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Palladium-Catalyzed Direct Mono- and Diarylation of Diphenydithienylethenes: A Useful Method for Enhancing Fluorescence Intensity and Aggregation-Induced Emission

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Abstract: In this study we report efficient method for the syntheses of mono- and diarylated diphenyldithienylethene (DPDTE) via a palladium-catalyzed C–H arylation reaction. These new derivatives showed amplified luminescent properties thanks to a change in polarity, particularly in the presence of an electron-withdrawing groups (EWG). Moreover, the arylated DPDTEs showed dual-emissive phenomena, including fluorescence in organic solvents and aggregation-induced emission.

Keywords: aggregation-induced emissions; CH functionalization; diphenyldithienylethene; palladium-catalyzed; thiophene

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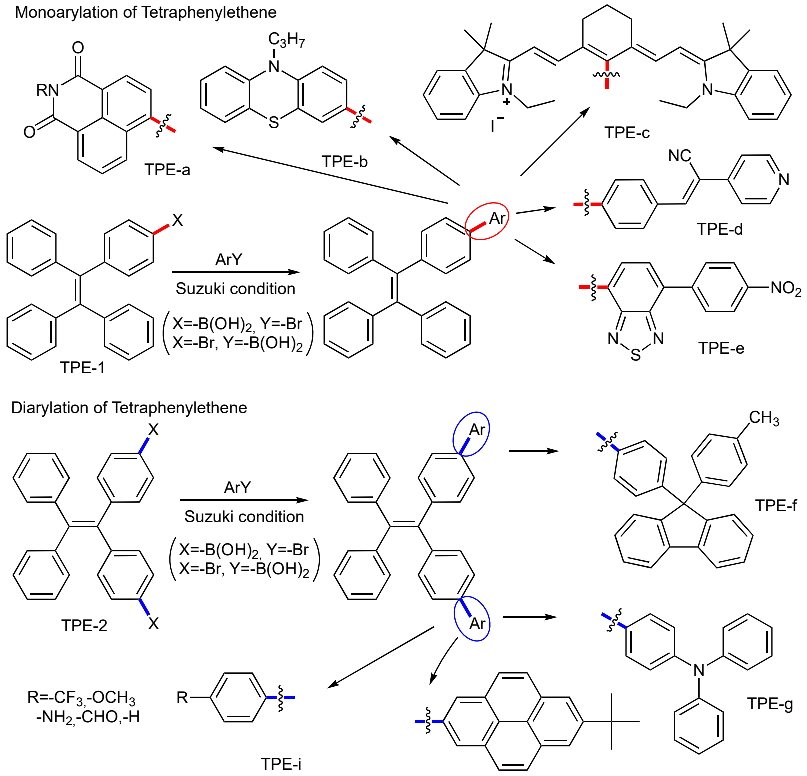
1. Introduction

Tetraarylethene (TAE) has become a well-known building block for luminescent organic material for its aggregation-induced emission (AIE) behavior [1,2]. The functionalization of TAE changed its physical properties, leading to its extensive applications in material science, synthetic and biological fields, supramolecular frameworks, and self-assemblies. For example, tetrafunctionalization at the para position of the phenyl ring of tetraphenylethene (TPE) provided interesting organic linkers for a metal–organic framework (MOF) involving platinum [3], mercury [4], silver [5], and palladium [6] and a covalent–organic framework (COF) via imine formation. TAEs showed weak emission at the aggregation state, but their emissive intensity could be amplified via MOF and COF formation. Diarylation of TPE can fine tune its physical properties to adapt to proposed applications. Diarylated TPEs possess not only AIE but also other interesting physical properties. In particular, TPE-f [7], in which TPE is combined with highly luminous fluorene groups, is an undoped organic light-emitting diode that exhibits deep-blue emissions, low turn-on voltage (3V), and high electroluminescence efficiency. TPE-g [8–10] with a triphenylamine moiety was fabricated as emissive layers in OLEDs because of its deep-blue emitter. TPE-h [11], which bears a pyridinyl group, exhibited an enhanced hole-transporting ability, blue emission, and excellent reversible mechanochromism. TPE-i [12–14] (Scheme 1), synthesized in high yields via the Suzuki–Miyaura reaction, showed different fluorescent colors and reversible mechanochromic luminescence with good reproducibility in a solid state. When R=CF_3, the compound was a self-recovering mechanochromic luminogen. When R=CHO, this group was functionalized after three steps to triethylmethylammonium bromide, which can be used as an ultrasensitive fluorescence biosensor.



Scheme 1. Monoarylation and diarylation of tetraphenylethene.

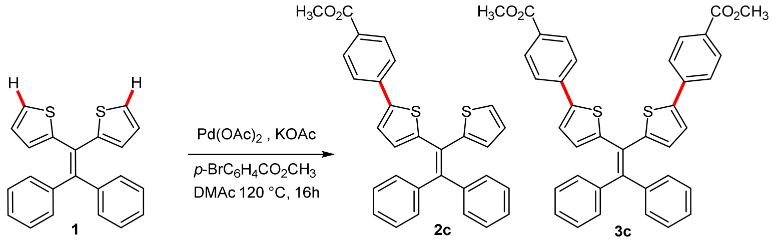
Monoarylated TPEs have been commonly synthesized by the Suzuki–Miyaura cross-coupling reaction. 1,8-Naphthalimide-based TPEs (TPE-a) are highly emissive luminophors having various mechanofluorochromic and aggregation-induced characteristics. Phenothiazine-substituted TPE (TPE-b) [15] showed strong emissions, strong AIE characteristics, and mechanofluorochromism in a solid state because its conformation was twisted by monoarylation. TPE has also been incorporated with heptamethine cyanine IR-780 in order to enhance its photosensitivity, photothermal response, and photostability in the near infrared region. TPE-c proved to be superior in rapid cell uptake and exhibited strong cytotoxicity to HeLa cells (IC_{50} = 3.3 μM). TPE-c [16] was an illustrative example of the relationship between an aggregation state and photophysical properties. It can be also applied in cell imaging and image-guided theranostics. A donor-accepter system could be designed by introducing an electron-withdrawing group (EWG) into TPE. For example, TPE-d [17] has a high polarity because its molecules consist of TPE as a donor group and an accepter group such as pyridyl or cyano. Their multistimulus-responsive fluorescent characteristics have been investigated and proven to have a relationship with AIE, mechanofluorescence, and acidochromism. These TPE derivatives are suitable for application in mechanosensors, acid or alkali fluorescence sensors, or in other opto-electronic applications. TPE-substituted benzothiadiazoles (TPE-e) [18] showed AIE and solvatochromic effects and have been applied to monitoring trace water fractions in organic solvents. The bond between TPE and the introduced aryl groups is commonly formed by the classical Suzuki–Miyaura cross-coupling reaction. The AIE effects of TPE, tetrathienylethene, and diphenyldithienylethene (DPDTE) have been thoroughly investigated. DPDTE is a good candidate for preparing new AIE luminogens because of the feasible arylation, via direct palladium-catalyzed C–H functionalization, of its thiophene moieties.

2. Results and Discussion

2.1. Synthesis

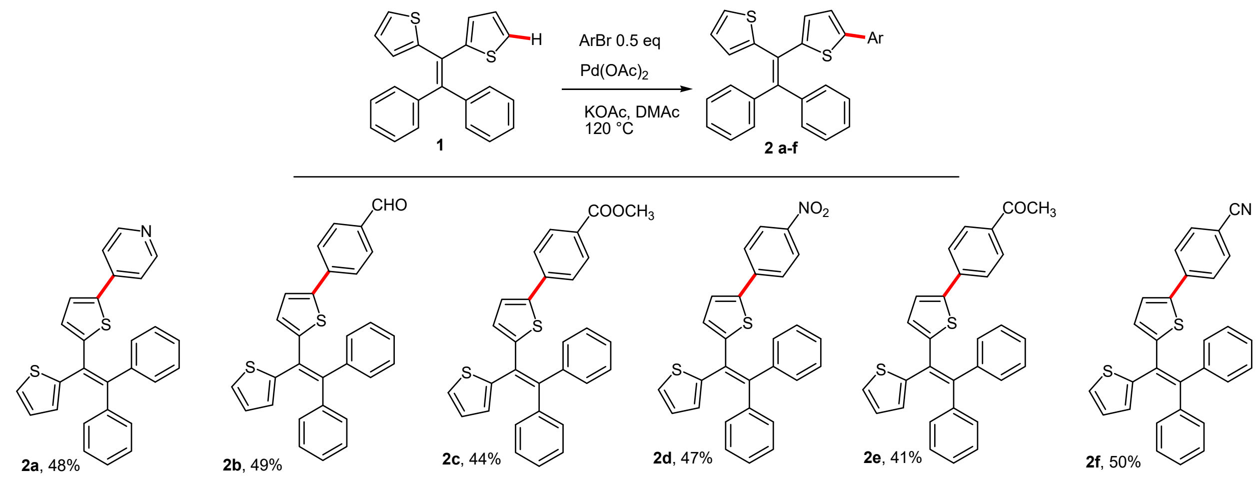
The starting material (DPDTE) was synthesized as described in the literature [19]. The reported procedure has been modified for gem-1,1-dibromo-2,2-dithienylethene and phenylboronic acid to give DPDTE with a 55% isolated yield. The palladium-catalyzed C–H functionalization of the thiophene and thienothiophene have been optimized by Doucet [20] and our group [21]. This ligand-free catalytic system consisted of only two components $Pd(OAc)_2$ and KOAc with DMAc as solvent, can be applied to various thiophene derivatives with good functional group tolerance. We have further optimized this condition by changing the ratio of **1** and *p*-$BrC_6H_4COOCH_3$ to obtain the monoarylated DPDTE (**2c**) and diarylated DPDTE (**3c**). A short screening of the reaction conditions is summarized in Table 1. The optimized conditions for the monoarylation of DPDTE were established with the ratio of **1** and aryl bromide as 1:0.5. With this optimized condition in hand, we successfully synthesized a number of monoarylated DPDTEs with moderate isolated yields (from 41 to 50%). The synthesized monoarylated DPDTEs are listed in the Scheme 2. The isolated yields of monoarylated DPDTEs were moderate. These conditions are suitable for a wide range of functional groups such as nitro, nitrile, aldehyde, acetyl, ester, and pyridine.

Table 1. Optimization of the arylation of DPDTE.



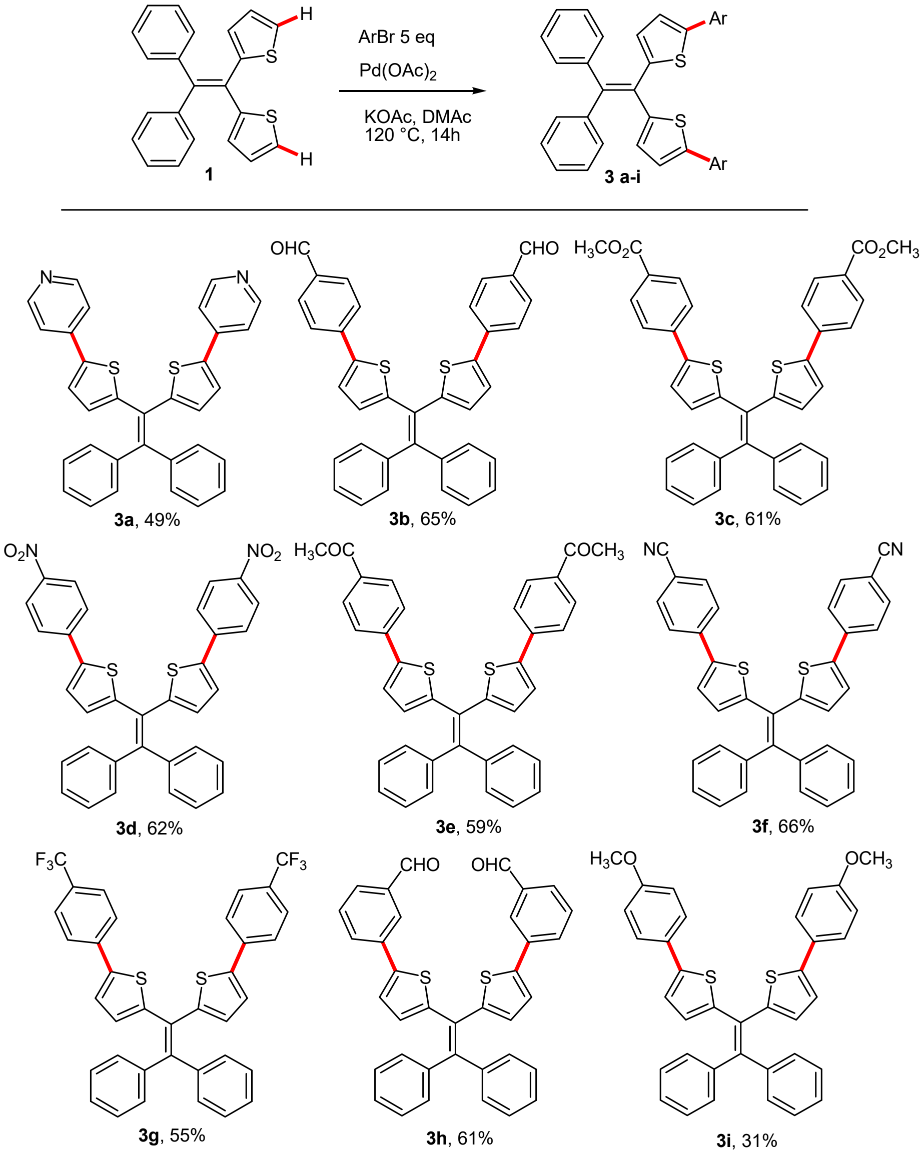
Entry	Ratio 1:ArBr	Yield (%) *	
		2c	3c
1	1:0.5	43	0
2	1:1	31	9
3	1:2	12	29
4	1:3	18	38
5	1:4	7	47
6	1:5	0	60

Reaction conditions: $Pd(OAc)_2$ 3 mol%, KOAc 3 eq., ratio (1:ArBr) listed in Table 1, 120 °C, 14 h. (ArBr = *p*-$BrC_6H_4CO_2CH_3$), *: isolated yield.



Scheme 2. Synthesis of monoarylated diphenyldithienylethenes **2a–f**.

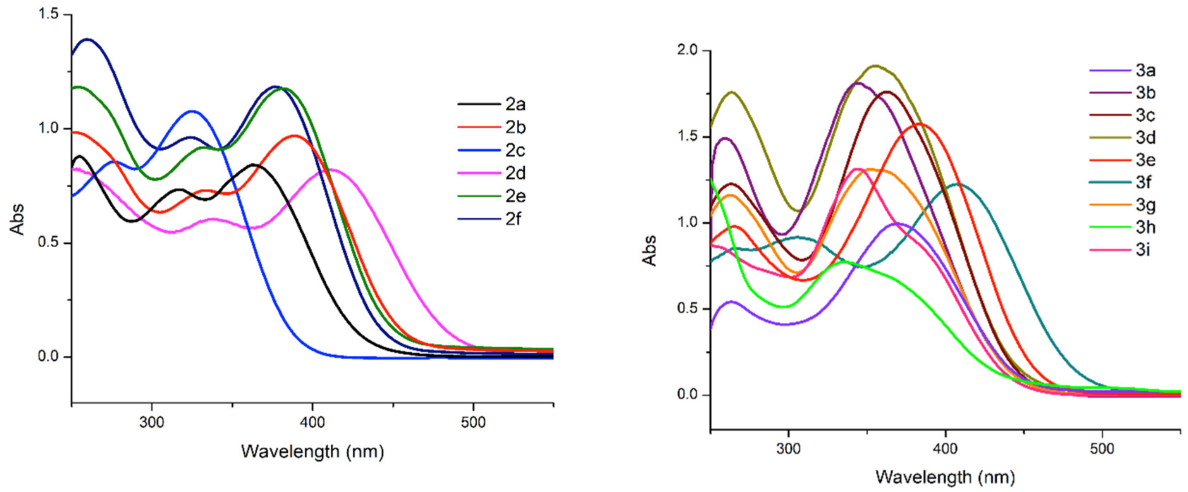
The diarylation could be obtained by increasing aryl bromides to 5 equivalents. Nine prepared compounds were synthesized and are showed in Scheme 3. The isolated yields varied from 31 to 66%, of which **3f** was obtained with the highest yield, while **3i** was isolated with the lowest yield. This result can be explained by the fact that electron-withdrawing substituents in aryl bromides led to easier oxidative additions of the palladium catalyst to the C–Br bond. The structures of all these compounds were confirmed by ^{1}H-NMR, ^{13}C-NMR and HRMS (see Supplementary Materials).



Scheme 3. Synthesis of diarylated diphenyldithienylethenes **3a–i**.

2.2. Photophysical Properties

Finally, in order to evaluate the photophysical properties of the mono- and diarylated DPDTEs, their UV-visible absorption and emission spectra were recorded in a chloroform solution at room temperature (Figure 1). The characteristic values, including λ_{abs} and λ_{em}, are listed in Table 2. The emission spectra of all these arylated DPDTE were characterized and shown in Figure 2, in which **2f** showed the highest intensive emission among all the synthesized compounds. These results suggested that the monoarylated products (**2a–f**) are more strongly emissive than the diarylated products (**3a–i**). This behavior could be explained by the fact that polarity of dissymmetric monoarylated DPDTEs is higher than that of the symmetric diarylated DPDTEs.



(**a**) (**b**)

Figure 1. Absorption spectra of the monoarylated DPDTEs (**2a**–**f**) (**a**) and diarylated DPDTEs (**3a**–**i**) (**b**) at 298 K in $CHCl_3$ solution (C = 10^{-5} M).

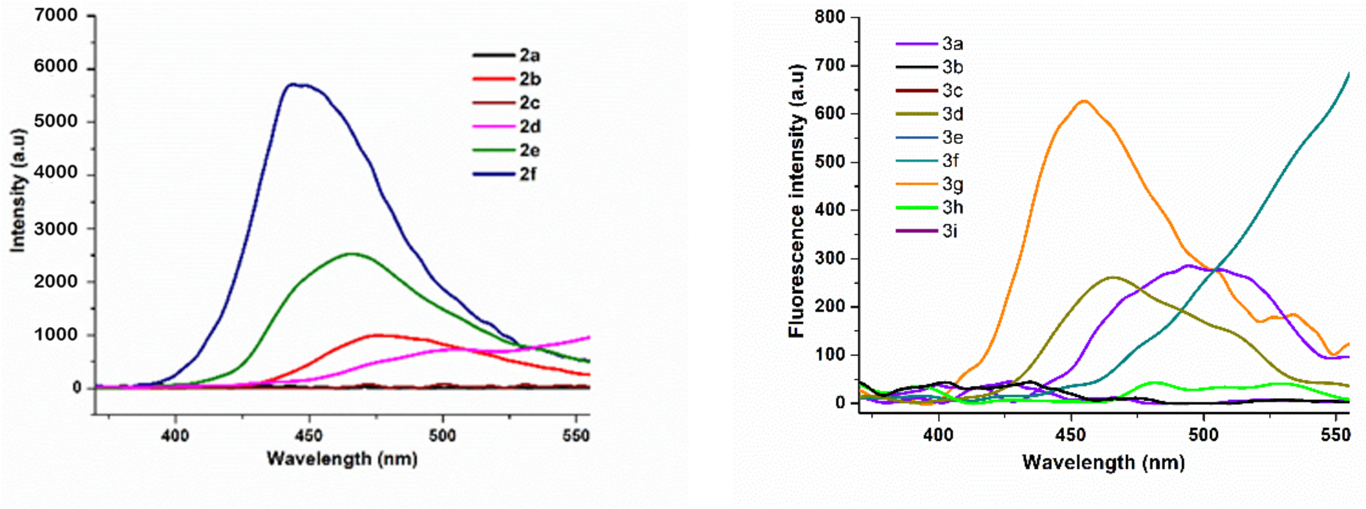
Table 2. Photophysical data of the arylated DPDTE (**2a**–**f**, **3a**–**i**).

	Absorption	**Emission at 298 K** [a]	
	λ_{abs} [a]/nm (ε 10^3/$M^{-1}cm^{-1}$)	λ_{em} [a]/nm	**Intensity(a.u)**
2a	256(73.5), 316(60.8), 363(70.4)	475	982.0
2b	334(18.1), 389(24.0)	476	1026.9
2c	277(21.4), 327(26.9)		<100
2d	337(25.0), 413(33.3)		<100
2e	253(25.0), 332(19.4), 385(24.4)	467	2536.7
2f	261(23.3), 323(16.2), 376(19.9)	446	5733.3
3a	263(21.8), 370(40.0)	495	284.8
3b	260(59.2), 344(72.5)		<100
3c	263(44.2), 362(62.9)		<100
3d	264(29.3), 357(31.9)		<100
3e	268(32.3), 384(52.7)		<100
3f	269(34.0), 306(36.6), 409(49.2)		<100
3g	263(29.0), 355(33.0)	452	621.7
3h	336(48.5)		<100
3i	253(36.2), 344(54.6), 385(36.5)		<100

[a] Measured in $CHCl_3$ solution at 298 K (C = 10^{-5} M), with 360 nm excitation.

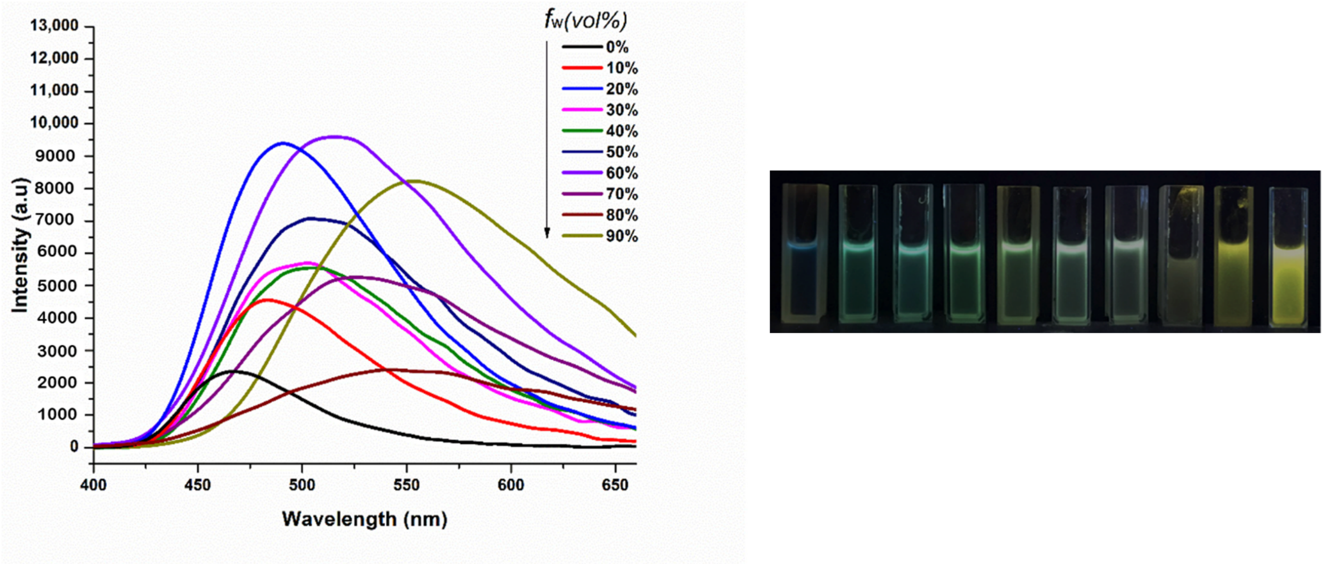
The aggregation-induced emissions of **2b** and **2e** are shown in Figures 3 and 4, respectively. A common feature of the electronic absorption spectra of the monoarylated DPDTEs is a set of three absorption bands characteristic of aromatic rings with intense and well-resolved absorption bands in the UV region (250–450 nm). However, spectrum **2c** has only two absorption bands in the spectrum cut-off. The ester is the weakest electron-withdrawing-group of the considered substituents, and **2c**'s three absorption bands do not shift to the longer wavelength as much as some other monoarylated DPDTEs do. Therefore, the band with the shortest wavelength falls outside the range of the screenshot diagram. Diarylated DPDTEs showed only two bands from 250 to 450 nm. This difference is due to the more symmetric structure of the diarylated derivatives in comparison to the monoarylated ones. Among those monoarylated DPDTEs, those with strong EWGs, such as **2b**, **2d**, **2e**, and **2f** showed increase in absorption intensity as well as in absorption wavelength due to the reduced-energy band gap between HOMO and LUMO of the molecules. Compound **2e** showed amazing fluorescence with increasing emission intensity: about 16-fold, from zero to about 17,500 a.u., while the percentage of water reached 90%. The emission color of

2e changed from blue to yellow and could be easily observed under UV light. In addition, its wavelength shifted from 450 to 545 nm, while for compound **2b**, when the H_2O ratio was increased, there was a gradual shift in emission wavelength. Interestingly, the color intensity increased from 2000 to 9000 a.u and was then reduced to 8200 a.u due to the quenching (ACQ) effect of aggregation. This aggregation may have been assisted by the hydrogen bonding of the gem-diol, which resulted from adding a water molecule to the aldehyde functional group.



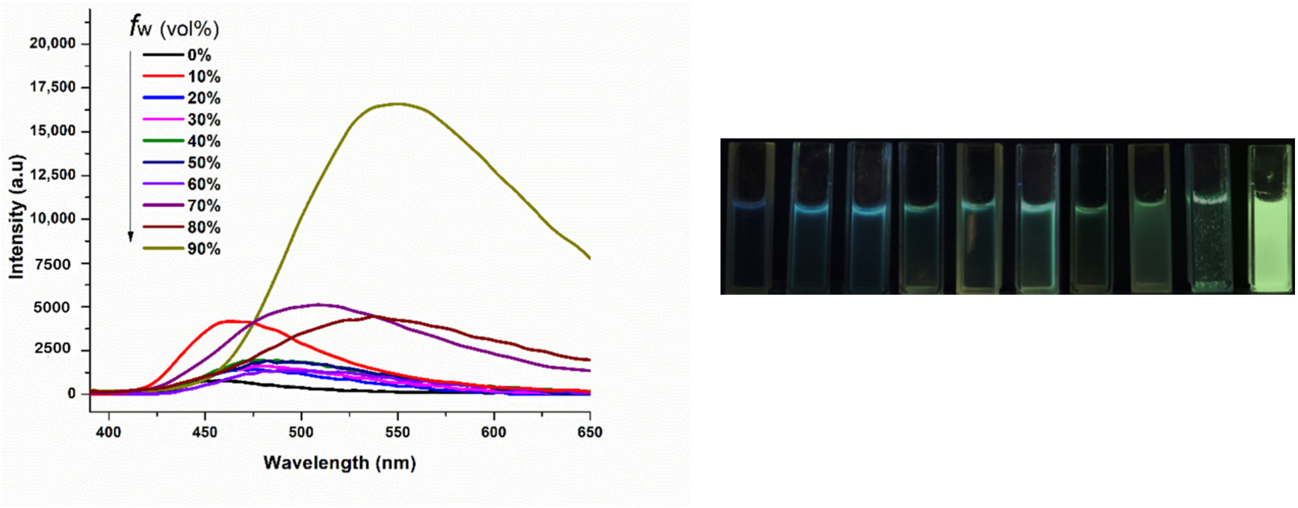
(**a**) (**b**)

Figure 2. Emission spectra of the monoarylated DPDTEs (**2a**–**f**) (**a**) and diarylated DPDTEs (**3a**–**i**) (**b**) in $CHCl_3$ at 298 K (C = 10^{-5} M) with λ_{ex} = 360 nm.



(**a**) (**b**)

Figure 3. (**a**) The AIE spectra of **2b** in THF/H_2O mixture, with λ_{ex} = 360 nm; (**b**) Photograph of **2b** in THF/H_2O mixture, under UV lamp (λ_{ex} = 365 nm).



(**a**) (**b**)

Figure 4. (**a**) The AIE spectra of **2e** in THF/H_2O mixture, with λ_{ex} = 360 nm; (**b**) Photograph of **2e** in THF/H_2O mixture, under UV lamp (λ_{ex} = 365 nm).

3. Materials and Methods

3.1. Materials

Reagents and solvents were obtained from commercial suppliers and used without further purification. Column chromatography was carried out using Merck Kieselgel 60 silica gel (particle size: 32–63 Å). Analytical TLC was performed using Merck precoated silica gel 60 F-254 sheets. All the C–H activation reactions were carried out under a nitrogen atmosphere. NMR spectroscopic data were acquired on Bruker Avance III spectrometer at 500 MHz for ^{1}H–NMR and 125 MHz for ^{13}C–NMR. HR–MS spectra were recorded on a 6500 series Q-TOF (Agilent) spectrometer. UV-Vis absorption spectra was measured on the UV-Vis Cary 60-Agilent spectrometer. Fluorescence spectra were recorded on Perkin Elmer FL 8500 spectrometer.

3.2. General Procedure for the CH Arylated Reaction

A suspension of DPDTE (69 mg, 0.2 mmol, 1.0 eq), $Pd(OAc)_2$ (1.0 mg, 0.006 mmol, 0.03 eq), KOAc (58 mg, 0.6 mmol, 3.0 eq), and 4-arylbromide (0.5 eq for monoarylation and 5.0 eq for diarylation) in degassed DMAc (5.0 mL) was stirred at 120 °C for 14 h under a nitrogen atmosphere. The insoluble impurities were filtered, and the combined filtrates were washed with water (3 × 30 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo to give a crude residue which was purified by column chromatography on silica gel (*n*-hexane) to give pure monoarylated (**2a–f**) and diarylated products (**3a–i**).

1-(2-(pyridine-4-yl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene **2a**: 40 mg (48%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 8.50 (2H, *d*, *J* = 6.5 Hz), *δ* 7.38 (2H, *d*, *J* = 6.0 Hz), *δ* 7.25–7.18 (10H, *m*), *δ* 7.15–7.13 (2H, *m*), *δ* 6.84–6.82 (2H, *m*), *δ* 6.76 (1H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 148.7, 144.8, 143.9, 143.3, 142.8, 142.7, 142.6, 140.4, 131.2, 131.1, 130.5, 129.9, 128.3, 128.0, 127.5, 127.3, 126.9, 126.7, 126.3, 125.9, 125.5, 119.7. HR-MS calcd for $C_{27}H_{20}NS_2$ ($[M+H]^+$): 422.1037, found: 422.1039.

1-(2-(4-formylphenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene **2b**: 44 mg (49%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 9.96 (1H, *s*), *δ* 7.81 (2H, *d*, *J* = 8.5 Hz), *δ* 7.60 (2H, *d*, *J* = 8.0 Hz), *δ* 7.26–7.14 (12H, *m*), *δ* 6.84 (2H, *d*, *J* = 3.0 Hz), *δ* 6.74 (1H, *d*, *J* = 3.5 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 191.4, 147.7, 145.0, 143.3, 143.0, 142.9, 142.8, 140.0, 134.9, 131.2, 130.6, 130.4, 129.9, 128.3, 128.0, 127.4, 127.2, 126.6, 126.3, 126.2, 125.7, 124.4. HR-MS calcd for $C_{29}H_{21}OS_2$ ($[M+H]^+$): 449.1034, found: 449.1064.

1-(2-(methyl 4-benzoate)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene **2c**: 42 mg (44%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.96 (2H, *d*, *J* = 8.5 Hz), *δ* 7.52 (2H, *d*, *J* = 8.5 Hz), *δ* 7.21–7.12 (12H, *m*), *δ* 6.83 (2H, *d*, *J* = 3.5 Hz), *δ* 6.72 (1H, *d*, *J* = 4.0 Hz), *δ* 3.91 (3H, *s*); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 166.8, 147.0, 145.1, 143.2, 143.0, 131.0, 130.7, 130.6, 130.2, 129.9, 128.6, 128.2, 128.0, 127.3, 127.1, 126.6, 126.3, 125.1, 123.8, 52.1. HR-MS calcd for $C_{30}H_{23}O_2S_2$ ([M+H]$^+$): 479.1139, found: 479.1136.

1-(2-(4-nitrophenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene **2d**: 44 mg (47%), orange solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 8.16 (2H, *d*, *J* = 9.0 Hz), *δ* 7.57 (2H, *d*, *J* = 9.0 Hz), *δ* 7.22–7.17 (10H, *m*), *δ* 7.14 (2H, *m*), *δ* 6.85–6.84 (2H, *m*), *δ* 6.75 (1H, *d*, *J* = 3.5 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 148.6, 146.4, 144.9, 143.7, 142.9, 142.8, 141.6, 140.5, 139.6, 131.3, 130.6, 129.9, 128.3, 128.0, 127.5, 127.3, 126.7, 126.3, 126.0, 125.6, 125.0, 124.3. HR-MS calcd for $C_{28}H_{19}NO_2S_2$ ([M]$^+$): 465.0857, found: 465.0822.

1-(2-(4-acetylphenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene **2e**: 38 mg (41%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.89 (2H, *d*, *J* = 8.5 Hz), *δ* 7.54 (2H, *d*, *J* = 8.5 Hz), *δ* 7.22–7.13 (12H, *m*), *δ* 6.84–6.83 (2H, *m*), *δ* 6.73 (2H, *d*, *J* = 4.0 Hz), *δ* 2.58 (3H, *s*, $-CH_3$); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 197.3, 147.2, 145.1, 143.1, 143.0, 142.9, 138.7, 135.6, 131.1, 130.6, 129.9, 129.0, 128.2, 127.9, 127.8, 127.3, 127.1, 126.6, 126.3, 125.2, 123.9, 26.5. HR-MS calcd for $C_{30}H_{23}OS_2$ ([M+H]$^+$): 463.1190, found: 463.1165.

1-(2-(4-nitrilphenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene **2f**: 45 mg (50%), orange solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.57 (2H, *d*, *J* = 8.5 Hz), *δ* 7.53 (2H, *d*, *J* = 8.5 Hz), *δ* 7.22–7.12 (12H, *m*), *δ* 6.85–6.83 (2H, *m*), *δ* 6.74 (1H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 147.9, 144.9, 143.4, 142.9, 142.8, 142.1, 138.5, 132.6, 131.1, 130.8, 130.6, 129.9, 129.8, 128.3, 128.0, 127.4, 127.2, 126.7, 126.3, 126.0, 125.6, 124.4, 118.9, 110.3. HR-MS calcd for $C_{29}H_{20}NS_2$ ([M+H]$^+$): 446.1037, found: 446.1021.

1,1-Di(2-(pyridine-4-yl)thien-5-yl)-2,2-diphenylethene **3a**: 49 mg (49%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 8.53 (4H, *brs*), *δ* 7.39 (4H, *d*, *J* = 4.5 Hz), *δ* 7.28 (2H, *d*, *J* = 4.0 Hz), *δ* 7.23–7.19 (10H, *m*), *δ* 6.83 (2H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 149.0, 148.0, 145.3, 142.4, 141.0, 131.5, 130.5, 128.3, 128.2, 127.8, 125.5, 125.3, 119.7. HR-MS calcd for $C_{32}H_{23}N_2S_2$ ([M+H]$^+$): 499.1303, found: 499.1291.

1,1-Di(2-(4-formylphenyl)thien-5-yl)-2,2-diphenylethene **3b**: 72 mg (65%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 9.96 (2H, *s*), *δ* 7.82 (4H, *d*, *J* = 8.5 Hz), *δ* 7.62 (4H, *d*, *J* = 8.0 Hz), *δ* 7.22–7.21 (12H, *m*), *δ* 6.82 (2H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 191.4, 147.0, 144.2, 143.2, 142.7, 139.9, 135.1, 131.4, 130.6, 130.4, 128.3, 128.1, 127.6, 125.7, 124.5. HR-MS calcd for $C_{36}H_{25}O_2S_2$ ([M+H]$^+$): 553.1296, found: 553.1309.

1,1-Di(2-(methyl 4-benzoate)thien-5-yl)-2,2-diphenylethene **3c**: 74 mg (61%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.97 (4H, *d*, *J* = 9.0 Hz), *δ* 7.53 (4H, *d*, *J* = 9.0 Hz), *δ* 7.21–7.19 (10H, *m*), *δ* 7.15 (2H, *d*, *J* = 4.0 Hz), *δ* 6.79 (2H, *d*, *J* = 4.0 Hz), *δ* 3.91 (6H, *s*); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 166.7, 146.4, 143.6, 143.5, 142.9, 138.5, 131.3, 130.6, 130.2, 128.7, 128.2, 127.4, 126.6, 125.1, 123.9, 52.1. HR-MS calcd for $C_{38}H_{28}O_4S_2$ ([M]$^+$): 612.1429, found: 612.1421.

1,1-Di(2-(4-nitrophenyl)thien-5-yl)-2,2-diphenylethene **3d**: 73 mg (62%), orange solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 8.18 (4H, *d*, *J* = 9.0 Hz), *δ* 7.59 (4H, *d*, *J* = 8.0 Hz), *δ* 7.24–7.19 (12H, *m*), *δ* 6.83 (2H, *d*, *J* = 3.5 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 147.7, 147.6, 146.6, 144.9, 142.5, 142.1, 140.3, 131.5, 130.5, 128.3, 127.8, 125.7, 125.6, 125.1, 124.4. HR-MS calcd for $C_{34}H_{23}N_2O_4S_2$ ([M+H]$^+$): 587.1099, found: 587.1078.

1,1-Di(2-(4-acetylphenyl)thien-5-yl)-2,2-diphenylethene **3e**: 68 mg (59%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): *δ* 7.91 (4H, *d*, *J* = 8.5 Hz), *δ* 7.56 (4H, *d*, *J* = 8.5 Hz), *δ* 7.17 (2H, *d*, *J* = 4.0 Hz), *δ* 7.23–7.19 (10H, *m*), *δ* 6.80 (2H, *d*, *J* = 4.0 Hz), *δ* 2.58 (6H, *s*); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): *δ* 197.2, 146.6, 143.8, 143.4, 142.8, 138.6, 135.7, 131.3, 130.6, 129.0, 128.2, 127.5, 125.3, 124.0, 26.5. HR-MS calcd for $C_{38}H_{28}O_2S_2$ ([M]$^+$): 580.1531, found: 580.1506.

1,1-Di(2-(4-cyanophenyl)thien-5-yl)-2,2-diphenylethene **3f**: 72 mg (66%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): δ 7.59 (4H, *d*, *J* = 8.5 Hz), δ 7.54 (4H, *d*, *J* = 8.5 Hz), δ 7.23–7.19 (10H, *m*), δ 7.16 (2H, *d*, *J* = 4.0 Hz), δ 6.80 (2H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): δ 147.1, 144.4, 142.6, 142.5, 138.4, 132.6, 131.4, 130.5, 128.3, 127.7, 125.7, 125.5, 124.5, 118.8, 110.5. HR-MS calcd for $C_{36}H_{22}N_2S_2$ ($[M]^+$): 546.1224, found: 546.1218.

1,1-Di(2-(4-trifluoromethylphenyl)thien-5-yl)-2,2-diphenyl ethene **3g**: 70 mg (55%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): δ 7.56 (8H, *s*), δ 7.22–7.19 (10H, *m*), δ 7.13 (2H, *d*, *J* = 4.0 Hz), 6.80 (2H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): δ 146.3, 143.7, 143.0, 142.8, 137.6, 131.2, 130.6, 129.3, 129.2, 129.0, 128.2, 127.5, 125.9, 125.8, 125.5, 123.8, 29.3. HR-MS calcd for $C_{36}H_{22}F_6S_2$ ($[M]^+$): 632.1067, found: 632.1065.

1,1-Di(2-(3-formylphenyl)thien-5-yl)-2,2-diphenyl ethene **3h**: 67 mg, 61%), yellow solid. ^{1}H-NMR δ_H (500 MHz, CDCl3, δ ppm): δ 10.01 (2H, *s*), δ 7.98 (2H, *t*), δ 7.74–7.72 (4H, *m*), δ 7.49 (2H, *t*, *J* = 7.5 Hz), δ 7.22–7.20 (10H, *m*), δ 7.14 (2H, *d*, *J* = 4.0 Hz), δ 6.80 (2H, *d*, *J* = 4.0 Hz); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): δ 192.0, 146.0, 143.5, 143.1, 142.9, 136.9, 135.3, 131.2, 131.1, 130.6, 129.5, 128.5, 128.2, 127.4, 126.4, 125.9, 123.4. HR-MS calcd for $C_{36}H_{24}O_2S_2$ ($[M]^+$): 552.1218, found: 552.1181.

1,1-Di(2-(4-methoxyphenyl)thien-5-yl)-2,2-diphenyl ethene **3i**: 34 mg, 31%), yellow solid. ^{1}H-NMR δ_H (500 MHz, $CDCl_3$, δ ppm): δ 7.41 (4H, *d*, *J* = 9.0 Hz), δ 6.85 (4H, *d*, *J* = 8.5 Hz), δ 6.92 (2H, *d*, *J* = 4.0 Hz), δ 7.23–7.16 (10H, *m*), δ 6.73 (2H, *d*, *J* = 3.5 Hz), δ 3.81 (6H, *s*); ^{13}C-NMR δ_C (125 MHz, $CDCl_3$, δ ppm): δ 159.2, 144.8, 144.0, 143.4, 131.0, 130.7, 128.2, 128.1, 127.5, 127.3, 127.0, 126.8, 125.8, 121.3, 114.2, 55.4. HR-MS calcd for $C_{36}H_{28}O_2S_2$ ($[M]^+$): 556.1531, found: 556.1507.

4. Conclusions

In conclusion, we developed an efficient palladium-catalyzed direct arylation of DPDTE with various aryl bromides. This efficient ligand-free reaction conditions can tolerate various functional groups. Therefore, our methodology is a useful tool for adjusting the polarity of DPDTE and to improve its fluorescent intensity. The photophysical property of the two monoarylated DPDTEs **2b** and **2e** were also characterized. In addition, the two diarylated DPDTEs **3a** and **3f** are undergoing further self-assembly study with metal ions that enhance their fluorescence since these DPDTEs contain potential coordination sites.

Supplementary Materials: The following is available online: supporting information with NMR spectra of compounds **2a–f**, **3a–i**.

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