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ARTICLE TYPE

# Highly Efficient and Facile Alkylation of 4*H*-Cyclopenta [2,1-b:3,4-b']dithiophene in Water

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A new and highly convenient method to perform alkylation of 4*H*-Cyclopenta [2,1-b:3,4-b']dithiophene (CPDT) in aqueous condition is reported. This method was also extended to successfully perform alkylation of 2,6-dibromo-4*H*-cyclopenta [2,1-b:3,4-b']dithiophene for the first time. This facile method has several advantages such as the exclusive use of water instead of high boiling toxic solvents, simple separation of the defect free dialkylated CPDT product and the use of mild reaction conditions. Despite using mild reagents and reaction conditions, to our delight, very high yields of up to 98% pure dialkylated CPDT products are obtained much more readily by this method in lesser time than literature procedures. The isolated products were identified by HRMS and solution NMR measurements to be solely the desired dialkylated product with the alkyl halides used here.

## Introduction

Organic electronic devices based on heterocyclic compounds, especially, thiophene derivatives have gained huge popularity since the past few decades due to their tunable structure as well as excellent photophysical, electrochemical, thermal and solution processable parameters.[1-17] These materials enable wide variety of functionalization and low cost light weight fabrication process on large-area substrates along with mechanical flexibility.[18]

Although thiophene oligomers and polymers have received immense attention, fused thiophenes are now gaining prominence due to their superior photophysical and device performances.[1-6,16] Fused bithiophenes such as, 4*H*-Cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) are structural analogs of fluorene molecule, and the "two biphenyl rings" in fluorene molecule conjoined with a methylene carbon bridge are replaced by "two thiophene rings". CPDT, which consists of rigidly planar bithiophene units with a $sp^3$-hybridized methylene bridge allows functionalization at the 4-position resulting in higher solubility and enhancing the processing ability in the resulting polymer.

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Electronic Supplementary Information (ESI) Available: Experimental details and scanned spectra of all the newly synthesized compounds are included.

4*H*-Cyclopenta[2,1-b:3,4-b']dithiophene has major application as semiconducting material out of the six possible isomers.[2-6,9-12] 4,4'-dialkyl CPDT, regarded as a fused-ring analogue of 3-alkyl thiophene and structural analogue of dialkylfluorene, possesses several advantages over both these systems.[8] In π-conjugated (semi) conducting copolymer systems, the 4,4'-dialkyl CPDT based oligomers and polymers having electron rich (donor) moieties, copolymerized with electron poor (acceptor) moieties are known to have tunable and narrow band gaps.[3-4] Hence, the development of an appropriate donor group is extremely critical to balance several device characteristics such as the charge carrier, trapping effects, band energetics and so on. 4,4'-dialkyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophenes have emerged as a key building block for polymer based materials in numerous applications such as organic field effect transistors (OFET),[4] organic solar cells,[3,9-12] optical sensors[5] and organic light-emitting diodes.[6]

Various synthetic methods have been utilized in the past to substitute the 4,4'-position of CPDT (Figure 1) by linear and branched alkyl chains to enhance their solubility and processability. These include mainly symmetrically,[7-12] asymmetrically,[14] in-plane,[15] and substituted C-4 alkylation reactions of CPDT. Few reports on the symmetrically substituted CPDT and their application in optoelectronic devices have also been demonstrated with superior device characteristics compared to polythiophenes.[3-4,16] It was observed that all these prior methods utilized high boiling organic solvents such as DMF, DMSO, toluene, etc. to perform the dialkylation of CPDT.[8-10,12] These reactions were reported to be air and water sensitive, harsh conditions such as hazardous and strong acids or strong bases were applied and in few cases metal catalysts were used to obtain the desired dialkylated products.[7-14] The first dialkylation of 4*H*-cyclopenta[2,1-b:3,4-b']dithiophene reported in 1994, used

lithiation method to obtain the dialkylated CPDT product in 35-47% yields.[7] Further improvements in the above method by using KOH in DMSO with catalytic amount of KI, NaI or KF resulted in 65-85% yields.[8-10] The use of NaH in DMF with KI was also reported to give desired dialkylated CPDT product with 57 % yield.[11] The dialkylation of CPDT using aq. KOH and TBAI in toluene as a solvent gave ~62 % yield.[12] These dialkylated CPDT yields could be improved up to 95 % in the presence of KOH and KI in DMSO.[13] The two step synthesis of dialkylated CPDT from 3-bromo-2,2'-bithophene by using n-BuLi and $H_2SO_4$ in 70% yields has also been reported.[14a] These developments over the years are proof of the enormous interest that CPDT molecule has generated. Despite the growing importance of these CPDT derivatives in numerous interdisciplinary applications, it is observed that all the synthetic routes use high boiling solvents, hazardous chemicals and adverse reaction conditions that are, in several cases, also air and water sensitive and are too expensive for practical purposes. Moreover, the formation of 4-alkyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene as the major impurity are very common by these methods.[8] The formation of these mono-substituted product even in small amounts are detrimental for unwanted impurity formation during device operation, which easily undergo oxidized product during exposure to oxygenated environment or during device fabrication or even when exposed to light.[16] Hence, these unfavorable synthetic routes having several drawbacks such as the use of expensive as well as harsh reagents along with high boiling solvents also require additional separation steps which make them less viable, incur higher costs of reactions, need additional precautions and special conditions for making defect-free dialkylated products. This encouraged us to investigate a simple route for synthesizing the dialkylated CPDT.

## Results and discussion

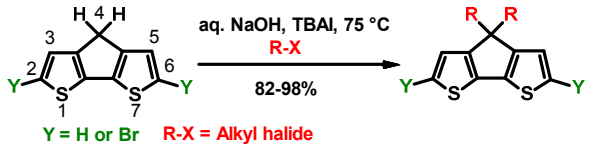


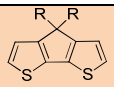
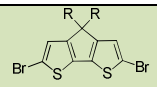
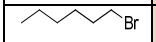
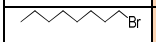
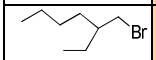
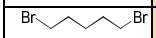
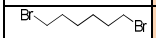
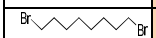
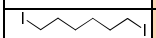
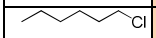
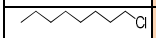

Figure 1: General synthetic scheme for synthesis of 4,4'-dialkylation of CPDT derivatives.

The development of new organic materials for optoelectronic device application relies on the improvement in the existing functionalization routes on the widely used aromatic and heterocyclic compounds. Benzene and thiophene are electron-rich units. Comparatively, thiophene has more electron-donating ability and strong electron-delocalization capability than benzene. Bithiophene units have more planarity or less rigidity compared to biphenyl units.[3e] In order to achieve superior polymer solubility and processability parameters, the fluorene and CPDT units with $sp^3$-hybridized carbon at the methylene bridge position are functionalized. Considering this requirement and the major drawbacks prevailing in the existing methods, we were encouraged to develop dialkylated CPDT by an alternate route that would be mild and friendly to the environment, reduce the cost, be safe and easier to perform, and yet high yields of the desired defect-free CPDT derivative could be accessible. In this manuscript, we report a facile, solvent free and high yielding method for the dialkylation of CPDT and 2,6-dibromo CPDT. To the best of our knowledge, there are no reports for the dialkylation reaction of 2,6-dibromo substituted CPDT (Figure 1, X = Br). For OPV and OFET devices, all existing methods report the alkylation of CPDT, followed by the bromination reaction to obtain the desired dialkylated CPDT with necessary bromides.[3-4,16] Our initial attempts, following an earlier reported procedure,[8] applied for the dialkylation of CPDT as well as 2,6-dibromo CPDT was partially successful, but the obtained yields of the products were very less (maximum ~40 %). Hence, it was necessary to develop an alternate and efficient route for obtaining dialkylated CPDT in high yields to realize higher quantities of functionalized CPDT for practical applications. Therefore, we performed the dialkylation reaction under various conditions to substantiate and overcome the basic problems and drawbacks in the existing reactions. Our attempts to perform dialkylation in atmospheric conditions resulted in the formation of a mixture of unwanted products in major amounts. The same reaction was now attempted after performing careful degassing of the reaction mixture comprising three freeze-thaw cycles. Stirring the reaction at room temperature for extended time did not give desired dialkylated CPDT which prompted us to slowly raise the temperature. During the course of 5 minutes we observed that the color of the reaction mixture changed into greenish black at 75 °C, however, no starting material was observed in the reaction mixture after ~3 h. We further continued performing the reaction using KF, KI, NaI reagents and DMSO, DMF, toluene solvent conditions and obtained product in 65-85 % yield.[8-10,12] However, separation of the product from these solvents was very tedious and loss of product while isolation was common. In order to overcome this isolation problem and make the reaction more viable, mild and environmentally friendly, the dialkylation reaction was performed in the absence of organic solvent. We observed that the dialkylated CPDT product yields obtained by this method were ~96 % with 1-bromo octane. The yield of CPDT dialkylation reaction could be improved above 80 % with all the alkyl halides, including chloro alkanes on addition of a phase transfer catalyst (PTC) such as tetrabutylammoniumiodide (TBAI). This modification in the reaction conditions resulted in the development of highly successful dialkylation reaction of CPDT without the use of any organic solvents, metal catalyst, inert gases, strong acids, and high pressure/temperature, yet 82-96 % (**Table 1**) isolated yield of the desired product 4,4'-dialkyl CPDT could be achieved with a variety of alkyl halides including chloro alkanes.

The initial reactions were performed by utilizing 5mL 50% aq. NaOH and TBAI and different 1°-alkyl halides at moderate temperature of ~35-40 °C assuming that the desired dialkylated product would be obtained at room temperature or in mild conditions. It was however, observed that the yield of dialkylated CPDT was less than 50 % with nearly all the alkyl halides. Raising the reaction temperature up to 75 °C enhanced the dialkylated CPDT yields up to 96 %. Before addition of the alkyl halide, the reaction mixture was thoroughly degassed by performing three freeze-thaw degassing repetitions, as mentioned above, to ensure the complete removal of oxygen. The reaction

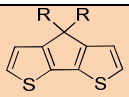
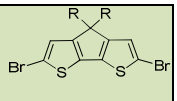
conditions were also optimized for appropriate base and their concentration. Diverse phase transfer catalysts and their quantities, the reaction temperature and time were also optimized by attempting dialkylation reactions with different alkyl halides.

**Table 1** Yields obtained for alkylation of CPDT, alkylation of 2,6-dibromo CPDT with various alkyl halides in aq. NaOH, TBAI as PTC at 75 °C.

| R-X(alkyl halide) | Entry |  Time (min) | Isolated Yield (%) | Entry |  Time (min) | Isolated Yield (%) |
|---|---|---|---|---|---|---|
|  | 1a | 150 | 94 | 1k | 45 | 96 |
|  | 1b | 150 | 96 | 1l | 45 | 98 |
|  | 1c | 150 | 90 | 1m | 45 | 92 |
|  | 1d | 150 | 88 | 1n | 45 | 91 |
|  | 1e | 180 | 82 | 1o | 45 | 83 |
|  | 1f | 180 | 92 | 1p | 45 | 94 |
|  | 1g | 180 | 90 | 1q | 45 | 91 |
|  | 1h | 180 | 90 | 1r | 45 | 92 |
|  | 1i | 240 | 82 | 1s | 105 | 84 |
|  | 1j | 240 | 84 | 1t | 105 | 85 |

The reaction of CPDT with linear and branched alkyl chains having chloro-, bromo- and iodoalkyl chains were attempted under similar reaction conditions. To perform dialkylation of CPDT, bromo alkanes are the most preferred substrates due to their better reactivity and lower costs compared to chloro- and iodo-alkanes. We report seven different types of bromo alkanes, which include linear alkyl chain, branched chain and dibromo-substituted alkyl chain derivatives (Table 1). Among these substrates, the highest yield of up to 96 % was obtained for the alkylation of CPDT with 1-bromo octane (Table 1, entry 1b). Subsequently, 1-bromo hexane (94 %), 1-bromo decane (90 %), 2-ethylhexyl bromide (88 %), 1,6-dibromo hexane (92 %), 1,5-dibromo pentane (82 %) and 1,8-dibromo octane (90 %) also reacted efficiently with CPDT to form their respective dialkylated CPDT products in high yields (Table 1, entry 1a to 1g). The reaction of CPDT with iodo and chloro terminated alkyl chains have never been attempted previously. We observed that, under similar reaction conditions, the yields of dialkylated CPDT with 1,6-diiodo hexane (90 %) were also very high (Table 1, entry 1h). The reaction of CPDT with lesser reactive chloro alkanes such as 1-chloro hexane (82 %) and 1-chloro octane (84 %) also gives good dialkylated CPDT yields within 4h under the same reaction conditions (Table 1, entry 1i and 1j). The above optimized reaction conditions (Table 1) of CPDT were also extended to perform the dialkylation of 2,6-dibromo CPDT. It was observed that the dialkylation of 2,6-dibromo CPDT with the alkyl halide substrates examined here required very less time to form the desired dialkylated product and nearly all the reactions confirmed that this dibromo CPDT had been completely reacted within an hour of the reaction (except with chloro halides) (Table 1, entry 1k and 1t). Due to the presence of the two electron withdrawing bromide groups on CPDT the reactivity of this substrate was higher compared to the unsubstituted CPDT. This trend is observed for the reactions with all the alkyl halide substrates with 2,6-dibromo CPDT under the same reaction conditions as reported for CPDT. The highest yield of 98 % in the case of 2,6-dibromo CPDT was also obtained on reacting with 1-bromooctane (Table 1, entry 1l). In the table 1, right columns, we have summarized the reaction time and the isolated yield of the dialkylation reaction products obtained with 2,6-dibromo CPDT. All the pure dialkylated products obtained above were extensively characterized by $^{1}$H NMR, $^{13}$C NMR, and high resolution mass spectroscopy (HRMS).(ESI, Figures S1-S48). We also observed that compared to all other dialkylation reactions of CPDT with dibromo alkanes, 1,5-dibromo alkane gives lesser yields of 82 % due to the formation of an unexpected byproduct occurring due to the attack of both the terminal bromine of this 1,5-dibromo pentane alkyl chain at the 4,4'-position of CPDT[14a,17] as well as 2,6-dibromo CPDT, which gets converted via ring cyclization into a stable six member ring. The byproduct 2,6-dibromo spiro[4,5] ([2,1-b; 3,4-b']dithieno)decane product was well characterized by $^{1}$H and $^{13}$C NMR, M.P. as well as single crystal X-ray crystallography analysis. (ESI Figures S49-S51).

**Table 2** Comparative reactivity study of CPDT and 2,6-dibromo CPDT alkylation with 1-bromooctane, TBAI (PTC) in presence of different types of base at 75 °C.

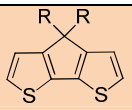
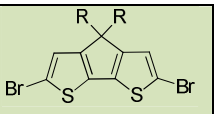
| Type of Base | Entry |  Time (min) | Isolated yield (%) | Entry |  Time (min) | Isolated yield (%) |
|---|---|---|---|---|---|---|
| NaOH | 2a | 150 | 96 | 2g | 45 | 98 |
| KOH | 2b | 150 | 95 | 2h | 45 | 96 |
| $K_2CO_3$ | 2c | 360 | 35 | 2i | 180 | 40 |
| $Na_2CO_3$ | 2d | 420 | 30 | 2j | 180 | 30 |
| $CH_3CO$ OK | 2e | 720 | X | 2k | 360 | X |
| No base | 2f | 1440 | X | 2l | 420 | X |

X = No reaction

Table 1 indicates that all the dialkylation reactions with CPDT as well as 2,6-dibromo CPDT were successful in 50 % aq. NaOH without the use of any additional organic solvents. Further, dialkylation of CPDT and 2,6-dibromo CPDT in the presence of various bases such as KOH, $K_2CO_3$, $Na_2CO_3$ and potassium acetate were also attempted with 1-bromooctane and TBAI (**Table 2**). It was observed that the dialkylated CPDT yields obtained with aq. KOH were nearly identical (table 2 entry 2b) to those obtained with aq. NaOH, however, very low yields of ~30-40 % were obtained in $K_2CO_3$ and $Na_2CO_3$ (table 2 entry 2c and 2d), whereas, no dialkylated CPDT product was obtained with potassium acetate (table 2 entry 2e). Dialkylation reactions performed in the absence of base with CPDT and 2,6-dibromo

CPDT did not give any product (table 2 entry 2f). This indicates that choosing an appropriate base is crucial for obtaining high dialkylation yields in shorter time.

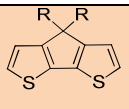
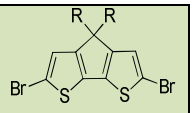
**Table 3** Comparative reactivity study of CPDT and 2,6-dibromo CPDT alkylation with 1-bromooctane and TBAI in presence of different quantities of aq. NaOH at 75 °C.

| Quantity of aq. NaOH | Entry |  | | Entry |  | |
|---|---|---|---|---|---|---|
| | | Time (min) | Isolated yield (%) | | Time (min) | Isolated yield (%) |
| 10 % | 3a | 420 | 40 | 3g | 240 | 45 |
| 20 % | 3b | 420 | 48 | 3h | 240 | 55 |
| 30 % | 3c | 360 | 65 | 3i | 180 | 70 |
| 40 % | 3d | 300 | 80 | 3j | 180 | 85 |
| 50 % | 3e | 150 | 96 | 3k | 45 | 98 |
| 60 % | 3f | 150 | 96 | 3l | 45 | 98 |

We have also optimized the quantity of aq. NaOH required for these reactions by reducing and increasing the quantity under identical reaction parameters (**Table 3**). It was observed that on decreasing the quantity of base from 50 % (w/w in water) to 40 %, 30 %, 20 % and 10 %, there was a significant drop in the desired dialkylated product to 80 %, 65 %, 48 % and 40 % under similar reaction conditions (Table 3 entry 3a to 3e). Further, increasing the quantity of base above 50 % did not alter the reaction yield or reduce the time of reaction (Table 3 entry 3f). Hence, all the reactions were performed in 50 % aq. NaOH. The effect of different type of bases on the dialkylated product yield with 2,6-dibromo CPDT as well as the quantity of NaOH are presented in table 2 and table 3. The reaction time and isolated yield summarized in these two tables confirm that 50 % aq. NaOH solution is appropriate for these dialkylation reaction with both CPDT as well as 2,6-dibromo CPDT.

The quantity and type of PTC also had a significant influence in obtaining the dialkylated products with these two CPDT derivatives in high yields. It was observed that the highest yield of 96 % and 98 % dialkylated CPDT and dialkylated 2,6-dibromo CPDT products were obtained with TBAI (**Table 4** entry 4a, 4h) in 50 % aq. NaOH. The reaction of 1-bromooctane with CPDT and 2,6-dibromo CPDT in presence of tetrabutylammoniumbromide (TBAB) gave 92 % of desired dialkylated product (Table 4 entry 4b, 4i) in 240 min and 80 min respectively. However, the dialkylated CPDT product yields obtained with tetrabutylammonium chloride (TBAC) and tetrabutylammonium fluoride (TBAF) were reduced to 70-75 % and 60-65 % respectively (Table 4 entry 4c, 4d, 4j and 4k) with the reaction taking up to 120-420 min to complete. The use of anionic and neutral surfactants such as SDS, and 15-crown-5 gave negligible to poor yields (15-40 %) under similar reaction conditions (Table 4 entry 4e, 4f, 4k and 4m). The dialkylation reaction with both CPDT as well as 2,6-dibromo CPDT did not proceed when performed in the absence of phase transfer catalyst (Table 4 entry 4g) indicating the vital role of phase transfer catalyst in this reaction.

**Table 4** Comparative reactivity study of CPDT and 2,6-dibromo CPDT alkylation with 1-bromooctane in presence of different types of PTCs in aq. NaOH at 75 °C. TBA-Tetrabutylammonium salts of halides.

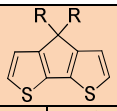
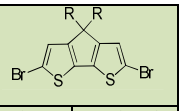
| Phase-transfer Catalyst (PTC) | Entry |  | | Entry |  | |
|---|---|---|---|---|---|---|
| | | Time (min) | Isolated Yield (%) | | Time (min) | Isolated Yield (%) |
| TBAI | 4a | 150 | 96 | 4h | 45 | 98 |
| TBAB | 4b | 240 | 92 | 4i | 80 | 92 |
| TBAC | 4c | 360 | 70 | 4j | 120 | 75 |
| TBAF | 4d | 420 | 60 | 4k | 180 | 65 |
| 15-crown-5 | 4e | 540 | 35 | 4k | 240 | 40 |
| Sodium dodecyl sulphate (SDS) | 4f | 420 | 15 | 4m | 180 | 15 |
| No PTC | 4g | 720 | X | 4n | 360 | X |

X = No reaction

Table 4 confirms that dialkylation of CPDT and 2,6-dibromo CPDT reactions with TBAI were most efficient and high yields of the desired dialkylated products are obtained in lesser reaction time compared to all other PTCs examined here. A general trend observed in these reactions indicated that the iodide containing PTC were most efficient compared to bromide, chloride and fluoride. The use of 15-crown-5 and SDS gave very less product yields requiring extended reaction time whereas reactions performed in the absence of PTC did not yield any dialkylated CPDT products.

After establishing that TBAI is the most suitable PTC for the dialkylation of CPDT and 2,6-dibromo CPDT, we investigated the accurate quantity that would be required for the best product yields. For optimization of the quantity of PTC, different mol % of TBAI was utilized in these reactions. The **table 5** depicts that 20 mol % of TBAI was sufficient for the successful dialkylation CPDT reactions. On adding 2.5 mol % of TBAI resulted in the formation of dialkylated CPDT and dialkylated 2,6-dibromo CPDT in 55-60 % yields (Table 5 entry 5a) in (480 minutes) 8 hours.Increasing the quantity of TBAI to 5 mol % and 7.5 mol % helped in enhancing the yields up to 80%, however, (480 minutes) 8 hours were required to achieve this yield (Table 5 entry 5b and 5c).A significant drop in reaction time as well as increase in the dialkylated product yields with both CPDT as well as 2,6-dibromo CPDT was achieved on increasing the quantity of TBAI up to 10 mol %.On further increasing the TBAI quantity to 20 mol % gave the maximum yield of 96-98% within 150 min (Table 5 entry 5e and 5l). Adding greater than 20 mol % of TBAI did not enhance the yields of desired product or reduce the reaction time (Table 5 entry 5e, 5f, 5g, 5l, 5m, and 5n).

**Table 5** Comparative reactivity study of CPDT and 2,6-dibromo CPDT alkylation with 1-bromooctane in presence of different quantities of TBAI at 75 °C.

| Different mol % of TBAI | Entry |  | | Entry |  | |
|---|---|---|---|---|---|---|
| | | Time (min) | Isolated Yield (%) | | Time (min) | Isolated Yield (%) |
| 2.5 | 5a | 480 | 55 | 5h | 240 | 60 |
| 5 | 5b | 480 | 70 | 5i | 240 | 75 |
| 7.5 | 5c | 480 | 78 | 5j | 240 | 80 |
| 10 | 5d | 240 | 92 | 5k | 120 | 95 |
| 20 | 5e | 150 | 96 | 5l | 45 | 98 |
| 50 | 5f | 150 | 96 | 5m | 45 | 98 |
| 100 | 5g | 150 | 96 | 5n | 45 | 98 |

## Conclusion

The introduction of dialkyl groups in 4*H*-Cyclopenta [2,1-b:3,4-b']dithiophene (CPDT) is the first step in achieving its solubility in various solvents for further functionalization reaction as well as their solution processing properties during optoelectronic device fabrication or sensor application. We developed a facile and highly economical methodology for the dialkylation of 4*H*-cyclopenta[2,1-b:3,4-b']dithiophene. This reaction avoided the use of any organic solvents, metal catalysts and no additional inert gases were applied while performing these reactions, yet high yield of up to 96% dialkylated CPDT were obtained. Furthermore, this methodology could also be extended, for the first time, to perform dialkylation of 2,6-dibromo CPDT under similar mild conditions. The yields of dialkylated product with 2,6-dibromo CPDT were even higher and required very less time to complete as compared to unsubstituted CPDT. 50 % aqueous NaOH and 20 mol % TBAI as phase transfer catalyst were found to be the most optimum to obtain the desired products. Dialkylation using even chloro alkanes, bromo and dibromo alkanes, and diiodo alkanes gave high yields with both CPDT and 2,6-dibromo CPDT. Importantly, these reactions work best in the absence of oxygen, whereas presence of water has virtually no effect on the reaction, thereby facilitating the reaction in aqueous medium. This simple methodology will facilitate the development and expansion of this environmentally friendly reaction and these fused thiophene derivatives in various interdisciplinary applications.

## Experimental Section:

**Materials:** Alkyl halides, CPDT and tetrabutylammonium halides, Milli-Q grade water, distilled solvents for workup and purification process. 4*H*-Cyclopenta [2,1-b:3,4-b']dithiophene and 2,6-dibromo-4*H*-Cyclopenta [2,1-b:3,4-b']dithiophene was purchased from Lumtech, Taiwan.

**General consideration:**

Compounds were purified by column chromatography using Silica Gel (60-120 mesh) with hexane as an eluent. $^1$H NMR (400 MHz and 600 MHz) and $^{13}$C NMR (100 MHz and 150 MHz) were recorded using $CDCl_3$ as solvent. Chemical shifts (δ) are reported in parts per million (ppm), internal reference (0.05% to 1 %) tetramethylsilane. Coupling constants (J) are reported in Hz singlet (s), doublet (d), triplet (t), multiplet (m), or broad (br). High resolution mass spectra were recorded on a Micromass Q-TOF ESI-MS instrument (model HAB273), X-ray data were collected on a diffractometer equipped with a CCD area detector using Mo.

*General Procedure Followed for the Dialkylation of 4H-Cyclopenta [2,1-b:3,4-b']dithiophene (CPDT).*

CPDT (0.2 g, 1.12 mmol), freshly prepared 50% aq. NaOH, and phase transfer catalyst tetrabutylammonium iodide (0.08 g, 20 mol %) were added into a round bottom flask. The flask was degassed thrice by applying freeze-thaw cycles to remove trace amounts of oxygen completely, followed by alkyl halide (2.8 mmol) addition via syringe (degassed) and the mixture heated at 75 °C continuously for 150-240 min. The reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum, and the crude was purified via column chromatography over silica / hexane.

*General Procedure Followed for the Dialkylation of 2,6-dibromo-4H-Cyclopenta [2,1-b:3,4-b']dithiophene (Br-CPDT)*

2,6-dibromo-4*H*-Cyclopenta [2,1-b:3,4-b']dithiophene (Br-CPDT) (0.2 g, 0.60 mmol), freshly prepared 50% aq. NaOH, and phase transfer catalyst tetrabutylammonium iodide (0.04 g, 20 mol %) were added into a round bottom flask. The flask was degassed thrice by applying freeze-thaw cycles to remove trace amounts of oxygen completely, followed by alkyl halide (1.48 mmol) addition via syringe (degassed) and the mixture heated at 75 °C continuously for 45-105 min. The reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum, and the crude was purified via column chromatography over silica / hexane.

*4,4'-Dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1a).*[7,9]

Yield: 0.365 g (94 %) as a light yellow color liquid. $^1$H NMR (600 MHz, $CDCl_3$): δ 7.10(d, 2H), 6.92(d, 2H), 1.84(m, 4H), 1.22(m, 4H), 1.14(m, 8H), 0.88(m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.32, 137.01, 124.61, 121.83, 53.44, 37.97, 31.85, 29.92, 24.70, 22.89, 14.35; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{21}H_{30}S_2$ 347.1867, found 347.1877.

*4,4'-Dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1b).*[8]

Yield: 0.433 g (96 %) as a light yellow color liquid. $^1$H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, *J*= 4.8 Hz, 2H), 6.90 (d, *J*= 5.4 Hz, 2H), 1.81(m, 4H), 1.34(m, 20H), 1.15(m, 4H), 0.84(t, 6H); $^{13}$C NMR(100 MHz, $CDCl_3$): δ 158.20, 136.72, 124.76, 121.82, 53.43, 37.97, 33.70, 30.62, 29.94, 29.61, 28.630, 24.64, 14.38; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{25}H_{38}S_2$ 403.2493, found 403.2497.

*4,4'-Bisdecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1c).*

Yield: 0.463 g (90 %) as a light yellow color liquid. $^1$H NMR (600 MHz, $CDCl_3$): δ 7.14(d, *J*= 4.8 Hz, 2H), 6.92 (d, *J*= 5.4 Hz, 2H), 1.87(m, 4H), 1.38(m, 4H), 1.32(m, 28H), 0.96(m, 6H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 158.30,136.63, 124.57, 121.81, 53.43, 45.32, 39.24, 33.79, 30.23, 29.91, 28.98, 27.46, 25.14, 22.63, 14.57; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{29}H_{46}S_2$ 459.3119, found 459.3119.

*4,4'-Bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1d).*[3m]

Yield: 0.397 g (88 %) as a light yellow color liquid.[1]H NMR (600 MHz, $CDCl_3$): δ 7.11(d, *J*= 4.8 Hz, 2H), 6.93(d, *J*= 5.4 Hz, 2H), 1.89(m, 4H), 0.99(m, 18H), 0.77(t, 6H), 0.61(t, 6H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 157.83, 137.01, 124.16, 122.55, 53.44, 43.45, 35.21, 34.35, 29.04, 27.48, 23.05, 14.33, 11.08; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{25}H_{38}S_2$ 403.2493, found 403.2493.

*4,4'-Bis-(5-bromopentyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1e).*

Yield: 0.397 g (82 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.14(d, *J*= 4.8 Hz, 2H), 6.89(d, *J*=5.4 Hz, 2H), 3.25(t, *J*=13.8 Hz, 4H), 1.85(m, 4H), 1.68(t, *J*= 13.2 Hz 4H), 1.26(m, 4H), 0.90(m, 4H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 157.62, 136.93, 125.06, 121.57, 53.22, 37.92, 34.04, 32.72, 29.11, 23.81; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{19}H_{24}Br_2S_2$ 476.9744, found 476.9752.

*4,4'-Bis-(6-bromohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1f).*[12]

Yield: 0.520 g (92 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.16(d, *J*=4.8 Hz, 2H), 6.92(d, *J*= 4.8 Hz, 2H), 3.32(t, *J*=6.6 Hz, 4H), 1.83(m, 4H), 1.73(t, *J*=7.8 Hz, 4H), 1.29(m, 4H), 1.15(m, 4H), 0.93(m, 4H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 157.85, 136.73, 124.83, 121.65, 53.24, 37.84, 34.12, 32.81, 29.85, 28.03, 24.29; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{21}H_{28}Br_2S_2$ 505.0057, found 505.0056.

*4,4'-Bis-(8-bromoctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1g).*

Yield: 0.565 g (90 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.15(d, *J*= 4.8 Hz, 2H), 6.92(d, *J*= 4.2 Hz, 2H), 3.36(t, *J*= 6.6 Hz, 4H), 1.82(m, 8H), 1.33(m, 4H), 1.15(m, 12H), 0.92(m, 4H).$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 158.15, 136.69, 124.70, 121.77, 53.39, 37.93, 34.21, 32.94, 30.01, 29.30, 28.80, 28.24, 24.59; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{25}H_{36}Br_2S_2$ 561.0683, found 561.0687.

*4,4'-Bis-(6-iodohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1h).*

Yield: 0.604 g (90 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.16(d, *J*= 4.2 Hz, 2H), 6.92(d, *J*= 4.8 Hz, 2H), 3.10(t, *J*= 7.2 Hz, 4H), 1.82(m, 4H), 1.68(m, 4H), 1.28(m, 4H), 1.15(m, 4H), 0.85(m, 4H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 154.36, 137.65, 124.53, 122.66, 44.36, 33.47, 31.85, 30.99, 28.70, 27.24, 7.22; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{21}H_{28}I_2S_2$ 598.9800, found 599.0084.

*2,6-Dibromo-4,4'-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1k).*

Yield: 0.288 g (96 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 6.94(s, 2H), 1.78(m, 4H), 1.27(m, 16H), 0.92(m, 6H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 156.13, 136.51, 124.77, 111.31, 55.23, 37.79, 31.79, 29.92, 24.63, 22.84, 14.34; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{21}H_{28}Br_2S_2$ 505.0057, found 505.0054.

*2,6-Dibromo-4,4'-dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1l).*[8]

Yield: 0.326 g (98 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 6.93(s, 2H), 1.72(m, 4H), 1.23(m, 20H), 1.11(m, 4H), 0.85(m, 6H); $^{13}C$ NMR (150 MHz, $CDCl_3$): 156.16, 136.50, 124.79, 111.27, 55.24, 37.74, 31.99, 30.17, 29.90, 29.49, 24.61, 22.90, 14.29;HRMS (ESI): m/z $[M+H]^+$calcd for $C_{25}H_{36}Br_2S_2$ 561.0683, found 561.0668.

*2,6-Dibromo-4,4'-didecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1m).*

Yield: 0.337 g (92 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 6.93 (s, 2H), 1.77(m, 4H), 1.26(m, 32H), 0.86(m, 6H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 156.17, 136.52, 124.80, 111.30, 55.25, 37.76, 32.15, 30.16, 29.93, 29.89, 29.76, 29.56, 24.65, 22.90, 14.34; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{29}H_{44}Br_2S_2$ 617.1309, found 617.1309.

*2,6-Dibromo-4,4'-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1n).*[3m]

Yield: 0.303 g (91 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 6.93(s, 2H), 1.81(m, 4H), 1.32(m, 18H), 0.86(t, 12H).$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 155.67, 136.87, 125.33, 111.048, 55.13, 43.29, 35.35, 29.89, 28.78, 23.62, 14.69, 11.28; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{25}H_{36}Br_2S_2$ 561.0683, found 561.0668.

*2,6-Dibromo-4,4'-bis(5-bromopentyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1o).*

Yield: 0.313 g (83 %) as a light yellow color liquid. $^1H$ NMR (600 MHz, $CDCl_3$): δ 6.89(s, 2H), 3.27(t, *J*= 6.6 Hz, 4H), 1.78(m, 4H), 1.70(t, *J*= 6.6 Hz, 4H), 1.25(m, 4H), 0.88(m, 4H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 155.46, 136.75, 124.52, 111.74, 54.96, 37.74, 33.97, 32.67, 28.65, 23.79; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{19}H_{22}Br_4S_2$ 634.7934, found 634.7934.

*2,6-Dibromo-4,4'-bis(6-bromohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1p).*[12]

Yield: 0.370 g (94 %.) as a light yellow color liquid. $^1H$ NMR (400 MHz, $CDCl_3$): δ 6.92(s, 2H), 3.34(t, *J*= 10.2 Hz, 4H), 1.77(m, 8H), 1.29(m, 4H), 1.15(m, 4H), 0.90(m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 155.73, 136.65, 124.62, 111.55, 55.06, 37.74, 34.14, 32.87, 29.22, 28.08, 24.41; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{21}H_{26}Br_4S_2$ 662.8247, found 662.8272.

*2,6-Dibromo-4,4'-bis(8-bromooctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1q).*

Yield: 0.388 g (91 %) as a light yellow color liquid. $^1H$ NMR (400 MHz, $CDCl_3$): δ 6.92(s, 2H), 3.34(t, *J*= 8 Hz, 4H), 1.77(m, 8H), 1.29(m, 4H), 1.15(m, 4H), 0.90(m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 152.06, 137.570, 125.32, 112.21, 55.98, 38.20, 33.68, 30.61, 30.07, 29.43, 28.66, 28.58, 24.06; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{25}H_{34}Br_4S_2$ 718.8873, found 718.8872.

*2,6-Dibromo-4,4'-bis(6-iodohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1r).*

Yield: 0.414 g (92 %) as a light yellow color liquid.[1]H NMR (600 MHz, $CDCl_3$): δ 6.97(s, 2H), 3.13(t, *J*= 6.6 Hz 4H), 1.78(m, 4H), 1.69(m, 4H), 1.29(m, 4H), 1.17(m, 4H), 0.92(m, 4H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 155.73, 136.65, 124.63, 111.57, 55.06, 37.74, 33.66, 30.38, 28.98, 24.38, 7.36; HRMS (ESI): m/z $[M+H]^+$calcd for $C_{21}H_{26}Br_2I_2S_2$ 756.7990, found 756.7992.

*X-ray crystallographic analysis of 2,6-Dibromo spiro[4,5]([2,1-b; 3,4-b']dithieno) decane:*

Single crystals of 2,6-Dibromo spiro[4,5]([2,1-b; 3,4-b']dithieno) decane were grown from $CHCl_3$ / hexane mixture. CCDC-1005162, the crystal parameters are available in the ESI. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.13(s, 2H), 1.76-1.63(m, 10H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 157.39, 135.86, 126.00, 110.95, 51.76, 42.05, 25.58, 22.92; M. P.- 84 °C.

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