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# SYNTHESIS AND BASIC OPTICAL PROPERTIES OF NEW π-CONJUGATED THIOPHENE-PYRIDINE CO-OLIGOMERS

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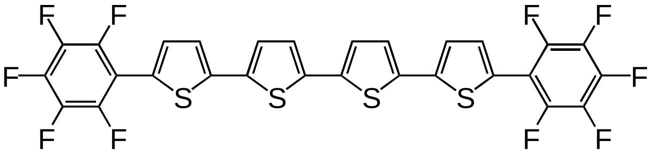
**Abstract** – Two series of π-conjugated thiophene-pyridine co-oligomers, Py-Th-$(Th)_m$-Th-Py (Py = pyridine unit; Th = thiophene unit; **4a**: m = 0; **5a**: m = 1; **6a**: m = 2) and Th-Py-$(Th)_m$-Py-Th (**4b**: m = 0; **5b**: m = 1; **6b**: m = 2), have been prepared by palladium- or nickel-promoted C-C coupling reaction in high yields. The π-π* absorption peak of Py-Th-$(Th)_m$-Th-Py (390-440 nm) is observed at a longer wavelength than that of Th-Py-$(Th)_m$-Py-Th (345-410 nm) with the same m number. These UV-vis data are considered to reflect a charge transfer (CT) interaction between the thiophene (donor) and pyridine (acceptor) units. **4a**-**6a**, **5b**, and **6b** show photoluminescence in a range of 430-540 nm and give quantum yields (Φ) of 20-40%. **4b** affords a high quantum yield of Φ = 71%. A linear correlation holds between the π-π* transition energy and the inverse of the number of the aromatic units [1/(m+4)] for the **4a**-**6a** and **4b**-**6b** series.

## INTRODUCTION

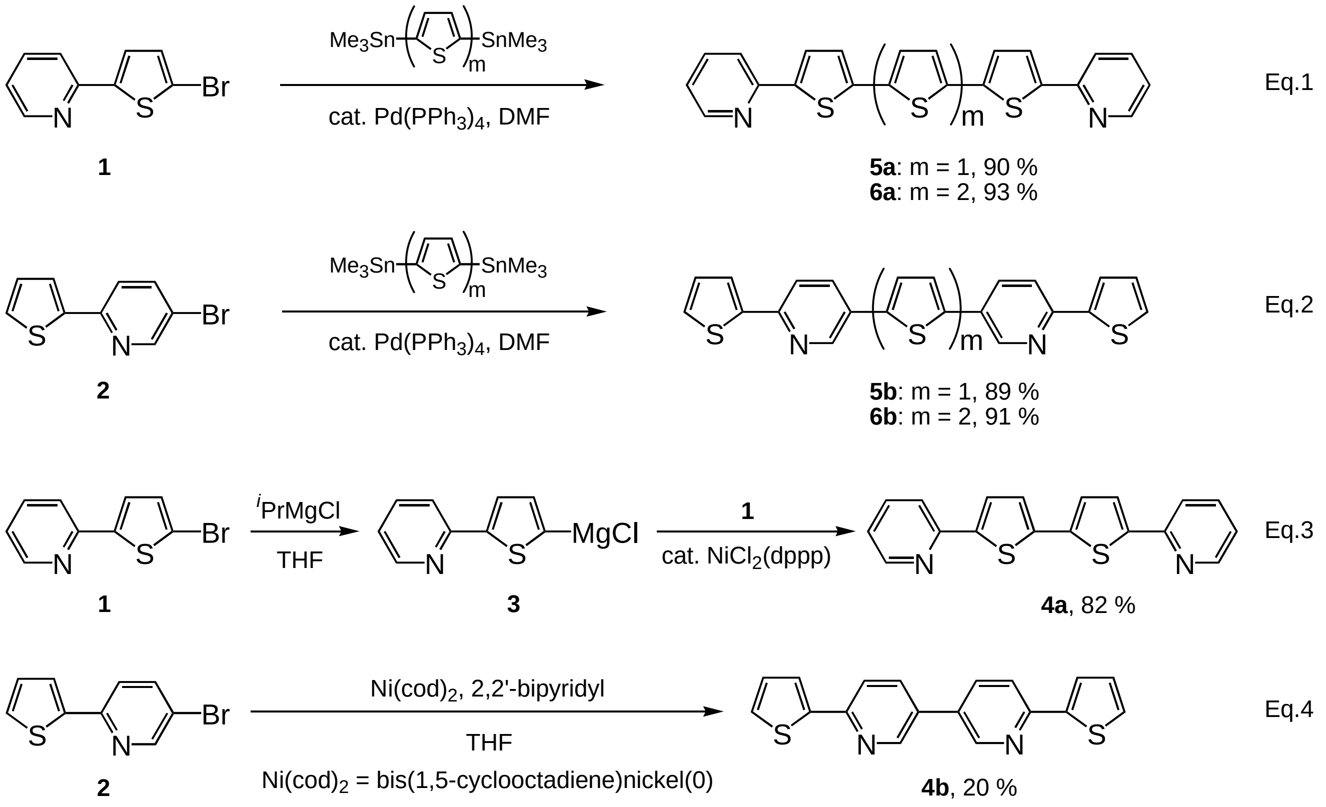
π-Conjugated heterocyclic polymers and oligomers are the subject of recent strong interest.[1] Applications of the compounds in electronic and optical devices are actively investigated. Some π-conjugated heterocyclic polymers have been adopted in industry. Thiophene[2] and pyridine[3] are most important building blocks of the π-conjugated compounds, and it is well-recognized that electronic functions of the π-conjugated compounds consisting of the thiophene unit or pyridine unit are controlled by π-excessive[2,4] nature of the thiophene unit and π-deficient[3,4] nature of the pyridine unit in the π-conjugated compounds. π-Conjugated co-oligomers and copolymers containing both π-excessive units and π-deficient units are another target of recent researches.[5,6] They show unique electronic and optical properties, which are considered to originate from an intramolecular charge-transferred (CT) electronic structure. Recently, Marks reported that the following compound having such a CT electronic structure serves as a good material for organic field-effect-transistor (FET).[5]



As described above, thiophene and pyridine are the important building block for π-conjugated oligomers and polymers. However, there has been no systematic research on π-conjugated co-oligomers of thiophene and pyridine, although copolymers of thiophene and pyridine have been reported.[6] Researches on the co-oligomers of thiophene and pyridine with controlled structure will give bases for better understanding and applications of π-conjugated molecules. We now report synthesis of a series of the thiophene-pyridine co-oligomers and basic optical properties of the co-oligomers.

## RESULTS AND DISCUSSION

Two series of thiophene-pyridine co-oligomers were prepared according to Scheme 1. As exhibited in Eq. 1, the palladium-catalyzed C-C coupling (Stille coupling)[7] of 2-bromo-5-(2-pyridyl)thiophene (**1**)[8] with 2,5-bis(trimethylstannyl)thiophene and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, respectively, gave the corresponding co-oliogomers with two 2-pyridyl terminal groups, Py-Th-$(Th)_m$-Th-Py (**5a**: m = 1, **6a**: m = 2), as an orange solid in high yields. Use of 2-(5-bromo-2-pyridyl)thiophene (**2**)[9] in a similar coupling afforded Th-Py-$(Th)_m$-Py-Th (**5b**: m = 1, **6b**: m = 2) with inner pyridine-2,5-diyl units as shown in Eq. 2. The tetramers, Py-Th-Th-Py (**4a**) and Th-Py-Py-Th (**4b**), were prepared by other types of organometallic C-C couplings. As depicted in Eq. 3, the coupling reaction[10] of the Grignard intermediate **3** with **1** in the presence of a catalytic amount of $NiCl_2$(dppp) [dppp = 1,3-bis(diphenylphosphino)propane] afforded a yellow solid of **4a** in 82% yield. Dehalogenative coupling[3,6] of **2** using a zerovalent nickel complex in DMF gave **4b** in 20% yield; the low yield was due to loss of the product in repeated purification of the compound. It was difficult to purify **4b**. All the obtained oligomers were partly soluble in organic solvents such as $CHCl_3$, and showed good solubility in formic acid. The TGA analysis revealed that these oligomers had high thermal stability. For example, the TGA curve of **5a** exhibited 10% weight loss temperature at about 365 °C.



**Scheme 1.** Synthetic route to the co-oligomers

The $^1$H NMR data of the oligomers in DCOOD are reasonable for their structures (cf. EXPERIMENTAL section). In acidic solvents, *N*-containing aromatic rings are usually protonated. Consequently, the $^1$H NMR data shown in Figure 1 are considered to correspond to those of protonated **6a** (chart a) and **6b** (chart b). For **6a**, the 2-pyridyl proton signals appear as a dd peak (H$^a$), a ddd peak (H$^c$), and a ddd peak (H$^b$) in a 1:1:1 peak area ratio; the H$^d$ signal is considered to be hidden under the strong peak of HCOOD (solvent impurity). The four doublet peaks observed at δ 8.07, 7.53, 7.49, and 7.37 are assigned to the thiophene protons as depicted in Figure 1(a).

The peaks of the pyridine rings in **6b** are shifted to a lower magnetic field (δ 9.1-8.3) as exhibited in Figure 1b. Signals of the three protons of the outer thiophene unit are observed at δ 8.13, 8.02 and 7.44; all of the peaks are observed as a doublet of doublets and the coupling patterns of the three signals are reasonable as shown in the Experimental part. Two doublet signals (or an AB quartet) observed at δ 7.80 and 7.56 are assigned to the protons of the inner thiophene ring.

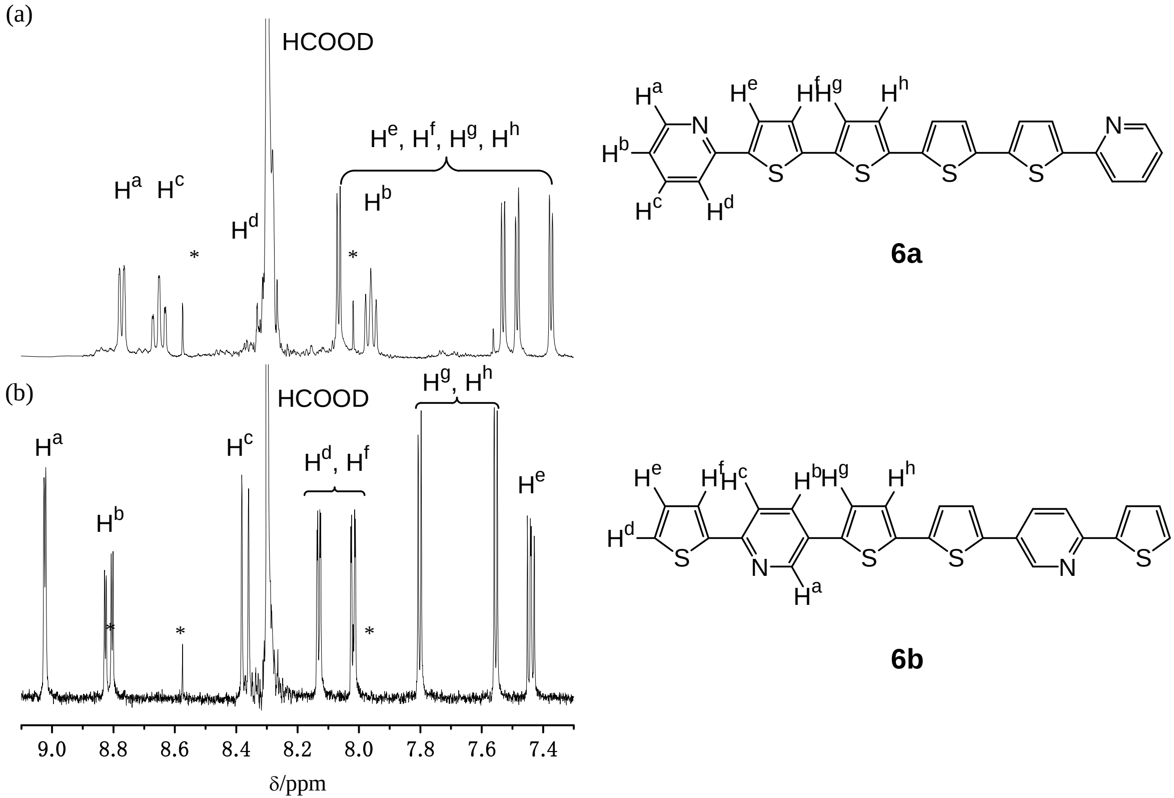


**Figure 1.** $^1$H NMR spectra of (a) **6a** and (b) **6b** in DCOOD at room temperature. Peaks with the * mark are due to the spinning side band of the solvent signal.

UV-vis spectra of the compounds are exhibited in Figure 2 and optical data of the co-oligomers are summarized in Table 1. The UV-vis peak reasonably shifts to a longer wavelength with extension of the π-conjugation length as shown in Figure 2 and Table 1.

The **a**-type co-oligomer gives the UV-vis peak at a longer wavelength than that of the corresponding **b**-type co-oligomer. For example, **6a** gives the UV-vis peak at 435 nm whereas **6b** affords the peak at 408 nm. In the case of **6b**, steric repulsion between the centered bithiophene unit and neighboring pyridine unit seems to cause some torsion of the main chain of the co-oligomer, and this seems to be the reason for **6b** to show $\lambda_{max}$ at the relatively shorter wavelength. A molecular structure of **6b** formed based on semiempirical PM5 calculation in the MOPAC2000 package of a computer program supports the torsion (by ca. 40 °) between the pyridine and neighboring thiophene rings in the main chain. On the other hand, such a steric repulsion in **6a** seems to be weak, and the semiempirical calculation of **6a** gives an essentially coplanar structure with an estimated torsion angle of 0.1 °. The difference in the coplanarity seems to account for the difference in the π-π* transition energy between **6a** and **6b**. Such a difference due to the different arrangement of aromatic rings was also found for co-oligomers of phenylene (Ph) and thiophene; i.e., between a Ph-(Th)$_n$-Ph (n = 1-4) series and a Th-(Ph)$_n$-Th (n = 1, 2) series.[11]

The $\lambda_{max}$ of **6a** (435 nm) is located at a longer wavelength than those of sexithiophene (403 nm) and the corresponding phenyl-capped bithiophene oligomer, Ph-Th-Th-Th-Th-Ph (423 nm). Because pyridine and benzene have a similar 6π electron system and they give the UV-vis peak at almost the same position ($\lambda_{max}$ = ca. 250 nm), the shift of the UV-vis peak of Ph-Th-Th-Th-Th-Ph to a longer wavelength observed with **6a** suggests that intramolecular charge transferred (CT) electronic state between the thiophene unit (donor) and pyridine unit (acceptor) contributes to the lowering of the π-π* transition energy. The **a**-type and **b**-type co-oligomers in non-acidic and polar solvents such as DMSO give the UV-vis peak (e.g., 430 nm for **6a** and 408 nm for **6b** in DMSO) at almost same position as those in $CHCl_3$. CT between the thiophene unit and pyridine unit is considered to occur, however, the effect of solvent polarity seems to be not large, possibly because of the symmetrical structure of the co-oligomes. In contrast, the absorption peaks of Py-Th-(Th)$_m$-Th-Py and Th-Py-(Th)$_m$-Py-Th in HCOOH were shifted to a longer wavelength compared to those in $CHCl_3$ (Table 1).

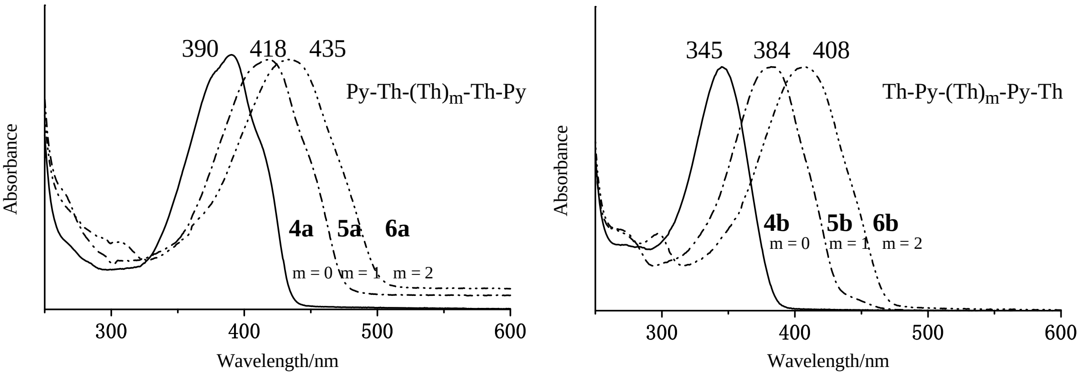


**Figure 2.** UV-vis spectra of **4a**, **5a**, and **6a** (left) and **4b**, **5b**, and **6b** (right) in $CHCl_3$.

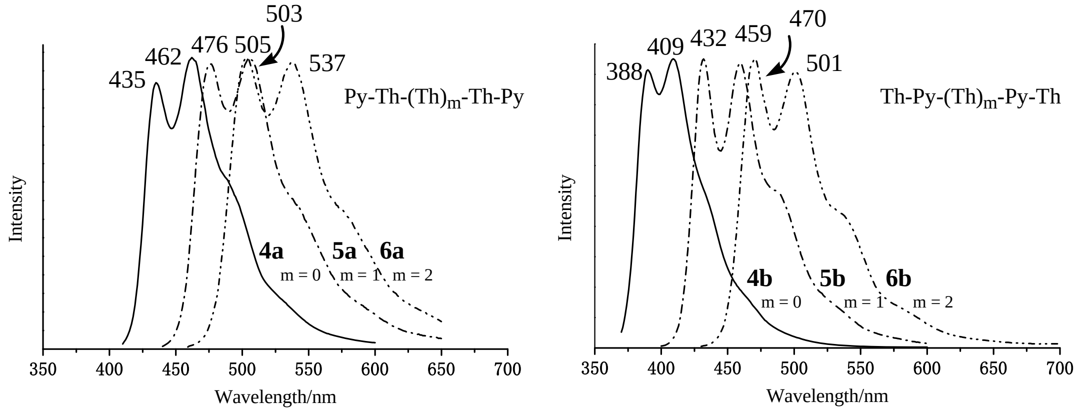


**Figure 3.** PL spectra of **4a**, **5a**, and **6a** (left) and **4b**, **5b**, and **6b** (right) in $CHCl_3$.

As depicted in Figure 3, the photoluminescence (PL) peak ($\lambda_{em}$) also moves to a longer wavelength with the increase in the number m in both the **a**- and **b**-series. All the PL spectra show structured emission peaks, which are usually assigned to coupling of electronic transition with ring vibration of the aromatic units.

The first main emission peaks of **4a**, **5a**, and **6a** appear at 435, 476, and 503 nm, respectively. The first main peaks of **4b**, **5b**, and **6b** appear at 388, 432, and 470 nm, respectively. The position of the first main emission peak agrees with the onset position of the UV-vis band for every case. **4b** gives a high quantum yield (Φ in Table 1) of 71% in PL. The quantum yields of other compounds are in a range from 17 to 37%; these values are comparable to those of Ph-$(Th)_n$-Ph.[11] The UV-vis and PL peaks were red-shifted in HCOOH. The shift in the acidic solvent suggests easier CT from the thiophene unit to the protonated pyridine unit.

**Table 1.** UV-vis and photoluminescence data of the co-oligomers

| compound | absorption, $\lambda_{max}$/nm | | photoluminescence, $\lambda_{em}$/nm (Φ)[a] | |
|---|---|---|---|---|
| | in $CHCl_3$ | in HCOOH | in $CHCl_3$ | in HCOOH |
| **4a** | 390 | 414 | 435, 462 (0.17) | 478 (0.21) |
| **5a** | 418 | 451 | 476, 505 (0.21) | 563 (0.19) |
| **6a** | 435 | 473 | 503, 537 (0.35) | 636 (0.10) |
| **4b** | 345 | 379 | 388, 409 (0.71) | 431 (0.43) |
| **5b** | 384 | 410 | 432, 459 (0.33) | 488 (0.28) |
| **6b** | 408 | 439 | 470, 501 (0.37) | 596 (0.07) |

[a] Φ = quantum yield.

Figure 4 depicts plots of the transition energy in the UV-vis absorption and photoluminescence vs. the inverse of the total aromatic units [1/n or 1/(m+4)] of the co-oligomers. A good linear correlation is observed between the transition energy and 1/n. Plots of $\lambda_{max}$ vs. 1/n also gave a good linear correlation and extrapolation of the straight line gives $\lambda_{max}$ of 530 nm at infinite n which agree with of $\lambda_{max}$ of poly(thiophene-2,5-diyl) at about 450 nm.[1]

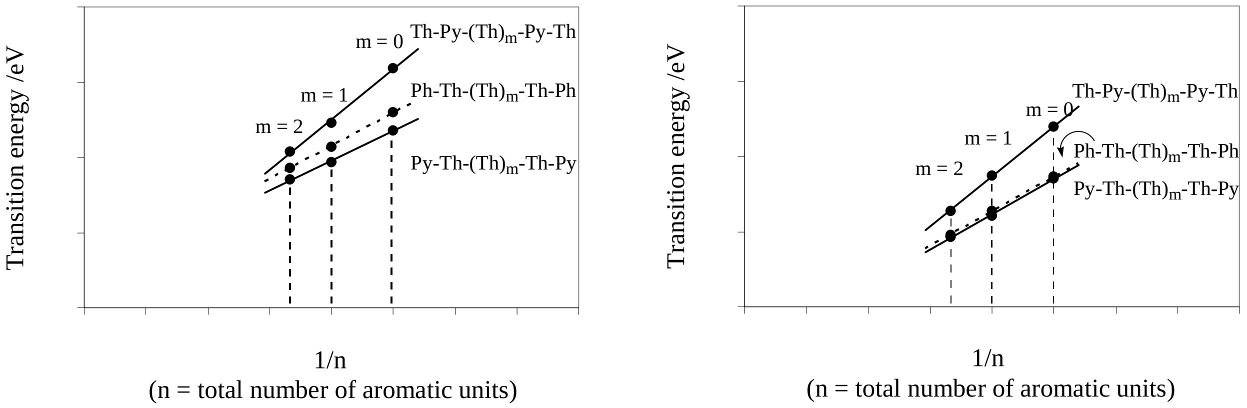


**Figure 4.** Plots of transition energy of Py-Th-$(Th)_m$-Th-Py (**4a**-**6a**) and Th-Py-$(Th)_m$-Py-Th (**4b**-**6b**) estimated by the data of $\lambda_{max}$ (left) and $\lambda_{em}$ (right) vs. the inverse of the total aromatic units [1/n or 1/(m+4)]. Data of the corresponding co-oligomers of thiophene and phenylene, Ph-Th-$(Th)_m$-Th-Py, extracted from ref. 11, are also shown (the broken lines).

As described above, the two **a**- and **b**-series of new π-conjugated thiophene-pyridine co-oligomers have been synthesized, and the basic optical properties of the co-oliogomers have been clarified.

## EXPERIMENTAL

2-Bromo-5-(2-pyridyl)thiophene (**1**),[6] 2-(5-bromo-2-pyridyl)thiophene (**2**),[7] $Pd(PPh_3)_4$,[12] $Ni(cod)_2$,[13] 2,5-bis(trimethylstannyl)thiophene,[14] and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene[15] were prepared according to the literature. $NiCl_2$(dppp) [dppp = 1,3-bis(diphenylphosphino)propane] and a THF solution of 2.0 M $^i$PrMgCl were purchased from Aldrich. NMR spectra were recorded on a JEOL EX-400 spectrometer. All $^1$H NMR chemical shifts are reported in ppm relative to HCOOD peak of formic acid-$d_2$ at δ 8.30. UV-vis spectra and photoluminescence spectra were measured with a Shimadzu UV-3100PC spectrometer and a Hitachi F-4010 spectrometer, respectively. The quantum yield (Φ) of the photoluminescence in solutions was calculated by comparing with the standard of quinine sulfate (ca. $10^{-5}$ M solution in 0.5 M $H_2SO_4$ with Φ of 54.6%). High resolution mass spectra (HRMS) were obtained with a JEOL JMS-700. TGA curves were taken using a Shimadzu thermometer TGA-50. Elemental analysis was carried out with a LECO CHNS-932 analyzer and a Yanaco YS-10 SX-Elements microanalyzer.

**Preparation of Py-Th-Th-Py (4a)** To a THF solution (15 mL) of **1** (0.53 g, 2.22 mmol) was added 1 mL of a THF solution of 2.0 M $^i$PrMgCl (2.00 mmol) at rt. After stirred for 1 h, $NiCl_2$(dppp) (5 mg) was added to the solution and the reaction mixture was stirred at rt for 24 h. The resulting suspension was poured into water and the reaction product was extracted with $CHCl_3$. The extract was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on alumina (first) and silica (second) with $CHCl_3$ to afford **4a** as a light yellow solid. 82% yield. $^1$H NMR (DCOOD, δ): 8.85 (dd, $J$ = 6.4 and 1.0 Hz, 2H), 8.72 (ddd, $J$ = 8.3, 6.4 and 1.0 Hz, 2H), 8.36 (d, $J$ = 8.3 Hz, 2H), 8.12 (d, $J$ = 4.1 Hz, 2H), 8.05 (dd, $J$ = 6.4 and 6.4 Hz, 2H), 7.73 (d, $J$ = 4.1 Hz, 2H). HRMS for $C_{18}H_{12}N_2S_2$: Calcd 321.0520 ($M+H^+$). Found 321.0511 ($M+H^+$).

**Preparation of Th-Py-Py-Th (4b)** To a dry THF (30 mL) solution containing $Ni(cod)_2$ (0.76 g, 2.77 mmol), 1,5-cyclooctadiene (1.3 mL), 2,2-bipydiyl (0.43 g, 2.77 mmol) was added **2** (0.54 g, 2.24 mmol). After stirred for 24 h at 60 ºC, the reaction mixture was poured into an aqueous ammonia. The reaction product was extracted with $CHCl_3$ and the extract was dried over $MgSO_4$. After removal of $CHCl_3$ by evaporation, the crude product was purified by column chromatography on silica with $CHCl_3$ (first), alumina with THF (second), and silica with THF (third) to yield **4b** as a light yellow solid. 20% yield. $^1$H NMR (DCOOD, δ): 9.30 (d, $J$ = 2.2 Hz, 2H), 9.08 (dd, $J$ = 8.3 and 2.2 Hz, 2H), 8.57 (d, $J$ = 8.3 Hz, 2H), 8.23 (dd, *J* = 4.0 and 1.2 Hz, 2H), 8.10 (dd, *J* = 5.0 and 1.2 Hz, 2H), 7.48 (dd, *J* = 5.0 and 4.0 Hz, 2H). HRMS for $C_{18}H_{12}N_2S_2$: Calcd 321.0520 (M+H$^+$). Found 321.0519 (M+H$^+$).

**Preparation of Py-Th-(Th)$_m$-Th-Py (5a: m = 1, 6a: m = 2) and Th-Py-(Th)$_m$-Py-Th (5b: m = 1, 6b: m = 2)** To a DMF (30 mL) solution of **1** (0.974 g, 4.1 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.820 g, 2.0 mmol) was added Pd($PPh_3$)$_4$ (30 mg, 0.025 mmol) at rt, and the mixture was stirred at 80 ºC for 24 h. After the resulting mixture was cooled to rt, a saturated aqueous solution of KF (50 mL) and aqueous ammonia (50 mL) were added to obtain an orange precipitate, which was collected by filtration. The precipitate was dissolved in formic acid, and the solution was poured into an excess amount of methanol, and the formed precipitate was corrected. The formed oligomer (**5a**) was dried under reduced pressure at 100 ºC. Preparation of **6a** was carried out analogously. Oliogomers (**5b** and **6b**) were prepared analogously by using **2**, instead of **1**.

**Py-Th-Th-Th-Py (5a):** 90% yield. $^1$H NMR (DCOOD, δ): 8.83 (dd, *J* = 6.1 and 1.0 Hz, 2H), 8.69 (ddd, *J* = 7.9, 7.9 and 1.0 Hz, 2H), 8.32 (d, *J* = 6.6 Hz, 2H), 8.10 (d, *J* = 4.2 Hz, 2H), 8.01 (ddd, *J* = 7.9 and 6.1 Hz, 2H), 7.60 (d, *J* = 4.2 Hz, 2H), 7.55 (s, 2H). Anal. Calcd. for $C_{22}H_{14}N_2S_3$: C, 65.64%; H, 3.51%; N, 6.96%. Found: C, 65.67%; H, 3.48%; N, 6.97%. The signal at δ 8.32 was hidden under the peak of HCOOD approximately at δ 8.3, and the peak position was determined on the basis of the HH-COSY spectrum of **5a**. The coupling pattern of the peak is given according to the coupling with the peak at δ 8.69, which is based on the HH-COSY spectrum.

**Py-Th-Th-Th-Th-Py (6a):** 93% yield. $^1$H NMR (DCOOD, δ): 8.77 (dd, *J* = 6.4 and 0.7 Hz, 2H), 8.65 (ddd, *J* = 6.4, 6.4 and 0.7 Hz, 2H), 8.32 (d, *J* = 6.4 Hz, 2H), 8.07 (d, *J* = 4.2 Hz, 2H), 7.96 (ddd, *J* = 6.4, 6.4 and 0.7 Hz, 2H), 7.53 (d, *J* = 4.2 Hz, 2H), 7.49 (d, *J* = 3.9 Hz, 2H), 7.37 (d, *J* = 3.9 Hz, 2H). Anal. Calcd. for $C_{26}H_{16}N_2S_4$: C, 64.43%; H, 3.33%; N, 5.78%. Found: C, 64.13%; H, 3.27%; N, 5.70%. The signal at δ 8.32 was hidden under the peak of HCOOD approximately at δ 8.3, and the peak position was determined on the basis of the HH-COSY spectrum of **6a**. The coupling pattern of the peak is given according to the coupling with the peak at δ 8.65, which is based on the HH-COSY spectrum.

**Th-Py-Th-Py-Th (5b):** 89% yield. $^1$H NMR (DCOOD, δ): 9.09 (d, *J* = 1.1 Hz, 2H), 8.88 (dd, *J* = 8.8 and 1.1 Hz, 2H), 8.41 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 3.9 Hz, 2H), 8.04 (d, *J* = 5.1 Hz, 2H), 7.93 (s, 2H), 7.45 (dd, *J* = 5.1 and 3.9 Hz, 2H). Anal. Calcd for $C_{22}H_{14}N_2S_3$: C, 65.64%; H, 3.51%; N, 6.96%. Found: C, 65.71%; H, 3.56%; N, 6.75%.

**Th-Py-Th-Th-Py-Th (6b):** 91% yield. $^1$H NMR (DCOOD, δ): 9.03 (d, *J* = 2.2 Hz, 2H), 8.83 (dd, *J* = 8.8 and 2.2 Hz, 2H), 8.37 (d, *J* = 8.8 Hz, 2H), 8.13 (dd, *J* = 3.9 and 1.0 Hz, 2H), 8.02 (dd, *J* = 4.9 and 1.0 Hz, 2H), 7.80 (d, *J* = 4.2 Hz, 2H), 7.56 (d, *J* = 4.2 Hz, 2H), 7.44 (dd, *J* = 4.9 and 3.9 Hz, 2H). Anal. Calcd for $C_{26}H_{16}N_2S_4$: C, 64.43%; H, 3.33%; N, 5.78%. Found: C, 64.08%; H, 3.35%; N, 5.67%.

## ACKNOWLEDGEMENTS

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