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<https://doi.org/10.1038/s42004-019-0228-y>

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Redox chemistry of π -extended tellurophenes

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In the past decade, the incorporation of tellurophene motifs into organic devices has been a promising strategy for the design of advanced materials. However, fundamental redox behavior of tellurophene-containing materials have never been comprehensively explored. Here, we report unique redox behavior of π -extended tellurophenes. The facile coordination of solvent molecules and/or anions becomes evident, in addition to the attachment of nucleophilic halides. This indicates that the tellurium center in oxidized 2,5-diphenyltellurophene is highly electron-deficient and easily yields coordinated structures. This coordination appears to trap the positive charge on the tellurium center rather than delocalizing it over the π -system. When no coordinating counter ion is present, however, oxidation appears to be delocalized over the entire π -system. Additionally, by using more delocalized structures, we show that coordination and charge-delocalization can co-exist. These results provide important insights to understand the properties of tellurophene-containing molecules and materials with extended π -systems.

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Redox reactions are important chemical and biochemical processes that occur in nature and a range of synthetic compounds of interest for catalysis and energy transfer and storage. Most of these reactions involve transition metal complexes, however, recent emphasis has been placed on main group inorganic compounds due to their lightweight and more abundant nature^{1–6}. In this context, tellurophene, a tellurium-containing five-membered aromatic ring^{7,8}, is of particular interest given that its π -delocalized nature resembles more traditional aromatic heterocycles and that it incorporates a metalloid that is capable of several stable oxidation states^{9–11}.

In the last decade, the incorporation of the tellurophene-motif into π -extended molecules and polymers has been recognized as a promising design for electronic devices, such as thin film transistors, light emitters, photovoltaics, and thermoelectrics^{12–25}. In comparison with thiophene-containing or selenophene-containing counterparts, characteristic properties derived from Te atom have been reported. For instance, replacing the sulfur (S) atoms in thiophenes with selenium (Se) and tellurium (Te) dramatically changes the electronic properties of these compounds^{7,8}. Tellurophene polymers have been shown to have a higher hole mobility than lighter analogs, presumably due to the high HOMO energy, as well as the increased polarizability of the heavy Te atoms. They are also more readily doped leading to conductive films at low loadings of dopant. Recent reports revealed that π -extended tellurophenes undergo quantitative reactions with certain oxidants to give a stable hypervalent Te(IV) state never before observed in thiophenes or selenophenes, owing to the metalloid nature of Te^{26–29}.

Considering that tellurophenes possess metalloid tellurium atoms in conjunction with organic π -system, their redox chemistry should be fundamentally different from other chalcogenophenes and other types of π -conjugated molecules. Despite the high level of interest in the electronic properties of tellurophenes, there is no complete picture of the redox chemistry. Except for the above-mentioned oxidative chemical transformation, which clearly traps the oxidation on the Te center, it is not clear if electrochemical oxidation will lead to delocalized or localized oxidized species.

Herein, we present a comprehensive investigation of the redox behavior of π -extended tellurophenes. Using a series of electrochemical methods and conditions we discover that stable localized and stable delocalized oxidized species can be prepared from tellurophenes. The results are important for improving our knowledge of main-group redox chemistry as well as π -extended systems.

Results

Electrochemical redox of 2,5-diphenyltellurophene (PT) in the presence of halides. Inspired by a previous report on the transformation of PT into PT- X_2 ($X = F, Cl, Br$) by reaction with halogen-based oxidants (XeF_2, ICl, Br_2) (Fig. 1a)²⁸, we began our investigation with the electrochemical equivalent reaction (Fig. 1b). Spectroelectrochemistry (SEC) was selected as a suitable means of confirming the desired chemical transformation, because PT- X_2 generates a characteristic absorption spectrum as a result of intramolecular charge-transfer (ICT)²⁸. Density functional theory (DFT) calculations for PT- X_2 suggest that ICT in PT- X_2 is assignable to the transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)²⁸. The HOMO of PT- X_2 is the delocalized π -orbital, while the LUMO has significant Te- X antibonding character²⁸.

SEC analyses of PT in $X^-/MeCN$ ($X = F, Cl, and Br$) suggested that the transformation of PT to PT- X_2 proceed readily via

anodic oxidation (see Fig. 2, Supplementary Fig. 1, Supplementary Table 1). Transformation of PT into PT- F_2 cleanly proceeded in 0.1 M $KF/PEG/MeCN$ electrolyte³⁰, accompanying two isosbestic points in the UV/vis spectra (Fig. 2a). In the course of the oxidation, the original absorption peak of PT at 342 nm, attributed to the $\pi-\pi^*$ transition, successively decreased, and formation of PT- F_2 was evidenced by the characteristic absorption peak at 393 nm (395 nm in previous report measured in CH_2Cl_2 ²⁸), which derives from the ICT of Te(IV) containing PT. Considering the extremely high oxidation potential of fluoride ions, this reaction should have proceeded through the oxidation of PT. The use of Bu_4NF as a fluoride source and electrolyte failed, presumably due to the residual water in Bu_4NF (THF solution).

Chlorination and bromination were also observed by applying 0.8 V vs. SCE in the presence of Et_4NX ($X = Cl, Br$) (Fig. 2b, c), while the reaction mechanism presumably differed to the formation of PT- F_2 . Since the oxidation potential of chloride and bromide are lower than PT, electrogenerated Cl_2 and Br_2 should have reacted with PT. After the reaction, inverting the polarity of working electrode to -0.4 V vs. SCE gave the precisely opposite change to the oxidation process, resulting in a spectrum identical to that of original PT (Fig. 2d). This result clearly indicated that this chemical process was reversible under electrochemical conditions.

Electrochemical redox of PT in the absence of halides. An important observation was made when we measured the SEC of PT in $Bu_4NBF_4/MeCN$, where no nucleophilic anion was present (Fig. 1c). The absorption spectrum of the oxidized species was unexpectedly quite similar to that of PT- X_2 (Fig. 3a). In general, the oxidation of conjugated oligomers results in broad absorption bands known as polaronic, π -dimeric, and bipolaronic bands³¹, as seen in the SEC analysis of 2,5-diphenylselenophene (PS, Supplementary Fig. 2). Hence, the absorption change seen in the case of PT was quite unusual. Based on assessments of the PT- X_2 absorption spectra, we believe that MeCN and/or BF_4^- anions in the electrolyte were coordinated to the Te center of the oxidized PT, giving various coordinated species. In the following section, we refer to these species as PT- L_2 . It should be noted that this assumed coordination appears to have stabilized the oxidized PT, as implied by the fully reversible redox behavior, with isosbestic points, observed in the SEC data (Fig. 3b).

To investigate the effect of the surrounding media on the generation of PT- L_2 , SEC was performed with various salt/solvent combinations (Supplementary Fig. 3). When MeCN was used as the solvent, the same absorption spectra appeared regardless of the anion (Supplementary Fig. 3a). However, using CH_2Cl_2 as the solvent (Gutman's donor number³²: MeCN = 14.1, $CH_2Cl_2 = 1$) resulted in slight changes in the absorption maximum depending on the anion species, suggesting the preferential coordination of anions (Supplementary Fig. 3b). The behavior observed in this work is comparable to that reported by Dutton and co-workers. They synthesized PT(OAc)(OTf) by the chemical oxidation of PT with a hypervalent iodine reagent³³. Considering the much lower donor numbers of ClO_4^- , BF_4^- and PF_6^- compared to AcO^- and TfO^- ³⁴, it is of note that even the use of such weak anions or a neutral donor (MeCN) resulted in coordination to the Te center of the oxidized PT.

Electrosynthesis of PT- L_2 . To improve our understanding of this oxidized species, PT- L_2 was produced on a bulk scale, employing an electrosynthetic approach in conjunction with a H-type cell containing 0.1 M $NaBF_4/MeCN$ as the electrolyte under nitrogen (Fig. 4a, b). Constant potential electrolysis of PT at 1.4 V vs. SCE

Fig. 1 The redox behavior of π -extended tellurophenes. Details of **a** are in ref. ²⁸. **b–g** represents the work described in this paper

Fig. 2 Spectroelectrochemistry of **PT** in the presence of halides. **a** Oxidation at 2.0 V vs. SCE for 170 s in 0.1 M KF/MeCN with PEG ($M_n = 200$) as an additive. **b** Oxidation at 0.8 V vs. SCE for 15 s in 0.1 M $\text{Et}_4\text{NBr}/\text{MeCN}$. **c** Oxidation at 0.8 V vs. SCE for 55 s in 0.1 M $\text{Et}_4\text{NCl}/\text{MeCN}$. **d** Reduction of **PT-Cl₂** at -0.4 V vs. SCE for 70 s

gave **PT-L₂** as a red colored species in solution. Although, the anodic electrolyte was a colorless suspension before the electrolysis due to the poor solubility of **PT** in acetonitrile, it changed to homogeneous solution in the course of the electrolysis. This color

was maintained so long as the solution was kept under nitrogen, while a black suspension was generated upon exposure to air. Thus, it appears that the coordination discussed above does in fact stabilize the oxidized species, but not under aerobic

Fig. 3 SEC data for **PT** in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{MeCN}$. **a** Oxidation at 1.0 V vs. SCE for 70 s. **b** Reduction at -1.0 V vs. SCE for 90 s

conditions. Despite our best attempts, single crystals of **PT-L₂** could not be obtained, presumably due to a significant amount of contamination by the supporting electrolyte.

We considered that this hemilabile species might be reactive toward other strong nucleophiles (Figs. 2d and 4a). After accumulating **PT-L₂** by bulk electrolysis, 3 eq. of Et_4NX ($\text{X} = \text{Cl}, \text{Br}$) or Bu_4NF were added to the compound, upon which a rapid change in the color of the solution was observed. After workup, **PT-X₂** ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) was obtained in moderate yields, up to 79% (Supplementary Fig. 4). This result indicates that **PT-L₂** is the equivalent of two-electron-oxidized **PT**.

^{125}Te NMR measurement was carried out for electrogenerated **PT-L₂**. After accumulating **PT-L₂** in divided cell according to the above-mentioned procedure, anodic solution was collected and solvent was removed under the reduced pressure. Residual solid was dissolved in CD_3CN , and ^{125}Te NMR spectrum was collected (Fig. 4c). The crude material showed a peak at 1368.4 ppm and no trace of signal for starting material was observed at 747.2 ppm²⁸. The peak appearance at 1368.4 ppm is remarkable considering that all the reported derivatives of diphenyltellurophene with Te (IV) center show peaks around 680–900 ppm (**PT-Cl₂**: 839.6 ppm²⁸, **PT-Br₂**: 769.9 ppm²⁸, **PT(OAc)₂**: 683 ppm³³, **PT(OAc)(OTf)**: 900 ppm³³).

DFT calculation of PT and PT-L₂. DFT calculations provided support for the stable geometry of **PT-L₂**. The optimized structures of **PT-L₂** ($\text{L} = \text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-$ or MeCN) confirmed the interaction of the Te center with the various L groups (Fig. 5a). Time-dependent (TD) DFT calculations demonstrate a strong absorption mainly contributed by HOMO–LUMO transition (Supplementary Fig. 5a, b, Supplementary Table 2). While the HOMO was found to consist of a typical π -orbital, the LUMO showed an antibonding Te–L character (Fig. 5b), in keeping with results previously reported for simulations of **PT-X₂** ($\text{X} = \text{F}, \text{Cl}, \text{Br}$)²⁸.

In the optimized structures, the C–C bond lengths between adjacent aryl groups were close to those expected for single bonds

(1.450–1.459 Å), while the dihedral angles ranged from 16.7° (MeCN) to 31.0° (PF_6^-) (Supplementary Table 3). When dicationic **PT** was optimized in the absence of a coordinating species, a planar structure was obtained having shortened C–C bonds (1.406 Å), in which the dihedral angles of adjacent aryl rings were also $<1^\circ$. This represents the quinoidal structure typically adopted by oxidized conjugated oligomers (Supplementary Table 3). These computational simulations indicate that the coordination of neutral or anionic donors to the Te center can hinder the delocalization of the positive charge over the entire π -system.

DFT calculations did not identify any optimized geometry for two-electron-oxidized **PT** in conjunction with $\text{BAR}_4^{\text{F}-}$. Attempts at optimization consistently failed, instead giving geometries with spatially separated **PT**²⁺ and $\text{BAR}_4^{\text{F}-}$, demonstrating the absence of an interaction. This result supports the spectroscopic observations.

Although the previous work reported that simulated absorption spectra by B3LYP theory gave better agreement with experimental data **PT** and **PT-Br₂** compared to those simulated with CAM-B3LYP theory²⁸, absorption spectra of **PT-L₂** ($\text{L} = \text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-$) were simulated better with CAM-B3LYP (Fig. 5b, Supplementary Fig. 5a, b, Supplementary Tables 2, 3). Absorption spectrum of dicationic MeCN adduct **PT-L₂** ($\text{L} = \text{MeCN}$) was simulated the best when the solvation of CH_2Cl_2 with CAM-B3LYP theory was taken into account (Supplementary Fig. 6). TD-DFT calculation of **PT-L₂** series ($\text{L} = \text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-$, MeCN) demonstrated that the absorptions appeared at the lower energy region were all dominantly contributed by the HOMO–LUMO transition, i.e. ICT-type absorption (Supplementary Table 2).

Oxidation of PT in weakly coordinating electrolyte. These results raised the question: is it possible to delocalize the positive charge over the **PT** π -system, as is commonly the case following the oxidation of thiophene/selenophene-containing conjugated oligomers? To answer this question, we employed an electrolyte composed of $\text{BAR}_4^{\text{F}-}$ ($\text{Ar}^{\text{F}} = \text{pentafluorophenyl}$) and CH_2Cl_2 (Fig. 1e). As expected, the absorption spectrum recorded in 0.1 M $\text{NaBAR}_4^{\text{F}}/\text{CH}_2\text{Cl}_2$ exhibited a drastic change, such that broad absorption peaks around 515 and 760 nm were observed (Fig. 6, blue line). This spectrum is similar to those generated by various conjugated oligomers in the radical cation state, namely polaronic band^{31,35}. Thus, the generation of **PT**^{•+} was anticipated, which was evidenced by the electron paramagnetic resonance (EPR) measurement (for detail, see the section “EPR measurement”). TD-DFT calculation was performed for **PT**^{•+} under various conditions (Supplementary Fig. 7a). TD-DFT simulation incorporating the solvation of CH_2Cl_2 with CAM-B3LYP theory gave the best suited data ($\lambda_{\text{max}} = 483, 623 \text{ nm}$) to the experimental result ($\lambda_{\text{max}} = 515, 760 \text{ nm}$) (Supplementary Table 2).

Interestingly, when CH_2Cl_2 was replaced by MeCN as the solvent the spectrum showed ICT-type absorption, with a peak maximum at 417 nm (Fig. 6, red line). This result conclusively demonstrates the coordination of MeCN to the Te center.

Comproportionation of MeCN -adduct, **PT-L₂** ($\text{L} = \text{MeCN}$), with **PT** was also investigated (Fig. 1f). **PT-L₂** ($\text{L} = \text{MeCN}$) was electrochemically generated in 0.1 M $\text{Bu}_4\text{NBAR}_4^{\text{F}}/\text{MeCN}$ using divided cell. After passing 2 F/mol, 1 eq. of **PT** dissolved in CH_2Cl_2 was added to the anodic chamber. UV–Vis absorption spectra were collected before and after the addition of **PT**. Upon the addition of **PT** into **PT-L₂** solution, no absorption increment at 530 and 760 nm derived from **PT**^{•+} was observed (Supplementary Fig. 8). Instead, simple overlaid spectra of **PT** and **PT-L₂** were obtained. This result conclusively demonstrates that there is no comproportionation reaction between **PT** and **PT-L₂** ($\text{L} = \text{MeCN}$).

Fig. 4 Electrochemical generation of **PT-L₂**. **a** Electrochemical generation of **PT-L₂** and following reaction with halides. **b** Photograph of electrochemical cell before (left) and after (middle) the electrolysis, and following addition of bromide (right). **c** Full and partial ^{125}Te NMR spectrum (94 MHz, CD_3CN) of **PT-L₂**

Cyclic voltammetry measurement. Based on the changes in absorption spectra depending on the electrolyte, we were prompted to acquire CV data for **PT** in various media (Fig. 7a). When CVs were recorded in MeCN containing BF_4^- or PF_6^- , all the oxidation waves were irreversible, and broad reduction currents appeared, presumably corresponding to the reduction of coordinated species. The electrochemical irreversibility remained when CH_2Cl_2 was used as the solvent with these same anions, although the oxidation potential shifted slightly in the positive direction. In contrast, the use of $\text{Bu}_4\text{NBAR}_4^-/\text{CH}_2\text{Cl}_2$ caused the **PT** to undergo quasi-reversible oxidation behavior, implying the absence of a nucleophilic reaction with the oxidized species. The oxidation again became irreversible when $\text{Bu}_4\text{NBAR}_4^-/\text{MeCN}$ was used, corresponding to the observation in Fig. 6. These CVs indicate that the oxidation of **PT** was intrinsically reversible but became irreversible upon coordination with the surrounding medium.

Further extension of π -system. At this point, it was hypothesized that the balance between the nucleophilicity of anions and the energetic advantage obtained from charge-delocalization determine the favored state. This would suggest that the extending π -system in the tellurophene should increase the energetic advantage associated with charge-delocalization, and possibly produce new absorption spectra.

Based on this hypothesis, we prepared 2,5-bis(2-(9,9'-dimethylfluorenyl))tellurophene (**FT**), in which the fluorenyl group enhances the charge-delocalization by extended π -system (Fig. 1g). CVs were obtained from **FT** using BF_4^- , PF_6^- , and BAR_4^-

in CH_2Cl_2 (Fig. 7b). Interestingly, **FT** showed quasi-reversible redox with PF_6^- and BAR_4^- . Encouraged by this result, we analyzed **FT** by SEC (Fig. 8a). Upon applying an oxidative potential in the presence of BF_4^- , **FT** exhibited ICT-type absorption (Fig. 8a, blue), while a polaronic band derived from $\text{FT}^{\bullet+}$ was observed in $\text{Bu}_4\text{NBAR}_4^-/\text{CH}_2\text{Cl}_2$ (Fig. 8a, green), in accordance with the results from the oxidation of **PT**. DFT and TD-DFT calculations supported the coordination of BF_4^- to the oxidized **FT** and the subsequent ICT-type absorption (Fig. 8b, Supplementary Figs. 5c, d and 9, Supplementary Tables 2, 4). TD-DFT calculation of $\text{FT}^{\bullet+}$ suggested the presence of two absorption bands around 600 and 900 nm (Supplementary Fig. 7b, Supplementary Table 2). The band at 600 nm was mainly contributed by singly occupied molecular orbital (SOMO) to α -LUMO transition, whereas the band at 900 nm was dominantly contributed by β -HOMO to β -LUMO transition. The former corresponds to the experimentally observed broad absorption around 500–700 nm region (Fig. 8a, green), while the latter was not observed due to the observation limit of the spectrometer.

Intriguingly, when $\text{Bu}_4\text{NPF}_6^-/\text{CH}_2\text{Cl}_2$ was used for the oxidation of **FL**, both ICT-type absorption and a polaronic band were observed (Fig. 8a, red). This result indicates the co-existence of two different states. This tendency can be explained based on the order of the donor numbers of the anions ($\text{BF}_4^- > \text{PF}_6^- > \text{BAR}_4^-$)^{33,36}. That is, PF_6^- possesses moderate nucleophilicity and thus generates two distinct states. However, even in the presence of PF_6^- , it is assumed that the coordinated form **FT-L₂** is more stable, because the ICT-type absorption

Fig. 5 Computational study of $\text{PT}^{\bullet+}$, PT^{2+} and PT-L_2 . **a** Optimized structure of $\text{PT}^{\bullet+}$, PT^{2+} and PT-L_2 ($\text{L} = \text{ClO}_4^-$, BF_4^- , PF_6^- , MeCN). **b** Energy levels of HOMO and LUMO in PT-L_2 ($\text{L} = \text{ClO}_4^-$, BF_4^- , PF_6^- , MeCN). TD-DFT calculations were performed with CAM-B3LYP/6-311 + g(2df, 2p)/SDD. For the calculation of dicationic PT-L_2 ($\text{L} = \text{MeCN}$), the solvation of CH_2Cl_2 was taken into account with the polarizable continuum model using the integral equation formalism variant. For the comparison of TD-DFT result of dicationic PT-L_2 ($\text{L} = \text{MeCN}$) under various sets of conditions, see Supplementary Fig. 6

intensity was much higher than that of the polaronic band. The optimized structure for FT-X_2 ($\text{X} = \text{PF}_6$) shows a typical coordinated form (Fig. 8b).

EPR measurement. EPR measurements were carried out for $\text{PT}^{\bullet+}$ and $\text{FT}^{\bullet+}$ (Supplementary Fig. 10a). PT or FT was oxidized in 0.1 M $\text{Bu}_4\text{NBAR}_4^{\text{F}}/\text{CH}_2\text{Cl}_2$ using H-type cell at room temperature under nitrogen atmosphere. Passing 1 F/mol of charge gave deep red or blue color solution in the anodic chamber for $\text{PT}^{\bullet+}$ and $\text{FT}^{\bullet+}$, respectively (Supplementary Fig. 10b). Solution of $\text{PT}^{\bullet+}$ maintained its color at low temperature (-30°C) under inert atmosphere, while leaving the solution at room temperature under inert atmosphere overnight resulted in the color change to brown and gave insoluble material. $\text{FT}^{\bullet+}$ showed deep blue color in solution (Supplementary Fig. 10b). The color was persistent even at room temperature under inert atmosphere overnight, indicating higher order stability of $\text{FT}^{\bullet+}$ compared to $\text{PT}^{\bullet+}$.

The anodic solution was degassed by freeze–pump–thaw cycle three times, then EPR spectrum was collected at room temperature immediately after preparing the sample. Both $\text{PT}^{\bullet+}$ and $\text{FT}^{\bullet+}$ samples showed EPR signals, demonstrating that

radical species are indeed generated via the anodic oxidation in weakly coordinating electrolyte (Supplementary Fig. 10c). Peak-to-peak line width (ΔB_{pp}) for $\text{PT}^{\bullet+}$ and $\text{FT}^{\bullet+}$ were 2.09 and 0.53 mT, respectively. The smaller splitting of $\text{FT}^{\bullet+}$ compared to $\text{PT}^{\bullet+}$ was attributed to the more delocalized nature of the spin in π -system. The spin density mapping simulated by DFT calculation also support the more delocalized spin distribution in $\text{FT}^{\bullet+}$ compared to $\text{PT}^{\bullet+}$ (Supplementary Fig. 10a).

Discussion

We have investigated the redox behavior of π -extended tellurophenes in various media. ICT-type absorption was observed during the anodic oxidation of PT , implying that solvent molecules and/or anions coordinated to Te and that oxidation is confined to the Te center. On the other hand, under weakly coordinating conditions (BAR_4^{F} anion in CH_2Cl_2) produced species that are clearly different from ICT-type absorption, demonstrating the generation of cationic PT with charge delocalization over the entire π -system. We have also successfully identified the conditions under which both the coordination and charge-delocalization states can co-exist, as a result of extending the π -system. One can regard these

Fig. 6 Oxidation of **PT** in the presence of weakly coordinating anion. SEC data for 1 mM **PT** before (dotted line) and after (solid line) oxidation in 0.1 M NaBARF₄/CH₂Cl₂ (blue) or 0.1 M NaBARF₄/MeCN (red)

(a) PT

(b) FT

Fig. 7 CV measurements of **PT** and **FT** in various electrolytes. CVs of (a) 1 mM **PT** and (b) 1 mM **FT** in (dotted lines) MeCN or (solid) CH₂Cl₂. The electrolyte was 0.1 M Bu₄NA (A = BF₄⁻, PF₆⁻ or BARF₄⁻). Scale bars in **a** and **b** indicate 10 and 5 μA, respectively

experiments as a means of better understanding intramolecular charge transportation in tellurophene-containing materials. We believe the findings reported herein will contribute to the improvement of such materials, as well as providing fundamental new insights into the chemistry of chalcogenophenes.

Methods

General considerations. All reagents and dehydrated solvents were from commercial source and used without further purification unless otherwise noted. Diethyl ether solution of isopropylmagnesium chloride (PrⁱMgCl, 1.0 M) was prepared by the previously reported procedure³⁷. Titanium(IV) isopropoxide

Fig. 8 SEC measurements and computational simulations of **FT**. **a** SEC data for 1 mM **FT** in CH₂Cl₂ with various salts. Neutral **FT** (dotted line), and oxidized **FT** in 0.1 M Bu₄NBF₄ (blue), 0.1 M Bu₄NPF₆ (red), 0.1 M Bu₄NBARF₄ (green). The BARF₄⁻ data were recorded before the full conversion to avoid absorbance values over the allowable range. Even following full conversion, **FT** does not show ICT-type absorption with BARF₄⁻. Inset: enlarged view of the polaron band in the red line plot. **b** Optimized structure of **FT**^{•+}, **FT**²⁺ and **FT-L**₂ (L = BF₄⁻, PF₆⁻)

[Ti(OPrⁱ)₄] was obtained from Sigma-Aldrich and distilled under reduced pressure. Diethyl ether was dried over sodium benzophenone ketyl and distilled under nitrogen. PS³⁸ and 1-(9,9-dimethylfluorene-2-yl)acetylene³⁹ were synthesized according to the reported procedure. Aqueous solution of NaBARF₄^F (Ar^F = pentafluorophenyl) was kindly supplied by Nippon Shokubai Co. Ltd. and NaBARF₄^F salt was obtained by evaporating the solvent. Bu₄NBARF₄^F was prepared by salt exchange of NaBARF₄^F and Bu₄NBr. NMR data for the synthesized materials are shown in Supplementary Figs. 11–14.

¹H and ¹³C NMR spectra were recorded on JEOL JNM EX-270 (¹H: 270.05 MHz, ¹³C: 67.8 MHz) spectrometer using CDCl₃ as a solvent. The chemical shifts for ¹H and ¹³C NMR spectra are given in δ (ppm) from internal tetramethylsilane (TMS) and CDCl₃, respectively. ¹²⁵Te NMR spectrum was recorded on JEOL ECP-300 (¹²⁵Te: 94 MHz) spectrometer using acetonitrile-d₃ as a solvent. EPR spectra were recorded using JES-RE3X EPR spectrometer. CV measurements were carried out using ALS 600A electrochemical analyzer or ALS 6005C electrochemical analyzer. SEC measurements were carried out using SEC2000-UV/Vis spectrometer system (BAS). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer.

Cyclic voltammetry measurement. Cyclic voltammetry measurements were performed in the three-electrode system equipped with Pt disk working electrode (ϕ = 1.6 mm), a Pt plate counter electrode (20 mm × 20 mm) and a SCE reference electrode in 0.1 M supporting electrolyte solution at a scan rate of 100 mV s⁻¹.

Spectroelectrochemistry. SEC measurements were performed in the three-electrode system equipped with a Pt gauze working electrode, a Pt wire counter electrode, and a SCE reference electrode in thin layer quartz glass spectroelectrochemical cell (1 mm thick) filled with 0.1 M supporting salt electrolyte containing 1 mM of substrates.

Electrosynthesis of PT-L₂ and subsequent reaction with halides. PT-L₂ was generated in bulk scale based on the electrosynthetic approach using an H-type cell. Bulk electrolysis was conducted in the H-type cell equipped with a Pt plate anode

(25 mm × 40 mm), a Pt cathode (20 mm × 20 mm) and an Ag wire as a pseudo-reference electrode. The applied potential was corrected into SCE value based on the potential difference of the ferrocene/ferrocenium redox pair. After putting magnetic stirrer bar, **PT** (0.1 mmol in anodic chamber) and NaBF₄ supporting electrolyte (20 mmol for each chamber), the cell atmosphere was replaced by nitrogen. NaBF₄ was employed because it can easily be removed by the wash with water. All the following procedure were conducted under the nitrogen flow. Dehydrated solvent (20 mL for each chamber) and trifluoromethanesulfonic acid (cathodic chamber, 20 mL) were added via syringe. 1.4 V vs. SCE was applied and electrolysis was continued until the electricity reaches 2 F/mol.

After accumulating **PT-L**₂ by electrolysis, 3 eq. of Et₄NX (X = Cl, Br, I) or Bu₄NF was added to the anodic chamber, accompanying rapid color change to leave some precipitate. This suspension was stirred for 15 min under nitrogen flow, then the anodic part was collected and concentrated under reduced pressure. Due to the nature of the product, column chromatography was not applicable for the purification. Instead, the crude materials were washed with deionized water, diethyl ether and hexane to remove NaBF₄ (supporting electrolyte) and Et₄NX. The resulting residue was characterized by ¹H NMR in CDCl₃, confirming the generation of **PT-X**₂ (X = Cl, Br) indicated by the characteristic singlet peak derived from the 3 and 4 position of tellurophene ring⁶. In regard with **PT-Cl**₂ and **PT-Br**₂, ¹H NMR showed peaks of **PT-X**₂ (X = Cl or Br), starting **PT** and residual solvent, thus the yield was calculated based on the weight of the mixture and the molar ratio of **PT-L**₂ and **PT** (Supplementary Fig. 4). The yields were 79% for **PT-Cl**₂ and 73% for **PT-Br**₂, respectively. Although the formation of **PT-F**₂ was also identified in ¹H NMR, due to the difficulty of eliminating alkylammonium contaminate, the yield was not calculated. The use of iodide as a nucleophile resulted in the recovery of **PT**, presumably due to the reductive elimination of iodine from the Te center, or the reduction of **PT-L**₂ by electron transfer from iodide. DFT calculation suggested that **PT-I**₂ is 7.2 kcal/mol more stable than the sum of the energy of **PT** and **I**₂. Hence, the electron transfer pathway between **PT-L**₂ and iodide seems more reasonable.

Comproportionation of oxidized 2,5-diphenyl tellurophene. Comproportionation between **PT** and **PT-L**₂ was investigated. **PT**^{•+} and **FT**^{•+} was generated in bulk scale based on the electrosynthetic approach using an H-type cell. Bulk electrolysis was conducted in the H-type cell equipped with a Pt plate anode (25 mm × 40 mm), a Pt cathode (20 mm × 20 mm) and an Ag wire as a pseudo-reference electrode. The applied potential was corrected into SCE value based on the potential difference of the ferrocene/ferrocenium redox pair. After putting a magnetic stirrer bar, **PT** (0.05 mmol in anodic chamber) and Bu₄NBAr₄^F supporting electrolyte (20 mmol for each chamber), the cell atmosphere was replaced by nitrogen. Dehydrated acetonitrile (20 mL for each chamber) was added via syringe. 1.4 V vs. SCE was applied and electrolysis was continued until the electricity reached 2 F/mol. After the electrolysis, an aliquot was collected from anodic solution and diluted dichloromethane 10 times and the UV-vis spectrum was recorded.

To an anodic solution containing **PT-L**₂ (L = MeCN) was added 1 eq of **PT** (0.05 mmol) dissolved in minimum amount of dichloromethane. After reacting for 10 min, an aliquot was collected from anodic solution and diluted dichloromethane 10 times and the UV-vis spectrum was recorded (Supplementary Fig. 8).

Electrochemical generation of **PT^{•+} and **FT**^{•+} for EPR measurement.** **PT**^{•+} and **FT**^{•+} were generated in bulk scale based on the electrosynthetic approach using an H-type cell. Bulk electrolysis was conducted in the H-type cell equipped with a Pt plate anode (10 mm × 10 mm), a Pt cathode (10 mm × 10 mm), and an Ag wire as a pseudo-reference electrode. The applied potential was corrected into SCE value based on the potential difference of the ferrocene/ferrocenium redox pair. After putting a magnetic stirrer bar, **PT** or **FT** (0.05 mmol in the anodic chamber) and Bu₄NBAr₄^F supporting electrolyte (10 mmol for each chamber), the cell atmosphere was replaced by nitrogen. Dehydrated dichloromethane (10 mL for each chamber) was added as a solvent. 1 F/mol of charge was passed under constant potential application (1.2 V vs. SCE for **PT** and 1.0 V vs. SCE for **FT**). After the electrolysis, the reaction mixture in the anodic chamber was transferred into the nitrogen-filled Schlenk flask. The solution was degassed by freeze-pump-thaw cycle three times. **PT**^{•+} showed deep red color in solution, and the color was persistent under an inert atmosphere at low temperature (−30 °C), while the color changed to brown and insoluble materials slowly precipitated out of the solution at room temperature. **PT**^{•+} showed deep blue color in solution, and the species was stable even at room temperature under an inert atmosphere.

The degassed solutions were charged into a tube and EPR measurements were performed at room temperature (Supplementary Fig. 10). Manganese oxide was used as an internal standard for the measurement of **PT**^{•+}.

DFT calculation. All calculations were performed using Gaussian 09 software. Geometry optimizations and frequency calculations were performed for all of the tellurophene derivatives at the B3LYP level of theory using LANL2DZ effective core potential for tellurium and iodine, and 6-31G(d) basis set for all other atoms. Frequency calculations were performed with the same basis set with scaling factor of 0.977⁴⁰. TD calculations were performed B3LYP or CAM-B3LYP level theory using SDD for Te, and 6-311G + (2df, 2p) basis set for all other atoms. For the calculation of dicationic **PT-L**₂ (L = MeCN), **PT**^{•+} and **FT**^{•+}, the solvation of CH₂Cl₂ or MeCN

was also taken into account with the polarizable continuum model using the integral equation formalism variant (effect of solvation in DFT calculation is summarized in Supplementary Figs. 6 and 7). The TD-DFT calculations were performed on the optimized geometries to determine the first 20 singlet transitions. Cartesian coordinates for optimized structures are shown in Supplementary Tables 5–18.

Data availability

All other relevant source data are available from the corresponding author upon reasonable request.

Received: 16 May 2019; Accepted: 17 October 2019;

Published online: 06 November 2019

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Acknowledgements

The authors thank Dr. Yoshihisa Sei in Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology, for EPR measurement. The authors thank Prof. Akihiro Shimizu at Osaka University for fruitful discussion. This study was financially supported by JSPS KAKENHI Grant numbers JP26708013, JP15H00724, and JP17H03095 (S.I.). N.S. also thanks JSPS for the financial support of his research fellowship (No. 16J07350). D.S.S. acknowledges the support by the NSERC of Canada.

Author contributions

S.I. conceived and directed the project. N.S., H.N., F.Z., and S.Y. designed and performed the experiments. S.I., D.S.S., and I.T. discussed results. S.I., D.S.S., and N.S. wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at <https://doi.org/10.1038/s42004-019-0228-y>.

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