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Reaction of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes with NBS—a route toward 2*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6(4*H*)-diones

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Solvent effects

ABSTRACT

In this paper we present a detailed study of the bromination reaction of cyclopentadithiophene (CPDT) derivatives, by means of NBS, giving access to either 2,6-dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes or 2*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6(4*H*)-diones (CPDT-2,6-diones). The CPDT-2,6-diones are fully characterized, including an X-ray single crystal structure of one of the representative materials. A mechanism leading to the formation of the latter, which arise as a new class of compounds within the CPDT family, is proposed and is supported by Gibbs free energy calculations. The influence of the solvent, reaction time, and the number of equivalents of NBS on the selectivity of the reaction is discussed.

1. Introduction

Organic photovoltaics (OPV) has emerged as a powerful and environmentally friendly technology that converts solar light into energy.[1] An appealing feature of organic solar cells is the relatively low production cost for large area modules by application of roll to roll printing techniques. Moreover, due to the high extinction coefficients of organic semiconductors, the thicknesses of the active layers can be in the order of hundreds of nanometers only, which may ultimately lead to light-weight, flexible and semi-transparent modules, particularly interesting for portable or wearable electronics and building integrated photovoltaics. With the solar photon flux peaking around 700 nm, various donor–acceptor materials—displaying a smaller band gap and broader absorption window—have recently been designed and used in bulk heterojunction organic solar cells.[2,3] Poly[(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6-diyl)-*alt*-(2,1,3-benzothiadiazole-4,7-diyl)] (**PCPDTBT**) (Fig. 1) was among the first low band gap copolymers to be explored for OPV applications, affording power conversion efficiencies above 2.8% in combination with a fullerene acceptor.[4] In the presence of a suitable processing additive, the efficiency was almost doubled, surpassing the 5% threshold.[5] As a result, **PCPDTBT** has become one of the workhorse low band gap materials in the field.[6] The copolymer, in which electron rich 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) and electron poor 2,1,3-benzothiadiazole units (BT) alternate along the backbone, is generally synthesized by Suzuki or Stille polycondensations,[7] occurring via a step-wise growth of the

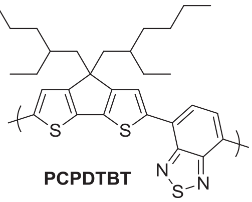

Fig. 1. Chemical structure of a **PCPDTBT** (4,4-bis(2-ethylhexyl)-substituted) low band gap copolymer.

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polymer chain and therefore requiring a precise 1:1 ratio of functionalities (halide and boronic ester or trialkyl tin, respectively). Not fulfilling this precise monomer feed ratio leads to the formation of low molecular weight species, which show poor optical properties and the resulting materials can, in consequence, not be used in the fabrication of highly efficient solar cell devices.

When Suzuki polycondensation (SPC) is chosen for the synthesis of **PCPDTBT**,[7c] the toxic tin side products generated in the Stille polycondensation are avoided. The SPC is usually carried out between the dibrominated CPDT and the bis(boronic acid pinacol ester) derivative of 2,1,3-benzothiadiazole. The latter can be synthesized in two steps starting from BT by direct bromination, using a mixture of bromine in hydrobromic acid,[8] followed by palladium catalyzed halogen-metal exchange in the presence of bis(pinacolato)diboron.[7b] On the other hand, dibrominated CPDT derivatives are obtained upon bromination using *N*-bromosuccinimide (NBS).[7d,9b] In order to obtain the precise 1:1 stoichiometry required in the SPC, high purity of the difunctional monomers is required. Coupling units bearing only one of these functionalities, i.e., boronic ester or bromine, act as end-cappers or 'dead end chains' and lead to the formation of lower molecular weight materials. Such monofunctional compounds must therefore carefully be removed by tedious purification or, ideally, not be formed during the transformations.

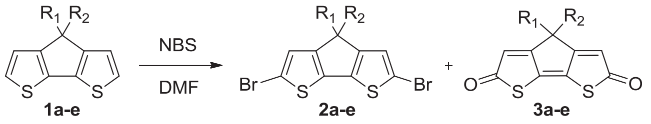
In this paper, we present a detailed study of the bromination reaction of CPDT derivatives, by means of NBS, giving access to both 2,6-dibromo-4,4-bis(alkyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes and 2*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6(4*H*)-diones (CPDT-2,6-diones), depending on the applied conditions.

2. Results and discussion

2.1. Synthetic exploration

The synthesis of CPDT derivatives has been studied intensively and has been improved steadily over the years. The groups of Gronowitz[10] and Wynberg[11] have dedicated long years of research to this class of compounds. Among the six isomers that can be obtained depending on the annulation of the two thiophene rings, 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene has gained much attention in the past years and is, to the best of our knowledge, the sole isomer that has been used in the synthesis of low band gap polymers for solar cell applications. The presence of solubilizing alkyl side chains on the bridging carbon atom is mandatory to obtain solution processable materials. Most synthetic protocols toward the CPDT scaffold involve multistep routes,[12] many of which use harsh reaction conditions and/or controversial reagents (such as the Wolff–Kishner reduction and the oxidation of secondary alcohols using pyridinium chlorochromate, respectively). More recently, CPDT derivatives bearing various functionalities in the side chains have been synthesized using a three-step approach.[13] This route enables the synthesis of both symmetrically and asymmetrically alkyl-substituted (linear or branched) CPDT derivatives and also allows introduction of ester-functionalized side chains by variation of the keto(ester) precursor. Regardless of the synthetic approach used for the synthesis of the CPDT scaffold, bromination in positions 2 and 6 of the fused aromatic unit is required to afford the CPDT monomer for SPC.[3c,14]

To brominate 4,4-bis(2-ethylhexyl)-substituted CPDT derivative **1a** (Scheme 1) and exclude the presence of the monobrominated derivative in the reaction mixture, we have conducted the bromination reaction (for 8–24 h in the dark and under inert atmosphere) by adding an excess of NBS (2.5 up to 3.2 equiv) to a 2 mM solution of the CPDT derivative in *N*,*N*-dimethylformamide (DMF). Under these conditions, no monobrominated product was detected and the yields of the isolated dibrominated CPDT **2a** (Scheme 1) were varying between 40 and 80%. Reactions which afforded 2,6-dibromo-CPDT **2a** in isolated yields as low as 40% have drawn our attention. The ^{1}H NMR spectra of the crude reaction mixtures (see Supplementary data, Fig. S1) showed, besides the expected triplet-like resonance pattern of the dibrominated CPDT **2a** (at δ=6.93 ppm) and the aliphatic protons of the alkyl side chains (in this case two 2-ethylhexyl groups), the presence of an additional triplet at δ=6.01 ppm. In the particular case shown in Fig. S1, both triplets were located in the low field region with the same integrated value, pointing to a 1:1 ratio of two products. The presence of a secondary product formed during the bromination reaction was also confirmed by GC–MS. It should be emphasized here that the resonance of the unique aromatic proton belonging to the dibrominated CPDT derivative **2a** (at δ=6.93 ppm) shows up as an 'apparent' triplet (there is no *J*-coupling) due to the presence of different stereoisomers. In the case where there is one linear and one branched (2-ethylhexyl) side chain (**2c** and **2d**), an apparent doublet was observed (Fig. S9 and 15), whereas in the case of two linear substituents (**2b**) only a sharp singlet was noticed (Fig. S4).



a $R_1 = R_2$ = 2-ethylhexyl, **b** $R_1 = R_2$ = dodecyl, **c** R_1 = 2-ethylhexyl, R_2 = octyl
d R_1 = 2-ethylhexyl, R_2 = methyl nonanoate, **e** $R_1 = R_2$ = ethyl

Scheme 1. Bromination of CPDTs **1a**–**e** with NBS, affording 2,6-dibromo-CPDTs **2a**–**e** and CPDT-2,6-diones **3a**–**e**.

Both reaction products were separated and purified by means of column chromatography (silica) to recover the dibrominated CPDT **2a** (clear oil, 40% yield) and the secondary product **3a** (yellow oil, 40% yield), respectively. Complete ^{1}H and ^{13}C NMR analysis, corroborated with GC–MS analysis and IR spectroscopy, allowed to identify the isolated secondary product as 4,4-bis(2-ethylhexyl)-2*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6(4*H*)-dione (**3a**) (Scheme 1), a new compound within the CPDT family. ^{1}H NMR analysis revealed that the triplet-like signal located around δ=6.01 ppm (Fig. S2) results from the protons in α position of the carbonyl groups, the latter being confirmed by the presence of a characteristic C=O resonance around δ=194 ppm in the ^{13}C NMR spectrum (Fig. S3) and by an absorption peak located at ν=1700 cm^{-1} in the IR spectrum. HRMS analysis provided the exact molar mass of the isolated product, in accordance with the proposed structure. The formation of the CPDT-2,6-dione was not limited to the bis(2-ethylhexyl) derivative, but was also encountered for a few analogous CPDT compounds **1b**–**d** (Scheme 1). The experiments that were conducted using 3.5 equiv of NBS in DMF allowed to isolate both the initially targeted dibrominated CPDTs **2a**–**d** and CPDT-2,6-diones **3a**–**d**. All novel materials were fully characterized by ^{1}H and ^{13}C NMR, (HR)MS and IR.

2.2. Single crystal X-ray diffraction

Single crystals suitable for X-ray diffraction analysis could be obtained for one of the CPDT-2,6-diones (**3c**) (Fig. 2), unambiguously proving the structure assignment. The structure is highly disordered, at least for the long alkyl chains. The CPDT system is quite rigid and planar, and the (first atoms of the) alkyl chains are positioned perpendicular with respect to the CPDT plane.

2.3. Reaction mechanism

Several processes can account for the formation of CPDT-2,6-diones **3a**–**d**: (1) Diels–Alder addition between singlet oxygen

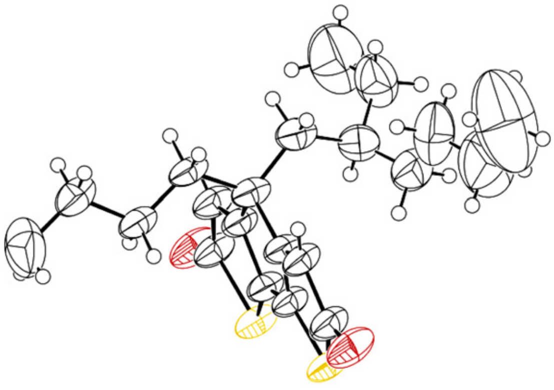


Fig. 2. Ortep representation of **3c** (R_1=2-ethylhexyl, R_2=octyl), showing thermal displacement ellipsoids drawn at the 50% probability level.

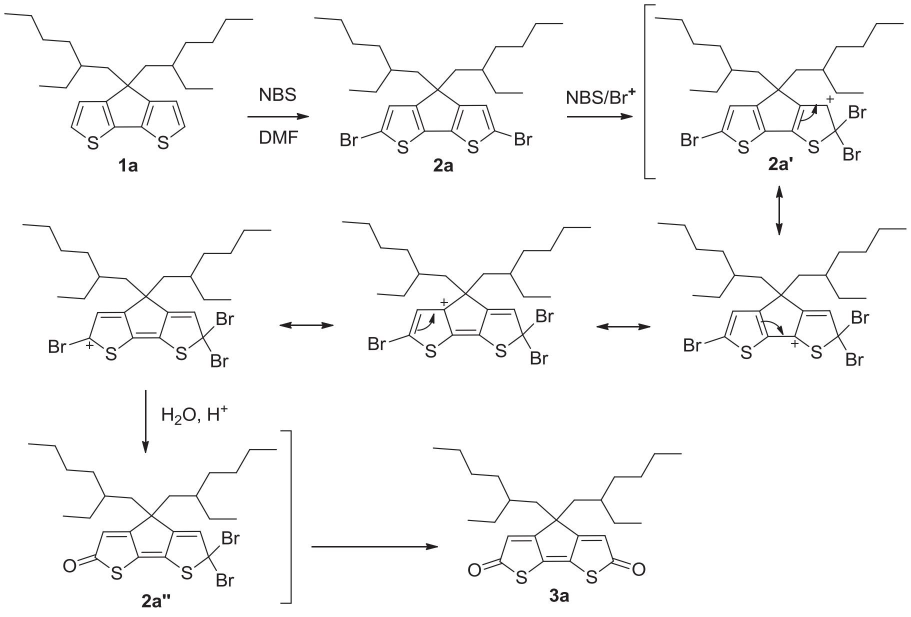
($^1O_2$) (presumably generated in situ) and the non-brominated CPDT derivative,[15] (2) hydrolytic opening of the thiophene ring followed by dehydrogenation via bromine and (3) overbromination of the dibrominated compound leading, upon aqueous work-up, to a thiolactone, followed by its fast oxidation (in air). To get more insight into the reaction path leading to the formation of the CPDT-2,6-diones, these possible mechanisms were analyzed.

(1) It is well known that thiophene derivatives, and especially photoactive materials, such as poly(3-alkylthiophenes), have a rather low photochemical stability, which, in the presence of air, leads to their degradation. The photodegradation products are believed to be formed via an adduct between the thiophene ring (part of the π-conjugated system in the case of polymers) and oxygen, generating carbonyl and sulfonic derivatives or that, alternatively, the pathway involves the side chains.[16] The fact that such degradations are considerably reduced or even absent when the thiophene derivatives are irradiated under inert atmosphere highlights the key role of oxygen in the formation of the photodegradation products. Since the bromination reaction of CPDT **1a** has been conducted in the dark and under inert atmosphere, this mechanism is not likely to take place. To verify the involvement of $^1O_2$, all further experiments were carried out under an oxygen-free atmosphere, using degassed solvents and chemicals. Additionally, only 2.1 equiv of NBS were used for a 1 mM solution of **1a** in DMF. Even when taking all these precautions, GC–MS and NMR analysis showed the formation of **3a** already after 2 h. At this stage of the reaction, also monobrominated CPDT was still present in low concentrations. After 3 h, when the monobrominated CPDT was not detected anymore, the reaction was stopped. These experiments showed that the exclusion of oxygen from the reaction medium does not completely avoid the formation of the CPDT-2,6-dione. Hence, the mechanism leading to the formation of compound **3a** probably does not involve $^1O_2$.

(2) In an attempt to brominate 2-bromo-3,5-di-*tert*-butylthiophene with bromine in an acetic acid–nitric acid mixture in the presence of silver nitrate, Gronowitz et al.[17] isolated the corresponding hydroxyfuranone in 70% yield. The formation of the latter was supposed to occur by hydrolytic opening of the thiophene ring followed by dehydrogenation via bromine. Also this mechanism does not seem to be responsible for the formation of compound **3a**, as the replacement of the sulfur atom in the CPDT ring was not observed.

(3) Upon bromination of naphtho[1,2-*c*]thiophene using a mixture of NBS in acetic acid, Lin et al.[18] have recovered the expected dibrominated compound together with two other secondary products, i.e., a thiolactone and a thioanhydride. Even though the bromination reaction was conducted for only 20 min, with just 2.0 equiv of NBS (an equimolar amount), the formation of the dibrominated compound was not exclusive, as three products were formed in a 1:0.6:1 ratio. The proposed mechanism involves further electrophilic attack of the dibrominated derivative leading to a tribrominated species, which affords the thiolactone upon aqueous work-up. Exposure of the latter to air leads to the formation of the thioanhydride.

By analogy, the same sequence of reactions, i.e., electrophilic attack followed by hydrolysis and fast oxidation, can account for the formation of CPDT-2,6-dione **3a** (Scheme 2). Here, overbromination at the 2-position of the CPDT ring affords the positively charged intermediate **2a′**, which is stabilized by several resonance forms. The resonance form bearing the positive charge at the 6-position leads, upon aqueous work-up, to thiolactone **2a″**. Surprisingly, this



Scheme 2. Proposed mechanism for the formation of CPDT-2,6-dione **3a**.

intermediate has never been detected by GC–MS or NMR analysis, suggesting that this compound is very efficiently converted to compound **3a**. The loss of aromaticity in compound **3a** is reflected in the chemical shift of the two protons belonging to the fused heterocycle located at δ=6.01 ppm, well below the normal chemical shift range of aromatic (CPDT) protons. The driving force for this transformation can be found in the formation of a stable quinoid derivative.[19] The CPDT-2,6-dione formation was enhanced by the use of an excess of NBS (vide infra), which suggests that, under these conditions, the CPDT-2,6-dione is thermodynamically favored, whereas the dibrominated CPDT derivative appears under more kinetic conditions. The crucial role of a bromonium intermediate in the NBS promoted rearrangement of 1,1-diarylmethylenecyclopentanes has recently been pointed out and supports the proposed reaction pathway.[20] Additionally, palladium mediated reactions between a series of variously substituted CPDT derivatives and sodium dicyanomethanide, followed by oxidation with aqueous bromine, have led to the formation of quinoid 2,6-dihydro-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene derivatives.[21]

2.4. Theoretical calculations

To support our assumption, theoretical calculations were carried out for the reactions involving the model compounds **1e**, **2e**, **2e″**, and **3e**, together with NBS, succinimide (NS), HBr, and water. The results, summarized in Fig. 3, showed that the formation of dibromo-CPDT **2e** from 4,4-diethyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**1e**) stabilizes the system by about 46.0 kcal/mol according to B3LYP/6-311+G(d,p) calculations, and by 50.1 kcal/mol when employing the MP2/6-311+G(d,p) method, indicating that the formation of the dibrominated compound is a thermodynamically favored process. Moreover, the formation of CPDT-2,6-dione **3e** further stabilizes the system by 62.6 [32.2] kcal/mol according to calculations carried out at the B3LYP/6-311+G(d,p) [MP2/6-311+G(d,p)] level. During the formation of dibromo-CPDT **2e**, part of the product reacts further with NBS to form **3e**, provided NBS is in excess, which is in agreement with the experimental findings. The calculations also indicated that the formation of the CPDT-2,6-dione derivative **3e** via intermediate **2e″** is thermodynamically favored, which substantiates the experimental hypothesis. The formation of **2e″** leads to an additional ΔG stabilization by 33.7 [19.3] kcal/mol with respect to **2e** and the transformation of the former to **3e** involves an additional stabilization by 28.9 [12.9] kcal/mol according to B3LYP/6-311+G(d,p) [MP2/6-311+G(d,p)] calculations.

Theoretically calculated NMR chemical shifts were in good agreement with the experimental ones. The B3LYP/6-311+G(2d,p) calculated ^{1}H NMR chemical shifts (corrected using the α/β linear regressions)[22] for the α and β hydrogen atoms on the thiophene rings of **1e** are δ=7.19 and 7.05 ppm, respectively, matching rather well the experimental values of δ=7.17 and 6.94 ppm for **1a**.[13a] For **2e**, the corresponding chemical shift for the β hydrogen atom decreased slightly to δ=6.90 ppm, close to the experimental value of δ=6.93 ppm for **2a**. The calculated ^{1}H NMR chemical shift of the β hydrogen atoms in **3e** appeared at 5.97 ppm, in line with the experimental shift at δ=6.01 ppm for **3a**. In addition, calculations on **2e″** showed that the β hydrogen atoms on the dibrominated and on the carbonyl sides have chemical shifts of δ=6.45 and 5.97 ppm, respectively. The resonance at δ=6.45 ppm can hence be applied as a fingerprint to detect the possible presence of **2e″**.

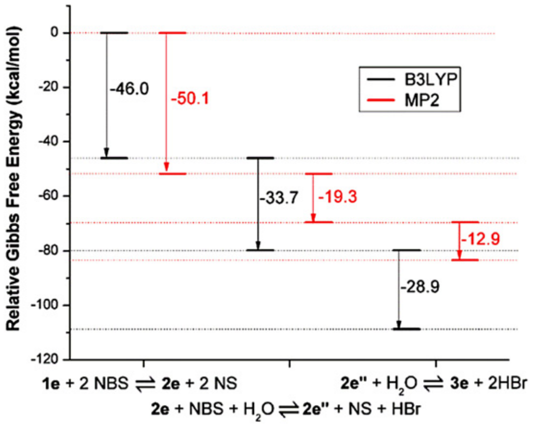


Fig. 3. Variation of the Gibbs free energy (kcal/mol) along the reaction coordinate.

2.5. Study of solvent effects

Knowing that in DMF the use of 4.0 equiv of NBS afforded the CPDT-2,6-dione **3c** (R_1=2-ethylhexyl, R_2=octyl) as the major reaction product (~73% yield; vide infra), we have investigated the influence of other solvents and/or solvent mixtures generally used for brominations using NBS. The polarity and protic character of the solvent were varied. As displayed in Table 1, the use of less polar solvents, such as chloroform ($CHCl_3$) or carbon tetrachloride (CCl_4), led exclusively to the formation of the dibrominated compound **2c**.

The use of polar protic solvents or a 1:1 mixture with a less polar solvent, such as acetic acid (AcOH) or an acetic acid/chloroform mixture, respectively, still afforded the dibrominated compound **2c** as the main reaction product, together with small amounts of CPDT-2,6-dione **3c** (the formation of **3c** being slightly enhanced in pure AcOH). These findings suggest that the formation of **3c** is favored in polar solvents. 1,2-Dimethoxyethane (DME) and DMF are both polar aprotic solvents, perfectly miscible with water. Moreover, the system NBS-DME is known as a powerful oxidizing medium for secondary alcohols.[21c,24] Surprisingly enough, bromination of **1c** appeared to proceed differently in these two solvents. In DME, the formation of **3c** did not occur at all, whereas in DMF the latter stands for the major reaction product. In acetone, **2c** was also the sole reaction product, the presence of **3c** not being detected. These results show that there is no correlation between the protic/aprotic character or the polarity of the solvent (mixture) and the product distribution (dibrominated CPDT vs CPDT-2,6-dione).

Table 1
Influence of the solvent (properties) on the bromination of **1c** (using 4.0 equiv of NBS)

Solvent (mixture)	**2c**:**3c** (%)	Dipole moment (*D*)[a]	Dielectric constant (ε)[a]	Miscibility with water
DMF	27:73	3.82	36.70	Yes
$CHCl_3$	100:0	1.01	4.81	No
CCl_4	100:0	0	2.24	No
AcOH	83:17	1.74	6.15	Yes
$CHCl_3$/AcOH (1:1)	96:4	—	—	—
DME	100:0	1.71	7.20	Yes
Acetone	100:0	2.88	21.0	Yes

[a] Ref. 25.

2.5.1. *In situ ^{1}H NMR experiments.*

To be able to follow the evolution of the reaction mixture in time, we have then performed a series of in situ ^{1}H NMR experiments. For this purpose, the bromination reaction was conducted directly in an NMR tube, in either DMF-d_7, $CDCl_3$, CH_3COOD or $CH_3COOD/CDCl_3$ (1:1 v/v).

2.5.1.1. *DMF-d_7.*

The first spectrum (after 5 min only) revealed the presence of the dibrominated CPDT **2c** together with traces of the monobrominated derivative. The last recorded spectrum (after 3 days) displayed almost no changes compared to the one recorded after 1 h, showing a main peak corresponding to the dibrominated product and two additional small peaks. The spectrum of the hydrolyzed sample, however, showed the resonance at δ=6.01 ppm, corresponding to the CPDT-2,6-dione **3c**, as the major signal, in an almost 9:1 ratio with respect to the dibrominated CPDT **2c** (δ=6.93 ppm), together with two other minor doublet-like signals at δ=6.30 and 7.10 ppm. GC–MS analysis of an aliquot collected after 1 h and the hydrolyzed sample (after 3 days) showed the same composition. These facts strongly suggest that the formation of the CPDT-2,6-dione is significantly accelerated upon hydrolysis and/or exposure to air. Under these conditions (4.0 equiv of NBS, DMF as a solvent) it became very clear that the reaction time has little or no influence on the formation of the CPDT-2,6-dione.

2.5.1.2. $CDCl_3$. The first spectrum (after 5 min) showed that the starting product was fully converted to the dibromo-CPDT **2c**. No traces of the monobrominated derivative or other secondary products could be detected at this stage of the reaction. The system looked stable and did not evolve in the next 5 h. No major changes, except for two minor doublet-like signals at δ=6.30 and 7.10 ppm, were noticed until the end of the experiment. After work-up, the ^1H NMR spectrum of the fully hydrolyzed mixture showed the presence of the dibrominated CPDT **2c** and small amounts of CPDT-2,6-dione **3c**. As in the DMF case, the two other minor doublet-like signals were equally present.

2.5.1.3. CH_3COOD and $CH_3COOD/CDCl_3$ (1:1 v/v). For the reactions performed in acetic acid or a mixture acetic acid/chloroform, in situ ^1H NMR experiments pointed again toward an increase in the percentage of the CPDT-2,6-dione **3c** upon aqueous work-up, this trend being enhanced in pure acetic acid.

Summarizing, in situ ^1H NMR experiments allowed to confirm the strong dependence of the reaction outcome on the solvent employed. No clear intermediates could be identified and/or isolated. The findings also point to a crucial change in composition upon aqueous work-up and support the suggested mechanism, i.e., overbromination followed by hydrolysis and fast conversion to the dione.

2.6. Influence of the number of equivalents of NBS on the product distribution

Having in mind that, provided NBS is in excess, the bromination reaction leads to the formation of two distinct classes of products, we were interested to obtain full control/selectivity toward the formation of either product. For this purpose we have decided to perform the bromination reaction of **1c** in DMF using an excess of NBS ranging from 2.1 to 5.0 equiv, the reaction time being limited to 3 h. This series of experiments (Table 2) pointed out that by using only a slight excess of NBS (2.1 or 2.5 equiv), the CPDT-2,6-dione formation could virtually be suppressed. The use of 3.0, 3.5, and 4.0 equiv of NBS afforded the CPDT-2,6-dione in 15, 50, and 73% yield, respectively, whereas the use of 5.0 equiv of NBS gave the CPDT-2,6-dione as the unique reaction product. The distribution of the mol fractions of **2c** and **3c** in the crude reaction mixture, as deduced from the integration of the protons located at δ=6.93 and 6.01 ppm in the ^1H NMR spectrum, respectively, showed a sigmoid variation with the number of equivalents of NBS used, which could be an indication of an autocatalytic reaction (Fig. 4).[23]

Table 2
Influence of the number of equivalents of NBS on the reaction product distribution **2c**:**3c**

Equiv NBS	**2c**:**3c**[a,b]
2.1	98:2
2.5	100:0
3.0	85:15
3.5	50:50
4.0	27:73
5.0	0:100

[a] Deduced from the integration of the protons situated at δ=6.93 and 6.01 ppm, belonging to compounds **2c** and **3c**, respectively; 3 h reaction at rt in DMF (c=0.02 mM).
[b] Within the ^1H NMR detection limit.

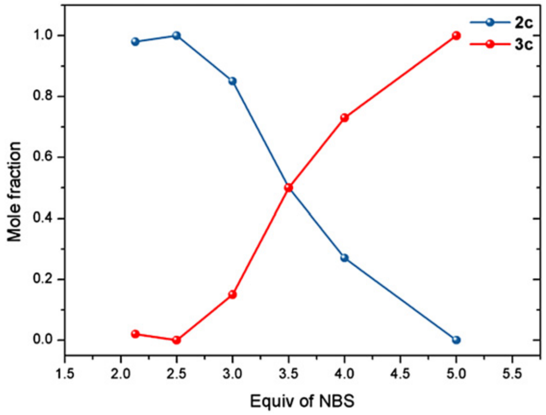


Fig. 4. Influence of the number of equivalents of NBS on the reaction product ratio **2c**:**3c** (experiments conducted in DMF).

3. Conclusions

In this study we have carefully investigated the bromination of a series of CPDT derivatives, with NBS as the bromine source. Among the parameters influencing the reaction, e.g., concentration of the starting product, solvent, reaction time and the presence/absence of oxygen, the solvent and the number of equivalents of NBS seemed to have a great impact on the yields of the dibrominated products and the 2*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6(4*H*)-dione secondary products. In DMF, full control over the reaction could be achieved by tuning the number of equivalents of NBS. The use of 2.1 equiv afforded the dibrominated CPDT derivatives as the unique reaction products. On the other hand, the use of 5.0 equiv led to exclusive formation of the CPDT-2,6-diones. The formation of the CPDT-2,6-diones is supposed to occur via a bromination-hydrolysis sequence, followed by fast conversion to the dione. The obtained insights are of relevance for all those involved in the synthesis and application of CPDT-based materials (notably in organic electronics). The chemical reactivity of this new class of compounds toward various transformations, e.g., reductions, Knoevenagel reactions, condensations, dimerizations, thionylations, etc., specific to carbonyl functionalities, is currently under investigation within our group, as is the exploration of the possible applications of the novel thienoquinoidal derivatives in organic electronics.[26]

4. Experimental section

4.1. Materials and methods

NMR chemical shifts (δ, in parts per million) were determined relative to the residual $CHCl_3$ absorption (7.26 ppm) or the ^{13}C resonance shift of $CDCl_3$ (77.16 ppm). Gas chromatography–mass spectrometry (GC–MS) analyses were carried out applying Chrompack Cpsil5CB or Cpsil8CB capillary columns. Exact mass measurements were performed in the EI mode at a resolution of 10,000. The structures of the model compounds were optimized using density functional theory (DFT) with the B3LYP hybrid exchange-correlation functional and the 6-311+G(d,p) basis set. All vibrational frequencies are real, confirming that these structures are minima. ΔG values were evaluated at the same level of approximation for T=298.15 K and P=1.0 atm. Based on the B3LYP/6-311+G(d,p) optimized structures, the chemical shifts of all systems were calculated with the same functional, the 6-311+G(2d,p) basis set, and the GIAO method to ensure origin-independence. The Møller–Plesset second-order perturbation theory (MP2) method was also employed to perform single point calculations on these geometries. For both B3LYP and MP2 electronic energies, the ΔG values were then evaluated by including the temperature-dependent contributions obtained at the B3LYP level. For both the structure optimizations and property calculations, the Polarizable Continuum Model (PCM) using the integral equation formalism (IEFPCM) was employed to account for solvent effects (DMF). All calculations were performed using Gaussian09.[27]

4.2. General procedure 1 (allowing to obtain both the dibrominated and the CPDT-2,6-dione products)

4,4-Bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (**1a**) (0.797 g, 1.98 mmol) was dissolved in DMF (100 mL) and the mixture was cooled to 0 °C by means of an ice bath (the reaction was performed in the dark and under N_2 balloon pressure). Subsequently, a solution of NBS (0.178 g, 5.97 mmol, 3.0 equiv) in DMF (100 mL) was added drop-wise during 30 min and the mixture was allowed to react at rt overnight. The mixture was again cooled down to 0 °C, water (100 mL) was added and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure afforded a dark yellow viscous oil. The crude mixture was purified by means of column chromatography (silica) using a gradient of hexane/ethyl acetate from 0% (isolation of the dibrominated CPDT **2a**) to 10% (isolation of the CPDT-2,6-dione **3a**).

*4.2.1. 2,6-Dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′] dithiophene (**2a**).*[7d] Light-yellow oil (0.400 g, 36%). ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.94/6.93/6.92 (3× s, intensity ratio 1/2/1, 2H), 1.85–1.75 (m, 4H), 1.32–1.21 (m, 2H), 0.90–0.85 (m, 16H), 0.80–0.76 (m, 6H), 0.64–0.60 (m, 6H).

*4.2.2. 4,4-Bis(2-ethylhexyl)-2H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6(4H)-dione (**3a**).* Yellow oil (0.342 g, 40%). GC–MS (EI) m/z=432 [M$^+$]; HRMS (EI) calcd for $C_{25}H_{36}O_2S_2$ 432.2157; found m/z=432.2166; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.02/6.01/6.00 (3× s, intensity ratio 1/2/1, 2H), 1.92–1.82 (m, 4H), 1.15–0.99 (m, 18H), 0.81 (t, J=6.0 Hz, 6H), 0.71 (t, J=6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=193.7 (C═O), 176.1, 145.7, 115.5 (CH), 52.1, 44.5 (CH_2), 35.6 (CH), 33.9 (CH_2), 28.2 (CH_2), 27.1 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 10.3 (CH_3); IR (NaCl, cm^{-1}) ν_{max}=3077 (w, unsaturated C–H), 2958/2927/2871/2857 (s, saturated C–H), 1700 (s, CO); UV–vis ($CHCl_3$, nm) λ_{max} (log ε)=278 (4.422), 381 (4.456).

*4.2.3. 2,6-Dibromo-4,4-didodecyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (**2b**).*[14] According to general procedure 1: 4,4-didodecyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (**1b**) (0.370 g, 0.718 mmol), NBS (0.383 g, 2.16 mmol, 3 equiv), DMF (50 mL), eluent hexane; light-yellow oil (0.510 g, 72%); GC–MS (EI) m/z=671/673/675 [M$^+$]; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.92 (s, 2H), 1.77–1.72 (m, 4H), 1.29–1.14 (m, 40H), 0.87 (t, J=6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=156.1, 136.4, 124.7, 111.2 (CH), 55.2, 37.7 (CH_2), 32.1 (CH_2), 31.1 (CH_2), 30.08 (CH_2), 29.78 (CH_2), 29.74 (CH_2), 29.5 (CH_2), 25.8 (CH_2), 24.6 (CH_2), 22.9 (CH_2), 14.3 (CH_3).

*4.2.4. 4,4-Didodecyl-2H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6(4H)-dione (**3b**).* Light-yellow oil (0.078 g, 20%); MS (CI) m/z=544 [M$^+$]; HRMS (EI) calcd for $C_{33}H_{52}O_2S_2$ 544.3409; found m/z=544.3370; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.01 (s, 2H), 1.86–1.82 (m, 4H), 1.29–1.20 (m, 40H), 0.87 (t, J=6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=194.3 (C═O), 176.1, 145.3, 115.1 (CH), 52.6, 39.4 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 29.77 (CH_2), 29.75 (CH_2), 29.70 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3); IR (NaCl, cm^{-1}) ν_{max}=3076 (w, unsaturated C–H), 2958/2923/2852 (s, saturated C–H), 1703 (s, CO); UV–vis ($CHCl_3$, nm) λ_{max} (log ε)=380 (4.497).

*4.2.5. Methyl-9-(2,6-dibromo-4-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-4-yl)nonanoate (**2d**).* According to general procedure 1: methyl 9-(4-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′] dithiophene-4-yl)nonanoate (**1d**) (0.315 g, 0.685 mmol), NBS (0.260 g, 1.46 mmol, 2.1 equiv), DMF (17.5 mL), eluent hexane/ethyl acetate 9:1; yellow oil (0.266 g, 63%); GC–MS (EI) m/z=616/618/620 [M$^+$]; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.92/6.91 (2× s, intensity ratio 1/1, 2H), 3.64 (s, 3H), 2.26 (t, J=7.5 Hz, 2H), 1.81 (t, J=4.8 Hz, 2H), 1.76–1.70 (m, 2H), 1.61–1.51 (m, 2H), 1.30–0.88 (m, 19H), 0.77 (t, J=6.9 Hz, 3H), 0.62 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=174.5 (CO–O), 155.9/155.8, 136.6/136.5, 125.0/124.9, 111.1/111.0 (CH), 55.1, 51.6 (CH_3), 41.7, 39.4 (CH_2), 35.4 (CH_2), 34.2 (CH), 34.1 (CH_2), 29.9 (CH_2), 29.31 (CH_2), 29.26 (CH_2), 29.18 (CH_2), 28.6 (CH_2), 27.4 (CH_2), 25.0 (CH_2), 24.3 (CH_2), 22.9 (CH_2), 14.2 (CH_3), 10.8 (CH_3); IR (NaCl, cm^{-1}) ν_{max}=3084 (w, unsaturated C–H), 2928/2855 (s, saturated C–H), 1739 (s, CO–O); UV–vis ($CHCl_3$, nm) λ_{max} (log ε)=250 (3.884), 339 (4.297).

4.3. General procedure 2 (allowing to push the reactions toward the formation of the CPDT-2,6-dione products)

4-(2-Ethylhexyl)-4-octyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (**1c**) (0.276 g, 0.68 mmol) was dissolved in DMF (10 mL) and the mixture was cooled down to 0 °C by means of an ice bath (the reaction was performed in the dark and under N_2 balloon pressure). Subsequently, a solution of NBS (0.484 g, 2.72 mmol, 4.0 equiv) in DMF (10 mL) was added drop-wise and the mixture was allowed to react at rt overnight. The mixture was again cooled down to 0 °C, water (100 mL) was added and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, and filtered. Evaporation of the solvent under reduced pressure afforded a dark yellow viscous oil. The crude mixture was purified by means of column chromatography (silica) using a gradient of hexane/ethyl acetate from 0% (isolation of the dibrominated compound **2c**) to 20% (isolation of the CPDT-2,6-dione **3c**).

*4.3.1. 2,6-Dibromo-4-(2-ethylhexyl)-4-octyl-4H-cyclopenta-[2,1-b:3,4-b′]dithiophene (**2c**).* Slightly yellow oil (0.060 g, 16%); GC–MS (EI) m/z=558/560/562 [M$^+$]; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.94/6.93 (2× s, intensity ratio 1/1, 2H), 1.83 (t, J=4.8 Hz, 2H), 1.78–1.72 (m, 2H), 1.27–0.89 (m, 21H), 0.86 (t, J=7.1 Hz, 3H), 0.79 (t, J=6.9 Hz, 3H), 0.64 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=155.9/155.8, 136.6/136.5, 125.0/124.9, 111.05/111.0 (CH), 55.1, 41.6 (CH), 39.4 (CH_2), 35.5 (CH_2), 34.1 (CH_2), 31.9 (CH_2), 30.0 (CH_2), 29.43 (CH_2), 29.40 (CH_2), 28.6 (CH_2), 27.4 (CH_2), 24.4 (CH_2), 22.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3), 14.2 (CH_3), 10.8 (CH_3); IR (NaCl, cm^{-1}) ν_{max}=3082 (w, unsaturated C–H), 2957/2926/2855 (w, saturated C–H); UV–vis ($CHCl_3$, nm) λ_{max} (log ε)=250 (3.984), 339 (4.282).

*4.3.2. 4-(2-Ethylhexyl)-4-octyl-2H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6(4H)-dione (**3c**).* Deep-yellow oil (0.205 g, 70%); GC–MS (EI) m/z=432 [M$^+$]; HRMS (EI) calcd for $C_{25}H_{36}O_2S_2$ 432.2157; found m/z=432.2164; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.01/6.00 (2× s, intensity ratio 1/1, 2H), 1.88–1.86 (m, 2H), 1.84–1.80 (m, 2H), 1.26–0.98 (m, 21H), 0.83 (t, J=6.9 Hz, 3H), 0.80 (t, J=6.9 Hz, 3H), 0.70 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=193.99/193.95 (C═O), 176.2/176.1, 145.4, 115.3/115.2 (CH), 52.3, 43.1 (CH), 40.9 (CH_2), 35.9 (CH_2), 33.8

(CH$_2$), 31.8 (CH$_2$), 29.7 (CH$_2$), 29.2 (CH$_2$), 28.3 (CH$_2$), 27.0 (CH$_2$), 24.4 (CH$_2$), 22.9 (CH$_2$), 22.6 (CH$_2$), 14.15 (CH$_3$), 14.10 (CH$_3$), 10.4 (CH$_3$); IR (NaCl, cm^{-1}) ν_{max}=3066 (w, unsaturated C–H), 2957/2926/2855 (s, saturated C–H), 1701 (s, CO); UV–vis (CHCl$_3$, nm) λ_{max} (log ε)=381 (4.253).

*4.3.3. Methyl-9-(4-(2-ethylhexyl)-2H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6(4H)-dione-4-yl)nonanoate (**3d**).* According to general procedure 2: methyl 9-(4-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-4-yl)nonanoate (**1d**) (0.100 g, 0.216 mmol), NBS (0.154 g, 0.866 mmol, 4.0 equiv), DMF (10 mL), eluent hexane/ethyl acetate 8:2; yellow oil (0.067 g, 63%); GC–MS (EI) *m*/*z*=490 [M$^+$]; HRMS (EI) calcd for $C_{27}H_{38}O_4S_2$ 490.2212; found *m*/*z*=490.2208; ^{1}H NMR (300 MHz, CDCl$_3$) δ=6.010/6.005 (2× s, intensity ratio 1/1, 2H), 3.66 (s, 3H), 2.28 (t, *J*=7.5 Hz, 2H), 1.89–1.81 (m, 4H), 1.63–1.54 (m, 2H), 1.28–1.05 (m, 19H), 0.82 (t, *J*=6.8 Hz, 3H), 0.72 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ=194.1 (CO), 176.2/176.1 (CO–O), 174.3, 145.5, 115.3 (CH), 52.4, 51.6 (CH$_3$), 43.2 (CH$_2$), 41.0 (CH$_2$), 35.9 (CH$_2$), 34.1 (CH), 33.9 (CH$_2$), 29.7 (CH$_2$), 29.2 (CH$_2$), 29.13 (CH$_2$), 29.08 (CH$_2$), 28.3 (CH$_2$), 27.1 (CH$_2$), 24.9 (CH$_2$), 24.4 (CH$_2$), 22.9 (CH$_2$), 14.1 (CH$_3$), 10.4 (CH$_3$); IR (NaCl, cm^{-1}) ν_{max}=3073 (w, unsaturated C–H), 2928/2855 (s, saturated C–H), 1739 (s, CO–O), 1700 (s, CO); UV–vis (CHCl$_3$, nm) λ_{max} (log ε)=381 (4.424).

4.4. General procedure 3 (used for the in situ ^{1}H NMR experiments)

A solution of **1c** in the corresponding deuterated solvent or solvent mixture was placed in an NMR tube, to which NBS (4.0 equiv) was then added as a solid. The mixture was well stirred by means of a vortex (the tube was protected from light by wrapping it in aluminum foil). The tube was placed in the NMR spectrometer and a first spectrum was recorded (generally 3–10 min after the addition of NBS). The reaction was allowed to run for 3 days, with spectra recorded every hour. At the end of the reaction, water was added and the aqueous layer was extracted with diethyl ether.

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Supplementary data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 912552. A copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Further supplementary data associated with this article (^{1}H and ^{13}C NMR spectra of **2b**–**d** and **3a**–**d**, and more details on the X-ray structure) can be found online at http://dx.doi.org/10.1016/j.tet.2013.01.026.

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