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Visible Light-Induced Synthesis of 3,4-Diarylthiophenes from 3,4-Diaryl-2,5-dihydrothiophenes

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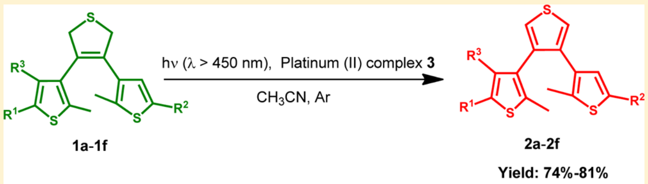
S Supporting Information

ABSTRACT: Using a catalytic amount of platinum(II) terpyridyl complex **3**, 3,4-diarylthiophenes (**2a–f**) could be synthesized from 3,4-diaryl-2,5-dihydrothiophenes (**1a–f**) under visible light (λ > 450 nm) irradiation in degassed CH_3CN. Spectroscopic study and product analysis reveal that the reaction is initiated by photoinduced electron transfer from 3,4-diaryl-2,5-dihydrothiophenes to platinum(II) complex **3**, leading to the formation of 3,4-diarylthiophenes.



INTRODUCTION

3,4-Disubstituted thiophenes are one of the most important classes of heterocyclic compounds, not only as key structural units with interesting biological activities but also as building blocks in the field of material sciences.[1,2] In particular, 3,4-diarylthiophenes are important because of their pharmacologic properties as anti-inflammatory agents[3] and their potential applications in organic electronic devices.[1,2] However, synthesis of 3,4-disubstituted heterocyclic compounds at one or more of the β positions is not easy because of the tendency toward aromatic substitution reactions at the more electronically favorable α positions of the heterocyclic ring. Although several approaches including Hinsburg condensation[4] and oxidative aromatization of the corresponding 3,4-disubstituted-2,5-dihydrothiophenes with hydrogen peroxide,[5] sulfuryl chloride,[6] bromine,[7] copper dibromide,[8] or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[9] have been employed to make 3,4-disubstituted thiophene derivatives, the use of toxic and expensive reagents, strict reaction conditions, difficulty in purification, and formation of poisonous gas as byproducts are problems that limit their widespread applications.

Photoredox transformations have recently attracted the attention of chemists owing to the generally mild conditions required for substrate activation and their suitability for "green reactions".[10−13] The use of visible light sensitization as a means to initiate organic reactions overcomes the lack of visible light absorbance by organic compounds, thus reducing side reactions often associated with photochemical reactions conducted with high energy ultraviolet light. Given the relatively long lifetime of the photoexcited state, the high quantum efficiency of its formation, and the exceptional chemical stability of its ground state,[14] square-planar platinum(II) terpyridyl complex was selected as a photocatalyst. Though this kind of complex has been exploited in the systems for photocatalytic hydrogen evolution,[15,16] there are few reports on the use of platinum(II) complexes in organic synthesis.[17] We reported that platinum(II) polypyridyl complexes could be used as sensitizers for photooxidation using molecular oxygen, where singlet oxygen was generated upon irradiation of light in visible region.[18] We also found that platinum(II) terpyridyl complexes could produce hydrogen photocatalytically from Hantzsch dihydropyridine derivatives and 3,4-diaryl-2,5-dihydropyrroles in quantitative yield.[19,20] Combined with our long-standing interest in visible light catalysis,[18−21] the present work is to study the preparation of 3,4-diarylthiophenes from 3,4-diaryl-2,5-dihydrothiophenes by a platinum(II) complex under visible light irradiation. Despite of the fact that direct irradiation of the 2,5-dihydrothiophene unit by ultraviolet light resulted in the formation of ring-closure product for photochromism,[22] we found that with visible light irradiation a catalytic amount of platinum(II) terpyridyl complex **3** is capable of producing 3,4-diarylthiophenes from 2,5-dihydrothiophene, far from that obtained under direct irradiation by ultraviolet light. Moreover, the mechanism of the visible-light initiated reaction is carefully examined by spectroscopic techniques.

RESULTS AND DISCUSSION

The photochemical reactions of 3,4-diaryl-2,5-dihydrothiophenes and the platinum(II) complex were investigated in CH_3CN at room temperature (Table 1). 3,4-Diaryl-2,5-dihydrothiophenes (**1a–f**) bearing different electronic substitutes, which can be easily prepared from very cheap starting materials by McMurry coupling of dicarbonyl compounds with $TiCl_4/Zn$,[22] were chosen to test the general feasibility of the reaction. The structure of **1c** can be functionalized by aldehyde, alcohol, acid, amide, imine groups, etc.[22] 3,4-Diaryl-2,5-dihydrothiophenes **1d–f** were used as examples to prove the effectiveness of the photocatalytic reactions for various functional groups.

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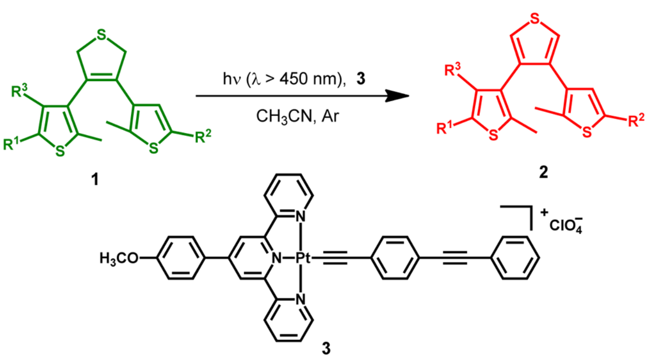
Table 1. Photocatalytic Reaction of 3,4-Diaryl-2,5-dihydrothiophenes by Platinum(II) Terpyridyl Complex 3[a]



entry	R^1	R^2	R^3	substrate	yield of **2**[b] (%)
1	H	H	H	**1a**	**2a**, 76
2	CH_3	CH_3	H	**1b**	**2b**, 81
3	Cl	Cl	H	**1c**	**2c**, 79
4	Cl	CHO	H	**1d**	**2d**, 78
5	CHO	CHO	H	**1e**	**2e**, 80
6	Cl	CHO	CHO	**1f**	**2f**, 74

[a] Reaction conducted with substrates **1** (1×10^{-2}–1×10^{-3} M) and platinum(II) terpyridyl complex **3** (1×10^{-5}–1×10^{-4} M) in degassed CH_3CN (50 mL) under irradiation by a 500 W high-pressure Hanovia mercury lamp. A glass filter was used to cut off light below 450 nm. [b] Isolated yield.

In a typical reaction, 50 mL of the solution of **1** (1×10^{-2}–1×10^{-3} M) and **3** (1×10^{-5}–1×10^{-4} M) in a Pyrex reactor was irradiated by a 500 W high-pressure Hanovia mercury lamp with argon current bubbled in. As shown in Figure 1a, the solution of **3** exhibits a broad absorption band in CH_3CN between 380 and 550 nm; a glass filter was used to cut off light below 450 nm, and thus only complex **3** was irradiated. Generally, the substrates were consumed completely in 8 h. After irradiation, the solvent was removed carefully under reduced pressure, and the products were isolated by extraction with ethyl acetate or purified by column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether = 1:10–2:1 and then characterized by ^1H NMR and MS spectroscopy. In contrast, irradiation of **1a** in the absence of complex **3** in CH_3CN at $\lambda > 450$ nm resulted in no product formation. Moreover, no products could be obtained when the reaction was carried out in the dark. Evidently, both light and **3** are essential for the dehydrogenation and a catalytic amount of **3** significantly accelerates the photochemical reaction to form 3,4-diarylthiophenes.

The generality of the photocatalyzed deprotonation reaction was tested by various functional groups. 3,4-Diaryl-2,5-dihydrothiophenes **1b–f** also underwent the reaction photocatalyzed by platinum(II) terpyridyl complex **3** under irradiation in degassed CH_3CN, resulting in the formation of deprotonation product 3,4-diarylthiophenes in a yield of 81% for **2b**, 79% for **2c**, 78% for **2d**, 80% for **2e**, and 74% for **2f**, respectively (Table 1).

This photocatalytic reaction process was clearly evidenced by UV–vis absorption and ^1H NMR spectra. In the following discussion, we used substrate **1a** as an example to show the spectral changes along with irradiation. Irradiation of **1a** and **3** in CH_3CN quickly decreased the absorbance at the typical bands of 300–350 nm for **1a**, accompanied by growth with a maximum at 290 nm, typical absorption of **2a** in the difference absorption spectra (Figure 1b). The well-defined isosbestic point at 302 nm suggests that **1a** and **2a** are present in the solution. This process was much clearer in the difference absorption spectra (inset, Figure 1b). ^1H NMR spectra before and after irradiation provide further evidence for this photochemical reaction. As shown in Figure 2, the typical signals of the starting material **1a** at 4.13, 6.69, 6.83 ppm disappeared while new signals appeared at 6.67, 6.72, 7.41 ppm, in line with those of pure **2a**. In spite of the conversion changing during irradiation, no secondary byproduct was detected throughout the reaction. On the basis of the consumption of the starting material of **1**, the conversion of the photoreaction was up to 97%.

To understand the primary process of the photocatalytic reaction, we examined the interaction between 3,4-diaryl-2,5-dihydrothiophenes and the complex. Platinum(II) complex **3** displays moderately intense $d\pi(Pt)\rightarrow\pi^*(trpy)$ metal-to-ligand charge-transfer (MLCT) transition luminescence with λ_{max} at 628 nm ($\tau = 270$ ns) in degassed CH_3CN at room temperature, which is readily quenched by 3,4-diaryl-2,5-dihydrothiophenes **1a**, and the quenching process follows Stern–Volmer kinetics with rate constant (k_q) of 10^9 M^{-1} s^{-1} (Table 2, Figure 3). Calculation of the free energy change (ΔG) by the Rehm–Weller equation revealed that the photoinduced electron transfer from **1** to the excited **3** was exothermic (Table 2). Since the energy of the singlet excited state of complex **3** is much lower than that of **1**, the singlet energy transfer from the

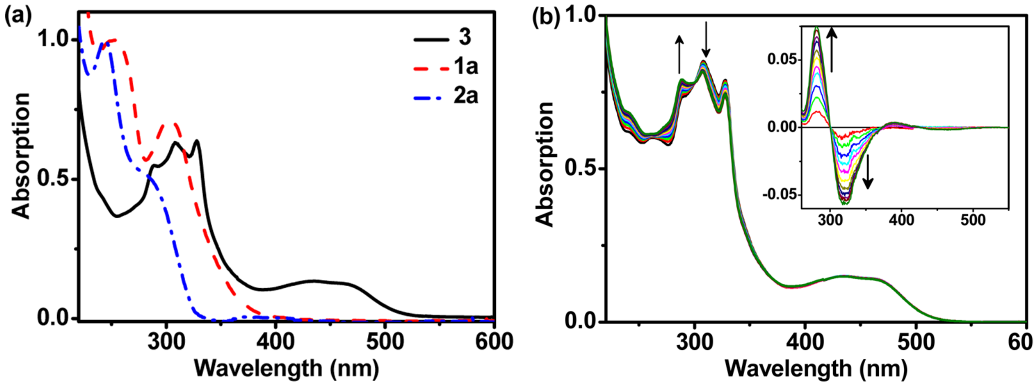


Figure 1. (a) UV–vis absorption spectra of **1a**, **2a**, and **3** in CH_3CN. (b) Absorption spectral change of **1a** (1.7×10^{-5} M) and **3** (1×10^{-5} M) in degassed CH_3CN as a function of time with irradiation at $\lambda > 450$ nm. Inset: difference absorption spectra with irradiation times 0, 3, 6, 9, 12, 15, 18, 21, 24, 30, 36, and 42 min, respectively.

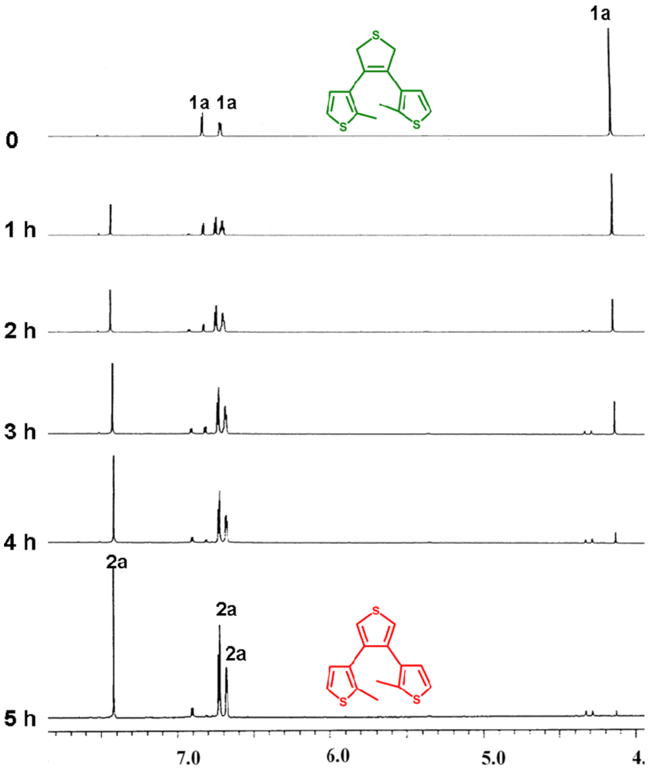


Figure 2. Partial ^{1}H NMR spectra of **1a** and **3** in degassed CD_3CN at different irradiation times. Because of the trace amount of **3**, the spectra only show the disappearance of **1a** and the appearance of **2a**.

Table 2. Rate Constant for Luminescence Quenching of Platinum(II) Complex 3 with Substrate 1 in CH_3CN (k_q), Oxidative Potential of 1 (ΔE_{ox}), and Free Energy Change (ΔG)

substrate	1a	1b	1c	1d	1e	1f
k_q (× 10^9 $M^{-1}s^{-1}$)	11.2	8.4	3.2	1.6	2.8	1.8
ΔE_{ox}/V[a]	1.47	1.43	1.62	1.51	1.46	1.56
ΔG/V[a]	−0.16	−0.20	−0.28	−0.12	−0.17	−0.07

[a] ΔG was calculated by the Rehm−Weller equation: $\Delta G = \Delta E_{ox} - \Delta E_{red} - \Delta E_{0,0} - e^2/\varepsilon a$, where ΔE_{ox} and ΔE_{red} versus NHE are oxidative and reductive potentials of **1** and **3**, respectively, which were measured by cyclic voltammetry in degassed CH_3CN solution with 0.1 M n-Bu_4NPF_6 as supporting electrolyte, scan rate 100 mV s^{-1}, working electrode: glassy carbon; reference electrode: Ag/Ag$^+$; ferrocene was used as external reference. ΔE_{red} is −0.53 V for **3** and $e^2/\varepsilon a$ is 0.05 V in CH_3CN. $\Delta E_{0,0}$ refers to the lowest excited energy of **3** in CH_3CN (2.11 V).

excited **3** to **1** is thermodynamically impossible; it is therefore reasonable to think that the photoinduced electron transfer is responsible for luminescence quenching and the products generation.

The photoinduced electron transfer is further evidenced by flash photolysis investigation at room temperature. Figure 4 displays the time-resolved absorption difference spectra for **3** and **3** with **1a**, respectively, in degassed CH_3CN solution. Upon laser pulse by 355 nm light, a strong transient absorption of the lowest ^{3}MLCT state for **3** emerged immediately with maximum at 470 nm, and the bleaching in the region of 400−500 nm may be attributed to the ground-state absorption of **3**. The decays could be well described by a monoexponential function with a lifetime of 270 ns. As **1a** was introduced into **3** ([**3**] = 8.0 × 10^{-5} M, [**1a**] = 4.8 × 10^{-4} M, [**3**]/[**1a**] = 1:6), the excited ^{3}MLCT absorption of **3** was progressively replaced by a series of new absorption throughout the near-UV and visible region with a maximum at 520 nm, which are possibly ascribed to the formation of the transient intermediates as one-electron-reduced platinum(II) complex according to the literature and our previous studies.[19,20,23] In this case, the transient decay of **3** at 520 nm could be well-described by biexponential function, with τ = 147 ns and 11.6 μs, respectively. The shorter lifetime of 147 ns was found to be consistent with the luminescence quenching experiment. Consequently, as **3** was excited, the photoinduced electron transfer from 3,4-diaryl-2,5-dihydrothiophene of **1a** to the excited complex **3** indeed took place. According to the lifetimes of **3** with the concentration of [**1a**] = 4.8 × 10^{-4} M, and **3** itself in CH_3CN, respectively, the rate constant for the photoinduced electron transfer can be estimated as k_{ET} = 6.5 × 10^9 M^{-1} s^{-1}, close to the diffusion limit. On the other hand, the longer lifetime of 11.6 μs at around 500 nm possibly resulted from the intermediate species of thiophene cation radical or thiophene radical formed by the electron transfer.[23] This assignment is based on the spectral features similar to those of thiophene cation radical and thiophene radical reported in the literature.[24]

On the basis of the above results, the photocatalytic deprotonation reaction from 3,4-diaryl-2,5-dihydrothiophenes to 3,4-diarylthiophenes can be rationalized in terms of mechanism shown in Figure 5. The photoinduced electron transfer from 3,4-diaryl-2,5-dihydrothiophenes **1** to the excited complex **3** produces thiophene cation radical $\mathbf{1}^{\bullet+}$ and one-electron-reduced platinum(II) complex $\mathbf{Pt(II)}^{\bullet-}$. The deprotonation of $\mathbf{1}^{\bullet+}$ radical cation leads to the formation of $\mathbf{1}^{\bullet}$ radical, and at the same time the reduced platinum(II) complex $\mathbf{Pt(II)}^{\bullet-}$ is in turn reacted with the proton to regenerate platinum(II) complex **Pt(II)**. Eventually, elimination of hydrogen atom from the respective radical intermediate of $\mathbf{1}^{\bullet}$ produces the dehydrogenation product 3,4-diarylthiophenes **2**.

■ CONCLUSION

In summary, we reported a facile method for the preparation of 3,4-diarylthiophenes from 3,4-diaryl-2,5-dihydrothiophenes by visible light catalysis. The inherent *green* character of light and platinum(II) terpyridyl complex are able to initiate the photocatalytic reaction leading to the formation of 3,4-diarylthiophenes with yields comparable to those obtained by the thermal synthetic methods. Mechanistic studies demonstrate that photoinduced electron transfer from 3,4-diaryl-2,5-dihydrothiophenes to platinum(II) complex **3** dominates the primary process of the deprotonation reaction.

■ EXPERIMENTAL SECTION

General Information. All reagents were purchased from commercial sources and used without treatment unless otherwise indicated. Acetonitrile for spectroscopic measurements and photochemical reactions was purified by the reported procedure.[25] HRMS was measured with a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer with ESI positive mode.

Synthesis of 3, 1a−f, and 2a−f. Platinum(II) terpyridyl complex **3** was prepared by the reaction of [Pt(trpy)Cl]Cl (trpy = 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine) with $HC{\equiv}CC_6H_4C{\equiv}CC_6H_5$-4, according to the literature method.[19]

3,4-Diaryl-2,5-dihydrothiophenes (**1a−f**) were synthesized from very inexpensive starting materials by McMurry coupling of dicarbonyl compounds with $TiCl_4$/Zn according to a reported method.[8,22] 3,4-

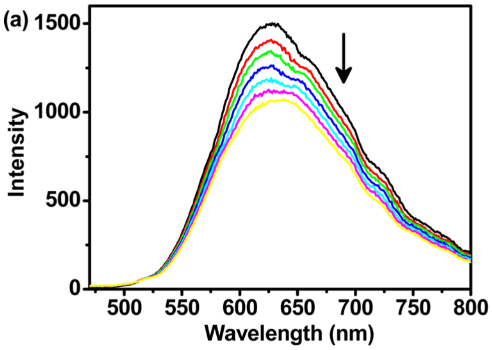


Figure 3. (a) Luminescence spectra of complex **3** (1.2×10^{-5} M) in degassed CH_3CN as a function of concentration of **1a** with excitation at 450 nm. (b) Stern−Volmer plot for luminescence intensity quenching of **3** by **1a**.

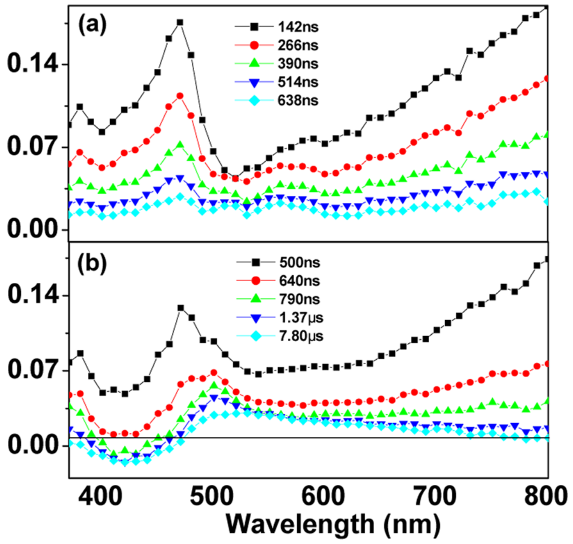


Figure 4. (a) Transient absorption spectra of **3** (8.0×10^{-5} M) in CH_3CN at room temperature. (b)Transient absorption spectra of **3** (8.0×10^{-5} M) with **1a** (4.8×10^{-4} M). λ_{ex} = 355 nm.

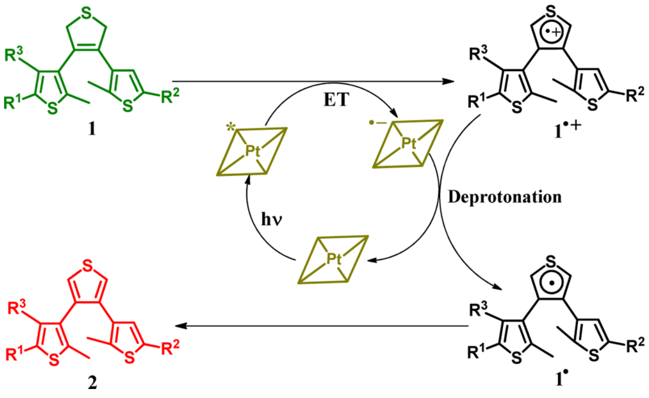


Figure 5. Possible pathways for the deprotonation of 3,4-diaryl-2,5-dihydrothiophenes.

Diarylthiophenes **2a**−**f** were obtained by the photocatalytic reaction and identified by ^{1}H NMR, ^{13}C NMR, and MS. In a typical reaction, the solution (50 mL) of **1** (1×10^{-2}−1×10^{-3} M) and **3** (1×10^{-5}−1×10^{-4} M) in a Pyrex reactor was irradiated by a 500 W high-pressure Hanovia mercury lamp with argon current bubbled in. The photoreaction was carried out in dry degassed CH_3CN solution at room temperature. After irradiation, the solvent was removed carefully under reduced pressure, and the products were isolated by extraction with ethyl acetate or purified by column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether = 1:10 to 2:1 and identified by ^{1}H NMR, ^{13}C NMR spectroscopy, MS, and IR.

*2,2′′-Dimethyl-2′,5′-dihydro-3,3′:4′,3′′-terthiophene (**1a**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 6.77 (d, 2H, J = 3.2 Hz), 6.64 (d, 2H, J = 3.2 Hz), 4.17 (s, 4H), 2.45 (s, 6H). EI-MS (m/z): M^+ calcd for $C_{14}H_{14}S_3$ 278.03, found 278.03.

*2,2″,5,5′′-Tetramethyl-2′,5′-dihydro-3,3′:4′,3′′-terthiophene (**1b**).* ^{1}H NMR (400 MHz, CD_3CN, ppm) δ: 6.50 (s, 2H), 4.03 (s, 4H), 2.32 (s, 6H), 1.87 (s, 6H). EI-MS (m/z): M^+ calcd for $C_{16}H_{18}S_3$ 306.06, found 306.06.

*5,5′′-Dichloro-2,2′′-dimethyl-2′,5′-dihydro-3,3′:4′,3′′-terthiophene (**1c**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 6.50 (s, 2H), 3.98 (s, 4H), 1.84 (s, 6H). EI-MS (m/z): M^+ calcd for $C_{14}H_{12}Cl_2S_3$ 345.95, found 345.93.

*5′′-Chloro-2,2′′-dimethyl-2′,5′-dihydro[3,3′:4′,3′′-terthiophene]-5-carbaldehyde (**1d**).* ^{1}H NMR (400 MHz, CD_3CN, ppm) δ: 9.73 (s, 1H, CHO), 7.63 (s, 1H), 6.76 (s, 1H), 4.10 (m, 4H), 2.14 (s, 3H), 1.90 (s, 3H). EI-MS (m/z): M^+ calcd for $C_{15}H_{13}ClOS_3$ 339.98, found 339.97.

*2,2′′-Dimethyl-2′,5′-dihydro[3,3′:4′,3′′-terthiophene]-5,5′′-dicarbaldehyde (**1e**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.75 (s, 2H), 7.43 (s, 2H), 4.16 (s, 4H), 2.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 182.1, 147.2, 140.8, 136.7, 134.8, 133.6, 42.8, 15.3. EI-MS (m/z): M^+ calcd for $C_{16}H_{14}O_2S_3$ 334.02, found 334.00.

*5-Chloro-2,2′′-dimethyl-2′,5′-dihydro[3,3′:4′,3′′-terthiophene]-4,5′′-dicarbaldehyde (**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 10.04 (s, 1H), 9.71 (s, 1H), 7.33 (s, 1H), 4.20 (m, 2H), 4.05 (m, 1H), 3.72 (m, 1H), 2.19 (s, 3H), 2.01 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 183.7, 182.3, 147.7, 141.6, 140.5, 137.0, 135.1, 134.7, 134.4, 134.4, 134.1, 131.4, 42.5, 42.0, 15.3, 13.6. EI-MS (m/z): M^+ calcd for $C_{16}H_{13}ClO_2S_3$ 367.98, found 367.97.

*2,2′′-Dimethyl-3,3′:4′,3′′-terthiophene (**2a**).* Pale yellow oil (16.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.29 (s, 2H), 6.72 (d, 2H, J = 3.5 Hz), 6.64 (d, 2H, J = 3.5 Hz), 2.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 139.9, 135.2, 134.8, 126.4, 125.4, 124.2, 15.4. EI-MS (m/z): M^+ calcd for $C_{14}H_{12}S_3$ 276.01, found 276.01.

*2,2′′,5,5′′-Tetramethyl-3,3′:4′,3′′-terthiophene (**2b**).* Yellow solid (17.8 mg, 81%). Mp: 87−89 °C. ^{1}H NMR (400 MHz, CD_3CN, ppm) δ: 7.28 (s, 2H), 6.32 (s, 2H), 2.32 (s, 6H), 2.08 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN, ppm) δ: 138.1, 135.9, 134.2, 133.9, 128.5, 124.6, 15.1, 13.8. EI-MS (m/z): M^+ calcd for $C_{16}H_{16}S_3$ 304.04, found 304.04.

*5,5′′-Dichloro-2,2′′-dimethyl-3,3′:4′,3′′-terthiophene (**2c**).* Yellow solid (17.2 mg, 79%). Mp: 114−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.21 (s, 2H), 6.49 (s, 2H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 139.9, 134.3, 132.6, 128.1, 125.4, 124.3, 13.9. EI-MS (m/z): M^+ calcd for $C_{14}H_{10}Cl_2S_3$ 343.93, found 343.93.

*5′′-Chloro-2,2′′-dimethyl[3,3′:4′,3′′-terthiophene]-5-carbaldehyde (**2d**).* Pale yellow amorphous solid (17.1 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.73 (s, 1H), 7.32 (s, 1H), 7.27 (m, 2H), 6.46 (s, 1H), 2.31 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 182.6, 147.4, 139.9, 138.7, 135.8, 135.2, 134.5, 132.3, 127.9, 125.8, 124.8, 124.7, 15.2, 13.9. HRMS (ESI) m/z calcd for

$C_{15}H_{12}ClOS_3$ (MH$^+$), 338.9733; found 338.9737. IR (KBr, cm^{-1}) ν: 3104, 2963, 2918, 2852, 2810, 1663, 1454, 1261, 1096, 1022, 871, 808.

*2,2′′-Dimethyl[3,3′:4′,3′′-terthiophene]-5,5′′-dicarbaldehyde (**2e**).* Green solid (17.5 mg, 80%). Mp: 117−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.70 (s, 2H), 7.34 (s, 2H), 7.30 (s, 1H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 182.5, 147.4, 140.1, 138.3, 135.1, 134.9, 125.3, 15.1. HRMS (ESI): m/z calcd for $C_{16}H_{13}O_2S_3$ (MH$^+$) 333.0072, found 333.0074. IR (KBr, cm^{-1}) ν: 3093, 2919, 2854, 2826, 1658, 1644, 1478, 1420, 1244, 1177, 1097, 861, 799.

*(R)-5-Chloro-2,2′′-dimethyl[3,3′:4′,3′′-terthiophene]-4,5′′-dicarbaldehyde (**2f**).* Yellow solid (16.1 mg, 74%). Mp: 152−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.66 (s, 2H), 7.30 (d, 1H, J = 3.2 Hz), 7.24 (d, 1H, J = 3.2 Hz), 7.13 (s, 1H), 2.37 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 183.6, 182.5, 147.8, 139.6, 139.0, 138.3, 135.7, 135.4, 134.8, 134.1, 133.6, 132.2, 125.7, 124.8, 15.1, 13.5. HRMS (ESI) m/z calcd for $C_{16}H_{12}ClO_2S_3$ (MH$^+$) 366.9683, found 366.9683. IR (KBr, cm^{-1}) ν: 3110, 2957, 2921, 2852, 2816, 2742, 1680, 1666, 1459, 1433, 1385, 1361, 1244, 1175, 1141, 1042, 863, 814.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **1a−f** and **2a−f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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