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Dicationic Heteroacenes Containing Thio- or Selenopyrylium Moieties

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Supporting Information

ABSTRACT: Dicationic heteroacenes that bear thio- or selenopyrylium moieties were synthesized by addition reactions of the corresponding diones with a Grignard reagent, followed by a dehydration reaction of the resulting diols with Brønsted acid. Alternatively, these dicationic heteroacenes were obtained from two-electron oxidations of the corresponding sulfur- or selenium-containing quinoids. The electronic structures of these dicationic heteroacenes were examined by NMR and UV-vis-NIR spectroscopy in conjunction with density functional theory calculations. The results of this



combined experimental and theoretical approach strongly imply effective conjugation of 22π -electrons in a system that is distributed over the entire pentacene framework.

■ INTRODUCTION

The synthesis of linearly fused polycyclic aromatic hydrocarbons has received considerable attention owing to their potential utility in organic photovoltaics, organic light-emitting diodes, and organic field-effect transistors. Among these promising small organic molecules, pentacene and its derivatives are known to be key components of highperformance organic thin-film devices.¹ Azapentacenes, i.e., isoelectronic analogues of pentacene containing nitrogen atoms, have recently attracted particular interest as a new and promising class of organic materials. Numerous synthetic routes to diaza- and tetraazapentacenes as well as their applications in organic field effect transistors materials have been reported.² Furthermore, diazadiborapentacene and thiaborin derivatives have been reported (Figure 1) and their unique structures and properties have been probed.³

Meanwhile, thio- and selenopyrylium salts represent a fundamental class of molecules in the field of organic chemistry that has attracted much attention in the last decade.⁴ To date, the synthesis of thio- or selenopyrylium-based acenic molecules, such as chalcogenpyrylium-containing naphthalenes,⁵ anthracenes,⁶ and tetracenes,⁷ has been reported. Theoretical investigations into these molecules have been also performed, and these predict characteristically small highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps.⁸ Thus, it was postulated that the electronic communication of p-orbitals between carbon and chalcogen atoms can decrease the optical band gap. In 1994, dicationic pentacene derivative F, which includes two thiopyrylium units, had been synthesized via a dehydration reaction of the corresponding thiopyranol precursor with a Brønsted acid.⁹ The ¹H NMR as well as UV-vis absorption spectra were recorded, and the latter revealed a red-edge absorption maximum at 778 nm. The result inspired us to explore the synthesis of new dicationic heteroacenes containing thio- or selenopyrylium moieties. For that purpose, we designed synthetic routes to 1a and 1b (Figure 2) via intramolecular Friedel-Crafts cyclizations of suitable precursors, which are based on a previous report on the synthesis of 2,5-arylchalcogenoterephthalic acid derivatives.¹⁰ More recently, Chi and co-workers have independently reported the synthesis of linear acenic derivative G, which bears thiopyrylium subunits, by two-electron oxidation of the corresponding quinoidal precursor, and revealed its solidstate structure.¹¹ As reports on the synthesis of pentacene analogues that contain sulfur atoms have remained scarce over the last decades, investigations on such synthetic approaches still remain a great challenge. Furthermore, synthetic investigations into dicationic pentacenes that bear selenium atoms have not been reported so far. Heteroacene 1b is the first example of its kind and provides valuable photophysical information on this class of compounds.

Herein, we report our concerted experimental and theoretical approach to develop a synthetic route to novel dicationic linear heteroacenes 1a and 1b, which bear thio- or selenopyrylium units (Figure 2), respectively, and we describe their electronic structures.

RESULTS AND DISCUSSION

Synthesis of Dicationic Heteroacenes 1a and 1b. Synthetic access to dicationic heteroacenes 1a and 1b was established via the following two pathways (Scheme 1): (i) treatment of dione derivatives 5a and 5b with arylmagnesium bromides, followed by dehydration reactions of the corresponding diol derivatives (6a and 6b) with a Brønsted acid; (ii) two-electron oxidation of conjugated quinoidal molecules 7a and 7b.

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Figure 1. Structures of selected diaza-, tetraazapentacenes, and pentacene analogues that contain nitrogen, boron, and/or sulfur atoms.



Figure 2. Chemical structures of 1a and 1b.

Initially, the nucleophilic substitutions of dibromophthalic acid ethyl ester 2 with benzenethiol 3a or benzeneselenol 3b provided phthalic acids 4a or 4b, which bear thioaryl or selenoaryl groups, in 72 and 20% yield, respectively (Scheme 2). Subsequent chlorination and Friedel-Crafts acylation of 4a afforded dione 5a in 91% vield. In the case of selenium analogue 4b, the sequence of chlorination and Friedel-Crafts acylation provided exclusively dione 5b in 25% yield and its molecular structure was confirmed by single-crystal X-ray

diffraction analysis (Figure S1). The results obtained indicate that the Friedel-Crafts reaction of phthaloyl dichloride 4b' involves an aryl migration via intermediate G through ipsoacylation (Scheme 3).¹² Treatment of diones 5a and 5b with tetramethylphenylmagnesium bromide in the presence of zinc chloride furnished diol derivatives 6a and 6b as diastereomeric mixtures in 51 and 28% yield, respectively (Scheme 4).

Meanwhile, treatment of diones 5a and 5b with tetramethylphenylmagnesium bromide, followed by a reaction with tin(II) chloride dihydrate afforded the corresponding quinoids 7a and 7b in 31 and 63% yield, respectively (Scheme 4). Prior to the chemical oxidations of 7a and 7b, the electrochemical behavior of 7a and 7b was examined by cyclic and differential pulse voltammetry. The corresponding voltammograms are shown in Figure 3. Reversible stepwise one-electron oxidation couples were observed between -0.10and +0.41 V for 7a and 7b (Table 1), suggesting that quinoids





1b (E = Se, R¹ = H, R² = *t*-Bu)

Scheme 2. Synthesis of 5a and 5b







Scheme 4. Synthesis of 1a and 1b



7a and 7b feature low oxidative potentials and that the resulting oxidized species are relatively stable in solution.

To synthesize dicationic heteroacenes 1a and 1b, we initially tried dehydrations of diols 6a and 6b using the Brønsted acid, tetrafluoroboric acid (Scheme 4). Upon adding an ethereal solution of tetrafluoroboric acid to a solution of 6a and 6b in dichloromethane at room temperature, the absorption for 6aand 6b in their UV-vis spectra disappeared. The solution was added dropwise to cooled hexane, and the brownish stable powder that precipitated was isolated by centrifugation. An elemental analysis of this brown powder (1a) or reddish purple powder (1b) revealed an elemental composition consistent with dication bis(tetrafluoroborate)s 1a and 1b, respectively, and this assignment was corroborated by multinuclear NMR spectroscopic analyses (vide infra).

Subsequently, oxidation reactions of quinoids 7a and 7b using $(NO)[BF_4]$ were monitored using UV-vis-NIR absorption spectroscopy. Upon treating 7a and 7b with one equivalent of $(NO)[BF_4]$ in CH_2Cl_2/CH_3CN (v/v = 9:1) at room temperature, the absorption bands for 7a and 7b disappeared in their UV-vis-NIR absorption spectra (Figure S2). Simultaneously, intense absorptions emerged in the NIR

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Figure 3. Cyclic (black) and differential pulse (red) voltammograms of 7a (left) and 7b (right).

Table 1. Observed Redox Potentials^{*a*} [V vs Fc/Fc^+] for 7a and 7b

	7a		7	'b
compd	first	second	first	second
$E_{\rm pa}$	-0.08	+0.49	-0.02	+0.48
$E_{\rm pc}$	-0.20	+0.34	-0.19	+0.30
$E_{1/2}$	-0.14	+0.41	-0.10	+0.39
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^aSupporting electrolyte: 0.1 M [n-Bu₄N][PF₆]; [7a]: 1.2 × 10⁻³ mol/L; [7b]: 5.0 × 10⁻³ mol/L (both in CH₂Cl₂); scan rate: 100 mV/s; room temperature.

region, which were assigned to the corresponding radical cations **8a** ($\lambda_{max} = 896/1094$ nm) and **8b** ($\lambda_{max} = 922/1128$ nm). These absorptions were attributed to $\pi - \pi^*$ electron transitions of the pentacene chromophores, which is supported by theoretical calculations (vide infra). Moreover, the red-edge absorption at $\lambda_{max} = 1094$ nm for sulfur analogue **8a** is comparable to that of previously reported radical cation E ($\lambda_{max} = 1092$ nm in CH₂Cl₂). The ESR spectra of **8a** and **8b** exhibited a broad signal at g = 2.004 and 2.010, respectively (Figure S3), which supports the presence of such radical species in solution.

Upon adding an excess of $(NO)[BF_4]$, the bands for 8a and 8b completely disappeared, under concomitant emergence of weak absorptions at 706/784 nm (8a) or 742/824 nm (8b) (Figure 4). These new bands can be attributed to dications 1a and 1b and are consistent with those of theoretically calculated dications 1a' and 1b' (vide infra). The red-edge absorptions correspond to $\pi - \pi^*$ electron transitions of the dicationic pentacene chromophore for sulfur and selenium analogues 1a and 1b, respectively. The red-edge absorption of the former is comparable to those of the previously reported dications F $(\lambda_{\text{max}} = 778 \text{ nm in } 0.05 \text{ M TfOH}-\text{CH}_3\text{CN})$ and **G** $(\lambda_{\text{max}} = 780 \text{ mm s})$ nm in CH₂Cl₂). The observed bathochromic shift for the rededge absorption maxima for 1a and 1b is larger than that between heteropentacene analogues A ($\lambda_{max} = 661$ nm in hexane), C ($\lambda_{max} = 681$ nm in hexane), D ($\lambda_{max} = 523$ nm in cyclohexane), and E (λ_{max} = 499 nm in cyclohexane) (Figure 1) and also between thiophene- and/or selenophene-containing heterocycles, such as I^{13} ($\lambda_{max} = 489$ nm in CH₂Cl₂), J^{13} ($\lambda_{max} = 481$ nm in CH₂Cl₂), K^{14} ($\lambda_{max} = 344$ nm in tetrahydrofuran (THF)), and L^{14} ($\lambda_{max} = 356$ nm in THF) (Figure 5). Thus, the observed decrease of the optical band gap can be reasonably rationalized in terms of a weak overlap of the π orbitals between the carbon-2p and sulfur-3p/ selenium-4p orbitals in the pentacene core of 1a and 1b.

NMR Spectroscopic Characterization of 1a and 1b. The molecular structures of 1a and 1b in solution were investigated by NMR spectroscopy. The NMR spectra of 1a



Figure 4. UV–vis–NIR absorption spectra of (a) 7a and (b) 7b upon addition of (NO)[BF₄] (1.0, 2.0, 3.0, 4.0, and 5.0 equivalents) in CH_2Cl_2/CH_3CN (v/v = 9:1) at room temperature.



Figure 5. Molecular structures of I-L.

and **1b** are shown in Figures S8–S10. The ¹H NMR spectra of **1a** and **1b** revealed deshielded resonances for all aromatic protons (<8 ppm) except for the tetramethylphenyl groups (Table 2), which are comparable to those of previously reported sulfur-containing acenes F and G. The most low-field-shifted signals for **1a** and **1b** can be assigned to the H6 protons at 9.58 and 9.68 ppm, respectively (cf. Table 2). Moreover, the resonances for the *ortho*-methyl groups of the tetramethylphenyl groups in **1a** and **1b** at 1.69 and 1.68 ppm, respectively, are upfield shifted, whereas the methyl groups at the metaposition resonate at 2.46 and 2.45 ppm, respectively. In their entirety, these results suggest the presence of a significant diatropic ring current in the pentacene subunits of **1a** and **1b**.

The ¹³C NMR spectra of **1a** and **1b** indicate a C_2 symmetric structure in solution (Figure S9), which is similar to those of the reported compounds F and G. Signals for atoms C1–C12 in **1a** and **1b** were observed at 127.5–167.2 ppm, whereas the

Fable 2. Observed and Calculated	¹ H NMR Chemical Shifts	[ppm]] for 1a/1b and 1a'/1	b′
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R ² , E	Ar	$\stackrel{H1}{\downarrow}$ R^1	2[BF ₄]			
	H6	$H4$ R^2	Ar = 2,3,5,6-Me₄C ₆ H			
1a (E = S, R ¹ = <i>t</i> -Bu, R ² = H3) 1b (E = Se, R ¹ = H2, R ² = <i>t</i> -Bu)						

compd	H1	H2	H3	H4	H6	CH ₃ ^c	CH_3^d	$C(CH_3)_3$
la ^a	8.06		8.69	8.89	9.58	1.69	2.46	1.34
1a' ^b	8.42		8.91	8.53	9.41	1.39	2.28	1.10
$1b^a$	8.26	8.01		9.02	9.67	1.69	2.45	1.55
16' ^b	8.48	8.18		8.64	9.32	1.20	2.26	1.34

^{*a*}Experimentally observed chemical shifts were recorded in CDCl₃/CD₃CN (v/v = 4:1). ^{*b*}Calculations were carried out at the GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(2d,p) level of theory. ^{*c*}Methyl groups are located at the 2,6-positions of the duryl substituents. ^{*d*}Methyl groups are located at the 3,5-positions of the duryl substituents.

most low-field-shifted signals at 176.3 ppm (for 1a) and 175.8 ppm (for 1b) were attributed to the C8 atoms of the chalcogenopyrylium ring (cf. Table S4). These experimentally observed chemical shifts of the pentacene core are substantially inconsistent with those of carbocations,¹⁵ such as the diphenylmethylium ($\delta = 201$) and triphenylcarbenium ($\delta = 212$) cations, indicating that 1a and 1b do not exhibit a localized carbocationic character in solution.

Although we could not detect ⁷⁷Se NMR resonance for **7b** in CDCl₃ at room temperature, we observed a singlet for dication 1b at 727.1 ppm in $CDCl_3/CD_3CN$ (v/v = 4:1) at room temperature (Figure S10). The resonance observed for 1b is low-field-shifted relative to neutral selenophene¹⁶ ($\delta = 613$) and benzo[b]selenophene¹⁶ (δ = 526), as well as slightly upfield shifted relative to that of monocationic selenopyrylium derivatives, such as selenopyrylium perchlorate¹⁷ (δ = 976 in CF₃COOD), selenopyrylium tetrafluoroborate¹⁸ (δ = 975.7 in CD₃CN), and 3-tert-butyl-2-benzoselenopyrylium tetrafluoroborate¹⁸ (δ = 890 in CD₃CN). The results of the ⁷⁷Se NMR analysis thus clearly suggest that 1b should be considered a cationic aromatic molecule. Accordingly, on the basis of this multinuclear NMR analysis, it seems feasible to conclude that in solution, 1a and 1b represent aromatic chalcogenopyryliumcontaining dicationic pentacenes.

Theoretical Investigations. To gain further insight into the electronic structures of 1a and 1b, we carried out theoretical calculations on radical cations 8a' and 8b' as well as dications 1a' and 1b', where the counter anions were omitted for simplicity. These molecules were optimized using density functional theory (DFT) methods implemented in the Gaussian 16 program,¹⁹ leading to C_{2h} symmetric optimized structures for 1a' and 1b' as well as 8a' and 8b'. For radical cations 8a' and 8b', assignment of the UV-vis-NIR absorption spectra was based on the results of time-dependent (TD)-DFT calculations at the UB3LYP/6-311+G(2d,p) level of theory. The experimentally observed absorption bands of 8a and 8b were assigned to singly occupied molecular orbital $(SOMO) \rightarrow LUMO$ and $SOMO - 1 \rightarrow SOMO$ transitions, i.e., symmetry-allowed $\pi - \pi^*$ transitions in the heteropentacene framework (Figure S4).²⁰ Thus, the theoretically predicted wavelengths match sufficiently well with the experimentally observed absorption bands in the UV-vis-NIR spectra.

In dicationic heteroacenes 1a' and 1b', the theoretically derived LUMOs and HOMO - 4 to HOMO - 7 are delocalized over the π^* - and π -orbitals of the heteropentacene

framework, respectively, whereas the HOMO to HOMO – 3 are localized exclusively on the π -electrons of the tetramethylphenyl groups (Figures S5 and S6). The results of TD-DFT calculations on 1a' and 1b' revealed that the predicted intense $\pi - \pi^*$ transitions can be assigned to the HOMO – 4 \rightarrow LUMO and HOMO – 6 \rightarrow LUMO transitions (Figure 6 and



Figure 6. HOMO - 6, HOMO - 4, and LUMOs (isovalue: 0.020) of dications 1a' and 1b' calculated at the B3LYP/6-311+G(2d,p) level of theory. Hydrogen atoms are omitted for clarity.

Table 3) and that the transition energies of selenium analogue 1b' are narrower than those of sulfur analogue 1a', which is in good agreement with the experimentally observed results.

Table 3. Summary of the TD-DFT Calculations on Dications 1a' and $1b'^{a}$

compd	$E (eV)^{b}$	$\lambda (nm)^{c}$	f^d	transition
1a'	1.632	759.7	0.0558	HOMO – 4 \rightarrow LUMO
	2.838	436.8	0.8282	HOMO $- 6 \rightarrow$ LUMO
1b′	1.550	799.7	0.0510	HOMO – $4 \rightarrow LUMO$
	2.683	462.1	1.0403	HOMO $- 6 \rightarrow$ LUMO

^{*a*}Calculations were carried out at the TD-B3LYP(PCM-CH₂Cl₂)/6-311+G(2d,p)//B3LYP/6-311+G(2d,p) level of theory. ^{*b*}Excitation energy. ^{*c*}Wavelength. ^{*d*}Oscillator strength.

The calculated ¹H and ¹³C NMR chemical shifts of **1a**' and **1b**' are summarized in Tables 2 and S4, respectively, together with the experimental results. The ¹H NMR resonances for the H1–H6 protons on the pentacene core were calculated to resonate < 8.18 ppm. Although resonances for the methyl groups, which are located at the 2,6-positions of the tetramethylphenyl subunits, are upfield shifted to 1.39 (**1a**') and 1.20 (**1b**') ppm, those at the 3,5-positions were shifted to 2.28 (**1a**') and 2.26 (**1b**') ppm. The calculated ¹³C NMR shifts

(Table S4) for the pentacene framework of 1a'/1b' are in good agreement with the experimentally observed chemical shifts. These results strongly suggest that dications 1a' and 1b', which contain thio- or selenopyrylium moieties, exhibit a diatropic ring current in the pentacene core.

The results of nucleus-independent chemical shift (NICS)^{21,22} calculations on 1a' and 1b' are summarized in Table 4 and show that the NICS(1)₂₇ values of the inner

Table 4. Calculated Nucleus-Independent Chemical Shifts (NICS) [ppm] of 1a' and $1b'^a$



 a Calculations were carried out at the GIAO-B3LYP/6-311+G-(2d,p)//B3LYP/6-311+G(2d,p) level of theory.

benzene rings are increased relative to those of the outer benzene and chalcogenopyrylium rings, reflecting that the heteropentacene framework of 1a' and 1b' exhibits a diatropic ring current due to their 22π -electron system.

A natural population analysis²³ of dications 1a' and 1b' revealed highly positive charges of +0.82 (1a') and +0.72 (1b') at the chalcogen atoms (Figure S7), whereas the pentacene framework consists of less polar carbon atoms; the observed charges (+0.14 to -0.23) indicate that form M should be the dominant resonance structure for 1a' and 1b' (Scheme 5). Therefore, the combined results of the theoretical survey suggest that 1a' and 1b' exhibit a cation-localized dicationic aromatic character with 22π -electrons.

CONCLUSIONS

We have reported the synthesis of pentacyclic dicationic heteroacenes 1a and 1b, which bear thio- or selenopyrylium moieties, via (i) addition reactions of the corresponding diones with a Grignard reagent followed by a dehydration reaction with Brønsted acid and (ii) via two-electron oxidation reactions of quinoids 7a and 7b. Heteroacenes 1a and 1b are thermally robust, which is due to the incorporation of tetramethylphenyl and tert-butyl groups. Heteroacenes 1a and 1b could potentially be used to build more complex thiopyrylium- or selenopyrylium-based heteroacene derivatives and also to synthesize promising prospective organic functional materials. The cationic sp²-type sulfur or selenium atoms introduced to replace the CH moieties in the pentacene unit lead to bathochromically shifted red-edge absorption and 22π electron aromaticity. Selenium analogue 1b is the first example of a heteropentacene that contains two selenopyrylium

subunits and that exhibits a substantially decreased optical band gap. Our study thus provides a reliable strategy for the fine-tuning of the molecular and electronic structure of aromatic ring systems by replacing individual atoms.

EXPERIMENTAL SECTION

General. All solvents were purified by standard methods. Preparative thin-layer chromatography was performed on Merck silica gel 60 PF254. Column chromatography was performed on silica gel 60N (Kanto Chemical) under an ambient atmosphere. ¹H (400 MHz) and ${}^{13}C$ NMR (101 Hz) spectra were recorded in CDCl₃ on a Bruker Avance spectrometer using the residual resonances of CHCl₃ $(\delta_{\rm H} = 7.26)$ and CDCl₃ $(\delta_{\rm C} = 77.0)$ as well as of DMSO-d₆ $(\delta_{\rm H} =$ 2.50; $\delta_{\rm C}$ = 39.5) as the internal standards to reference the ¹H and ¹³C NMR spectra. ¹⁹F (376 MHz) and ⁷⁷Se (76.3 MHz) NMR spectra were recorded on a Bruker Avance spectrometer using CFCl₃ ($\delta_{\rm F}$ = 0.00) and 90% Me₂Se in C₆D₆ ($\delta_{Se} = 0.00$) as the external standards. The assignment of the signals was typically accomplished on the basis of one-dimensional (homodecoupling and DEPT) and two-dimensional (COSY, HMQC, and HMBC) NMR techniques. Unless otherwise stated, all ¹³C and ¹⁹F NMR experiments were performed using broad-band ¹H decoupling. Electron ionization (EI) and electrospray ionisation time-of-flight (ESI-TOF) mass spectral data were obtained on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively. Absorption spectra were recorded on a JASCO V-550 UV-vis or a Shimadzu UV-3600 UV-vis-NIR spectrometer. Electrochemical experiments were carried out with an ALS 617D electrochemical analyzer using a glassy carbon disk working electrode, a Pt wire counter electrode, and Ag/0.01 M (1 M = 1 mol/dm^3) AgNO₃ reference electrode. The measurements were carried out at ambient temperature in CH₂Cl₂ containing 0.1 M [n-Bu₄N][PF₆] as the supporting electrolyte using a scan rate of 100 mV/s. Elemental analyses were carried out on a JM11 CHN analyzer by J-Science Lab. All melting points were determined on a Yanaco micro-melting point apparatus or a Mettler Toledo MP90 melting point system and are uncorrected.

Materials. Unless stated otherwise, all materials were purchased from common commercial chemical suppliers and used without further purification. All reactions were carried out under an inert atmosphere of argon or nitrogen. The synthesis of **4a** and **5a** was accomplished using modified procedures reported previously.^{10,11} Di(4-*tert*-butylphenyl)diselenide²⁴ and 3-bromo-1,2,4,5-tetramethylbenzene²⁵ were prepared according to previously reported procedures.

Synthesis of Phthalic Acid 4a.¹⁰ Diethyl 2,5-dibromoterephthalate (1.00 g, 2.63 mmol), 4-tert-butylbenzenethiol (2.30 mL, 13.2 mmol), and potassium carbonate (2.18 g, 15.8 mmol) were dissolved in dimethylformamide (DMF) (15 mL) and stirred for 20 h at 120 °C, before the reaction mixture was poured into water (150 mL). The aqueous layer was washed with ethyl acetate and acidified by addition of a solution of hydrochloric acid. The resulting yellow suspension was filtered, and the thus obtained solid was washed with water and dried under reduced pressure to afford phthalic acid 4a (0.932 g, 1.88 mmol, 72%) as a yellow solid. 4a: mp > 300 °C; ¹H NMR (DMSO d_6) δ 7.52 (d, J = 8.0 Hz, 4H, ArH), 7.44 (d, J = 8.0 Hz, 4H, ArH), 7.29 (s, 2H, ArH), 1.31 (s, 18H, CH₃); ¹³C NMR (DMSO- d_6) δ 166.3 (C), 152.1 (C), 137.6 (C), 134.4 (CH), 131.0 (C), 129.3 (CH), 128.4 (C), 127.0 (CH), 34.5 (C), 30.9 (CH₃); HRMS (EI, positive mode) (m/z): [M]⁺ calcd for C₂₈H₃₀O₄S₂, 494.1586; found, 494.1574.

Scheme 5. Conceivable Resonance Structures for Dications 1a' and 1b'



Synthesis of Phthalic Acid 4b. Diethyl 2,5-dibromoterephthalate (1.00 g, 2.63 mmol), di(4-tert-butylphenyl)diselenide (2.23 g, 1.58 mmol), and potassium carbonate (2.18 g, 15.8 mmol) were dissolved in DMF (20 mL). Sodium borohydride (0.597 g, 15.8 mmol) was added to the solution at room temperature, and the solution was stirred for 20 h at 120 °C. The solution was allowed to cool to room temperature and then poured into water (20 mL). After the solution was filtered, the filtrate was washed with ethyl acetate. The aqueous layer was acidified by addition of a solution of hydrochloric acid, and the resulting yellow suspension was filtered. The thus obtained solid was washed with water and dried under reduced pressure to afford phthalic acid 4b (0.317 g, 0.36 mmol, 20%) as a yellow solid. 4b: mp > 300 °C; ¹H NMR (DMSO- d_6) δ 7.57 (d, J = 8.4 Hz, 4H, ArH), 7.50 (d, J = 8.4 Hz, 4H, ArH), 7.44 (s, 2H, ArH), 1.31 (s, 18H, CH₃); ¹³C NMR (DMSO- d_6) δ 166.8 (C), 152.2 (C), 136.6 (CH), 135.3 (C), 131.1 (C), 131.0 (C), 127.0 (CH), 124.8 (C), 34.5 (C), 31.0 (CH₃); ⁷⁷Se NMR (DMSO- d_6) δ 447.4 (s); HRMS (ESI-TOF, negative mode) (m/z): $([M - H]^{-})$ calcd for $C_{28}H_{29}O_4^{80}Se_2$ 589.0396; found, 589.0388; anal. calcd for C₂₈H₃₀O₄Se₂: C, 57.15; H, 5.14%; found: C, 56.92; H, 5.26%.

Synthesis of Dione **5a**.¹⁷ A solution of phthalic acid **4a** (0.500 g, 1.01 mmol) in DMF (1 mL) and thionyl chloride (10 mL) was stirred for 4 h at room temperature, before all volatile substances were removed under reduced pressure. After a solution of titanium tetrachloride (3.0 mL, 10 mmol) in dichloromethane (20 mL) was added, the resulting reaction mixture was stirred for 16 h at room temperature. Then, the reaction mixture was poured into water (20 mL) and the organic layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and dried under reduced pressure to afford dione **5a** (0.424 g, 0.924 mmol, 91%) as an orange powder. **5a**: ¹H NMR (CDCl₃) δ 8.85 (s, 2H, ArH), 8.64 (d, J = 2.0 Hz, 2H, ArH), 7.74 (dd, J = 2.0, 8.4 Hz, 2H, ArH), 7.56 (d, J = 8.4 Hz, 2H, ArH), 1.42 (s, 18H, CH₃); MS (EI, positive mode) (m/z): [M]⁺ calcd for C₂₈H₂₆O₂S₂, 459; found, 459.

Synthesis of Dione 5b. A solution of phthalic acid 4b (0.250 g, 0.424 mmol) in DMF (1 mL) and thionyl chloride (5.1 mL) was stirred for 4 h at room temperature, before all volatiles were removed under reduced pressure. A solution of aluminum trichloride (1.40 g, 10.5 mmol) in carbon disulfide (10 mL) was added, and the resulting mixture was stirred for 16 h at room temperature. Then, the reaction mixture was poured into water (20 mL) and the organic layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and dried under reduced pressure to give an orange solid (0.278 g). Purification of the crude orange solid by recrystallization from dichloromethane afforded dione **5b** (0.059 g, 0.12 mmol, 25%) as an orange powder. **5b**: mp > 300 °C; ¹H NMR (CDCl₃) δ 8.93 (s, 2H, ArH), 8.59 (d, J = 8.4 Hz, 2H, ArH), 7.63 (d, J = 2.0 Hz, 2H, ArH), 7.53 (dd, J = 8.4, 2.0 Hz, 2H, ArH), 1.40 (s, 18H, CH₃); ¹³C NMR (CDCl₃) δ 81.1 (C), 156.9 (C), 135.6 (C), 132.6 (C), 131.9 (C), 131.5 (CH), 131.4 (CH), 128.4 (C), 125.0 (C), 124.8 (C), 35.4 (C), 30.9 (CH₃); ⁷⁷Se NMR (CDCl₃) δ 340.5 (s); HRMS (ESI-TOF, positive mode) (m/z): ([M $(+ Na]^{+}$ calcd for $C_{28}H_{26}NaO_2^{80}Se_2$, 577.0161; found, 577.0175; anal. calcd for C28H26O2Se2: C, 60.88; H, 4.74%; found: C, 60.99; H, 4.55%

Synthesis of Diol **6a**. A suspension of 3-bromo-1,2,4,5tetramethylbenznene (0.465 g, 2.18 mmol), magnesium turnings (0.106 g, 4.36 mmol), and zinc chloride (0.009 g, 0.07 mmol) in THF (10 mL) was stirred for 4 h under reflux. After cooling to room temperature, the suspension was added to a solution of dione **5a** (0.100 g, 0.218 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred for 20 h under reflux, before being poured into a saturated solution of ammonium chloride. The resulting suspension was filtered, and the organic layer of the filtrate was extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and dried under reduced pressure to give a crude brown solid. Separation of the crude brown solid by column chromatography on silica gel (eluent: dichloromethane) afforded diol **6a** as a diastereomeric mixture (0.081 g, 1.1 mmol, 51%). **6a**: orange solid; mp 190–191 °C; ¹H NMR (CDCl₃) δ 7.17 (dd, J = 8.2 Hz, 2.1 Hz, 1H, ArH), 7.09 (dd, J = 8.2 Hz, 2.1 Hz, 1H, ArH), 7.09 (dd, J = 8.2 Hz, 2.1 Hz, 1H, ArH), 7.04–7.02 (m, 3H, ArH), 6.97 (d, J = 8.2 Hz, 1H, ArH), 6.85 (d, J = 2.1 Hz, 1H, ArH), 6.55 (d, J = 2.0 Hz, 1H, ArH), 6.44 (s, 1H, ArH), 4.86 (s, 1H, ArH), 2.32–2.21 (m, 15H, CH₃), 1.92–1.87 (m, 9H, CH₃), 1.05 (s, 9H, CH₃), 1.03 (s, 9H, CH₃); HRMS (ESI-TOF, positive mode) (m/z): ([M – OH]⁺) calcd for C₄₈H₅₃OS₂, 709.3532; found, 709.3524; anal. calcd for C₄₈H₅₄O₂S₂: C, 79.29; H, 7.49%; found: C, 79.01; H, 7.28%.

Synthesis of Diol 6b. A suspension of bromo-2,3,5,6-tetramethylbenznene (0.465 g, 2.18 mmol), magnesium turnings (0.106 g, 4.36 mmol), and zinc chloride (0.036 g, 0.26 mmol) in THF (10 mL) was stirred for 4 h under reflux. After cooling to room temperature, the suspension was added to a solution of dione 5b (0.100 g, 0.181 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred for 20 h under reflux, before being poured into a saturated solution of ammonium chloride. The resulting suspension was filtered, and the organic layer of the filtrate was extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and dried under reduced pressure to give a crude brown solid. Separation of the crude brown solid by column chromatography on silica gel (eluent: dichloromethane) afforded diol 6b as a diastereomeric mixture (0.041 g, 0.45 mmol, 28%). 6b: orange solid: mp 165–167 °C; ¹H NMR (CDCl₃) δ 7.23 (d, J = 2.0 Hz, 1H, ArH), 7.17 (d, J = 2.0 Hz, 1H, ArH), 7.02 (s, 2H, ArH), 6.95 (dd, J = 8.4, 2.0 Hz, 1H, ArH), 6.88 (dd, J = 8.8, 2.0 Hz, 1H, ArH), 6.75 (d, J = 8.4 Hz, 1H, ArH), 6.60 (s, 1H, ArH), 6.49 (d, J = 8.8 Hz, 1H, ArH), 5.10 (s, 1H, ArH), 2.31-2.21 (m, 15H, CH₃), 1.91 (s, 3H, CH₃), 1.89 (s, 3H, CH₃), 1.87 (s, 3H, CH₃), 1.23 (s, 18H, CH₃); ⁷⁷Se NMR (CDCl₃) δ 359.7 (s), 345.0 (s); HRMS (ESI-TOF, positive mode) (m/z): ([M - OH]⁺) calcd for C₄₈H₅₃O⁸⁰Se₂, 805.2421; found, 805.2429; anal. calcd for C48H54O2Se2: C, 70.23; H, 6.63%; found: C, 70.41; H, 6.80%.

Synthesis of Quinoid 7a. A suspension of bromo-2,3,5,6tetramethylbenznene (0.465 g, 2.18 mmol), magnesium turnings (0.106 g, 4.36 mmol), and zinc chloride (0.020 g, 0.15 mmol) in THF (10 mL) was stirred for 4 h under reflux. After cooling to room temperature, the suspension was added to a solution of dione 5a (0.100 g, 0.218 mmol) in THF (10 mL) at room temperature. Then, the reaction mixture was stirred for 20 h under reflux, before being poured into a solution of tin(II) chloride dihydrate (0.984 g, 4.36 mmol), 1.0 mol/L hydrochloric acid (3.0 mL), and water (1.0 mL) at room temperature. After the solution was stirred for 2 h at room temperature, the solution was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Separation of the crude residue was accomplished by column chromatography on silica gel (hexane/ dichloromethane = 10:1, v/v), which afforded quinoid 7a (0.047 g, 0.33 mmol, 31%) as a red powder. 7a: mp > 300 °C; ¹H NMR $(CDCl_3) \delta 7.01 \text{ (s, 2H, ArH}, 6.92 \text{ (dd, } J = 8.2, 2.0 \text{ Hz, 2H, ArH}),$ 6.81 (d, J = 8.2 Hz, 2H, ArH), 6.34 (d, J = 2.0 Hz, 2H, ArH), 5.72 (s, 2H, ArH), 2.28 (s, 12H, CH₃), 1.96 (s, 12H, CH₃), 1.01 (s, 18H, CH₃); HRMS (ESI-TOF, positive mode) (m/z): $([M + Na]^+)$ calcd for C48H52NaS2, 715.3408; found, 715.3412; anal. calcd for C48H52S2: C, 83.19; H, 7.56%; found: C, 82.90; H, 7.30%. Satisfactory ¹³C NMR data of 7a could not be obtained due to its low solubility in common organic solvents.

Synthesis of Quinoid **7b**. A suspension of bromo-2,3,5,6tetramethylbenznene (0.386 g, 1.81 mmol), magnesium turnings (0.088 g, 3.6 mmol), and zinc chloride (0.020 g, 0.15 mmol) in THF (10 mL) was stirred for 4 h under reflux. After cooling to room temperature, the suspension was added to a solution of dione **5b** (0.100 g, 0.218 mmol) in THF (10 mL) at room temperature. Then, the reaction mixture was stirred for 20 h under reflux, before being poured into a solution of tin(II) chloride dihydrate (0.816 g, 3.62 mmol), 1.0 mol/L hydrochloric acid (3.0 mL), and water (1.0 mL) at room temperature. After stirring for 2 h at room temperature, the solution was extracted with dichloromethane. The organic layer was separated and dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Separation of the crude residue by column chromatography on silica gel (eluent: hexane) afforded quinoid 7b (0.089 g, 1.0 mmol, 63%) as a red powder. 7b: mp > 300 °C; ¹H NMR (CDCl₃) δ 7.09 (d, J = 2.0 Hz, 2H, ArH), 7.02 (s, 2H, ArH), 6.82 (dd, J = 8.4, 2.0 Hz, 2H, ArH), 6.34 (d, J = 8.4 Hz, 2H, ArH), 6.04 (s, 2H, ArH), 2.28 (s, 12H, CH₃), 1.95 (s, 12H, CH₃), 1.21 (s, 18H, CH₃); ¹³C NMR (CDCl₃) δ 150.2 (C), 137.7 (C), 133.9 (C), 132.9 (C), 132.4 (C), 130.9 (C), 130.7 (CH), 130.0 (C), 128.6 (C), 128.3 (CH), 128.1 (C), 124.2 (CH), 124.0 (CH), 121.5 (CH), 34.4 (C), 30.9 (CH₃), 20.2 (CH₃), 16.3 (CH₃); MS (ESI-TOF, positive mode) (m/z): [M]⁺ calcd for C₄₈H₅₂⁸⁰Se₂, 788; found, 788; anal. calcd for C₄₈H₅₂Se₂: C, 73.27; H, 6.66%; found: C, 73.30; H, 6.79%.

Reaction of Diol **6a** with Tetrafluoroboric Acid. An ethereal solution of tetrafluoroboric acid (53%, 0.044 g, 0.27 mmol) was added to a solution of diol **6a** (0.020 g, 0.028 mmol) in dichloromethane (5 mL) at room temperature. After stirring the solution for 30 min, the absorption bands of **6a** in the UV–vis–NIR spectrum had disappeared and those for **1a** were detected. The solution was added dropwise to cooled hexane (50 mL) to afford a brown suspension. Separation of the suspension using a centrifuge afforded dicationic salt **1a** (6.2 mg, 0.061 mmol, 23%) as a brown powder. **1a**: mp 280 °C (dec.); anal. calcd for $C_{48}H_{52}B_2F_8S_2$: C, 66.52; H, 6.05%; found: C, 66.32; H, 6.08%.

Reaction of Quinoid **7a** *with Nitrosonium Tetrafluoroborate.* A 0.43 mol/L solution of nitrosonium tetrafluoroborate in CD₃CN (100 μL) was added to a solution of quinoid **7a** (5.0 mg, 7.2 μmol) in CDCl₃ (448 μL) and CD₃CN (12 μL) at room temperature. The formation of **1a** was detected by NMR spectroscopy. **1a**: ¹H NMR (CDCl₃/CD₃CN = 8:2) δ 9.58 (s, 2H, ArH), 8.89 (d, *J* = 8.8 Hz, 2H, ArH), 8.69 (dd, *J* = 9.0 Hz, 2.0 Hz, 2H, ArH), 8.06 (d, *J* = 2.0 Hz, 2H, ArH), 7.51 (s, 2H, ArH), 2.46 (s, 12H, CH₃), 1.69 (s, 12H, CH₃), 1.34 (s, 18H, CH₃); ¹³C NMR (CDCl₃/CD₃CN = 8:2) δ 176.3 (C), 156.6 (C), 152.9 (C), 141.6 (CH), 139.6 (C), 130.9 (C), 129.7 (CH), 128.4 (CH), 35.7 (C), 29.8 (CH₃), 19.3 (CH₃), 16.9 (CH₃); ¹⁹F NMR (CDCl₃/CD₃CN = 8:2) δ -146.67 (s, [¹⁰BF₄]⁻), -146.71 (s, [¹¹BF₄]⁻); HRMS (ESI-TOF, positive mode) (*m*/*z*): ([M – BF₄]⁺) calcd for C₄₈H₅₂BF₄S₂, 779.3540; found, 779.3543.

Reaction of Diol **6b** with Tetrafluoroboric Acid. An ethereal solution of tetrafluoroboric acid (53%, 0.044 g, 0.27 mmol) was added to a solution of diol **6b** (0.041 g, 0.050 mmol) in dichloromethane (5 mL) at room temperature. After the solution had been stirred for 30 min, the absorption for diol **6b** disappeared in the UV–vis–NIR spectrum and **1b** was detected. The solution was added dropwise to cooled hexane (50 mL) to give a brown suspension. Separation of the suspension using a centrifuge afforded dicationic salt **1b** (0.015 g, 0.092 mol, 34%) as a reddish purple powder. **1b**: mp 256 °C (dec.); anal. calcd for $C_{48}H_{52}B_2F_8Se_2$: C, 60.03; H, 5.46%; found: C, 59.82; H, 5.29%.

Reaction of Quinoid 7b with Nitrosonium Tetrafluoroborate. A 0.43 mol/L solution of nitrosonium tetrafluoroborate in CD₃CN (88 μ L) was added to a solution of quinoid 7b (5.0 mg, 6.4 μ mol) in CDCl₃ (448 μ L) and CD₃CN (24 μ L) at room temperature. The formation of 1b was detected by NMR spectroscopy. 1b: ¹H NMR $(CDCl_3/CD_3CN = 8:2) \delta 9.67 (s, 2H, ArH), 9.02 (d, J = 2.0 Hz, 2H)$ ArH), 8.26 (d, J = 9.2 Hz, 2H, ArH), 8.02 (dd, J = 9.2 Hz, 2.0 Hz, 2H, ArH), 7.47 (s, 2H, ArH), 2.45 (s, 12H, CH₃), 1.69 (s, 12H, CH₃), 1.55 (s, 18H, CH₃); ¹³C NMR (CDCl₃/CD₃CN = 8:2) δ 175.8 (C), 167.2 (C), 161.8 (C), 143.5 (C), 139.4 (CH), 137.4 (CH), 135.1 (C × 2), 133.9 (CH), 131.5 (CH), 130.7 (C), 130.5 (C), 127.5 (CH), 37.5 (C), 29.3 (CH₃), 19.0 (CH₃), 16.7 (CH₃) (one quaternary ¹³C NMR signal for 1b cannot be assigned due to its low solubility in common organic solvents.); ¹⁹F NMR (CDCl₃/CD₃CN = 8:2) δ -146.12 (s, $[^{10}BF_4]^-$), -146.17 (s, $[^{11}BF_4]^-$); ⁷⁷Se NMR (CDCl₃/ $CD_3CN = 8:2$) δ 727.1 (s); HRMS (ESI-TOF, positive mode) (m/z): $([M - BF_4]^+)$ calcd for $C_{48}H_{52}BF_4^{80}Se_2$, 875.2429; found, 875.2438.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00100.

X-ray diffraction analysis; ESR spectra of 8a and 8b; theoretical calculations; ¹H, ¹³C, and ⁷⁷Se NMR spectra of 1a and 1b (PDF)

Accession Codes

CCDC 1896933 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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