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SHORT COMMUNICATION

Saturated NHC Derived Dichalcogen Dications

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Dedicated to Prof. Manfred Scheer on the Occasion of his 65th Birthday

Abstract. Herein, the synthesis and characterization of dicationic dichalcogenide compounds $[(SIPr)E]_2(OTf)_2$ (**3a-E**) (E = S, Se, Te) based on a saturated N-heterocyclic carbene (NHC), SIPr [SIPr = $C\{N(Dipp)CH_2\}_2$, Dipp = 2,6-$i\mathrm{Pr}_2C_6H_3$] are reported. Treatment of SIPr (**1a**) with elemental chalcogens affords the heavier ketone derivatives (SIPr)E (**2a-E**), which readily undergo oxidative E–E coupling reactions with triflic anhydride to yield the corresponding products **3a-E**. Compounds **3a-E** are air-stable crystalline solids and were characterized by NMR and UV/Vis spectroscopy as well as by X-ray diffraction methods.

Introduction

N-Heterocyclic carbenes (NHCs) **I** are very versatile carbon-donor neutral ligands in transition metal[1] as well as in main-group element[2] chemistry and play key roles in synthesis and catalysis (Figure 1).[3] In recent years, NHCs have been also recognized as very interesting building blocks for the development of new ligand sets[4] and molecular frameworks with open-shell electronic structures.[5] N-Heterocyclic olefins (NHOs **II-E**; E = CY_2, Y = H, alkyl or aryl group)[6] and N-heterocyclic imines (NHIs **II-E**; E = NY, Y = H, $SiMe_3$, alkyl group),[7] which are formally derived by the combination of an NHC and a CY_2 or NY unit (Figure 1), have made remarkable progresses in molecular science. Among main-group compounds, the use of NHCs in the isolation of compounds **III-E** featuring a diatomic E_2 moiety[8] is remarkable as they may formally be considered as organic solvent soluble allotropes of main-group elements.[9] Indeed, they exhibit interesting electronic structures and reactivity, including transfer of E_2 (or E) moiety on to a different substrate from **III-E**.[10] Cyclic alkyl amino carbenes (cAACs) have also been found to be useful in accessing similar compounds.[11]

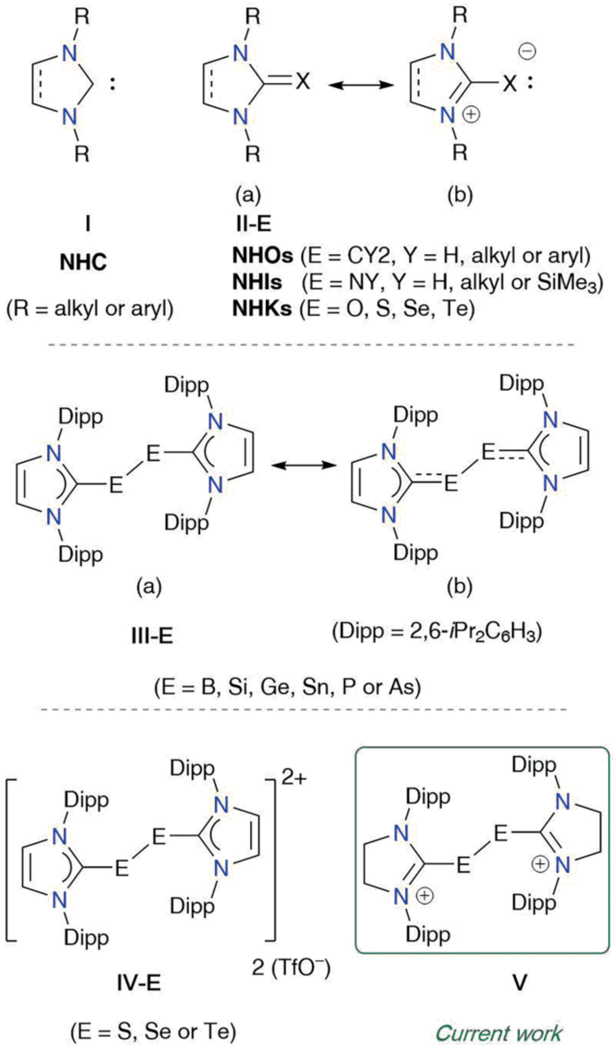

Figure 1. NHC (**I**), NHOs, NHIs, and NHKs (**II-E**) derived from an NHC. Diatomic main-group compounds **III-E** stabilized by an NHC. Unsaturated NHC-derived dichalcogen dications **IV-E**.

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Dicationic compounds **IV-E** (E = S, Se or Te) obtained by the oxidative E–E coupling of the corresponding N-heterocyclic ketones (NHKs) **II-E** can be regarded as structural diatomic analogues of neutral compounds **III-E**. Indeed, several compounds **IV-E** (E = S,[12] Se,[12] and Te[13]) also based on a similar unsaturated bulky NHC (IPr = C{(NDipp)CH}$_2$; Dipp = 2,6-iPr$_2$C$_6$H$_3$) have been isolated. Nonetheless, compounds **IV-S** and **IV-Se** were characterized by elemental analysis, IR spectroscopy, and X-ray diffraction but no NMR spectroscopic data was provided. The nature of the C$_{(NHC)}$=E bond of **II-E** and thus the properties of derived species directly depends on the donor-acceptor properties of NHCs.[14] Therefore, **II-E** featuring a weak π-accepting NHC are stronger π-donors compared to those derived from electrophilic NHCs such as SIPr [SIPr = C{(NDipp)CH$_2$}$_2$]. (NHC)Se compounds are useful candidates for the experimental determination of electronic properties of NHCs by ^{77}Se NMR spectroscopy.[14d,15] A systematic NMR analysis of the oxidative coupling products **IV-E** of (IPr)Se and (IPr)Te would be useful in complementing to the electronic property of NHCs. The saturated analogue of IPr, the SIPr, is more electrophilic than IPr and thus exhibits superior π-acceptor ability than IPr. Interestingly, while related compounds (SIPr)E[16] (E = S or Se) have been reported, their dicationic derivatives **V** remain thus far unknown.

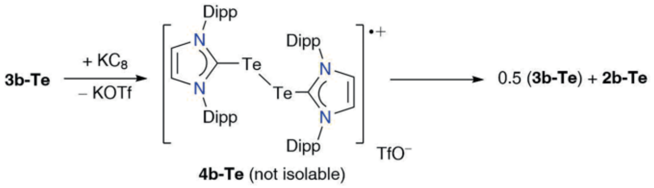
Herein, we report the synthesis and characterization of the dichalcogen dications [(SIPr)E$_2$(SIPr)](OTf)$_2$ (**3a-E**) (E = S, Se, Te) featuring an electrophilic NHC, SIPr. Moreover, we present missing NMR spectroscopic data of hitherto known unsaturated derivatives [(IPr)E$_2$(IPr)](OTf)$_2$ (**3b-E**) (E = S and Se) as well as provide a comparative study on NMR and structural properties of these two classes of compounds.

Results and Discussion

Synthesis

Compounds (SIPr)S (**2a-S**)[16b] and (SIPr)Se (**2a-Se**)[15b] were prepared according to previously reported methods using SIPr (**1a**) and elemental sulfur and selenium, respectively. Similarly, treatment of SIPr (**1a**) with tellurium powder affords compound **2a-Te** as an off-white solid in 82 % yield (Scheme 1). Reaction of a dichloromethane solution of **2a-E** (E = S, Se or Te) each with triflic anhydride (Tf$_2$O)[13] yielded compounds **3a-E** as crystalline solids. By employing a similar method,[13] hitherto known compounds **3b-S** and **3b-Se**[12,17] are also accessible in 82–92 % yield from (IPr)S (**1b-S**)[18] and (IPr)Se (**1b-Se**).[15b] While the exact mechanism of the formation of **3a-E** and **3b-E** is currently not known, Tf$_2$O seems to serve as one-electron oxidant to generate triflate anion and [CF$_3$SO$_2$] radical. The former is present as a counter anion in **3a-E** and **3b-E**, whereas as the latter possibly reacts with CH$_2$Cl$_2$ to form CF$_3$SO$_2$Cl or decomposes into CF$_3$ and SO$_2$. To identify the possible side products, a colorless CD$_2$Cl$_2$ solution of **2a-S** in an NMR tube was treated with Tf$_2$O and analyzed by NMR spectroscopy (Figures S37 and S38, Supporting Information). The ^{1}H NMR spectrum exhibits the complete consumption of **2a-S** and the clean formation of **3a-S**. The ^{19}F{^{1}H} NMR spectrum shows three main signals at –72.3, –74.4, and –79.1 ppm. The signals at –72.3 and –79.1 are characteristic of Tf$_2$O (unreacted) and the TfO$^-$ anion, respectively, whereas the remaining signal at δ = –74.4 ppm may be assigned to CF$_3$SO$_2$Cl.[19]

Treatment of **3b-Te** with one equivalent of KC$_8$ led to the formation of a 1:1 mixture of dication **3b-Te** and the tellurone **2b-Te** as evidenced by the ^{1}H NMR spectrum of the resulting mixture, suggesting the decomposition of the putative radical cation **4b-Te** into **3b-Te** and **2b-Te** (Scheme 2).

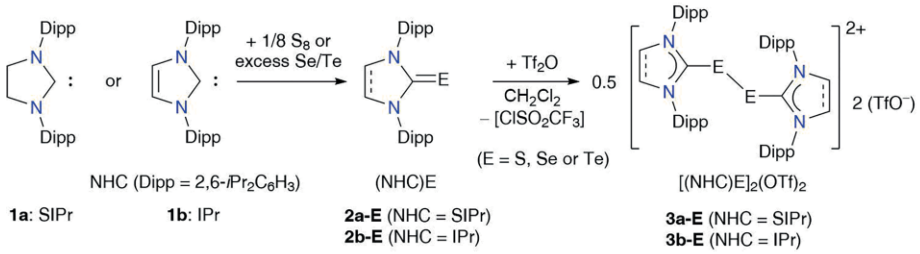


Scheme 2. Reaction of **3b-Te** with KC$_8$.

These findings are in line with the cyclovoltammetric analyses of the dications **3a-E** and **3b-E** (acetonitrile, NBu$_4$PF$_6$, 100 mV·s^{-1}), which show no reversible redox event in the –2.5 V to +2.5 V region.

NMR Studies

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a-E**, **3a-E**, and **3b-E** exhibit expected resonances for the NHC units (see the Supporting Information for NMR plots). Selected ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} or ^{125}Te{^{1}H} NMR values of **2a-E**, **2b-E**, **3a-E**, and **3b-E** are given in Table 1. As expected, the ^{1}H NMR signal for the backbone CH$_2$ protons of the dications **3a-E** (**3a-S** 4.69, **3a-Se** 4.34, **3a-Te** 4.34 ppm) has been downfield shifted compared to that of the corresponding neutral precursors **2a-E** (**2a-S** 4.06, **2a-Se** 4.05, **2a-Te** 4.07 ppm). The downfield shifting



Scheme 1. Synthesis of **2a-E** and **2b-E** and their one-electron oxidation to **3a-E** and **3b-E**, respectively.

Table 1. Selected ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{125}Te{^{1}H} NMR chemical shifts / δ ppm for **2a-E**, **3a-E**, **2b-E**, and **3b-E**.

	Solvent	$^1H_{backbone}$	$^{13}C\{^1H\}_{CE}$	$^{77}Se\{^1H\}$	$^{125}Te\{^1H\}$
2a-S	$CDCl_3$	4.06	184	–	–
3a-S	CD_3CN	4.69	147	–	–
2b-S	$CDCl_3$	6.84	167	–	–
3b-S	CD_3CN	8.45	139	–	–
2a-Se	$CDCl_3$	4.05	184	191	–
3a-Se	CD_3CN	4.34	164	498	–
2b-Se	$CDCl_3$	7.01	162	91	–
3b-Se	CD_3CN	8.01	154	430	–
2a-Te	$CDCl_3$	4.07	168	–	81
3a-Te	CD_3CN	4.34	160	–	582
2b-Te	CD_3CN	7.46	147	–	–65
3b-Te	CD_3CN	8.01	146	–	525

of the ^{1}H NMR signal for the backbone CH protons of IPr-derivatives (**3b-E** vs. **2b-E**) is more pronounced (**3b-S/ 2b-S** 8.09/ 6.84, **3b-Se/ 2b-Se** 8.01/ 7.01, and **3b-Te/ 2b-Te** 8.01/ 7.20 ppm) with respect to those of SIPr (**3a-E** vs. **2a-E**). This may be because of the aromatic nature of the 1,3-imidazole ring of IPr, which usually upsurges with increasing Lewis acidity of the C2-substituent. The downfield shifting in both cases, however, becomes smaller from S to Se to Te, which is consistent with the decreasing electronegativity in the group.

The ^{13}C{^{1}H} NMR spectra of **2-E** and **3-E** reveal interesting features. The ^{13}C{^{1}H} NMR spectra of dications **3-E** exhibit a resonance (**3a-S** 147, **3a-Se** 164, **3a-Te** 160 ppm; **3b-S** 139, **3b-Se** 154, **3b-Te** 146 ppm) for the chalcogen-bound carbene carbon atoms, which is at a higher field from that of neutral precursors **2-E** (**2a-S** 184, **2a-Se** 184, **2a-Te** 168 ppm; **2b-S** 167, **2b-Se** 162, **2b-Te** 147 ppm). The larger downfield ^{13}C{^{1}H} NMR values for the C_E nuclei of **2a-E** compared to **2b-E** are in line with the greater π-acceptor property of SIPr than IPr.[14c] The values for sulfur and selenium compounds (**2**) are comparable but the same for the tellurium derivatives (**2-Te**) is small (i.e. higher shielding). This may be rationalized as a weaker π-character of the C=Te bond compared to C=S and C=Se bonds of **2-E**. Not surprisingly, the chemical shifts for both **2a-Te** (147 ppm) and **3b-Te** (146 ppm) as well as **2b-Te** (168 ppm) and **3b-Te** (160 ppm) remain virtually unchanged. The ^{77}Se{^{1}H} NMR signal of both **3a-Se** (498 ppm) as well as **3b-Se** (430 ppm) is shifted by 322 ± 14 ppm to lower field than that of **2a-Se** (191 ppm) and **2b-Se** (91 ppm), respectively. A similar trend in the ^{125}Te{^{1}H} NMR spectra of **3a-Te** (582 ppm) and **3b-Te** (525 ppm) with respect to that of **2a-Te** (81 ppm) and **2b-Te** (–65 ppm), is in agreement with the formation of dicationic compounds **3**.

X-ray Diffraction Analysis

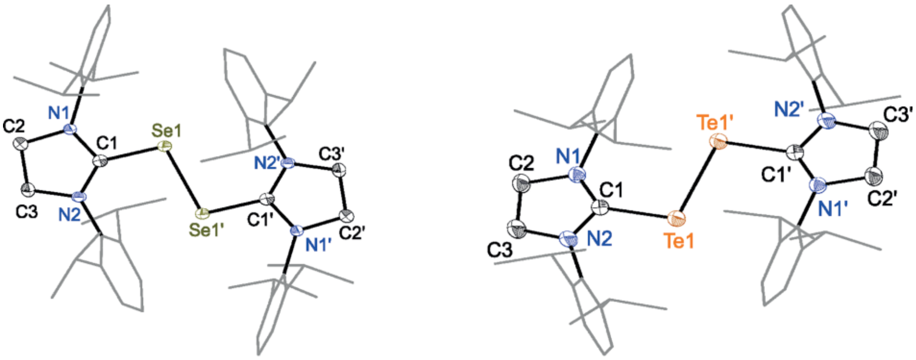
The hitherto unknown solid-state structure of compound **2a-S** (Figure S39, Supporting Information) was determined by single-crystal X-ray diffraction analysis.[16b] **2a-S** is isostructural to **2b-S** and thus, the C–S bond length of **2a-S** [1.656(5) Å] and **2b-S** [1.670(1) Å] are equal within three standard deviations.[17] Moreover, the N–C–N bond angle of **2a-S** [111.0(4)°] is wider than that of **2b-S** [104.6(2)°].

The solid-state molecular structures of **3a-Se** and **3a-Te** (Figure 2 and Figures S40 and S41, Supporting Information) exhibit a *trans*-bent arrangement along the E–E bond (Table 2). The Se–Se bond length of **3a-Se** [2.429(1) Å] and Te–Te bond length of **3a-Te** [2.789(1) Å] are comparable with that of IPr-derivatives **3b-Se** [2.427(5) Å][12] and **3b-Te** [2.792(1) Å],[13] respectively. The Se–Se bond length in neutral organodiselenides (RSeSeR) ranges from 2.24 to 2.39 Å and is dependent on the nature of the substituent (R = halide or an aryl or alkyl group).[20] The Se–Se bond length of **3a-Se** [2.429(1) Å] is intermediate of the bond lengths (2.23–2.98 Å) observed for dimeric dialkyl diselenium cations $[(RSe_2R)^+]_2$ (R = Me or Et).[21] The E–E bond lengths of **3a-Se** [2.429(1) Å] and **3b-Te** [2.789(1) Å] are longer than those of the corresponding neutral RSe–SeR [2.319(4) Å, R = C_6H_5; 2.339(2) Å, R = 2,6-$Mes_2C_6H_3$][22] and RTe–TeR [2.711(1) Å, R = 2,6-$Mes_2C_6H_3$][22b] as well as of the radical cations $[RSe–SeR]^{\bullet+}$ [2.289(1) Å, R = C_6H_5; 2.289(7) Å, R = 2,6-$Mes_2C_6H_3$] and $[RTe–TeR]^{\bullet+}$ [2.662(1) Å, R = 2,6-$Mes_2C_6H_3$].[23]

The C2–C3 bond lengths of **3a-Se** [1.521(5) Å] and **3a-Te** [1.524(3) Å] are within three standard deviations equal to that of **2a-S** [1.535(7) Å] and slightly longer than that of **2a-Se** [1.508(4) Å].[15a] The C1–E1–E1′ bond angles of **3a-Se** [101.3(1)°] and **3a-Te** [98.6(1)°] are larger than those of **3b-Se** [94.8(1)°] and **3b-Te** [89.3(1)°]. This is in line with the puckered structure of the C_3N_2 ring of SIPr.

UV/Vis Spectroscopy

Compounds **3a-S** and **3b-S** are pale yellow solids and thus their UV/Vis spectra show no (for **3a-S**) or a very weak (at 490 nm for **3b-S**) absorption in the visible region. The latter is consistent with its UV/Vis absorption (474 nm) measured in the solid-state.[12] While the UV/Vis spectrum of **3a-Se** (orange solid) shows a shoulder at 505 nm, those of **3b-Se** (violet solid), **3a-Te** (violet solid) and **3b-Te** (green solid) measured in acetonitrile exhibit a characteristic broad absorption maximum at 507 nm, 571 nm, and 630 nm, respectively. As reported previously,[13] the highest occupied molecular orbital (HOMO) of **3b-Te** is mainly the lone pairs of the Te_2 unit, whereas the lowest unoccupied molecular orbital (LUMO) is the σ*-orbital at the Te_2 moiety. Based on TD-DFT analysis,



3a-Se **3a-Te**

Figure 2. Solid-state molecular structures of **3a-Se** and **3a-Te**. Hydrogen atoms and triflate counter anions are omitted for the sake of clarity. For **3a-Se** only one of two crystallographically independent molecules is shown, each of which is located at an inversion center (see Figure S38, Supporting Information). Thermal displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths /Å and angles /° for **3a-Se**: Se1–Se1′ 2.429(1), Se1–C1 1.908(3), C1–N1 1.331(4), C1–N2 1.320(4), C2–N1 1.480(4), C3–N2 1.490(4), C2–C3 1.521(5), C1–Se1–Se1’ 101.3(1), N1–C1–N2 112.5(3); for **3a-Te**: Te1–Te1’ 2.789(1), Te1–C1 2.115(1), C1–N1 1.322(2), C1–N2 1.324(2), C2–N1 1.490(2), C3–N2 (1.481(2), C2–C3 1.524(3), C1–Te1–Te1’ 98.6(1), N1–C1–N2 112.0(1).

Table 2. Selected bond lengths /Å and angles /° for the dications in **3a-Se**, **3b-Se**, **3a-Te**, and **3b-Te**.

	E–E	C–E	C–N	N–C–N	C–E–E	Reference
3a-Se a)	2.429(1)	1.908(3)	1.331(4) 1.320(4)	112.5(3)	101.3(1)	This work
3b-Se	2.427(5)	1.885(2)	1.349(3) 1.351(3)	107.2(2)	94.8(1)	[12]
3a-Te a)	2.789(1)	2.115(1)	1.322(2) 1.324(2)	112.0(1)	98.6(1)	This work
3b-Te	2.792(1)	2.095(3)	1.352(4) 1.351(4)	106.6(2)	90.4(3)	[13]

a) Symmetry-generated from a half molecule in the asymmetric unit.

the absorption at λ_{max} = 630 nm for **3b-Te** may be assigned to HOMO→LUMO transition.[13] The same absorption for the **3a-Te** (571 nm) featuring a more electrophilic carbene (SIPr) is, however, blue-shifted compared to that of **3b-Te** containing a rather weak electrophilic carbene (IPr). This suggests a larger HOMO–LUMO energy gap in the former. Electrophilic NHCs such as SIPr stabilize the HOMO, leading to a larger HOMO–LUMO energy gap. This has also been shown previously with related phosphorus[24] and arsenic[25] compounds reported by this laboratory. Moreover, the replacement of a lighter element by a heavier element leads to the narrowing of HOMO–LUMO energy gap. This clearly rationalizes the successive red-shifting of the corresponding absorption band in the UV/Vis spectra of **3-E** derivatives (Figure 3).

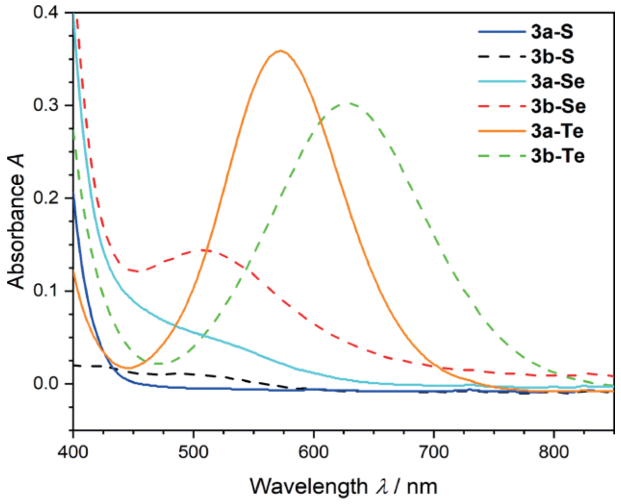


Figure 3. UV/Vis spectra of **3a-E** (solid lines) and **3b-E** (dashed lines) in acetonitrile (c = 10^{-3} M).

Conclusions

In conclusion, we have reported the synthesis and characterization of ionic dichalcogen compounds **3a-E** (E = S, Se, and Te) derived from a saturated NHC (SIPr). In addition, the missing spectroscopic information about the hitherto known related IPr-derivatives **3b-E** has been presented. A comparative study on the spectroscopic and structural parameters of these two classes of compounds has been provided. Further electrochemical analysis of these compounds is currently underway in this laboratory, which may lead to corresponding open-shell radical cations or anions upon their one-electron oxidation or reduction.

Experimental Section

All syntheses and manipulations were carried out in an inert gas atmosphere (Ar or N$_2$) using standard Schlenk techniques or a glove box (MBraun LABMasterPro). Solvents were dried with appropriate drying agents, distilled, and stored over 3 Å molecular sieves prior to use. Deuterated solvents were dried with appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500, Bruker Avance III 500 HD or Bruker NEO 600 spectrometer. Chemical shifts (in δ, ppm) are referenced to the solvent residual signals of CDCl$_3$ (^{1}H, 7.26; ^{13}C, 77.16) and CD$_3$CN (^{1}H, 1.94; ^{13}C, 1.32). UV/Vis spectra were recorded on a ThermoFischer Evolution 300 spectrophotometer. Elemental analyses were carried out with a EURO EA Element Analyzer. IPr and SIPr were prepared following literature protocols.[26] S$_8$ was sublimed prior to use and stored under an argon atmosphere. Se powder and Te powder were dried in vacuo and stored under an argon atmosphere. Tf$_2$O was distilled prior to use and stored in a nitrogen atmosphere. Single crystal X-ray diffraction analyses were performed on Rigaku Supernova diffractometers.

Synthesis of (SIPr)Te (2a-Te): A 30 mL THF suspension of SIPr (4.0 g, 10.2 mmol) and Te powder (1.3 g, 10.2 mmol) was stirred at room temperature overnight. Filtration through a plug of Celite afforded a light-yellow filtrate. The volatiles were removed in vacuo to obtain **2a-Te** as an off-white solid in 82 % (4.4 g) yield. $C_{27}H_{38}N_2Te$ (518) (**2a-Te**): calcd. C 62.58, H 7.39, N 5.41 %; found: C 63.01, H 7.77, N 5.64 %. **^{1}H NMR** (500 MHz, CDCl$_3$, 298 K): δ = 7.45 (t, J = 7.7 Hz, 2 H, *p*-C$_6$*H*$_3$), 7.27 (d, J = 6.7, 4 H, *m*-C$_6$*H*$_3$), 4.07 (s, 4 H, NC*H*), 3.05 [hept, J = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.47 [d, J = 6.7 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.34 [d, J = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$]. **^{13}C{^{1}H} NMR** (126 MHz, CDCl$_3$, 298 K): δ = 168.2 (*C*Te), 147.0 (*i*-*C*$_6$H$_3$), 136.4 (*o*-*C*$_6$H$_3$), 129.7 (*p*-*C*$_6$H$_3$), 124.7 (*m*-*C*$_6$H$_3$), 52.6 (N*C*H$_2$), 29.4 [*C*H(CH$_3$)$_2$], 25.2 [CH(*C*H$_3$)$_2$], 24.6 [CH(*C*H$_3$)$_2$]. **^{125}Te{^{1}H} NMR** (158 MHz, CDCl$_3$, 298 K): δ = 80.8 ppm.

General Procedure for the Preparation of Compounds 3a-E and 3b-E: To a precooled (–40 °C) dichloromethane solution (10 mL) solution of (NHC)E (**2a-E** or **2b-E**, E = S, Se or Te; NHC = SIPr for **2a** and IPr for **2b**) was added Tf$_2$O (1 equiv.). The resulting suspension was stirred overnight at room temp. The volatiles were removed under vacuum and the residue was washed with toluene (10 mL × 3) to obtain the dicationic compounds [(NHC)E]$_2$(OTf)$_2$ (**3a-E** or **3b-E**, E = S, Se or Te; NHC = SIPr for **a** and IPr for **b**).

[(SIPr)S]$_2$(OTf)$_2$ (3a-S): Reagents: **2a-S** (1.02 g, 2.41 mmol), Tf$_2$O (0.42 mL, 0.7 g 2.4 mmol). Yield: 76 % (1.1 g), bright yellow solid. $C_{56}H_{76}F_6N_4O_6S_4$ (1143) (**3a-S**): calcd. C 58.72, H 6.86, N 4.89 %; found: C 58.67, H 6.42, N 4.74 %. **^{1}H NMR** (500 MHz, CD$_3$CN, 298 K): δ = 7.63 (t, J = 7.8 Hz, 4 H, *p*-C$_6$*H*$_3$), 7.48 (d, J = 7.8 Hz, 8 H, *m*-C$_6$*H*$_3$), 4.69 (s, 8 H, NC*H*$_2$), 2.96 [hept, J = 6.9 Hz, 8 H, C*H*(CH$_3$)$_2$], 1.37 [d, J = 6.7 Hz, 24 H, CH(C*H*$_3$)$_2$], 1.33 [d, J = 6.7 Hz, 24 H, CH(C*H*$_3$)$_2$]. **^{13}C{^{1}H} NMR** (126 MHz, CD$_3$CN, 298 K): δ = 159.8 (*C*S), 147.2 (*i*-*C*$_6$H$_3$), 133.3 (*o*-*C*$_6$H$_3$), 130.5 (*p*-*C*$_6$H$_3$), 126.9 (*m*-*C*$_6$H$_3$), 55.7 (N*C*H$_2$), 30.3 [*C*H(CH$_3$)$_2$], 26.6 [CH(*C*H$_3$)$_2$], 23.2 [CH(*C*H$_3$)$_2$]. **^{19}F{^{1}H} NMR** (471 MHz, CD$_3$CN, 298 K): δ = –79.3 ppm.

[(IPr)S]$_2$(OTf)$_2$ (3b-S): Reagents: **2b-S** (0.5 g, 1.2 mmol), Tf$_2$O (0.20 mL, 0.3 g, 1.2 mmol). Yield: 60 % (0.4 g), off-white solid. $C_{56}H_{72}F_6N_4O_6S_4$ (1139) (**3b-S**): calcd. C 58.93.72, H 6.53, N 4.91 %; found: C 59.24, H 6.52, N 4.71 %. **^{1}H NMR** (500 MHz, CD$_3$CN, 298 K): δ = 8.45 (s, 4 H, NC*H*), 7.75 (t, J = 7.9 Hz, 4 H, *p*-C$_6$*H*$_3$), 7.57 (d, J = 7.9 Hz, 8 H, *m*-C$_6$*H*$_3$), 2.25 [sept, J = 6.8 Hz, 8 H, C*H*(CH$_3$)$_2$], 1.32 [d, J = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$], 1.23 [d, J = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$] ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD$_3$CN, 298 K): δ = 146.2 (*C*S), 134.2 (*p*-*C*$_6$H$_3$), 133.1 (N*C*H), 126.6 (*p*-*C*$_6$H$_3$), 126.77 (*m*-*C*$_6$H$_3$), 30.4 [*C*H(CH$_3$)$_2$], 26.1 [CH(*C*H$_3$)$_2$], 22.6 [CH(*C*H$_3$)$_2$] ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD$_3$CN, 298 K): δ = –79.4 ppm. **UV/Vis** (acetonitrile, 10^{-3} M): λ (ε) [nm (M^{-1} cm^{-1})] = 491 (11).

[(SIPr]Se]$_2$(OTf)$_2$ (3a-Se): Reagents: **2a-Se** (0.6 g, 1.3 mmol), Tf$_2$O (0.23 mL, 0.4 g, 1.4 mmol).Yield: 84 % (0.7 g), orange solid. Single crystals suitable for X-ray diffraction analysis were obtained by storing a saturated acetonitrile solution of **3a-Se** at room temperature overnight. $C_{56}H_{76}F_6N_4O_6S_2Se_2$ (1237) (**3a-Se**): calcd. C 54.36, H 6.19, N 4.53 %; found: C 54.70, H 6.66, N 4.34 %. **^{1}H NMR** (500 MHz, CD$_3$CN, 298 K): δ = 7.53 (t, J = 7.8 Hz, 4 H, *p*-C$_6$*H*$_3$), 7.31 (d, J = 7.7 Hz, 8 H, *m*-C$_6$*H*$_3$), 4.34 (s, 8 H, NC*H*$_2$), 2.76 [hept, J = 7.0 Hz, 8 H, C*H*(CH$_3$)$_2$], 1.19 [d, J = 6.6 Hz, 24 H, CH(C*H*$_3$)$_2$], 1.09 [d, J = 6.7 Hz, 24 H, CH(C*H*$_3$)$_2$]. **^{13}C{^{1}H} NMR** (126 MHz, CD$_3$CN, 298 K): δ = 164.9 (*C*Se), 148.6 (*i*-*C*$_6$H$_3$), 134.4 (*o*-*C*$_6$H$_3$), 129.4 (*p*-*C*$_6$H$_3$), 127.2 (*m*-*C*$_6$H$_3$), 56.3 (N*C*H$_2$), 30.0 [*C*H(CH$_3$)$_2$], 25.9 [CH(*C*H$_3$)$_2$], 24.1 [CH(*C*H$_3$)$_2$]. **^{19}F{^{1}H} NMR** (471 MHz, CD$_3$CN, 298 K): δ = –79.3 ppm. **^{77}Se{^{1}H} NMR** (95 MHz, CDCl$_3$, 298 K): δ = 497.5 ppm. **UV/Vis** (acetonitrile, 10^{-3} M): λ (ε) [nm (M^{-1} cm^{-1})] = 505 (53).

[(IPr]Se]$_2$(OTf)$_2$ (3b-Se): Reagents: **2b-Se** (1.1 g, 2.1 mmol), Tf$_2$O (0.38 mL, 0.6 g, 2.1 mmol). Yield: 92 % (1.2 g), violet solid. $C_{56}H_{72}F_6N_4O_6S_2Se_2$ (1233) (**3b-Se**): calcd. C 54.45, H 6.04, N 4.54 %; found: C 54.79, H 5.79, N 4.11 %. **^{1}H NMR** (500 MHz, CD$_3$CN, 298 K): δ = 8.02 (s, 4 H, NC*H*), 7.69 (t, J = 7.8 Hz, 4 H, *p*-C$_6$*H*$_3$), 7.41 (d, J = 7.8 Hz, 8 H, *m*-C$_6$*H*$_3$), 2.06 [hept, J = 6.8 Hz, 8 H, C*H*(CH$_3$)$_2$], 1.09 [d, J = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$], 1.00 [d, J = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$]. **^{13}C{^{1}H} NMR** (126 MHz, CD$_3$CN, 298 K): δ = 146.9 (*C*Se), 134.9 (*p*-*C*$_6$H$_3$), 130.9 (N*C*H), 130.0 (N*C*N) 126.8 (*m*-*C*$_6$H$_3$), 30.2 [*C*H(CH$_3$)$_2$], 25.2 [CH(*C*H$_3$)$_2$], 23.2 [CH(*C*H$_3$)$_2$]. **^{19}F{^{1}H} NMR** (471 MHz, CD$_3$CN, 298 K): δ = –79.4 ppm. **^{77}Se{^{1}H} NMR** (95 MHz, CDCl$_3$, 298 K): δ = 430.3 ppm. **UV/Vis** (acetonitrile, 10^{-3} M): λ (ε) [nm (M^{-1} cm^{-1})] = 507 (144).

[(SIPr]Te]$_2$(OTf)$_2$ (3a-Te): Reagents: **2a-Te** (1.0 g, 2.0 mmol), Tf$_2$O (0.33 mL, 0.5 g, 2.0 mmol). Yield: 92 %, (1.2 g), violet solid. Single crystals suitable for X-ray diffraction analysis were obtained by storing a saturated acetonitrile solution of **3a-Te** at room temperature overnight. $C_{56}H_{76}F_6N_4S_2Te_2$ (1335) (**3a-Te**): calcd. C 50.32, H 5.88, N 4.19 %; found: C 49.75, H 5.68, N 3.92 %. **^{1}H NMR** (500 MHz, CD$_3$CN, 298 K): δ = 7.47 (t, J = 8.3 Hz, 4 H, *p*-C$_6$*H*$_3$), 7.29 (d, J = 7.7 Hz, 8 H, *m*-C$_6$*H*$_3$), 4.34 (s, 8 H, NCH$_2$), 2.79 [hept, J = 7.0 Hz, 8 H, C*H*(CH$_3$)$_2$], 1.31 [d, J = 6.9 Hz, 24 H, CH(C*H*$_3$)$_2$], 1.21 [d, J = 6.7 Hz, 24 H, CH(C*H*$_3$)$_2$]. **^{13}C{^{1}H} NMR** (126 MHz, CD$_3$CN, 298 K): δ = 160.4 (*C*Te), 149.7 (*i*-*C*$_6$H$_3$), 134.3 (*o*-*C*$_6$H$_3$), 131.2 (*p*-*C*$_6$H$_3$), 127.4 (*m*-*C*$_6$H$_3$), 56.0 (N*C*H$_2$), 29.9 [*C*H(CH$_3$)$_2$], 25.6 [CH(*C*H$_3$)$_2$], 24.3 [CH(*C*H$_3$)$_2$]. **^{19}F{^{1}H} NMR** (471 MHz, CD$_3$CN, 298 K): δ = –79.4 ppm. **^{125}Te{^{1}H} NMR** (158 MHz, CDCl$_3$, 298 K): δ = 582.1 ppm. **UV/Vis** (acetonitrile, 10^{-3} M): λ (ε) [nm (M^{-1} cm^{-1})] = 571 (358).

Supporting Information (see footnote on the first page of this article): NMR spectra and crystallographic details of compounds **2-E** and **3-E**.

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