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Role of Alkyl Substituent and Solvent on the Structural, Thermal, and Magnetic Properties of Binary Radical Salts of 1,2,3,5-Dithia- or Diselenadiazolyl Cations and the TCNQ Anion

Anni I. Taponen, Awatef Ayadi, Noora Svahn, Manu K. Lahtinen, Mathieu Rouzières, Rodolphe Clérac,* Heikki M. Tuononen,* and Aaron Mailman*



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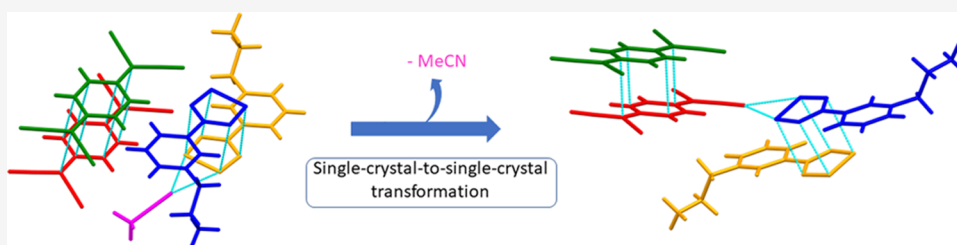
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ABSTRACT: The synthesis, structural, thermal, and magnetic properties of a series of simple binary organic salts based on the radical anion of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 4-(*N*-alkylpyridinium-3-yl)-1,2,3,5-dithiadiazolyl (DTDA), 1^R ($R = \text{Et, Pr, Bu}$), radical cations and their heavier selenium analogues (DSDA), 2^R , are described. Single-crystal X-ray structural analyses reveal that short alkyl substituents on the pyridinium moiety of DTDA/DSDA cations lead to crystallization of isostructural acetonitrile (MeCN) solvates $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Pr}}\cdot\text{MeCN}$, $2^{\text{Et}}\cdot\text{MeCN}$, and $2^{\text{Pr}}\cdot\text{MeCN}$ with *trans*-cofacial DTDA radical cation and eclipsed-cofacial TCNQ radical anion dimers. A slight increase in the substituent chain length to butyl affords the solvate $1^{\text{Bu}}\cdot 0.5\text{MeCN}$ or the nonsolvate 1^{Bu} . The nonsolvate 1^{Bu} can be exclusively isolated using propionitrile (EtCN), whereas the isostructural selenium analogue 2^{Bu} crystallizes from MeCN. The crystal packing in $1^{\text{Bu}}\cdot 0.5\text{MeCN}$ and $1^{\text{Bu}}/2^{\text{Bu}}$ is distinctively different: rare one-dimensional (1D) columnar π -stacks of evenly spaced TCNQ radical anions with periodic distortions along the vertical stacking direction and *cis*-cofacial DTDA dimers in $1^{\text{Bu}}\cdot 0.5\text{MeCN}$ vs discrete, non-eclipsed-cofacial TCNQ dimers and *trans*-antiarafacial DTDA/DSDA dimers in $1^{\text{Bu}}/2^{\text{Bu}}$. The nonsolvated structure 1^{Pr} with *trans*-cofacial DTDA and non-eclipsed-cofacial TCNQ dimers can be isolated from EtCN. Single-crystal and powder X-ray diffraction methods confirmed a thermally driven, irreversible, single-crystal-to-single-crystal structural transformation between $1^{\text{Pr}}\cdot\text{MeCN}$ and 1^{Pr} . Thermogravimetric analyses of all nonsolvated salts show varied, yet robust, thermal behavior, while the thermal behavior of the solvates is consistent with more facile lattice solvent loss from structures with longer *N*-alkyl chains. Variable-temperature magnetic susceptibility measurements indicate that all structures are diamagnetic at low temperatures. However, thermally populated magnetic states could be observed for $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Et}}\cdot\text{EtCN}$, $1^{\text{Pr}}\cdot\text{MeCN}$, $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, 1^{Bu} , and 2^{Bu} at higher temperatures. This can be correlated with desolvation and structural changes that lead to the generation of weakly antiferromagnetically coupled non-eclipsed-cofacial TCNQ dimers, in agreement with results from density functional theory (DFT) calculations.

INTRODUCTION

Ion-paired molecular solids containing the ubiquitous electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) have been extensively investigated for constituents of new functional materials exhibiting conductive, optical, and/or magnetic properties. A quintessential example of this class of compounds is the 1:1 charge transfer complex between TCNQ and tetrathiafulvalene (TTF), reported in 1973.¹ It was the first example of an organic solid showing metal-like behavior over a large temperature range and maximum electrical conductivity on par with typical metallic elements, such as copper. This system has been intensively explored even to this day, leading to many groundbreaking results. For example, bringing

individual crystals of TTF and TCNQ into direct, mechanical contact, a process dubbed crystal laminating, has been found to create stable and reproducible conducting layers with high carrier density without the need of dopants.² Recently, nanostructured TTF–TCNQ was found to exhibit excellent electromagnetic performance and electromagnetic interference

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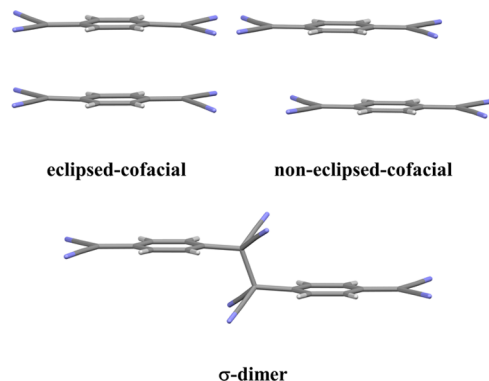


shielding effectiveness, opening up the possibility to develop electromagnetic response materials based on charge transfer systems.³

The TTF–TCNQ charge transfer complex has a unique and well-defined crystal structure in which the formally ionic constituents form alternating and evenly spaced columnar stacks consisting of noneclipsed subunits. As a result, the stacks behave as decoupled, quasi-one-dimensional (1D) electronic systems that lead to the observed conductivity at high temperatures. However, at very low temperatures, the TTF–TCNQ system becomes an insulator owing to two Peierls transitions that occur independently at 38 and 54 K for TTF and TCNQ, respectively.⁴ The evenly spaced, uniform columnar packing of TCNQ^{•−} radical anions is relatively uncommon; however, it is observed, for example, in the *N*-methylphenazinium (NMP) salt that also shows high electrical conductivity for an organic species, though several orders of magnitude less than that of TTF–TCNQ.^{5,6}

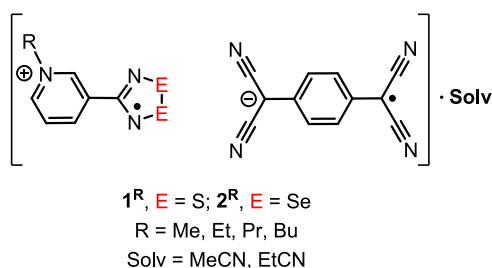
By far the most common packing type in ion-paired TCNQ salts involves the formation of discrete π -dimers of TCNQ^{•−} radical anions with either an eclipsed or noneclipsed geometry (Chart 1). The former geometry typically involves a transversal

Chart 1. Three Most Common Modes of Dimerization for the 7,7',8,8'-Tetracyanoquinodimethane Radical Anion (TCNQ^{•−})



offset of *ca.* 1.0 Å, while the latter is characterized by a longitudinal offset of *ca.* 2.1 Å (Chart 2).⁷ In both cases, the unpaired electrons in the dimers are antiferromagnetically coupled *via* strong π – π interactions, whereas systems with noneclipsed geometry often exhibit thermally accessible triplet states.^{8,9} In addition to π -dimerization, TCNQ^{•−} radical anions

Chart 2. Illustration of the Structures of the Binary Salts 1^R and 2^R, and Their Acetonitrile (MeCN) or Propionitrile (EtCN) Solvates, Consisting of a 1,2,3,5-Dithiadiazolyl (DTDA; E = S) or 1,2,3,5-Diselenadiazolyl (DSDA; E = Se) Radical Cation and a TCNQ Radical Anion



have been found to form σ -dimers in the solid state with long (1.6–1.7 Å) and thereby weak C–C bonds. There are only a dozen structurally characterized examples of σ -dimers of TCNQ^{•−} reported to date,^{9–20} with the first example being the *N*-ethylphenazinium (NEP) salt, [NEP][TCNQ].²¹ It is striking that such a simple methyl-to-ethyl substitution in the cationic moiety has such a profound influence on the structure of the anion (evenly spaced π -stacks in [NMP][TCNQ] *vs* σ -dimers in [NEP][TCNQ]) and, therefore, to the physical properties of the compound (highly conducting *vs* insulating).

The majority of simple binary salts of the TCNQ^{•−} radical anion contain diamagnetic counter cations, though there are examples of salts with radical cations.^{22,23} Recently, we decided to introduce an additional spin to the system by combining TCNQ^{•−} with the 4-(*N*-methylpyridinium-3-yl)-1,2,3,5-dithiadiazolyl radical cation (3-MePyDTDA^{•+}) by solution methods to afford the solvates 1^{Me}·MeCN and 1^{Me}·EtCN, where 1^{Me} = [3-MePyDTDA^{•+}][TCNQ^{•−}].²⁴ Such ion-paired salts of molecular radicals can lead to new functional materials with interesting magnetic and/or conductive properties. We showed that the desolvation of 1^{Me}·MeCN and 1^{Me}·EtCN containing π -dimers of both 3-MePyDTDA^{•+} and TCNQ^{•−} affords the nonsolvate 1^{Me} that, in turn, undergoes a reversible first-order phase transition associated with structural interconversion between two discrete and noninteracting TCNQ^{•−} radicals ($S = 1/2$) and their C–C-bonded σ -dimers ($S = 0$). The magnetic bistability observed for 1^{Me} results from the structural flexibility of the π -dimer of 3-MePyDTDA^{•+} and the intermolecular $S^{\delta+} \cdots N^{\delta-}$ interactions between 3-MePyDTDA^{•+} and TCNQ^{•−} radicals that allow the formation and breakup of the C–C bond in TCNQ^{•−} dimers (1.656(8) Å) without other structural changes.

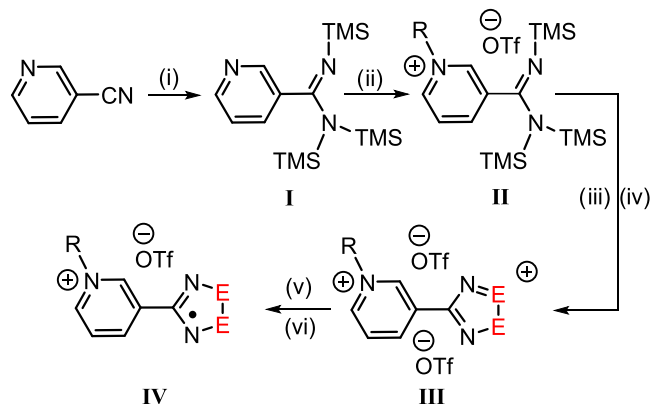
In this study, we continue our investigations on the radical-ion salts of DTDA^{•+} and TCNQ^{•−} by probing the effect the alkyl chain length on the pyridinium moiety of the DTDA^{•+} radical cation has on the solid-state architecture. As a first approximation, the replacement of the methyl group by a longer alkyl chain is expected to affect the steric properties of the cation alone because the SOMO of DTDA^{•+} is invariant to such substitution. Combined with the pliability of longer alkyl chains, the increased steric repulsion should favor the formation of nonsolvated crystal structures that, in turn, could be advantageous for the formation of σ -dimers of TCNQ^{•−} and possibly new magnetically bistable systems composed of organic radicals. As a further modification to the molecular structure, we performed an atom-to-atom replacement and investigated the behavior of selenium analogues of DTDA^{•+}, that is, 4-(*N*-alkylpyridinium-3-yl)-1,2,3,5-diselenadiazolyl radical-cations (DSDA^{•+}). The primary motivation for these investigations comes from the well-studied *N*-alkylphenazinium salts of TCNQ^{•−} discussed above, in which case the identity of the cationic alkyl chain (methyl, ethyl, or butyl) influences not only the TCNQ^{•−} dimerization mode but also the resultant physical properties. Moreover, despite the known role that the cation plays in the solid-state structure and properties of TCNQ^{•−} salts, only a few systematic studies have been reported on the topic to date.

EXPERIMENTAL SECTION

General Methods and Procedures. Full experimental details for the synthesis and characterization of the precursors I–IV (see Scheme 1) and the salts 1^{Et}·MeCN, 1^{Pr}·MeCN, 1^{Bu}·0.5MeCN, 1^{Et}·EtCN, 1^{Pr},

1^{Bu} , $2^{\text{Et}}\cdot\text{MeCN}$, $2^{\text{Pr}}\cdot\text{MeCN}$, and 2^{Bu} (Scheme 2), are given in the Supporting Information.

Scheme 1. Synthetic Sequence to the Triflate Salts of 4-(*N*-Alkylpyridinium-3-yl)-1,2,3,5-dithiadiazolyl ($E = \text{S}$) and 4-(*N*-Alkylpyridinium-3-yl)-1,2,3,5-diselenadiazolyl ($E = \text{Se}$) Radical Cations, IV^{a}



^aReagents and general conditions: (i) $\text{LiN}(\text{TMS})_2\cdot\text{Et}_2\text{O}$, THF, reflux, 16 h, TMSCl; (ii) ROTf, Et_2O , RT, 16 h; (iii) excess S_2Cl_2 or quantitative SeCl_2 , MeCN, RT, 16 h; (iv) excess TMSOTf, MeCN, RT, 3 h; (v) NBu_4I , MeCN, RT, 3 h; (vi) AgOTf, MeCN, 2 h.

X-ray Crystallography. Variable-temperature single-crystal X-ray diffraction studies were performed on Agilent SuperNova equipped with Atlas CCD detector, dual micro-focus X-ray source (Cu and Mo), and multilayer optics to generate Cu $K\alpha$ ($\lambda = 1.54184 \text{ \AA}$) or Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Crystals were mounted on MiTeGen micro-mounts using Fomblin oil or glass fibers using Wacker silicone paste for low- (<273 K) and high-temperature (>273 K) data collections, respectively. Data acquisitions, reductions, twinning, and analytical face/index-based absorption corrections were made using CrysAlis^{PRO} (v. 39.46).²⁵ The structures were solved using ShelXT program²⁶ and refined on F^2 by full-matrix least-squares techniques with the ShelXL program as implemented in Olex (v. 1.2) program package²⁷ that utilizes the ShelXL-2013 module.²⁸ C–H hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 (aromatic) or 1.5 (aliphatic) times the host atom. Crystallographic data of compounds $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Pr}}\cdot\text{MeCN}$, $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, $1^{\text{Et}}\cdot\text{EtCN}$, 1^{Pr} , 1^{Bu} , $2^{\text{Et}}\cdot\text{MeCN}$, $2^{\text{Pr}}\cdot\text{MeCN}$, and 2^{Bu} are compiled in Tables 1 and 2; crystallographic data of derivatives of IV are given in the Supporting Information (Tables S1 and S2). In the case of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, poor crystallinity and/or the combination of severe nonmerohedral twinning was persistent across several samples that led to poor data quality. The atom connectivity and crystal packing, however, were clearly

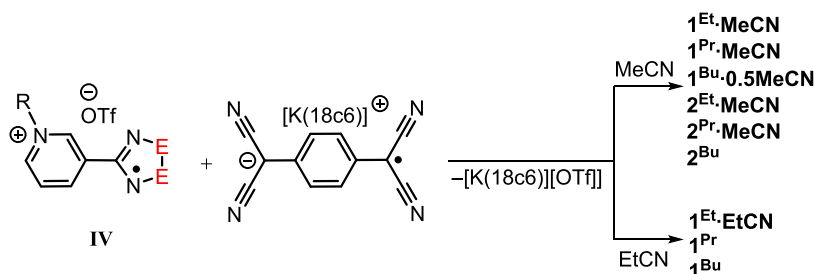
established and consistent between two independent data sets. Full crystallographic details are available in the Supporting Information.

Powder X-ray Diffraction. Powder X-ray diffraction measurements were performed on PANalytical X'Pert PRO MPD diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$; 45 kV, 40 mA). In routine experiments, a freshly crystallized and lightly hand-ground powder sample was prepared on zero-background signal generating silicon plate using petrolatum jelly as an adhesive. Diffraction intensities were recorded from spinning samples. In variable-temperature work, a lightly ground sample was placed into an Anton Paar TTK450 temperature-controlled chamber equipped with an automated sample-stage height controller. Diffraction data were acquired by an X'Celerator detector using 2θ ranges of 3–60 and 4–40° in routine and variable-temperature experiments, respectively. A step size of 0.017° and counting times from 60 to 240 s per step were used based on the sample to acquire sufficient diffraction intensities. In variable-temperature measurements, samples were heated/cooled with a heating/cooling rate of 10 K min^{-1} under a nitrogen atmosphere. Each powder pattern was recorded isothermally at the chosen temperature. The diffractometer was aligned using a silicon powder standard material (SRM 640, National Institute of Standards & Technology), and the temperature was calibrated by monitoring the solid-state phase transition of KNO_3 from orthorhombic to trigonal structure (402 K). Data processing and Pawley fits were performed with the program X'Pert HighScore Plus (v. 4.9).²⁹ The unit cell parameters of the powder samples were refined by Pawley analysis using the corresponding single-crystal structure parameters as the basis of least-squares refinements. Variables used in the fits were zero-offset, polynomial background, sample displacement, and unit cell parameters along with peak profile parameters including peak width, shape, and asymmetry.³⁰

Thermogravimetric Analyses (TGA). Thermogravimetric analyses were performed on a PerkinElmer STA 600 simultaneous thermal (TG/DSC) analyzer using open platinum pan under a nitrogen atmosphere (40 mL min^{-1} flow rate) with a heating rate of 10 K min^{-1} over 295–873 K for DTDA and 295–573 K for DSDA variants. Temperature calibration was performed with an indium standard (PerkinElmer, melting point = 429.60 K) and weight calibration by a standard weight of 50.00 mg at room temperature. All samples were freshly prepared and dried *in vacuo* prior to measurements where 3–8 mg of sample was typically used. Recorded TGA data were processed using the Pyris Manager software (v. 13). The desolvation and decomposition temperatures were determined as extrapolated onset values.

Magnetic Susceptibility Measurements. Magnetic measurements were performed on a Quantum Design SQUID MPMS-XL magnetometer housed at the Centre de Recherche Paul Pascal (CRPP) operating at temperatures between 1.8 and 400 K for dc magnetic fields ranging from –7 to 7 T. Measurements were performed on polycrystalline samples $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Et}}\cdot\text{EtCN}$, $1^{\text{Pr}}\cdot\text{MeCN}$, and $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, and the nonsolvates 1^{Bu} and 2^{Bu} (21.7, 24.6, 35.1, 24.9, 33.3, and 18.8 mg, respectively) and introduced in a sealed double polyethylene/polypropylene bags (3 cm \times 0.5 cm \times 0.02

Scheme 2. Double-Displacement Reaction between IV and $[\text{K}(\text{18c6})][\text{TCNQ}]$ Leads to the Radical-Ion Salts $1^{\text{Et,Pr}}\cdot\text{MeCN}$, $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, $2^{\text{Et,Pr}}\cdot\text{MeCN}$, and 2^{Bu} in MeCN, and $1^{\text{Et}}\cdot\text{EtCN}$ and $1^{\text{Pr,Bu}}$ in EtCN (1, $E = \text{S}$; 2, $E = \text{Se}$).



1, $E = \text{S}$; 2, $E = \text{Se}$

Table 1. Crystallographic Data for Compounds $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Et}}\cdot\text{EtCN}$, $1^{\text{Pr}}\cdot\text{MeCN}$, 1^{Pr} , $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, and 1^{Bu}

	$1^{\text{Et}}\cdot\text{MeCN}$	$1^{\text{Et}}\cdot\text{EtCN}$	$1^{\text{Pr}}\cdot\text{MeCN}$	1^{Pr}	$1^{\text{Bu}}\cdot 0.5\text{MeCN}$	1^{Bu}
CCDC	2181980	2181982	2181983	2181987	2182780	2181986 ^b
formula	$\text{C}_{22}\text{H}_{16}\text{N}_8\text{S}_2$	$\text{C}_{23}\text{H}_{18}\text{N}_8\text{S}_2$	$\text{C}_{23}\text{H}_{18}\text{N}_8\text{S}_2$	$\text{C}_{21}\text{H}_{15}\text{N}_7\text{S}_2$	$\text{C}_{46}\text{H}_{35}\text{N}_{15}\text{S}_4$	$\text{C}_{22}\text{H}_{17}\text{N}_7\text{S}_2$
molecular weight (g mol^{-1})	456.55	470.57	470.59	429.52	926.13	443.54
T (K)	120.00(10)	120.00(10)	120.00(10)	120.00(10)	120.00(10)	120.00(10)
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.6768(7)	8.6669(5)	8.8121(5)	8.4212(5)	13.442(3)	6.8439(3)
b (Å)	10.4354(11)	10.4645(6)	10.8960(6)	8.4510(5)	13.464(3)	11.1768(5)
c (Å)	11.9119(10)	13.1169(8)	11.7291(6)	14.1533(8)	13.959(5)	14.2752(7)
α (°)	98.978(8)	74.971(5)	98.130(4)	84.671(5)	92.94(2)	93.617(4)
β (°)	90.426(7)	82.518(5)	92.145(4)	80.088(5)	107.47(3)	90.731(4)
γ (°)	96.364(8)	83.520(4)	97.591(5)	85.166(4)	111.98(2)	106.931(4)
V (Å ³)	1058.46(17)	1135.27(12)	1103.29(11)	985.54(10)	2196.1(11)	1041.99(9)
Z	2	2	2	2	2	2
ρ_{calc} (g cm^{-3})	1.432	1.377	1.416	1.447	1.401	1.414
absorption ($\mu\text{ mm}^{-1}$)	0.280	0.264	0.271	0.295	2.425	0.281
$F(000)$	472.0	488.0	488.0	444.0	960.0	460.0
2θ range for data collection (deg)	3.978–57.762	4.044–57.77	3.812–57.812	4.852–57.706	6.754–137.994	4.928–57.918
index ranges	$-9 \leq h \leq 11$ $-14 \leq k \leq 14$ $-15 \leq l \leq 14$	$-10 \leq h \leq 11$ $-13 \leq k \leq 13$ $-16 \leq l \leq 17$	$-11 \leq h \leq 9$ $-14 \leq k \leq 13$ $-14 \leq l \leq 13$	$-11 \leq h \leq 11$ $-11 \leq k \leq 10$ $-17 \leq l \leq 19$	$-16 \leq h \leq 16$ $-16 \leq k \leq 16$ $-16 \leq l \leq 16$	$-8 \leq h \leq 9$ $-14 \leq k \leq 14$ $-19 \leq l \leq 18$
reflections collected	7601	8934	8432	12,717	11,546	17,696
independent reflections	4739 [$R_{\text{int}} = 0.0190$, $R_{\text{sigma}} = 0.0383$]	5121 [$R_{\text{int}} = 0.0226$, $R_{\text{sigma}} = 0.0406$]	4941 [$R_{\text{int}} = 0.0184$, $R_{\text{sigma}} = 0.0361$]	4573 [$R_{\text{int}} = 0.0395$, $R_{\text{sigma}} = 0.0456$]	11546 [$R_{\text{int}} = 0.2257^a$, $R_{\text{sigma}} = 0.1951$]	4920 [$R_{\text{int}} = 0.0279$, $R_{\text{sigma}} = 0.0234$]
data/restraints/ parameters	4739/0/291	5121/0/300	4941/0/300	4573/0/272	11546/236/492	4920/0/281
goodness-of-fit on F^2	1.047	1.067	1.041	1.085	1.114	1.170
final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0366$ $wR_2 = 0.0861$	$R_1 = 0.0406$ $wR_2 = 0.0938$	$R_1 = 0.0387$ $wR_2 = 0.0946$	$R_1 = 0.0526$ $wR_2 = 0.1602$	$R_1 = 0.1617$ $wR_2 = 0.3912$	$R_1 = 0.0720$ $wR_2 = 0.1941$
final R indices [all data]	$R_1 = 0.0464$ $wR_2 = 0.0922$	$R_1 = 0.0548$ $wR_2 = 0.1013$	$R_1 = 0.0460$ $wR_2 = 0.1002$	$R_1 = 0.0659$ $wR_2 = 0.1710$	$R_1 = 0.2663$ $wR_2 = 0.4381$	$R_1 = 0.0746$ $wR_2 = 0.1952$
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å^{-3})	0.29/−0.26	0.33/−0.44	0.35/−0.31	0.98/−0.61	2.88/−0.83	0.69/−0.51

^aValue for R_{int} is determined for the major component of the twin refinement. See the Supporting Information for details. ^bSee also CCDC 2181985.

cm; typically 20–40 mg) in a glovebox with a controlled argon atmosphere. Prior to the experiments, the field-dependent magnetization was measured at 100 K on each sample to detect the presence of any bulk ferromagnetic impurity. As expected for paramagnetic or diamagnetic materials, a perfectly linear dependence of the magnetization that extrapolates to zero at zero dc field was systematically observed; the samples appeared to be free of any ferromagnetic impurities. The magnetic susceptibilities were corrected for the sample holder and the intrinsic diamagnetic contributions.

Density Functional Theory. Singlet–triplet gaps were calculated for TCNQ and DTDA dimers using the structural data from low- and high-temperature crystal structures of 1^{Pr} and 1^{Bu} . The calculations were performed with the functionals PBE1PBE-D3BJ^{31–36} and LC- ω hPBE^{37–40} using def2-TZVP basis sets.⁴¹ The geometries of the dimers were extracted from the solid-state X-ray structures, and the positions of the hydrogen atoms were optimized at the PBE1PBE-D3BJ/def2-TZVP level of theory prior to energy calculations. Broken-symmetry solutions were used for the singlet states while high-spin reference determinants were employed for the triplet states. Two different methods were used as these kinds of calculations are known to be highly sensitive to the choice of density functional. As expected, the singlet–triplet gaps calculated with the two methods differ quantitatively, but the results are in good qualitative agreement with all structural features, notably the separation of the dimers in the solid

state, and show that the TCNQ dimers have singlet–triplet gaps that are always smaller than those calculated for the DTDA dimers.

RESULTS AND DISCUSSION

Synthesis. A synthetic route to DTDA radical cation derivatives and the corresponding DSDA congeners,⁴² both as their triflate (OTf^-) salts, **IV**, was achieved by modification of our previously reported methodology (Scheme 1).⁴³ In brief, N,N,N' -tris(trimethylsilyl)-3-pyridineimidamide **I** was readily obtained as a viscous yellow oil that could be purified by fractional vacuum distillation and subsequently alkylated with N -alkyl triflates to afford the corresponding N -alkylpyridinium triflates,⁴⁴ **II**, as moisture-sensitive salts. Cyclocondensation of **II** with sulfur monochloride (S_2Cl_2) or freshly prepared selenium dichloride (SeCl_2),⁴⁵ followed by subsequent meta-thesis with trimethylsilyl trifluoromethanesulfonate (TMSOTf), provided access to the double triflate salts **III**. The dications in these salts could be readily reduced to the monocation radicals with tetrabutylammonium iodide and converted to their more soluble triflate salts by subsequent treatment with silver triflate (AgOTf). Repeated recrystalliza-

Table 2. Crystallographic Data for Compounds $2^{\text{Et}}\cdot\text{MeCN}$, $2^{\text{Pr}}\cdot\text{MeCN}$, and 2^{Bu}

	$2^{\text{Et}}\cdot\text{MeCN}$	$2^{\text{Pr}}\cdot\text{MeCN}$	2^{Bu}
CCDC	2181981	2181984	2182311
formula	$\text{C}_{22}\text{H}_{16}\text{N}_8\text{Se}_2$	$\text{C}_{23}\text{H}_{18}\text{N}_8\text{Se}_2$	$\text{C}_{22}\text{H}_{17}\text{N}_7\text{Se}_2$
molecular weight (g mol ⁻¹)	550.35	564.37	537.34
<i>T</i> (K)	120.00(10)	120.00(10)	120.00(10)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.7199(5)	8.8519(5)	6.8553(3)
<i>b</i> (Å)	10.4193(5)	10.8610(7)	11.2539(10)
<i>c</i> (Å)	12.0089(6)	11.8794(7)	14.3128(7)
α (°)	98.783(4)	98.194(5)	94.004(6)
β (°)	90.104(4)	91.479(5)	90.361(4)
γ (°)	96.494(4)	97.549(5)	106.859(6)
<i>V</i> (Å ³)	1071.16(10)	1119.48(12)	1053.77(12)
<i>Z</i>	2	2	2
ρ_{calc} (g cm ⁻³)	1.706	1.674	1.694
absorption (μ mm ⁻¹)	3.480	3.332	4.593
<i>F</i> (000)	544.0	560.0	532.0
2θ range for data collection (deg)	3.982–59.322	3.824–57.768	8.232–153.464
index ranges	–11 ≤ <i>h</i> ≤ 12 –13 ≤ <i>k</i> ≤ 13 –16 ≤ <i>l</i> ≤ 16	–11 ≤ <i>h</i> ≤ 11 –13 ≤ <i>k</i> ≤ 10 –15 ≤ <i>l</i> ≤ 15	–8 ≤ <i>h</i> ≤ 6 –13 ≤ <i>k</i> ≤ 14 –18 ≤ <i>l</i> ≤ 18
reflections collected	8141	8194	6856
independent reflections	5162 [$R_{\text{int}} = 0.0178$, $R_{\text{sigma}} = 0.0313$]	5006 [$R_{\text{int}} = 0.0283$, $R_{\text{sigma}} = 0.0661$]	6856 [$R_{\text{int}} = 0.1026^a$, $R_{\text{sigma}} = 0.0173$]
data/restraints/parameters	5162/0/291	5006/0/300	6856/0/282
goodness of fit on F^2	1.077	1.020	1.055
final <i>R</i> indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0293$ $wR_2 = 0.0747$	$R_1 = 0.0402$ $wR_2 = 0.0687$	$R_1 = 0.0516$ $wR_2 = 0.1498$
final <i>R</i> indices [all data]	$R_1 = 0.0351$ $wR_2 = 0.0778$	$R_1 = 0.0693$ $wR_2 = 0.0777$	$R_1 = 0.0557$ $wR_2 = 0.1532$
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.85/–0.73	0.61/–0.54	1.33/–1.22

^aValue for R_{int} is determined for the major component of the twin refinement.

tion from degassed acetonitrile (MeCN) and/or propionitrile (EtCN) afforded **IV** as analytical pure solids in moderate to high yields (Supporting Information).

A double-displacement reaction between **IV** and the highly soluble salt $[\text{K}(18\text{c}6)][\text{TCNQ}]$, prepared according to literature procedures,^{24,46} gave 1:1 salts of *N*-alkylated DTDA/DSDA cations and TCNQ anion (**1^R**, E = S; **2^R**, E = Se; R = Et, Pr, Bu) see (Scheme 2). When the syntheses of **1** and **2** were performed in MeCN, crystalline products **1^{Et}·MeCN**, **1^{Pr}·MeCN**, **2^{Et}·MeCN**, and **2^{Pr}·MeCN** with one solvent molecule per asymmetric unit were obtained. In the case of E = S and R = Bu, the crystalline solvate **1^{Bu}·0.5MeCN** was formed, whereas the corresponding selenium derivative **2^{Bu}** crystallized without any lattice solvent molecules. Substitution of MeCN with EtCN in the double-displacement reaction gave the solvate **1^{Et}·EtCN** along with two nonsolvated structures **1^{Pr}** and **1^{Bu}**. Unfortunately, similar reactions of the selenium derivatives of **IV** could not be carried out in EtCN due to solubility issues.

Crystal Structures of the Salts IV. Crystals of triflate salts of the *N*-alkylated radical cations **IV** (E = S, Se; R = Et, Pr, Bu) were obtained from MeCN and structurally characterized by single-crystal X-ray diffraction (Tables S1 and S2, Supporting Information). All salts display strong ion-pairing between the triflate anion and the DTDA/DSDA rings. The DTDA/DSDA radicals adopt a *trans*-cofacial dimerization mode in all cases except for E = S and R = Bu (monoclinic, space group I_2/a), where the rare twisted-cofacial mode was found with the butyl

chain in an *anti-anti-anti* conformation that protrudes above the plane of the almost coplanar pyridinium and DTDA rings (Figure 1), which are twisted by $\phi = 4.8^\circ$ (ϕ is defined as the angle between the mean planes through all nonhydrogen atoms of the pyridinium and DTDA/DSDA rings, respectively). In the case of E = Se and R = Bu derivative (triclinic, space group $P\bar{1}$), the pyridinium and DSDA rings are not coplanar ($\phi = 10.4^\circ$), and the butyl chain adopts an *anti-gauche-anti* conformation that extends laterally from the pyridinium ring (Figure 1). Despite the two different modes of dimerization found for the derivatives of **IV**, the interplanar separation $\delta_{\text{DTDA/DSDA}}$, defined as the centroid-to-centroid distance between the two $-\text{CN}_2\text{S}_2/-\text{CN}_2\text{Se}_2$ rings of the dimer, falls into very narrow ranges of 3.05–3.12 and 3.17–3.19 Å for the DTDA and DSDA dimers, respectively. In all structures of **IV**, the dimers adopt a one-dimensional (1D) head-over-tail π -stacking pattern like that found in related triflate salts of *N*-methylpyridinium-DTDA derivatives.⁴³

Crystal Structures of Ethyl Derivatives 1^{Et}·MeCN, 1^{Et}·EtCN, and 2^{Et}·MeCN. Compounds **1^{Et}·MeCN**, **1^{Et}·EtCN**, and **2^{Et}·MeCN** crystallize in a triclinic unit cell (space group $P\bar{1}$) and are isostructural with the previously reported methyl derivative **1^{Me}·MeCN**. Their asymmetric unit comprises one DTDA/DSDA cation, one TCNQ anion, and one solvent molecule. The DTDA/DSDA radicals are dimerized in *trans*-cofacial manner, while the TCNQ radicals form eclipsed-cofacial dimers. Together the cations and anions generate repeating $\text{A}^+ - \text{A}^+ \cdots \text{B}^- - \text{B}^-$ stacking motifs (Figure 2). The

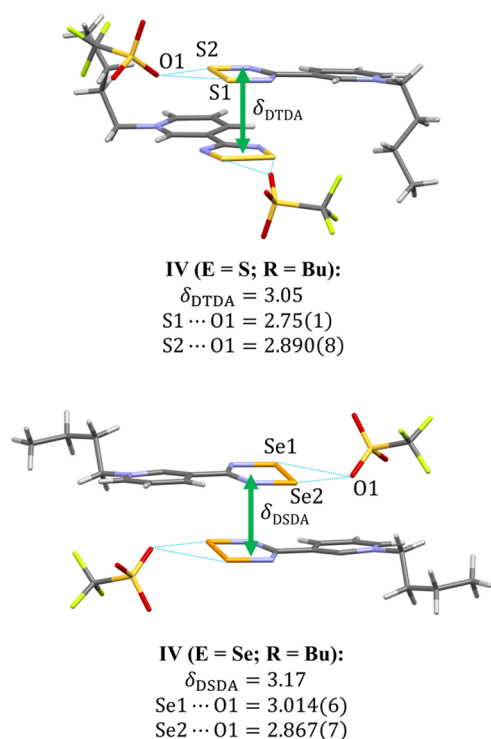


Figure 1. Representative view of packing and most important intermolecular interactions in *N*-butyl derivatives of **IV** along with key distances (Å). Minor components of disordered *N*-butyl chains in **IV** (E = S, R = Bu) have been omitted for clarity.

interplanar separation δ_{DTDA} is nearly identical in **1^{Et}·MeCN** and **1^{Et}·EtCN**, 3.15 and 3.16 Å, respectively, and falls within the typical range for *trans*-cofacial DTDA dimers (3.06–3.30 Å) determined from structural data deposited for all DTDA/DSDA radical (or radical cation) derivatives in the Cambridge Structural Database (CSD).⁴⁷ The corresponding δ_{DSDA} distance in **2^{Et}·MeCN** is 3.17 Å and, prior to this work, only one structurally characterized example of a DSDA dimer in *trans*-cofacial arrangement had been reported.⁴⁸ The centroid-to-centroid distance between two TCNQ radicals, δ_{TCNQ} , is slightly below 3.3 Å in **1^{Et}·MeCN**, **1^{Et}·EtCN**, and **2^{Et}·MeCN**, as is typical for eclipsed-cofacial TCNQ dimers with minor transversal offset (Table S3, Supporting Information). The DTDA/DSDA and pyridinium rings are nearly coplanar ($\phi =$

0.9–6.9; Table S3, Supporting Information) in all **1^{Et}·MeCN**, **1^{Et}·EtCN**, and **2^{Et}·MeCN**, which is entirely expected based on existing structural data. Calculations for the phenyl-substituted DTDA radical have shown that $\phi = 0$ represents a minimum on the potential energy surface and that even minor perturbations can lead to significant twist angles between the pyridinium and DTDA/DSDA rings.⁴⁹ The solvent molecules form supramolecular CN \cdots S/Se interactions with DTDA/DSDA that altogether span a narrow range of 2.888(2)–2.999(2) Å and are significantly shorter than the sum of van der Waals radii for nitrogen and sulfur/selenium atoms (*ca.* 3.35/3.45 Å, respectively). A network of weak C–H \cdots N hydrogen bonds further connects the solvent molecules and DTDA/DSDA cations to TCNQ anions.

Crystal Structures of Propyl Derivatives 1^{Pr}·MeCN, 2^{Pr}·MeCN, and 1^{Pr}. Compounds **1^{Pr}·MeCN** and **2^{Pr}·MeCN** are isostructural with the ethyl derivatives (triclinic unit cell, space group *P*1) and contain *trans*-cofacial DTDA/DSDA dimers and eclipsed-cofacial TCNQ dimers forming A⁺–A⁺ \cdots B[–]–B[–] stacking motifs (Figure 2). The key metrical parameters in **1^{Pr}·MeCN** and **2^{Pr}·MeCN**, such as the centroid-to-centroid distances $\delta_{\text{DTDA/DSDA}}$ (3.14 and 3.18 Å, respectively) and δ_{TCNQ} (3.25 and 3.27 Å, respectively) as well as CN \cdots S/Se interactions between solvent molecules and DTDA/DSDA cations (2.897(2)–3.007(4) Å), are all similar to those in **1^{Et}·MeCN**, **1^{Et}·EtCN**, and **2^{Et}·MeCN**.

When the double-displacement reaction between **IV** (E = S; R = Pr) and [K(18c6)][TCNQ] was performed in EtCN, **1^{Pr}** could be crystallized without any solvent molecules in the crystal lattice (Table 1). The crystal structure of **1^{Pr}** (triclinic unit cell, space group *P*1) shows DTDA radical cations dimerized in *trans*-cofacial manner (Figure 3). In comparison to the solvate **1^{Pr}·MeCN**, the DTDA and pyridinium rings in **1^{Pr}** are not coplanar and the DTDA rings have slipped further on top of each other, though the δ_{DTDA} distance remains essentially unchanged at 3.11 Å (Table S4, Supporting Information). As in **1^{Pr}·MeCN**, the TCNQ anions form cofacial dimers in **1^{Pr}**, but they adopt a noneclipsed geometry with 2.1 Å longitudinal offset (Table S4, Supporting Information), leading to a significantly increased δ_{TCNQ} distance, 3.73 Å, compared to **1^{Pr}·MeCN**. Overall, the DTDA cations form head-over-tail π -stacks A⁺–A⁺ \cdots A⁺–A⁺ and TCNQ dimers form staircase-like B[–]–B[–] \cdots B[–]–B[–] packing motifs in **1^{Pr}** that are connected by supramolecular CN \cdots S

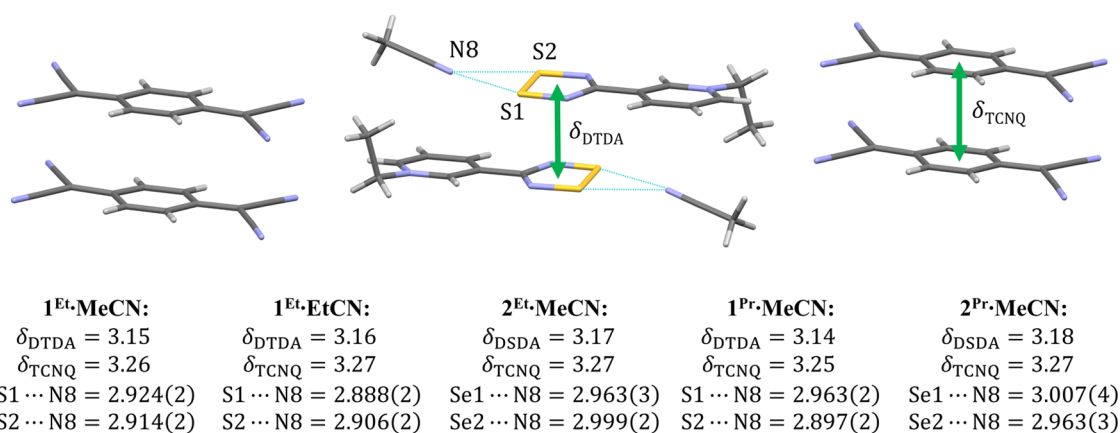


Figure 2. Representative view of packing and most important intermolecular interactions in **1^{Et}·MeCN** and key distances (Å) in the isostructural series **1^{Et}·MeCN**, **1^{Et}·EtCN**, **2^{Et}·MeCN**, **1^{Pr}·MeCN**, and **2^{Pr}·MeCN**.

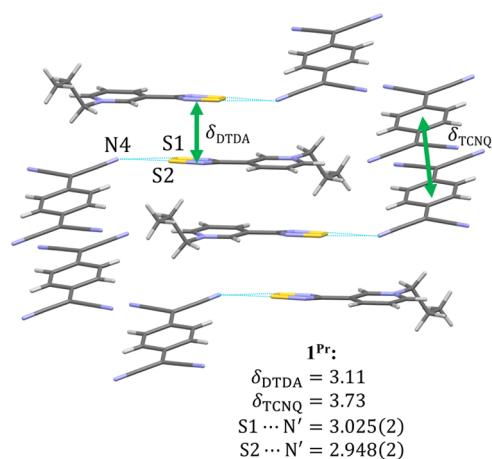


Figure 3. Representative view of packing and most important intermolecular interactions in **1^{Pr}** along with key distances (Å).

interactions (2.948(2) and 3.025(2) Å) as well as weak C–H...N hydrogen bonds. The *N*-propyl substituents adopt an *anti-gauche* conformation in **1^{Pr}** as opposed to the *anti-anti* conformation found in the solvate **1^{Pr}·MeCN**.

The structure of **1^{Pr}** can also be compared to that of **1^{Me}** at low temperatures. Even though the solvates **1^{Me}·MeCN** and **1^{Pr}·MeCN** are isostructural, the position adopted by the longer *N*-alkyl chain in the structure of **1^{Pr}** and the associated steric effects prevent the formation of C–C-bonded σ -dimers of TCNQ radicals similar to that happens upon desolvation of **1^{Me}·MeCN** to **1^{Me}**. Hence, **1^{Pr}** is not expected to show bistability upon increasing the temperature (*vide infra*).

Crystal Structures of Butyl Derivatives 1^{Bu}·0.5MeCN, 1^{Bu}, and 2^{Bu}. The crystal structure of **1^{Bu}·0.5MeCN** (triclinic unit cell, space group *P* $\bar{1}$) has two DTDA cations, two TCNQ anions, and only one solvent molecule in the asymmetric unit. The DTDA radicals are arranged in a typical manner to *cis*-cofacial dimers that together form $\text{A}^+ - \text{A}^+ \cdots \text{A}^+ - \text{A}^+$ stacks with alternating orientation of the dimeric subunits (Figure 4). The intradimer S...S distances are almost identical, 2.984(7) and

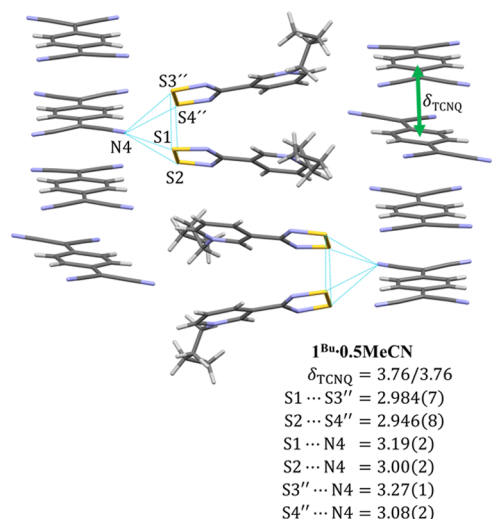


Figure 4. Representative view of packing and most important intermolecular interactions in **1^{Bu}·0.5MeCN** along with key distances (Å). Solvent molecules and disordered *N*-butyl chains have been omitted for clarity.

2.946(8) Å, and within the typical range for *cis*-cofacial DTDA dimers (2.90–3.20 Å) determined from structural data deposited in the CSD.⁴⁷ The DTDA dimers in **1^{Bu}·0.5MeCN** are significantly wedged with a tilt angle of 12.2° that arises from the steric demand of the butyl substituents in a lateral *anti-gauche-anti* conformation like that found in **IV** (E = Se; R = Bu). The wedged arrangement is not uncommon for DTDA radicals but typically observed in the case of halogenated substituents, such as trifluoromethyl- and fluoro- and chlorophenyls.^{50,51} The TCNQ anions form evenly spaced staircase-like $\text{B}^- \cdots \text{B}^- \cdots \text{B}^-$ stacks with two virtually identical δ_{TCNQ} distances, 3.756 and 3.76 Å, and a noneclipsed geometry with 2.0 Å longitudinal offset and negligible transversal offset (Table S4, Supporting Information). However, the neighboring TCNQ radicals are not perfectly aligned but are rotated with respect to each other along the π -stacking direction, with the largest rotational angle observed for every fourth anion (Figure S1, Supporting Information). This creates a rare 1D stacking motif with a periodic distortion of every fourth TCNQ radical anion that results in stacking faults similar to those previously encountered in crown complexes of alkali metal salts of TCNQ.⁵² The DTDA and TCNQ stacks are connected by supramolecular $\text{CN} \cdots \text{S}$ interactions (3.00(2)–3.27(1) Å) as well as weak C–H...N hydrogen bonds. The solvent molecules are embedded in the space between neighboring stacks.

Interestingly, the double-displacement reaction between **IV** (E = Se; R = Bu) and $[\text{K}(18\text{c}6)][\text{TCNQ}]$ in MeCN gave the nonsolvated derivative **2^{Bu}**. The corresponding sulfur derivative **1^{Bu}** could also be synthesized in bulk by performing the analogous double-displacement reaction in EtCN; trace amounts of this product were also formed in MeCN and could be separated from **1^{Bu}·0.5MeCN** based on crystal morphology and characterized by X-ray crystallography.

Compounds **1^{Bu}** and **2^{Bu}** are isostructural with one DTDA/DSDA cation and one TCNQ anion in the asymmetric unit (triclinic unit cell, space group *P* $\bar{1}$). The DTDA/DSDA cations are in a rare *trans*-antarafacial arrangement (*trans*-cofacial in **1^{Pr}**) and form head-over-tail $\text{A}^+ - \text{A}^+ \cdots \text{A}^+ - \text{A}^+$ π -stacking motifs (Figure 5). The intradimer S...S distance in **1^{Bu}** is 3.172(2) Å and falls to the lower end of the typical range for *trans*-antarafacial DTDA dimers (3.13–3.44 Å) determined from structural data deposited in the CSD. The corresponding Se...Se distance in **2^{Bu}** is 3.241(1) Å and is comparable to the data reported for the two other structurally characterized examples of such an arrangement of DSDA radicals (3.215(2)–3.334(2) Å).^{48,53} However, this comparison is not entirely warranted because the radicals are charge neutral in all published examples and coordinated to two metal centers in one of the two cases. The twist angle between DTDA/DSDA and pyridinium rings is 22.6 and 23.5° in **1^{Bu}** and **2^{Bu}**, respectively, and thereby significantly greater than in any of the other structures reported. This is presumably due to the weak C–H...N hydrogen-bond network that assembles the TCNQ and pyridinium rings into an almost coplanar arrangement, while simultaneously allowing the DTDA/DSDA cations and TCNQ anions to connect by supramolecular $\text{CN} \cdots \text{S}$ (2.869(3) Å and 2.962(3) Å) and $\text{CN} \cdots \text{Se}$ (2.937(5) and 3.017(6) Å) interactions. Like the case of **1^{Pr}**, the TCNQ dimers adopt a noneclipsed geometry with *ca.* 2.2 Å longitudinal offset and negligible transversal offset (Table S4, Supporting Information). The dimers form staircase-like $\text{B}^- - \text{B}^- \cdots \text{B}^- - \text{B}^-$ stacks with two vastly differing δ_{TCNQ} distances, 3.70 and 5.18 Å in

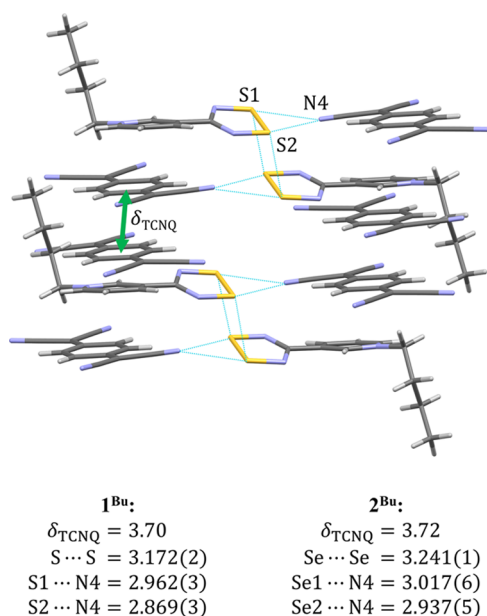


Figure 5. Representative view of packing and most important intermolecular interactions in 1^{Bu} and key distances in isostructural compounds 1^{Bu} and 2^{Bu} (Å).

1^{Bu} and 3.72 and 5.19 Å in 2^{Bu} . The *N*-butyl substituents adopt an *anti-anti-anti* conformation in 1^{Bu} and 2^{Bu} , as opposed to the *anti-gauche-anti* conformation found in the solvate $1^{\text{Bu}} \cdot 0.5\text{MeCN}$, preventing the formation of C–C-bonded σ -dimers of TCNQ.

Thermal Behavior of Crystalline Solvates of 1 and 2.

The crystallographic data discussed above clearly show the effect of the crystallization solvent and the *N*-alkyl chain length on the dimerization mode of DTDA/DSDA (*cis*-cofacial, *trans*-cofacial, or *trans*-antarcfacial) and TCNQ radicals (eclipsed-cofacial or non-eclipsed-cofacial). Interestingly, none of the three nonsolvated structures 1^{Pr} , 1^{Bu} , and 2^{Bu} revealed a σ -dimer of TCNQ akin to the low-temperature (LT) phase of 1^{Me} , indicating that the *N*-methyl substituent plays a role in

facilitating the formation of a C–C bond between TCNQ radicals in 1^{Me} . However, it can also be argued that solvent molecules in the crystal lattice of $1^{\text{Me}} \cdot \text{MeCN}$ and $1^{\text{Me}} \cdot \text{EtCN}$ are essential for obtaining the right initial arrangement of cations and anions that then reorganizes upon desolvation to yield the σ -bonded dimer in 1^{Me} . To investigate this further, and to reveal other interesting physical properties for this series of radical-ion salts, the thermal behavior of the solvates $1^{\text{Et}} \cdot \text{MeCN}$, $1^{\text{Pr}} \cdot \text{MeCN}$, $1^{\text{Bu}} \cdot 0.5\text{MeCN}$, $1^{\text{Et}} \cdot \text{EtCN}$, $2^{\text{Et}} \cdot \text{MeCN}$, and $2^{\text{Pr}} \cdot \text{MeCN}$ was investigated by thermogravimetric analysis (TGA).

The recorded TGA curves allowed the establishment of onset temperatures for the loss of lattice solvent and the %-weight losses calculated from the data were consistent with the stoichiometries established by single-crystal X-ray crystallography (Table S5 and Figures S2–S10, Supporting Information). The variable behavior of the investigated solvates in the release of the solvent, before the onset of decomposition at temperatures >450 K, reflects the varying strength of interactions between solvent molecules and radical ions in the crystal structures of $1^{\text{Et}} \cdot \text{MeCN}$, $1^{\text{Et}} \cdot \text{EtCN}$, $1^{\text{Pr}} \cdot \text{MeCN}$, $1^{\text{Bu}} \cdot 0.5\text{MeCN}$, $2^{\text{Et}} \cdot \text{MeCN}$, and $2^{\text{Pr}} \cdot \text{MeCN}$ (*vide supra*).

The thermal behavior of the solvates $1^{\text{Et}} \cdot \text{MeCN}$ and $1^{\text{Et}} \cdot \text{EtCN}$ observed in their TGA curves indicated that the solvent is gradually removed from these structures with onset temperatures of 387 and 396 K, respectively. There is only a narrow plateau between the occurrence of desolvation and thermal decomposition at 472 and 452 K for $1^{\text{Et}} \cdot \text{MeCN}$ and $1^{\text{Et}} \cdot \text{EtCN}$, respectively (Table S5, Figures S2 and S3, Supporting Information). For this reason, we did not attempt a single-crystal-to-single-crystal (SCSC) transformation in these two cases even though the structures contain the shortest *N*-alkyl substituents with the least influence on the packing of TCNQ radicals. The selenium analogue $2^{\text{Et}} \cdot \text{MeCN}$ undergoes a more facile desolvation with an onset temperature of 385 K and decomposition at 452 K. This system was not investigated any further, however, because its *trans*-cofacial DSDA and eclipsed-cofacial TCNQ dimers are strongly

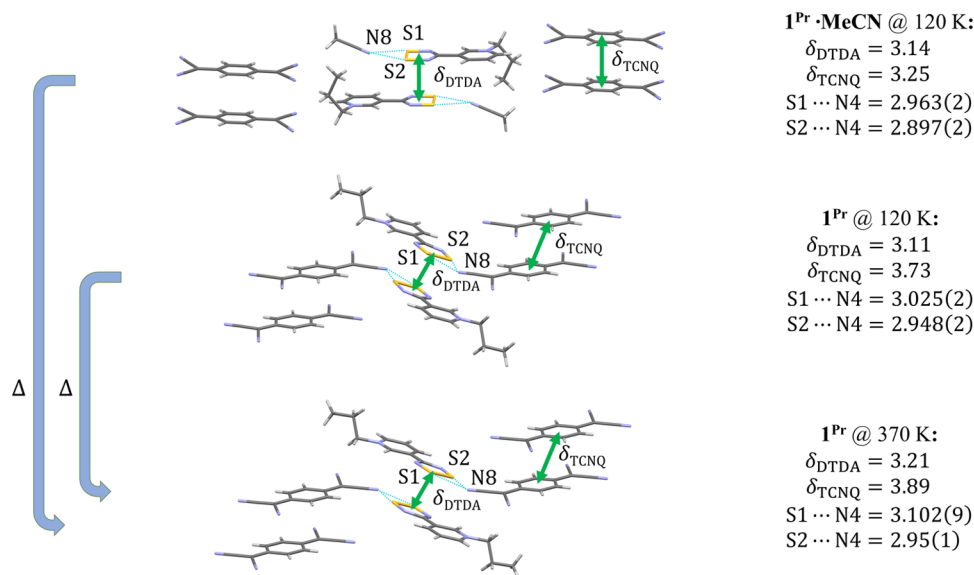


Figure 6. Illustration of changes to the solid-state structure of $1^{\text{Pr}} \cdot \text{MeCN}$ upon desolvation to 1^{Pr} and temperature change from 120 to 370 K along with key distances (Å).

antiferromagnetically coupled, preventing significant changes to both structure and properties upon desolvation.

The two isostructural analogues $1^{\text{Pr}}\cdot\text{MeCN}$ and $2^{\text{Pr}}\cdot\text{MeCN}$ displayed a similar behavior in TGA with facile loss of lattice solvent at 354 and 358 K, respectively, and high thermal stability up to >450 K. The robust thermal behavior observed for the salts suggested that an SCSC transformation might be realized in these cases and was attempted for $1^{\text{Pr}}\cdot\text{MeCN}$. Again, given the strongly antiferromagnetically coupled *trans*-cofacial DSDA and eclipsed-cofacial TCNQ dimers in $2^{\text{Pr}}\cdot\text{MeCN}$, we did not pursue investigations on this system any further.

Careful heating of single crystals of $1^{\text{Pr}}\cdot\text{MeCN}$ on the goniometer head up to 370 K led to the acquisition of a high-temperature (HT) structure by single-crystal X-ray diffraction that revealed an SCSC transformation to the nonsolvated 1^{Pr} structure with a triclinic unit cell (space group $P\bar{1}$). The HT crystal structure of 1^{Pr} is comparable to the LT data discussed above (Table S6, Supporting Information) and shows *trans*-cofacial DTDA dimers and non-eclipsed-cofacial TCNQ dimers with 2.1 Å longitudinal offset and negligible transversal offset (Figure 6). As expected, both δ_{DTDA} and δ_{TCNQ} distances have significantly increased in the HT structure, while the CN \cdots S interactions between cations and anions are much less affected by the change in temperature from 120 to 370 K. The nature of the SCSC transformation observed for $1^{\text{Pr}}\cdot\text{MeCN}$ effectively confirms that desolvation alone is not sufficient to yield a σ -bonded TCNQ dimer, but the size of the *N*-alkyl substituent plays a key role in the process.

The thermally induced desolvation of $1^{\text{Pr}}\cdot\text{MeCN}$, its phase purity, and the associated SCSC transformation to 1^{Pr} were confirmed in the bulk by variable-temperature powder X-ray diffraction experiments (Tables S7 and S8 and Figures S11–S13, Supporting Information). Subsequent Pawley refinement of the unit cell parameters for each of the powder samples was found to be structurally like the corresponding single-crystal structures. Traces of 1^{Pr} appear in the bulk of $1^{\text{Pr}}\cdot\text{MeCN}$ before heating, suggesting that the difference in crystal lattice enthalpy between the solvated and nonsolvated structures is very small. Variable-temperature powder X-ray experiments indicate that the loss of lattice solvent occurs readily above 377 K, with only residual traces of $1^{\text{Pr}}\cdot\text{MeCN}$ visible in the diffractograms. These results are consistent with the data from TGA (Table S5 and Figure S4, Supporting Information).

In the case of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, the solvent molecules in the crystal lattice do not interact strongly with the DTDA radical cation, that is, there are no CN \cdots S interactions in the structure. Instead, the solvent seems to play the role of a space filler in $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, as indicated by the comparatively low onset temperature for solvent loss at 361 K with decomposition taking place at 457 K (Table S5 and Figure S5, Supporting Information). Unfortunately, the poor quality of single crystals of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$ prevented further investigation of any possible SCSC transformation, but powder X-ray diffraction experiments showed the bulk material to be consistent with the single-crystal structure (Table S7 and Figure S14, Supporting Information).

Both the nonsolvated structures 1^{Bu} and 2^{Bu} contain rare *trans*-antafacial DTDA/DSDA dimers, and Pawley refinement of the unit cell parameters for each of the powder samples was found to be consistent with the corresponding single-crystal structures (Table S8, Figures S15 and S16, Supporting Information). In the case of 1^{Bu} , the nonsolvated

material could be obtained from EtCN as sizable single crystals, and an HT single-crystal structure was determined for it at 370 K (Table S6 and Figure S17, Supporting Information). Upon heating, the S \cdots S distance was found to increase significantly from 3.172(2) to 3.312(1) Å, but the value is still within the typical range for DTDA dimers (3.13–3.44 Å). The staircase-like π -stacking of TCNQ dimers along the *a*-axis is maintained in the HT structure of 1^{Bu} , but the δ_{TCNQ} distance has increased from 3.70 to 3.78 Å with very minor changes seen in longitudinal and transversal offsets (Table S4, Supporting Information).

Magnetic Measurements and Computational Investigations. Based on our previous experience with $1^{\text{Me}}\cdot\text{MeCN}$ and $1^{\text{Me}}\cdot\text{EtCN}$ that exhibit thermal hysteresis near room temperature due to lattice solvent loss and subsequent first-order phase transition between a paramagnetic HT and a diamagnetic LT phase, the bulk magnetic properties of the solvates $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Et}}\cdot\text{EtCN}$, $1^{\text{Pr}}\cdot\text{MeCN}$, and $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, and the nonsolvates 1^{Bu} and 2^{Bu} were explored. Variable-temperature magnetic susceptibility data using a static field of 1.0 T were collected between 1.85 and 400 K, with different thermal cycling to probe the *in situ* desolvation of the different solvated materials.

All samples are essentially diamagnetic below 300 K, as expected for π -dimers of DTDA and TCNQ radicals with only a very low concentration of spin-defect impurities (Figure 7).

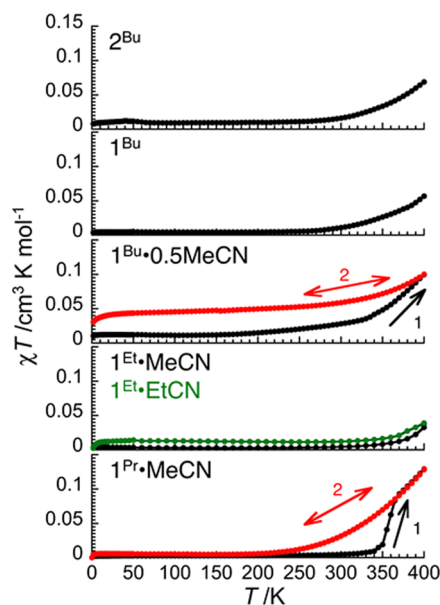


Figure 7. Temperature dependence of the χT product for $1^{\text{Pr}}\cdot\text{MeCN}$, $1^{\text{Et}}\cdot\text{MeCN}$, $1^{\text{Et}}\cdot\text{EtCN}$, $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, 1^{Bu} , and 2^{Bu} at 1 T (χ , the dc magnetic susceptibility, is defined as M/H per mole of complex).

The solvates $1^{\text{Et}}\cdot\text{MeCN}$ and $1^{\text{Et}}\cdot\text{EtCN}$ remained diamagnetic up to 350 K. Above this temperature, only a small increase of the χT product is observed (Figure 7) that is consistent with gradual loss of lattice solvent observed in TGA above 385 K. The magnetic properties upon subsequent cooling from 400 K remain quantitatively unchanged, indicating that solvated and desolvated 1^{Et} materials possess roughly the same magnetic properties.

In the solvates $1^{\text{Pr}}\cdot\text{MeCN}$ and $1^{\text{Bu}}\cdot 0.5\text{MeCN}$, the loss of lattice solvent was evidenced by a steady increase in χT during the first heating cycle with onset temperatures consistent with

data from TGA (Figures 7, S4 and S5, Supporting Information). A subsequent cooling and heating cycle did not follow the same track of the initial heating. In the case of $\mathbf{1}^{\text{Bu}}\cdot\mathbf{0.5MeCN}$, the loss of lattice solvent led to a small concentration of spin-defect impurities ($\sim 10\%$) that presumably arise from isolated TCNQ radicals within the 1D π -stacks or defect sites generated during desolvation. In the nonsolvated material $\mathbf{1}^{\text{Bu}}$, a modest thermal population of the excited magnetic states was observed above 300 K. For $\mathbf{1}^{\text{Pr}}\cdot\mathbf{MeCN}$, the maximum value of the χT product, *ca.* $0.15 \text{ cm}^3\text{K mol}^{-1}$, was recorded at the highest possible temperature of the experiment (400 K, Figure 7). The value is much lower than expected for an ideal $S = 1/2$ system, $0.375 \text{ cm}^3\text{K mol}^{-1}$. The resulting plot of χT vs T plot for $\mathbf{1}^{\text{Pr}}\cdot\mathbf{MeCN}$ after loss of lattice solvent is consistent with thermally populated magnetic states above 250 K that, based on the structural data, arise from the weakly interacting noneclipsed TCNQ dimers in $\mathbf{1}^{\text{Pr}}$. This was probed with DFT using the PBE1PBE and LC- ω hPBE (values reported in parentheses) functionals together with the def2-TZVP basis sets. The calculations revealed a singlet–triplet (S–T) gap of 5 (3) kJ mol^{-1} for the TCNQ dimer in the geometry that it adopts in the HT structure of $\mathbf{1}^{\text{Pr}}$ compared to the S–T gap of 22 (13) kJ mol^{-1} calculated for the DTDA dimer in a similar manner. Corresponding S–T gaps calculated from the LT structure are 12 (8) and 31 (19) kJ mol^{-1} for TCNQ and DTDA, respectively. These values agree with the structural data, that is, the TCNQ radicals are well separated at both temperatures and have small S–T gaps, while the energy gaps calculated for the DTDA radicals are in both cases higher due to δ_{DTDA} being much smaller than δ_{TCNQ} in both structures.

The crystal structures of the isostructural nonsolvates $\mathbf{1}^{\text{Bu}}$ and $\mathbf{2}^{\text{Bu}}$ both showed DTDA/DSDA radicals with a rare *trans*-antarafacial dimerization mode along with non-eclipsed-cofacial TCNQ dimers. The variable-temperature magnetic behavior of $\mathbf{1}^{\text{Bu}}$ and $\mathbf{2}^{\text{Bu}}$ was found to be nearly identical (Figure 7) with thermally populated magnetic states increasing steadily above *ca.* 300 K. The magnetic behavior was found to follow the same track during repeated heating and cooling cycles, as expected based on the available structural data. This magnetic behavior is tentatively attributed to the small S–T gap afforded by the non-eclipsed-cofacial TCNQ dimer geometry at higher temperatures. S–T gaps calculated for TCNQ and DTDA dimers in the geometries they adopt in the HT structure of $\mathbf{1}^{\text{Bu}}$ are 11 (8) and 23 (14) kJ mol^{-1} , respectively. Corresponding values calculated from the LT structure are 19 (13) and 36 (21) kJ mol^{-1} for TCNQ and DTDA, respectively. The calculated values are in accordance with the structural data and show the S–T gaps to be smaller for TCNQ dimers at both temperatures.

CONCLUSIONS

In this work, we have provided a detailed account of the preparation, structural, thermal, and magnetic characterization of a series of simple binary organic radical salts obtained by partnering the ubiquitous 7,7,8,8-tetracyanoquinodimethane radical anion (TCNQ $^-$) with 4-(*N*-alkylpyridinium-3-yl)-1,2,3,5-dithiadiazolyl radical cations (DTDA $^{+}$) and their selenium analogues (DSDA $^{+}$).

When using shorter-alkyl-chain substituents ethyl and propyl, the binary salts crystallized as isostructural acetonitrile solvates $\mathbf{1}^{\text{Et}}\cdot\mathbf{MeCN}$, $\mathbf{1}^{\text{Pr}}\cdot\mathbf{MeCN}$, $\mathbf{2}^{\text{Et}}\cdot\mathbf{MeCN}$, and $\mathbf{2}^{\text{Pr}}\cdot\mathbf{MeCN}$. In these structures, the DTDA and DSDA radicals are dimerized

in *trans*-cofacial manner and form supramolecular CN \cdots S/Se interactions with the solvent, whereas the TCNQ radicals form eclipsed-cofacial dimers. A slight increase in the alkyl chain length to butyl, however, led to a distinctly different solvate structure $\mathbf{1}^{\text{Bu}}\cdot\mathbf{0.5MeCN}$ in which the DTDA radicals form *cis*-cofacial dimers with the solvent molecules settled in the space between butyl substituents while the TCNQ radicals are arranged to a rare 1D columnar stacking motif containing periodic distortions along the vertical stacking direction. Changing the solvent from MeCN to EtCN or replacing sulfur for selenium both favored the isolation of nonsolvated structures in the case of $\mathbf{1}^{\text{Pr}}$, $\mathbf{1}^{\text{Bu}}$, and $\mathbf{2}^{\text{Bu}}$; the solvate $\mathbf{1}^{\text{Et}}\cdot\mathbf{EtCN}$ was also obtained. In the nonsolvated structures, the DTDA and DSDA dimers are either in *trans*-cofacial ($\mathbf{1}^{\text{Pr}}$) or *trans*-antarafacial ($\mathbf{1}^{\text{Bu}}$ and $\mathbf{2}^{\text{Bu}}$) arrangement, while the TCNQ radicals adopt noneclipsed dimer geometry with substantial longitudinal offset.

The results from this work confirmed our expectation that the steric repulsion and pliability of longer-alkyl-chain substituents on the cation favor the formation of nonsolvated crystal structures. This was found to be particularly true for crystallizations from EtCN that led exclusively to nonsolvates in the case of $\mathbf{1}^{\text{Pr}}$ and $\mathbf{1}^{\text{Bu}}$; analogous selenium derivatives could not be crystallized from this solvent due to the low solubility of precursor salts **IV** (E = Se, R = Et, Pr, Bu). In all crystal structures containing one solvent molecule per ion, the solvents work as structure-driving agents and arrange the DTDA and DSDA cations to *trans*-cofacial dimers held in place by supramolecular CN \cdots S/Se interactions. Partially solvated and nonsolvated crystal structures show significantly more variation in the arrangement of the ions in the solid state, and there exists no clear structure-driving factor in these cases. Unfortunately, none of the crystal structures obtained in this work revealed the formation of σ -dimers of TCNQ radicals even though $\mathbf{1}^{\text{Pr}}\cdot\mathbf{MeCN}$ was found to be isostructural with $\mathbf{1}^{\text{Me}}\cdot\mathbf{MeCN}$ and could be thermally desolvated to $\mathbf{1}^{\text{Pr}}$. Clearly, the *N*-alkyl group in $\mathbf{1}^{\text{Pr}}$ compared to $\mathbf{1}^{\text{Me}}$ is sufficiently bulky to direct the TCNQ radicals to form their most favorable arrangement, non-eclipsed-cofacial dimers, not only in $\mathbf{1}^{\text{Pr}}$ but also in all nonsolvated crystal structures reported in this work.

All nonsolvated salts displayed varied but robust thermal behavior, while the thermal behavior of the solvates revealed a clear trend for the loss of lattice solvent becoming more facile for systems with longer alkyl chains. The thermally induced desolvation of $\mathbf{1}^{\text{Pr}}\cdot\mathbf{MeCN}$, its phase purity, and the associated SCSC transformation to $\mathbf{1}^{\text{Pr}}$ were confirmed in the bulk by variable-temperature powder X-ray diffraction experiments. Variable-temperature magnetic susceptibility measurements showed that all investigated structures are diamagnetic at low temperatures. However, thermally populated paramagnetic states could be observed in all investigated cases above 250 K and, in particular, for the nonsolvated systems $\mathbf{1}^{\text{Pr}}$, $\mathbf{1}^{\text{Bu}}$, and $\mathbf{2}^{\text{Bu}}$. This behavior was tentatively assigned to the noneclipsed geometry of TCNQ radical dimers in these structures that leads to a longer separation between the radical ions at higher temperatures and, consequently, to small singlet–triplet gaps. This interpretation was supported by results from DFT calculations.

Considered as a whole, the systematic investigation of structural and solvent effects on the crystal structure, thermal, and magnetic properties of the simple binary salts **1** and **2** and their solvates has provided structural insight that can be applied to related systems in the design of new functional

molecular materials. In this context, the selenium analogue of $1^{\text{Me}}\cdot\text{MeCN}$, namely, $2^{\text{Me}}\cdot\text{MeCN}$, appears as an interesting target system. Based on the results reported herein, the S-to-Se atom replacement is not expected to lead to desolvation and the crystal structure of $2^{\text{Me}}\cdot\text{MeCN}$ is predicted to be isostructural with $1^{\text{Me}}\cdot\text{MeCN}$. Consequently, 2^{Me} might be a suitable platform to observe σ -dimers of TCNQ radicals in the solid state, possibly leading to bistability like that established in the case of $1^{\text{Me}}\cdot\text{MeCN}$. Synthetic work toward this and related systems are currently underway.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.2c00795>.

Full experimental details for all compounds and computational details, including NMR and IR spectral data, TG curves, PXRD patterns, and variable-temperature single-crystal diffraction data (PDF)

Accession Codes

CCDC 2181974, 2181976–2181977, 2181980–2181989, 2182178, 2182311, 2182459, 2182640, 2182780, and 2207551 contain 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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Role of Alkyl Substituent and Solvent on the Structural, Thermal, and Magnetic Properties of Binary Radical Salts of 1,2,3,5-Dithia- or Diselenadiazolyl Cations and the TCNQ Anion

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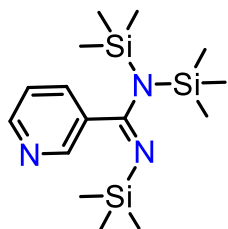
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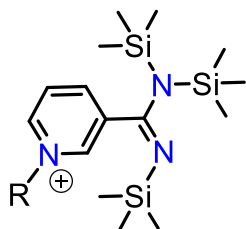
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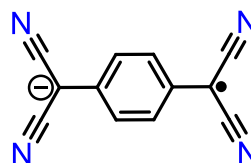
Illustrative presentations of common abbreviations:



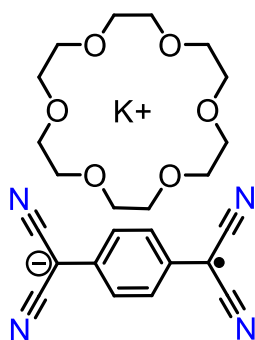
3-pyN₂TMS₃
I



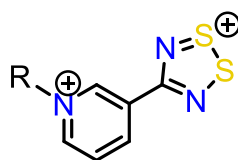
3-RpyN₂TMS₃⁺
cation in II



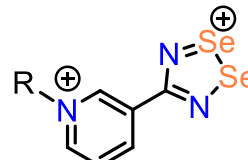
TCNQ^{•-}



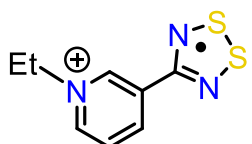
[K(18c6)][TCNQ]



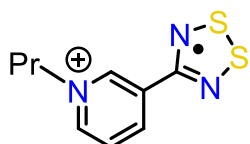
3-RpyDTDA²⁺
cation in III (E = S)



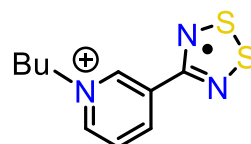
3-RpyDTDA²⁺
cation in III (E = Se)



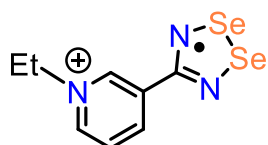
3-EtpyDTDA^{•+}
IV (E = S, R = Et)



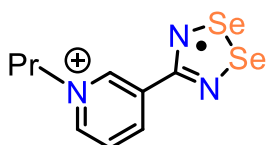
3-PrpyDTDA^{•+}
IV (E = S, R = Pr)



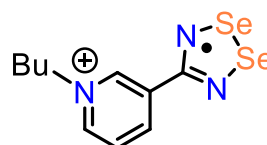
3-BupyDTDA^{•+}
IV (E = S, R = Bu)



3-EtpyDSDA^{•+}
IV (E = Se, R = Et)



3-PrpyDSDA^{•+}
IV (E = Se, R = Pr)



3-BupyDSDA^{•+}
IV (E = Se, R = Bu)

General methods and procedures

The reagents 3-cyanopyridine, sulfur monochloride (S_2Cl_2), 18-crown-6 (18c6), 7,7,8,8-tetracyanoquinodimethane (TCNQ), ethyl trifluoromethanesulphonate (EtOTf), benzyltriethylammonium chloride ([BzEt₃N][Cl]), and potassium metal were purchased commercially and used as received, except for 18c6 which was recrystallized from acetonitrile (MeCN) and vacuum dried at 35°C according to a literature procedure.¹ The solvents, MeCN, propionitrile (EtCN), dichloromethane (DCM), diethyl ether (Et₂O), and tetrahydrofuran (THF) were of at least reagent grade and used as received unless otherwise noted. Both MeCN and EtCN were successively distilled from P₂O₅ and CaH₂, while Et₂O and THF were distilled from LiAlH₄ and Na/benzophenone prior to use.

All reactions and manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. The precursors (E)-*N,N,N'*-tris(trimethylsilyl)-3-pyridineimidamide and *N*-alkyl triflates (ROTf, R = Pr, Bu) were prepared by modified literature procedures and purified by vacuum distillation prior to use.^{1,2} The salt [K(18c6)[TCNQ] was prepared according to a previously reported procedure.³

All infrared (IR) spectra were recorded on a Bruker Alpha FTIR spectrometer housed inside an argon filled glove box using a single reflectance diamond ATR or a universal transmission module as Nujol mulls (previously dried over Na metal) on KBr plate. A minimum of 16 scans were recorded at a 4 cm⁻¹ resolution. For convenience, all spectra are plotted using normalized %-transmittance versus the wavenumber ($T = 10^{-A}$, where A is the absorbance; $A = \log(1/R)$ with R being the reflectance for ATR FTIR measurements without ATR correction).

NMR spectra were recorded on Bruker Avance III HD 300 MHz and 500 MHz spectrometers using anhydrous deuterated solvents and were referenced internally to the solvent residual peak.⁴

Elemental analyses (C, H, and N) were performed in house using an Elementar EL III elemental analyzer on samples prepared using tin foil pans under an argon atmosphere.

NOTE. All of the double chloride salts, *i.e.* 3-RpyDTDA[Cl]₂, and iodide salts, *i.e.* 3-RpyDTDA[I], and their DSDA variants (R = Et, Pr, Bu) were used without further purification throughout this work. The double chloride and iodide salts are all poorly soluble in common (NMR and EPR) solvents and are extremely hygroscopic- and/or air-sensitive and, therefore, must be handled with care under a dry nitrogen or argon atmosphere. The subsequent metathesis to the more soluble triflate (CF₃SO₃⁻) anion allows analytically pure salts to be readily obtained that were fully characterized by spectroscopic and analytical methods. In all cases, the FT-IR spectra provide a routine and robust measurement of the fundamental molecular vibrations of these salts. Unwanted hydrolysis/oxidation products can be readily identified by the presence of broad N–H (3400–3000 cm⁻¹) and strong S–O stretching vibrations (1415–1300 cm⁻¹).

1.1 Preparation of [3-EtpyN₂TMS₃][OTf]

A solution of 3-pyN₂TMS₃ (4.37 g, 12.9 mmol) in 18 ml of Et₂O was cooled to 0 – 5 °C in an ice-water bath while neat EtOTf (2.00 ml, 20.0 mmol) was added dropwise to the solution over a period of 5 min. The reaction mixture was allowed to gradually warm up to room temperature and stirred for 16 h to afford a yellow solution. The volatiles were removed by flash distillation to give a viscous yellow oil which was triturated with 2 × 5 ml of dry toluene. The resulting off-white solid was collected by filtration and dried *in vacuo*. Yield: 4.80 g (9.31 mmol, 72 %). ¹H NMR (δ, CD₃CN, ppm): 8.73 (d, 1H, Ar-H, *J* = 6.1 Hz), 8.66 (s, 1H), 8.40 (dt, 1H, Ar-H, *J* = 8.1 and 1.4 Hz), 8.04 (t, 1H, Ar-H, *J* = 7.0 Hz), 4.63 (q, 2H, N-CH₂, *J* = 7.4 Hz), 1.60 (t, 3H, CH₂-CH₃, *J* = 7.3 Hz), 0.12 (s, 27H).

1.2 Preparation of [3-EtpyDTDA][Cl]₂

A solution of S₂Cl₂ (6.00 ml, 74.3 mmol) in 20 ml of MeCN was added dropwise to a solution of [3-EtpyN₂TMS₃][OTf] (6.39 g, 12.3 mmol) in 40 ml of MeCN cooled to 0 – 5 °C in an ice-water bath. The mixture was allowed to warm to room temperature with stirring for 18 h and then filtered. Solid [BzEt₃N][Cl] (3.17g, 13.9 mmol) was added to the filtrate to afford an orange precipitate. The mixture was stirred for 15 min after which the orange solid was collected by filtration, washed with 2 × 20 ml of MeCN and 3 × 20 ml of DCM, and dried *in vacuo*. Yield: 3.13 g (11.2 mmol, 91 %).[§] IR (ATR, cm⁻¹): 3078 (m), 3044 (m), 2991 (m), 2960 (m), 2243 (m), 1690 (w), 1639 (m), 1590 (w), 1509 (w),

[§] The double chloride salts can be contaminated with variable amounts of sulfur which can lead to higher-than-expected theoretical yields. Therefore, no analytical data was recorded, and the products are used without further purification.

1479 (w), 1455 (w), 1409 (s), 1343 (w, sh), 1240 (w), 1195 (s), 1150 (w), 1096 (w), 1032 (w), 995 (m), 948 (m), 897 (m), 855 (s), 807 (w), 710 (s), 692 (m), 681 (m, sh), 639 (w), 622 (w, sh), 572 (m), 547 (s), 521(m), 453 (w), 434 (w).

1.3 Preparation of [3-EtpyDTDA][OTf]₂

To a slurry of crude [3-EtpyDTDA][Cl]₂ (3.13 g, 11.2 mmol) in 40 ml of MeCN was added an excess of TMSOTf (4.80 ml, 26.5 mmol), giving a pale yellow solid in a clear colourless solution. The mixture was stirred for 90 min at room temperature and then gently refluxed before hot filtering. The solvent volume was reduced by half *in vacuo*. Subsequent storing of the solution for 48 h at -20 °C gave clear colourless crystals which were collected by filtration and dried *in vacuo*. Yield: 3.03 g (5.95 mmol, 53 %). ¹H NMR (δ, CD₃CN, ppm): 9.84 (s, 1H, Ar-H), 9.47 (dt, 1H, Ar-H, *J* = 8.3 and 1.4 Hz), 9.09 (d, 1H, Ar-H, *J* = 6.2 Hz), 8.41 (t, 1H, Ar-H, *J* = 7.2 Hz) 4.83 (q, 2H, N-CH₂-CH₃, *J* = 7.4 Hz), 1.73 (t, 3H, CH₂-CH₃, *J* = 7.3 Hz). Elemental analysis calculated (found) for C₁₀H₉F₆N₃O₆S₄: C, 23.58 (23.54); H, 1.78 (1.85); N, 8.25 (8.29).

1.4 Preparation of [3-EtpyDTDA][I]

A degassed solution of NBU₄I (4.00 g, 10.8 mmol) in 40 ml of MeCN was poured onto solid [3-EtpyDTDA][OTf]₂ (2.63 g, 5.17 mmol) and the mixture was stirred for 3 h at room temperature to afford a lustrous bronze micro-crystalline solid that was collected by filtration, washed with 2 × 20 ml of DCM, and dried *in vacuo*. Yield: 0.970 g (2.87 mmol, 56 %). IR (ATR, cm⁻¹): 3053 (w), 1636 (w), 1509 (w), 1481 (w), 1456 (w), 1381 (w), 1248 (s), 1224 (s), 1179 (m), 1163 (m), 1095 (w, sh), 1028 (s), 938 (w), 836 (w), 814 (w), 795 (m), 775 (m), 755 (w), 677 (m), 634 (s), 575 (m), 514 (s), 443 (w).

1.5 Preparation of radical-cation IV (E = S, R = Et)

Solid AgOTf (0.775 g, 3.02 mmol) was added to a suspension of [3-EtpyDTDA][I] (0.954 g, 2.82 mmol) in 20 ml of MeCN and the mixture was stirred for 2 h at room temperature. Solid AgI was cannula filtered to afford a dark orange-brown filtrate that was concentrated to dryness by flash distillation. Repeated recrystallization from MeCN at -20 °C afforded an analytically pure product as lustrous green-bronze plates. Yield: 0.461 g (1.28 mmol, 45 %). IR (ATR, cm⁻¹): 3127 (w), 3070 (w), 1705 (w), 1642 (m), 1569 (w), 1522 (w), 1465 (m), 1371 (w), 1338 (w), 1261 (w, sh), 1240 (s, sh), 1222 (s), 1152 (s), 1091 (w, sh), 1022 (s), 985 (w, sh), 920 (w), 861 (m), 830 (m), 783 (s), 775 (m, sh), 736 (w, sh), 700 (w), 632 (s), 573 (s), 516 (s), 430 (m). Elemental analysis calculated (found) for C₉H₉F₃N₃O₃S₃: C, 30.00 (29.85); H, 2.52 (2.47); N, 11.66 (11.74).

1.6 Preparation of $1^{\text{Et}}\cdot\text{MeCN}$

A solution of **IV** (**E** = **S**; **R** = **Et**) (0.058 g, 0.161 mmol) in 7 ml of MeCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of $[\text{K}(\text{18c6})][\text{TCNQ}]$ (0.084 g, 0.165 mmol) in 7 ml of MeCN was allowed to slowly diffuse into the former over a 24 h period. This afforded lustrous violet-black plate-like crystals which were collected by suction filtration on a small, sintered glass Buchner funnel, washed with 5 ml of MeCN, and air dried. Yield: 0.049 g (0.117 mmol, 66 %). IR (Nujol mull, cm^{-1}): 2254 (vw), 2178 (m), 2157(m, sh), 1635 (vw), 1582 (w), 1501 (w), 1350 (m), 1261 (w), 1208 (vw), 1174 (w), 1098 (vw), 986 (vw), 826 (vw), 797 (w), 779 (vw, sh), 678 (vw), 521 (vw). Elemental analysis calculated (found) for $\text{C}_{22}\text{H}_{16}\text{N}_8\text{S}_2$: C, 57.88 (57.79); H, 3.53 (3.53); N, 24.54 (24.53).

1.7 Preparation of $1^{\text{Et}}\cdot\text{EtCN}$

A solution of **IV** (**E** = **S**; **R** = **Et**) (0.041 g, 0.114 mmol) in 8 ml of EtCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of $[\text{K}(\text{18c6})][\text{TCNQ}]$ (0.084 g, 0.165 mmol) in 10 ml of EtCN was allowed to slowly diffuse into the former over a 24 h period. This afforded lustrous violet-black block-shaped crystals which were collected by suction filtration on a small, sintered glass Buchner funnel, washed with EtCN, and air dried. Yield: 0.042 g (0.089 mmol, 78 %). IR (ATR, cm^{-1}): 2248 (vw), 2207 (vw), 2170 (m), 2146 (m), 2119 (m, sh), 1993 (w), 1558 (m), 1511 (w, sh), 1503 (m), 1471 (w, sh), 1454 (w, sh), 1415 (w), 1318 (s), 1248 (m, sh), 1218 (vw, sh), 1150 (s), 1130 (s), 1101 (s), 983 (m, sh), 957 (s), 836 (m), 826 (s), 791 (m), 808 (m), 791 (m), 718 (m), 697 (s), 679 (s), 591 (w), 598 (w), 524 (w), 518 (m), 473 (m). Elemental analysis calculated (found) for $\text{C}_{23}\text{H}_{18}\text{N}_8\text{S}_2$: C, 58.71 (58.66); H, 3.86 (3.770); N, 23.81(23.00).

1.8 Preparation of $[\mathbf{3}\text{-PrpyN}_2\text{TMS}_3][\text{OTf}]$

A solution of **3-pyN₂TMS₃** (5.05 g, 15.0 mmol) in 15 ml of Et₂O was cooled to 0 – 5 °C in an ice-water bath while neat PrOTf (2.10 ml, 15.1 mmol) was added dropwise to the solution over a period of 5 min. The reaction mixture was allowed to gradually warm up to room temperature and stirred for 16 h to afford a yellow solution. The volatiles were removed by flash distillation to give a viscous yellow oil, which was triturated with 2 × 5 ml of dry toluene and dried *in vacuo*. Product solidified after 48 h. Yield: 6.34 g (12.0 mmol, 85 %). ¹H NMR (δ , CD₃CN, ppm): 8.69 (d, 1H, Ar-H, J = 5.9 Hz), 8.64 (s, 1H, Ar-H), 8.37 (d, 1H, Ar-H, J = 8.2 Hz), 8.05 (t, 1H, Ar-H, J = 7.1 Hz), 4.53 (t, 2H, N-CH₂-CH₂, J = 7.5 Hz), 2.01** (sext, 2H, CH₂-CH₂-CH₃, J = 7.5 Hz), 0.97 (t, 3H, CH₂-CH₃ J = 7.4

** Peak is partially obscured by the residual solvent (MeCN) peak in CD₃CN (δ = 1.94).

Hz), 0.12 (s, 27H).

1.9 Preparation of [3-PrpyDTDA][Cl]₂

A solution of S₂Cl₂ (4.50 ml, 56.6 mmol) in 60 ml of MeCN was added dropwise to a solution of [3-prpyN₂TMS₃][OTf] (5.00 g, 9.44 mmol) in 75 ml of MeCN cooled to 0 – 5 °C in an ice-water bath. The mixture was allowed to warm to room temperature with stirring for 18 h. Solid [BzEt₃N][Cl] (4.35 g, 19.1 mmol) was added and a bright orange solid was collected by filtration after 2 h of stirring and washed with 3 × 30 ml of MeCN, 3 × 30 ml of DCM, and dried *in vacuo*. Yield: 3.23 g (Expected: 2.80 g).[§] IR (ATR, cm⁻¹): 2966 (m), 2933 (m), 2876 (m), 2752 (m, br), 2658 (m, br), 1685 (w), 1634 (w), 1589 (vw), 1544 (vw), 1505 (m), 1446 (m), 1407 (s), 1312 (w), 1203 (w), 1161 (m), 1118 (s), 1032 (vw), 942 (vw), 900 (vw), 834 (w), 779 (w), 753 (m), 679 (s), 638 (w, sh), 573 (vw), 530 (m), 508 (w, sh), 461 (vw), 420 (w).

1.10 Preparation of [3-PrpyDTDA][OTf]₂

To a slurry of crude [3-PrpyDTDA][Cl]₂ (3.23 g, 10.9 mmol) in 50 ml of MeCN was added an excess of TMSOTf (4.93 ml, 27.2 mmol), giving a white solid in a clear greyish solution. The mixture was stirred for 3 h at room temperature and then gently refluxed before hot filtering. The solvent volume was reduced by half *in vacuo* and the resulting crystalline off-white solid was recrystallized twice from 2 × 25 ml of EtCN. After 48 h at -20 °C, clear colourless crystals were obtained and collected by filtration and dried *in vacuo*. Yield: 3.36 g (6.42 mmol, 59 %). ¹H NMR (δ, CD₃CN, ppm): 9.83 (s, 1H, Ar-H), 9.49 (s, 1H, Ar-H), 9.08 (s, 1H, Ar-H), 8.41(s, Ar-H) 1H, 4.73 (t, 2H, N-CH₂-CH₂, *J* = 7.4 Hz), 2.11 (sext, 2H, CH₂-CH₂-CH₃, *J* = 7.4 Hz), 1.04 (t, 3H, CH₂-CH₃, *J* = 7.4 Hz). Elemental analysis calculated (found) for C₁₁H₁₁F₆N₃O₆S₄: C, 25.24 (24.93); H, 2.12 (2.078); N, 8.03 (8.00).

1.11 Preparation of [3-PrpyDTDA][I]

A degassed solution of NBu₄I (4.88 g, 13.2 mmol) in 40 ml of MeCN was poured onto a solution of [3-PrpyDTDA][OTf]₂ (3.36 g, 6.42 mmol) in 25 ml of MeCN and the mixture was stirred for 16 h at room temperature to afford a micro-crystalline green-bronze solid that was collected by filtration, washed with 2 × 10 ml of MeCN, 20 ml of DCM, and dried *in vacuo*. Yield: 2.11 g (6.00 mmol, 94 %). IR (ATR, cm⁻¹): 3047 (w), 2960 (w), 2872 (w), 1626 (w), 1497 (w), 1452 (w), 1373 (m), 1334 (w), 1261 (m), 1220 (w), 1175 (m), 1124 (m), 1028 (m), 953 (w), 904 (vw), 826 (w), 802 (m), 753 (s), 749 (s), 681 (s), 634 (s), 575 (vw), 502 (s), 451 (w).

1.12 Preparation of radical-cation IV (E = S, R = Pr)

To a solution of [3-PrpyDTDA][I] (2.11 g, 6.00 mmol) was poured a solution of AgOTf (1.63 g, 6.35 mmol) in 35 ml of MeCN and stirred for 2 h at room temperature. Solid AgI was cannula filtered and the solution was flash distilled to dryness *in vacuo*. The resulting product was recrystallized from 20 ml of MeCN. Yield: 1.01 g (2.70 mmol, 45 %). IR (ATR, cm^{-1}): 3053 (vw), 2978 (vw), 2949 (vw), 2888 (vw), 1640 (vw), 1509 (vw), 1467 (vw), 1465 (vw), 1418 (vw), 1383 (m), 1271 (s, sh), 1250 (s), 1222 (s), 1193 (m, sh), 1146 (s), 1026 (s), 965 (m, sh), 906 (m), 836 (m), 806 (m), 781 (s), 755 (m), 677 (s), 634 (s), 573 (s), 512 (s), 441 (m). Elemental analysis calculated (found) for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{N}_3\text{O}_3\text{S}_3$: C, 32.08 (31.97); H, 2.96 (3.022); N, 11.22 (11.34).

1.13 Preparation of $1^{\text{Pr}}\cdot\text{MeCN}$

A solution of IV (E = S; R = Pr) (0.042 g, 0.112 mmol) in 7 ml of MeCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.062 g, 0.122 mmol) in 7 ml of MeCN was allowed to slowly diffuse into the former over a 24 h period. This afforded dark-orange needles which were collected by suction filtration on a small, sintered glass Buchner funnel, washed with 5 ml of MeCN, and air dried. Yield: 0.043 g (0.091 mmol, 81 %). IR (ATR cm^{-1}): 3076 (vw), 2253 (w), 2173 (m, sh), 2154 (s), 1633 (w), 1564 (m), 1500 (m), 1465 (m), 1309 (s), 1210 (m, sh), 1129 (s), 1100 (s), 984 (m), 948 (m), 839 (m), 822 (m), 805 (m, sh), 785 (m), 755 (m, sh), 714 (m, sh), 671 (s), 612 (m), 588 (m), 574 (m), 562 (m), 544 (m), 518 (s), 499 (m), 477 (s), 441 (m), 423 (m). Elemental analysis calculated (found) for $\text{C}_{23}\text{H}_{18}\text{N}_8\text{S}_2$: C, 58.71 (58.72); H, 3.86 (3.81); N, 23.81 (23.37).

1.14 Preparation of 1^{Pr}

A solution of IV (E = S, R = Pr) (0.040 g, 0.107 mmol) in 7 ml of EtCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.056 g, 0.110 mmol) in 7 ml of EtCN was allowed to slowly diffuse into the former over a 24 h period. This afforded dark-orange needles which were collected by suction filtration on a small, sintered glass Buchner funnel, washed with EtCN, and air dried. Yield: 0.031 g (0.072 mmol, 68 %). IR (ATR cm^{-1}): 3053 (w), 3030 (w), 2643 (w), 2171 (s), 2147 (s), 1691 (vw), 1635 (vw), 1579 (m), 1503 (m), 1459 (m), 1351 (m), 1302 (w, sh), 1241 (w, sh), 1208 (w, sh), 1176 (s), 1130 (m, sh), 1023 (w, sh), 972 (w), 817 (m), 782 (m), 714 (w), 677 (m), 618 (w), 575 (vw, sh), 543 (vw), 513 (w), 473 (m). Elemental analysis calculated (found) for $\text{C}_{21}\text{H}_{15}\text{N}_7\text{S}_2$: C, 58.72 (59.21); H, 3.52 (3.42); N, 22.83 (22.52).

1.15 Preparation of [3-BupyN₂TMS₃][OTf]

A solution of 3-pyN₂TMS₃ (5.00 g, 14.8 mmol) in 40 ml of Et₂O was cooled to 0 – 5 °C in an ice-water bath while neat BuOTf (2.50 ml, 15.8 mmol) was added dropwise to the solution over 5 min. The reaction was allowed to gradually warm up to room temperature and stirred for 16 h to afford a yellow solution. The volatiles were removed by flash distillation to give a viscous yellow oil, which was triturated with 3 × 5 ml of dry toluene and dried *in vacuo*. Product solidified after 72 h. Yield: 7.31 g (13.4 mmol, 91 %). ¹H NMR (δ, CD₃CN, ppm): 8.70 (d, 1H, Ar-H, *J* = 6.1 Hz), 8.64 (s, 1H, Ar-H), 8.37 (dt, 1H, Ar-H, *J* = 8.1 and 1.4 Hz), 8.04 (dd, 1H, Ar-H, *J* = 6.2 and 1.5 Hz), 4.56 (t, 2H, N-CH₂-CH₂, *J* = 7.6 Hz), 1.37 (sext, 2H, CH₂-CH₂-CH₃, *J* = 7.5 Hz), 0.97 (t, 3H, CH₂-CH₃, *J* = 7.3 Hz), 0.12 (s, 27H).

1.16 Preparation of [3-BupyDTDA][Cl]₂

A solution of S₂Cl₂ (6.50 ml, 81.4 mmol) in 20 ml of MeCN was added dropwise to a solution of [3-BupyN₂TMS₃][OTf] (7.31 g, 13.4 mmol) in 60 ml of MeCN cooled to 0 – 5 °C in an ice-water bath. The mixture was allowed to warm to room temperature and gently refluxed for 18 h. Solid [BzEt₃N][Cl] (6.13 g, 26.9 mmol) was added and the resulting mixture was filtered after 1 h of stirring. Bright orange solid was washed with 4 × 20 ml of MeCN and 3 × 20 ml of DCM. Yield: 2.09 g (6.75 mmol, 50 %). [§] IR (ATR, cm⁻¹): 3070 (w), 2864 (w), 1632 (w), 1501 (w), 1471 (w), 1416 (s), 1356 (w), 1315 (w), 1283 (w), 1181 (w, sh), 1165 (m), 1120 (m), 1083 (vw), 1030 (vw), 965 (m), 914 (w, sh), 902 (m), 816 (s), 787 (w), 732 (w), 694 (s), 681 (m, sh), 622 (w), 579 (vw), 545 (s).

1.17 Preparation of [3-BupyDTDA][OTf]₂

To a slurry of crude [3-BupyDTDA][Cl]₂ (2.09 g, 6.75 mmol) in 30 ml of EtCN was added an excess of TMSOTf (3.00 ml, 16.6 mmol), giving a white solid in a faint yellow solution. The mixture was stirred for 5.5 h at room temperature and then gently refluxed before hot filtering. The solvent volume was decreased to 20 ml and the product was kept for 72 h at –20 °C to afford clear off-white crystals. Yield: 2.91 g (5.41 mmol, 81 %). ¹H NMR (δ, CD₃CN, ppm): 9.86 (s, 1H, Ar-H), 9.48 (s, 1H, Ar-H), 9.10 (s, 1H, Ar-H), 8.40 (s, Ar-H) 1H, 4.77 (t, 2H, N-CH₂-CH₂, *J* = 7.6 Hz), 2.07 (pent, 2H, CH₂-CH₂-CH₂, *J* = 7.6 Hz), 1.45 (sext, 2H, CH₂-CH₂-CH₃, *J* = 7.5 Hz), 1.00 (t, 3H, CH₂-CH₃, *J* = 7.3 Hz). Elemental analysis calculated (found) for C₁₂H₁₃F₆N₃O₆S₄: C, 26.82 (26.65); H, 2.44 (2.39); N, 7.82 (7.84).

1.18 Preparation of [3-BupyDTDA][I]

A degassed solution of NBu₄I (3.04 g, 8.23 mmol) in 40 ml of MeCN was poured onto a solution of

[3-BupyDTDA][OTf]₂ (2.10 g, 3.91 mmol) in 20 ml of MeCN and the mixture was stirred for 2.5 h at room temperature to afford a micro-crystalline bronze colored solid that was collected by filtration, washed with 2 × 20 ml of MeCN, 2 × 20 ml of DCM, and dried *in vacuo*; Yield: 0.704 g (1.92 mmol, 49 %). IR (ATR, cm⁻¹): 3111 (vw), 3076 (vw), 3027 (w), 2956 (w), 2917 (w, sh), 1632 (w), 1589 (vw), 1507 (m), 1460 (m), 1375 (m), 1336 (w), 1273 (w), 1183 (m), 1144 (w), 930 (w), 826 (w), 814 (s), 773 (s), 679 (s), 665 (w, sh), 520 (s), 502 (m), 449 (m).

1.19 Preparation of radical-cation IV (E = S, R = Bu)

A solution of AgOTf (0.627 g, 2.44 mmol) in 40 ml of MeCN was degassed twice and poured onto solid **[3-BupyDTDA][I]** (0.852g, 2.33 mmol). The mixture was stirred for 2 h at room temperature. Solid AgI was cannula filtered, volatiles were removed from the filtrate *in vacuo* and the product recrystallized twice from 10 ml of MeCN. Repeated recrystallization from MeCN at -20 °C afforded analytically pure lustrous green-bronze plates. Yield: 0.659 g (1.70 mmol, 73 %). IR (ATR, cm⁻¹): 3065 (w), 2966 (w), 2943 (w), 2882 (w), 1363 (w), 1511 (w), 1469 (w), 1452 (w, sh), 1440 (vw, sh), 1389 (m), 1275 (s), 1252 (s), 1220 (s), 1195 (m, sh), 1183 (m), 1142 (s), 1028 (s), 961 (m), 951 (m), 842 (m), 810 (m), 775 (m), 755 (m), 740 (w, sh), 681 (m), 632 (s), 571 (s), 512 (s), 439 (m). Elemental analysis calculated (found) for C₁₁H₁₃F₃N₃O₃S₃: C, 34.02 (33.90); H, 3.37 (3.33); N, 10.82 (10.92).

1.20 Preparation of 1^{Bu}·0.5MeCN

A solution of **IV (E = S; R = Bu)** (0.077g, 0.198 mmol) in 10 ml of MeCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.104 g, 0.205 mmol) in 10 ml of MeCN was allowed to slowly diffuse into the former over a 24 h period. This afforded violet-black needles which were collected by suction filtration on a small, sintered glass Buchner funnel, washed with 5 ml of MeCN, and air dried. Yield: 0.042 g (0.0453 mmol, 46 %). IR (Nujol mull, cm⁻¹): 2215 (vw), 2175 (s), 2154 (s), 1628 (vw), 1581 (m), 1508 (s), 1259 (w), 1177 (s), 1134 (m, sh), 1091 (m, sh), 1018 (w), 987 (w), 820 (w), 810 (w, sh), 773 (w), 679 (vw), 583 (vw), 524 (vw), 510 (vw), 479 (vw), 418 (s), 410 (s, sh). Elemental analysis calculated (found) for C₄₆H₃₇N₁₅S₄: C, 59.53 (59.66); H, 4.02 (4.21); N, 22.64 (22.17).

1.21 Preparation of 1^{Bu}

A solution of **IV (E = S; R = Bu)** (0.040 g, 0.103 mmol) in 7 ml of EtCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.053 g, 0.104 mmol) in 7 ml of EtCN was allowed to slowly diffuse into the former over a 24 h period. This afforded dark orange plank-like needles which were collected by suction filtration on a small, sintered glass

Buchner funnel, washed with 5 ml EtCN, and air dried. Yield: 0.012 g (0.013 mmol, 13 %). IR (ATR, cm^{-1}): 2150 (s), 1575 (s), 1504 (s), 1463 (m, sh), 1137 (s), 1275 (m, sh), 1210 (w), 1164 (s), 1134 (s, sh), 986 (w), 817 (m), 786 (m), 712 (m), 681 (m), 582 (w), 540 (w), 509 (m), 476 (m). Elemental analysis calculated (found) for $\text{C}_{22}\text{H}_{17}\text{N}_7\text{S}_2$: C, 59.57 (59.60); H, 3.86 (3.701); N, 22.11, (22.14).

1.22 Preparation of [3-EtpyDSDA][Cl]₂

A solution of [3-EtpyN₂TMS₃][OTf] (5.10 g, 9.88 mmol) in 20 ml of MeCN was added dropwise to a freshly prepared solution of SeCl₂ (2.89 g, 19.3 mmol) in 40 ml of MeCN. The mixture was stirred for 2 h at room temperature. Solid [BzEt₃N][Cl] (3.37 g, 14.8 mmol) was added and the mixture was stirred for 2 h before a bright orange solid was collected by filtration and washed with 4 × 20 ml of MeCN and 2 × 10 ml of DCM. Yield: 3.23 g (8.59 mmol, 87 %). IR (ATR, cm^{-1}): 3061 (w), 3049 (w), 2954 (w), 2750 (vw, sh), 1691 (m), 1630 (vw), 1497 (w), 1469 (w, sh), 1452 (w), 1442 (w, sh), 1387 (w), 1316 (w), 1279 (vw), 1208 (vw), 1173 (m), 1130 (w), 1093 (vw), 1032 (vw), 981 (vw), 906 (vw), 902 (vw), 840 (w), 787 (w), 773 (w), 712 (s), 696 (s), 683 (s), 647 (m, sh), 622 (vw, sh), 567 (vw), 524 (vw).

1.23 Preparation of [3-EtpyDSDA][OTf]₂

To a suspension of crude [3-EtpyDSDA][Cl]₂ (0.656 g, 1.75 mmol) in 40 ml of MeCN was added an excess of TMSOTf (0.80 ml, 4.351 mmol), giving a clear yellow solution. The mixture was stirred for 1 h at room temperature and then gently refluxed before hot filtering. The solvent volume was reduced by half *in vacuo* and subsequent cooling of the solution for 16 h at -20 °C afforded pale yellow needles. Yield: 0.818 g (1.36 mmol, 78 %). ¹H NMR (δ , CD₃CN, ppm): 9.99 (s, 1 H), 9.63 (s, 1H, Ar-H), 9.20 (s, 1H, Ar-H), 8.24 (s, 1H, Ar-H), 4.84 (q, 2H, $J = 7.3$ Hz), 1.70 (t, 3H, $J = 7.3$ Hz). Elemental analysis calculated (found) for $\text{C}_{10}\text{H}_9\text{F}_9\text{N}_3\text{O}_6\text{S}_2\text{Se}_2$: C, 19.91 (19.92); H, 1.50 (1.486); N, 6.97 (7.128).

1.24 Preparation of [3-EtpyDSDA][I]

A degassed solution of NBu₄I (1.063 g, 2.878 mmol) in 20 ml of MeCN was added to a degassed solution of [3-EtpyDSDA][OTf]₂ (0.798 g, 1.323 mmol) in 20 ml of MeCN and the mixture was stirred for 2 h at room temperature to afford a greenish-bronze precipitate that was collected by filtration, washed with MeCN and DCM, and dried *in vacuo*. The crude product was collected and used without further purification. Yield: 0.517 g (1.197 mmol, 90 %). IR (ATR, cm^{-1}): 3062 (w), 2962 (w), 1703 (vw), 1630 (w), 1495 (w), 1452 (w), 1387 (vw), 1322 (m), 1267 (m), 1224 (w, sh), 1173 (s), 1122 (m), 1071 (w, sh), 1030 (m), 985 (w, sh), 948 (vw), 914 (vw), 879 (vw), 816 (w), 785

(m), 730 (w), 698 (s), 679 (m, sh), 620 (s), 573 (w), 518 (w), 459 (w).

1.25 Preparation of radical-cation IV (E = Se; R = Et)

A solution of AgOTf (0.318 g, 1.239 mmol) in 25 ml of MeCN was degassed twice and poured onto solid [3-EtpyDSDA][I] (0.506 g, 1.17 mmol). The mixture was stirred for 2 h at room temperature and then gently refluxed. Solid AgI was cannula filtered to afford a dark red solution that gave a lustrous copper-bronze crystalline solid upon cooling to room temperature. The volatiles were removed *in vacuo* and the crude product was recrystallized twice from MeCN to afford an analytically pure product. Yield: 0.441 g (0.972 mmol, 83 %). IR (ATR, cm^{-1}): 3064 (vw, sh), 3058 (vw), 1634 (vw), 1503 (w), 1481 (vw), 1456 (vw), 1389 (vw), 1334 (w), 1269 (m, sh), 1248 (s), 1226 (s), 1191 (w, sh), 1177 (w, sh), 1163 (m, sh), 1144 (s), 1134 (m, sh), 1028 (s), 936 (w, sh), 812 (w), 783 (w), 757 (w, sh), 740 (w), 704 (m), 679 (m), 630 (s), 571 (m), 514 (m), 465 (m). Elemental analysis calculated (found) for $\text{C}_9\text{H}_9\text{F}_3\text{N}_3\text{O}_3\text{SSe}_2$: C, 23.80 (23.68); H, 2.00 (2.089); N, 9.25 (9.18).

1.26 Preparation of $2^{\text{Et}}\cdot\text{MeCN}$

A solution of IV (E = Se; R = Et) (0.070 g, 0.154 mmol) in 13 ml of MeCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.078 g, 0.154 mmol) in 10 ml of MeCN was allowed to slowly diffuse into the former over a 24 h period at $-20\text{ }^\circ\text{C}$. Small orange needles were afforded, which were collected by filtration, washed with 5 ml MeCN, and dried *in vacuo*. Yield: 0.035 g (0.068 mmol, 44 %). IR (ATR, cm^{-1}): 3072 (w), 2253 (m), 2173 (s, sh), 2154 (s), 1632 (w), 1574 (m), 1497 (m), 1473 (m), 1331 (m), 1208 (w), 1163 (m), 1129 (m, sh), 979 (w), 873 (w, sh), 822 (m), 803 (m), 783 (w), 746 (w), 715 (w), 701 (m), 677 (m), 632 (m), 615 (w), 564 (w), 541 (w), 506 (w), 479 (m), 463 (w). Elemental analysis calculated (found) for $\text{C}_{22}\text{H}_{16}\text{N}_8\text{Se}_2$: C, 48.01 (47.83); H, 2.93 (2.931); N, 20.36 (20.29).

1.27 Preparation of [3-PrpyDSDA][Cl]₂

A solution of [3-PrpyN₂TMS₃][OTf] (6.00 g, 11.3 mmol) in 25 ml of MeCN was added dropwise to a freshly prepared solution of SeCl₂ (3.21 g, 21.4 mmol) in 40 ml of MeCN. The mixture was stirred for 6 h at room temperature. Solid [BzEt₃N][Cl] (5.16 g, 22.7 mmol) was added and the mixture was stirred for 16 h before a bright orange solid was collected by filtration and washed with 3×15 ml of MeCN and 3×10 ml of DCM. Yield: 4.18 g (10.72 mmol, 95 %). IR (ATR, cm^{-1}): 3070 (w), 2964 (w), 2933 (w, sh), 1687 (w), 1628 (w), 1540 (vw), 1491 (w), 1493 (w), 1471 (w), 1456 (w, sh), 1393 (w), 1322 (vw), 1267 (w), 1210 (vw), 1181 (w, sh), 1163 (m), 1110 (w), 1030 (vw), 938 (vw), 916 (vw), 900 (vw), 836 (w), 812 (w), 781 (m), 761 (w), 757 (w), 717 (m, sh), 706 (m), 691 (s), 681 (m,

sh), 636 (m), 510 (vw), 467 (m).

1.28 Preparation of [3-PrpyDSDA][Otf]₂

To a slurry of crude [3-PrpyDSDA][Cl]₂ (4.18 g, 10.7 mmol) in 30 ml of MeCN was added an excess of TMSOTf (5.00 ml, 27.6 mmol), giving a white solid in an orange solution. The mixture was stirred for 3 h at room temperature and then gently refluxed before hot filtering. The volatiles were removed *in vacuo* and the filtrate was recrystallized from 20 ml of EtCN. Subsequent cooling of the solution to -20 °C for 18 h gave clear yellow crystals. Yield: 4.65 g (7.53 mmol, 70 %). ¹H NMR (δ, CD₃CN, ppm): 9.83 (s, 1H), 9.51 (s, 1H), 9.076 (s, 1H), 8.30 (s, 1H), 4.73 (t, 2H, N-CH₂-CH₂, *J* = 7.5), 2.10 (sext, 2H, CH₂-CH₂-CH₃ *J* = 7.4), 1.03 (t, 3H, CH₂-CH₃, *J* = 7.3 Hz). Elemental analysis calculated (found) for C₁₁H₁₁F₆N₃O₆S₂Se₂: C, 21.40 (21.19); H, 1.80 (1.741); N, 6.81 (6.81).

1.29 Preparation of [3-PrpyDSDA][I]

A degassed solution of Nbu₄I (2.12 g, 5.73 mmol) in 40 ml of MeCN was poured onto solid [3-PrpyDSDA][Otf]₂ (1.78 g, 2.89 mmol) and the mixture was stirred for 12 h at room temperature to afford a micro-crystalline green-bronze solid. The solid was collected by filtration, washed with 20 ml of MeCN, and dried *in vacuo*. Yield: 0.802 g (1.80 mmol, 62 %). IR (ATR, cm⁻¹): 3043 (vw), 2958 (vw), 2870 (vw), 1622 (vw), 1489 (w), 1454 (w), 1326 (w), 1271 (m), 1254 (m), 1238 (w, sh), 1169 (s), 1120 (m), 1075 (vw, sh), 1030 (m), 822 (vw, sh), 806 (w), 757 (vw), 734 (vw), 697 (s), 681 (s), 636 (m, sh), 620 (s), 575 (vw, sh), 506 (vw), 504 (vw), 459 (m).

1.30 Preparation of radical-cation IV (E = Se; R = Pr)

A solution of AgOTf (0.471 g, 1.83 mmol) in 40 ml of MeCN was poured to a solid [3-PrpyDSD][I] (0.802 g, 1.80 mmol). The mixture was stirred for 2 h at room temperature. Solid AgI was cannula filtered to afford a dark red solution that was concentrated *in vacuo* and kept at -20 °C for 16 h. Dark golden-brown crystals were collected by filtration and dried *in vacuo*. Yield: 0.532 g (1.14 mmol, 63 %). IR (ATR, cm⁻¹): 3053 (vw), 2976 (vw), 2947 (vw), 2888 (vw), 1638 (vw), 1501 (vw), 1460 (vw), 1462 (vw), 1334 (w), 1269 (m, sh), 1244 (s, sh), 1220 (s), 1193 (w, sh), 1177 (w), 1148 (s), 1130 (m, sh), 1026 (s), 904 (vw), 802 (m), 742 (m), 710 (m), 679 (s), 632 (vs), 573 (m), 514 (s), 465 (m). Elemental analysis calculated (found) for C₁₀H₁₁F₃N₃O₃SSe₂: C, 25.65 (25.20); H, 2.37 (2.30); N, 8.98 (9.05).

1.31 Preparation of 2^{Pr}·MeCN

A solution of IV (E = Se, R = Pr) (0.070 g, 0.150 mmol) in 13 ml of MeCN was degassed by three

freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.076 g, 0.150 mmol) in 10 ml of MeCN was allowed to slowly diffuse into the former over a period of 24 h at -20 °C. This afforded dark orange plank-like needles which were collected by filtration on a small, sintered glass Buchner funnel, washed with 5 ml of MeCN, and dried *in vacuo*. Yield: 0.068 g (0.119 mmol, 80 %). IR (ATR, cm^{-1}): 2254 (w), 2173 (s, sh), 2154 (s), 1626 (w), 1578 (s), 1499 (m), 1462 (m), 1375 (w), 1333 (s), 1210 (w), 1163 (s), 1125 (m, sh), 1094 (m, sh), 986 (w), 942 (w), 924 (w), 864 (vw), 820 (m), 817 (m), 749 (w), 715 (m), 700 (m), 677 (s), 632 (m), 625 (m, sh), 564 (w), 541 (w), 526 (vw), 496 (vw), 477 (m), 432 (vw). Elemental analysis calculated (found) for $\text{C}_{23}\text{H}_{18}\text{N}_8\text{Se}_2$: C, 48.95 (48.63); H, 3.21 (3.072); N, 19.85 (19.89).

1.32 Preparation of [3-BupyDSDA][Cl]₂

A solution of [3-BupyN₂TMS₃][OTf] (4.73g, 8.69 mmol) in 35 ml of MeCN was added dropwise to a freshly prepared solution of SeCl₂ (2.47 g, 16.5 mmol) in 40 ml of MeCN. The mixture was stirred for 5 h at room temperature. Solid [BzEt₃N][Cl] (4.36 g, 19.1 mmol) was added and the mixture was stirred 16 h before a bright orange solid was collected by filtration and washed with 3 × 20 ml of MeCN and 2 × 10 ml of DCM. Yield: 2.43 g (6.02 mmol, 73 %). IR (ATR, cm^{-1}): 3070 (w), 2954 (w), 2923 (w), 2866 (w), 1683 (w), 1626 (w), 1487 (m), 1467 (m, sh), 1434 (w, sh), 1397 (m), 1356 (w), 1322 (w), 1303 (w), 1275 (w), 1246 (w), 1210 (w), 1169 (w, sh), 1159 (m), 1112 (w), 1083 (vw), 1032 (vw), 959 (w, sh), 932 (w, sh), 918 (w), 842 (w), 824 (vw, sh), 779 (s), 738 (w), 742 (w, sh), 708 (s), 691 (s), 685 (m, sh), 636 (s), 622 (w, sh), 577 (w, sh), 512 (vw), 467 (w, sh), 451 (w), 420 (vw).

1.33 Preparation of [3-BupyDSDA][OTf]₂

To a slurry of crude [3-BupyDSDA][Cl]₂ (2.43 g, 6.02 mmol) in 30 ml of EtCN was added an excess of TMSOTf (2.80 ml, 13.24 mmol), forming a white solid in a grey solution. The mixture was stirred for 3 h at room temperature and then gently refluxed before hot filtering. The volatiles were removed *in vacuo* and the resulting off-white solid was recrystallized from 18 ml of EtCN at 4 °C giving yellow crystals. Yield: 2.00 g (3.17 mmol, 53 %). ¹H NMR (δ , CD₃CN, ppm): 9.89 (s, 1 H), 9.562 (s, 1H), 9.11 (s, 1H), 8.27 (s, 1H), 4.76 (t, 2 H, N-CH₂-CH₂, $J = 7.6$ Hz), 2.05 (pent, 2H, CH₂-CH₂-CH₂ $J = 7.6$ Hz) 1.46 (sext, 2H, CH₂-CH₂-CH₃, $J = 7.5$ Hz), 1.00 (t, 3H, CH₂-CH₃, $J = 7.4$ Hz).^{††} Elemental analysis calculated (found) for $\text{C}_{11}\text{H}_{13}\text{F}_3\text{N}_3\text{O}_3\text{SSe}_2$: C, 22.83 (22.68); H, 2.08 (2.116); N, 6.66 (6.809).

^{††} Signals attributed to residual propionitrile (EtCN) were found in the ¹H-NMR at δ 2.36 and 1.21 ppm, hence the crystalline solid was dried in an Abderhalden drying apparatus (78 °C and 10^{-3} bar) before performing an elemental analysis.

1.34 Preparation of [3-BupyDSDA][I]

A degassed solution of NBu₄I (2.709 g, 7.33 mmol) in 20 ml of MeCN was added to a yellow solution of [3-BupyDSDA][OTf]₂ (2.20 g, 3.48 mmol) in 40 ml of MeCN and the mixture was stirred for 2 h at room temperature to afford a micro-crystalline green-bronze solid. The solid was collected by filtration and washed with 20 ml of MeCN, 2 × 20 ml of DCM, and dried *in vacuo*. Yield: 1.09 g (2.37 mmol, 68 %). IR (ATR, cm⁻¹): 3064 (w), 2958 (w), 2929 (w), 2868 (w), 1624 (w), 1491 (w), 1452 (w), 1378 (vw), 1324 (w), 1256 (s), 1222 (m, sh), 1191 (w), 1167 (s), 1122 (s), 1085 (m, sh), 1028 (s), 928 (w), 879 (w), 802 (m), 730 (w), 700 (s), 681 (s), 610 (s, sh), 620 (s), 596 (m, sh), 516 (m), 459 (m).

1.35 Preparation of radical-cation IV (E = Se, R = Bu)

A solution of AgOTf (0.730 g, 2.84 mmol) in 40 ml of MeCN was poured to a solid [3-BupyDSDA][I] (1.09 g, 2.37 mmol). The mixture was stirred for 2 h at room temperature. Solid AgI was cannula filtered to afford a dark purple solution that was concentrated *in vacuo* and kept at 4 °C. Dark golden-brown crystals were collected by filtration and dried *in vacuo*. Yield: 0.719 g (1.49 mmol, 63 %). IR (ATR, cm⁻¹): 3066 (vw), 3053 (vw), 2968 (vw), 2943 (vw), 2882 (vw), 2870 (vw), 1632 (vw), 1503 (w), 1469 (vw, sh), 1460 (vw), 1385 (vw), 1336 (w), 1267 (s), 1244 (s), 1224 (s), 1175 (m, sh), 1154 (s), 1128 (m, sh), 1028 (s), 838 (vw, sh), 810 (w), 785 (vw, sh), 744 (w, sh), 742 (w, sh), 708 (m), 679 (m), 632 (s), 573 (m), 561 (w, sh), 514 (m), 467 (m). Elemental analysis calculated (found) for C₁₁H₁₃F₃N₃O₃SSe₂: C, 27.40 (27.12); H, 2.72 (2.695); N, 8.71 (8.73).

1.36 Preparation of 2^{Bu}

A solution of IV (E = Se; R = Bu) (0.050 g, 0.103 mmol) in 8 ml of MeCN was degassed by three freeze-pump-thaw cycles and a similarly degassed solution of [K(18c6)][TCNQ] (0.052 g, 0.103 mmol) in 7 ml of MeCN was allowed to slowly diffuse into the former over a period of 24 h at -20 °C. This afforded lustrous violet-black plate-like crystals which were collected by suction filtration on a small, sintered glass Buchner funnel, washed with 5 ml of MeCN, and dried *in vacuo*. Yield: 0.023 g (0.042 mmol, 40 %). IR (ATR, cm⁻¹): 2184 (m, sh), 2170 (s, sh), 2150 (s), 1629 (w, sh), 1574 (s), 1506 (m), 1476 (m, sh), 1463 (m, sh), 1353 (s), 1331 (s), 1212 (w), 1173 (s), 1128 (m, sh), 977 (w), 975 (w), 933 (w), 819 (m), 788 (w, sh), 741 (w), 717 (w, sh), 698 (m, sh), 688 (s), 636 (m), 579 (w), 543 (w), 526 (w), 509 (w), 476 (m), 442 (vw). Elemental analysis calculated (found) for C₂₂H₁₇N₇Se₂: C, 49.18 (48.94); H, 3.19 (3.232); N, 18.25 (18.21).

Low-temperature single crystal X-ray crystallography

Table S1. Crystallographic data for compounds **IV** (**E = S; R = Et, Pr, Bu**).

Compound	IV (E = S; R = Et)	IV (E = S; R = Pr)	IV (E = S; R = Bu)
CCDC Code	2181974	2182640	2182459
Formula	C ₉ H ₉ F ₃ N ₃ O ₃ S ₃	C ₁₀ H ₁₁ F ₃ N ₃ O ₃ S ₃	C ₁₁ H ₁₃ F ₃ N ₃ O ₃ S ₃
Molecular weight (g·mol ⁻¹)	360.37	374.40	388.42
<i>T</i> (K)	120.00(10)	120.00(10)	120.00(10)
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>I</i> 2/ <i>a</i>
<i>a</i> (Å)	6.4483(3)	6.6590(2)	13.2956(2)
<i>b</i> (Å)	7.3299(5)	7.3288(3)	7.7822(10)
<i>c</i> (Å)	14.9331(14)	15.4747(8)	31.2747(5)
α (°)	101.804(7)	102.466(4)	90
β (°)	90.012(6)	94.228(4)	101.0000(10)
γ (°)	90.042(5)	93.284(3)	90
<i>V</i> (Å ³)	690.89(9)	733.31(5)	3176.51(8)
<i>Z</i>	2	2	8
ρ_{calc} (g·cm ⁻³)	1.732	1.696	1.624
μ (mm ⁻¹)	0.584	5.111	4.743
<i>F</i> (000)	366.0	382.0	1592.0
Crystal size (mm ³)	0.222 × 0.04 × 0.018	0.234 × 0.073 × 0.03	0.349 × 0.044 × 0.024
Radiation (Å)	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for data collection (°)	5.574 to 58.098	5.872 to 153.734	5.758 to 153.494
Reflections collected	4651	5723	19106
Independent reflections	3134	5723	3351
Data/restraints/parameters	[<i>R</i> _{int} = 0.0410, <i>R</i> _{sigma} = 0.0747] 3134/0/191	[<i>R</i> _{int} = 0.0322 ^a , <i>R</i> _{sigma} = 0.1010] 5723/0/201	[<i>R</i> _{int} = 0.0246, <i>R</i> _{sigma} = 0.0164] 3351/0/237
Goodness-of-fit on <i>F</i> ²	1.165	1.087	1.056
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0622, <i>wR</i> ₂ = 0.1489	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.1271	<i>R</i> ₁ = 0.0266, <i>wR</i> ₂ = 0.0707
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0816, <i>wR</i> ₂ = 0.1639	<i>R</i> ₁ = 0.0488, <i>wR</i> ₂ = 0.1306	<i>R</i> ₁ = 0.0282, <i>wR</i> ₂ = 0.0723
Largest diff. peak/hole / e Å ⁻³	0.68/−0.61	0.53/−0.45	0.47/−0.34

^a Value for *R*_{int} is determined for the major component of the twin refinement.

Table S2. Crystallographic data for compounds **IV** (**E = Se; R = Et, Pr, Bu**).

Compound	IV (E = Se; R = Et)	IV (E = Se; R = Pr)	IV (E = Se; R = Bu)
CCDC Code	2182178	2181976	2181977
Formula	C ₉ H ₉ F ₃ N ₃ O ₃ SSe ₂	C ₁₀ H ₁₁ F ₃ N ₃ O ₃ SSe ₂	C ₁₁ H ₁₃ F ₃ N ₃ O ₃ SSe ₂
Molecular weight (g·mol ⁻¹)	454.17	468.20	482.22
<i>T</i> (K)	120.00(10)	120.00(10)	120.00 (10)
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	6.4334(4)	6.6041(5)	6.4600(7)
<i>b</i> (Å)	7.4835(5)	7.4279(8)	7.5264(6)
<i>c</i> (Å)	15.0493(18)	15.7145(18)	16.8572(14)
α (°)	101.816(8)	76.902(9)	97.838(7)
β (°)	90.593(8)	84.880(8)	93.333(8)
γ (°)	90.503(5)	87.889(7)	90.995(7)
<i>V</i> (Å ³)	709.10(11)	747.71(13)	810.31(13)
<i>Z</i>	2	2	2
ρ_{calc} (g·cm ⁻³)	2.127	2.080	1.976
μ (mm ⁻¹)	8.380	7.971	7.381
<i>F</i> (000)	438.0	454.0	470.0
Crystal size (mm ³)	0.125 × 0.047 × 0.021	0.157 × 0.042 × 0.013	0.32 × 0.21 × 0.024
Radiation (Å)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for data collection (°)	6.000 to 154.348	5.794 to 140	5.302 to 153.28
Reflections collected	3632	4087	4724
Independent reflections	3632	2727	4724
	[<i>R</i> _{int} = 0.0741 ^a , <i>R</i> _{sigma} = 0.0403]	[<i>R</i> _{int} = 0.0502, <i>R</i> _{sigma} = 0.0756]	[<i>R</i> _{int} = 0.0767 ^a , <i>R</i> _{sigma} = 0.0351]
Data/restraints/parameters	3632/0/192	2727/0/200	4723/0/210
Goodness-of-fit on <i>F</i> ²	1.065	1.062	1.048
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0367, <i>wR</i> ₂ = 0.0989	<i>R</i> ₁ = 0.0790, <i>wR</i> ₂ = 0.2114	<i>R</i> ₁ = 0.0631, <i>wR</i> ₂ = 0.1875
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0455, <i>wR</i> ₂ = 0.1011	<i>R</i> ₁ = 0.0984, <i>wR</i> ₂ = 0.2309	<i>R</i> ₁ = 0.0745, <i>wR</i> ₂ = 0.1954
Largest diff. peak/hole / e Å ⁻³	0.88/−0.65	2.66/−1.54	2.45/−1.18

^a Value for *R*_{int} is determined for the major component of the twin refinement.

Table S3. Longitudinal (Δx) and transversal offsets (Δy) of TCNQ radical-anions in solvates **1^{Et}·MeCN**, **1^{Et}·MeCN**, **1^{Pr}·MeCN** **1^{Et}·EtCN**, **1^{Bu}·0.5MeCN**, **2^{Et}·MeCN**, and **2^{Pr}·MeCN** together with the centroid-to-centroid distances (d) and offset angles (α and β) from which the offsets are derived. Twist angles (ϕ) between two mean planes determined by all non-hydrogen atoms of the pyridinium and DTDA/DSDA rings in the DTDA/DSDA cation-radicals.

Compound	d (Å)	α (°)	β (°)	Δx (Å)	Δy (Å)	ϕ
1^{Et}·MeCN	3.26	89.6	88.8	0.02	0.07	5.6
1^{Et}·EtCN	3.27	88.5	89.9	0.07	0.01	6.9
1^{Pr}·MeCN	3.25	89.8	81.6	0.01	0.50	0.9
1^{Bu}·0.5MeCN	3.76	58.4	89.2	1.97	0.06	2.8/5.8 ^a
2^{Et}·MeCN	3.27	88.7	90.0	0.07	0	6.1
2^{Pr}·MeCN	3.27	88.9	84.0	0.06	0.34	1.9

^a There are two crystallographically independent DTDA cation-radicals in the asymmetric unit.

Table S4. Longitudinal (Δx) and transversal offsets (Δy) of TCNQ radical-anions in non-solvates **1^{Pr}**, **1^{Bu}**, and **2^{Bu}** at both low (120 K, LT) and high temperature (300 or 370 K, HT) together with the centroid-to-centroid distances (d) and offset angles (α and β) from which the offsets are derived. Twist angles (ϕ) between two mean planes determined by all non-hydrogen atoms of the pyridinium and DTDA/DSDA rings in the DTDA/DSDA cation-radicals .

Compound	d (Å)	α (°)	β (°)	Δx (Å)	Δy (Å)	ϕ
LT- 1^{Pr} (120 K)	3.73	56.2	88.3	2.08	0.11	8.1
HT- 1^{Pr} (370 K)	3.89	57.5	89.6	2.09	0.02	7.8
LT- 1^{Bu} (120 K)	3.70	54.9	89.3	2.13	0.05	22.6
HT- 1^{Bu} (370 K)	3.78	55.9	89.7	2.12	0.02	15.5
LT- 2^{Bu} (120 K)	3.72	54.6	89.1	2.15	0.06	23.5
HT- 2^{Bu} (300 K)	3.76	55.7	89.5	2.12	0.04	19.2

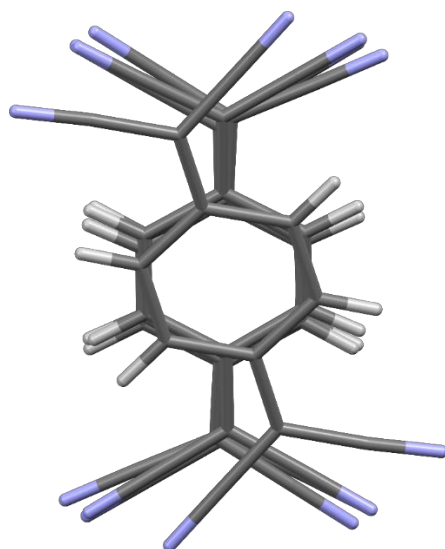


Figure S1. Illustration of stacking of TCNQ^{-•} radical-anions in **1^{Bu}•0.5MeCN** emphasizing the periodic distortion of the TCNQ with respect to the vertical stacking axis.

Thermogravimetric analyses

Table S5. Thermogravimetric data for **1^{Et}·MeCN**, **1^{Et}·EtCN**, **1^{Pr}·MeCN**, **1^{Pr}**, **1^{Bu}·0.5MeCN**, **1^{Bu}**, **2^{Et}·MeCN**, **2^{Pr}·MeCN**, and **2^{Bu}**.

Compound	Desolvation onset (K / °C)	Decomposition onset (K / °C)	Theoretical weight loss (%)	Experimental weight loss (%)
1^{Et}·MeCN	387 / 114	472 / 199	8.99	9.14
1^{Et}·EtCN	396 / 123	452 / 179	11.65	11.26
1^{Pr}·MeCN	354 / 81	467 / 194	8.72	8.50
1^{Pr}	-	464 / 191	-	-
1^{Bu}·0.5MeCN	361 / 88	457 / 184	4.40	4.84
1^{Bu}	-	444 / 171	-	-
2^{Et}·MeCN	385 / 112	452 / 179	7.43	7.24
2^{Pr}·MeCN	358 / 85	450 / 177	7.25	7.12
2^{Bu}	-	447 / 174	-	-

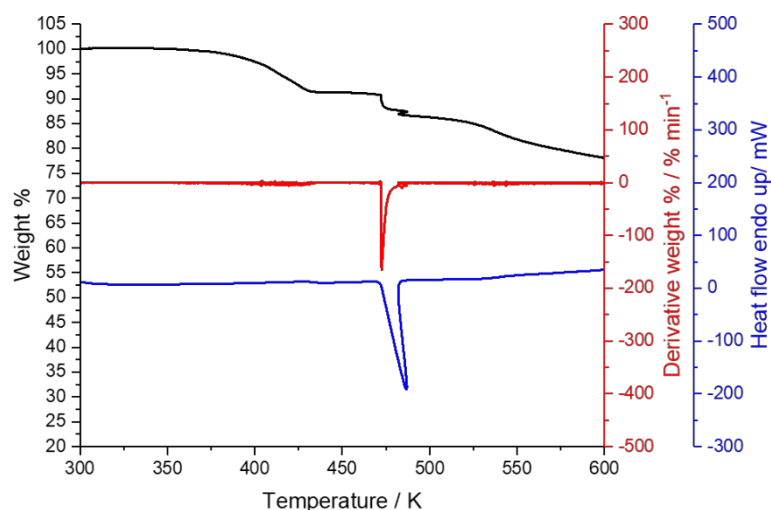


Figure S2. TGA analysis (black) of **1^{Et}·MeCN** at 300 – 600 K with a heating rate of 10 K min⁻¹. The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue.^{††}

^{††} A temporary over heating of the sample and nominal change in the heating rate caused by highly exothermic (decomposition) event briefly effects the appearance of the heat flow curve near the event.

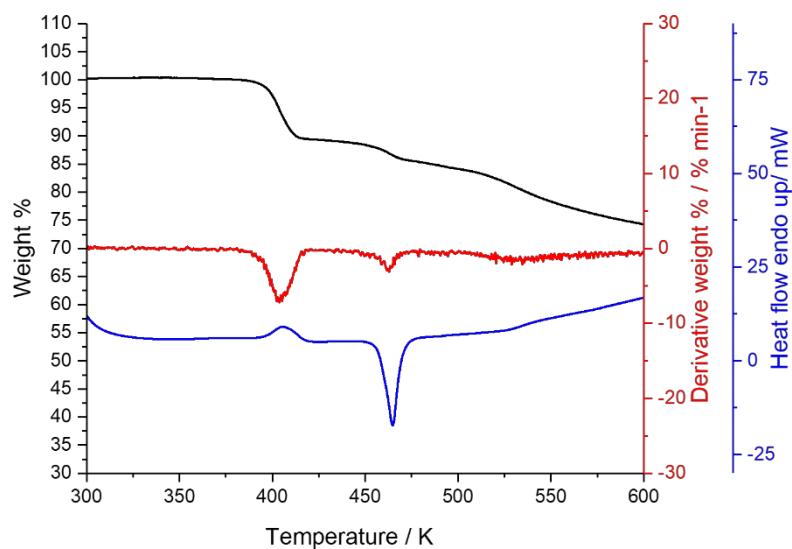


Figure S3. TGA analysis (black) of $1^{\text{Et}}\cdot\text{EtCN}$ at 300– 600 K with a heating rate of 10 K min^{-1} . The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue.

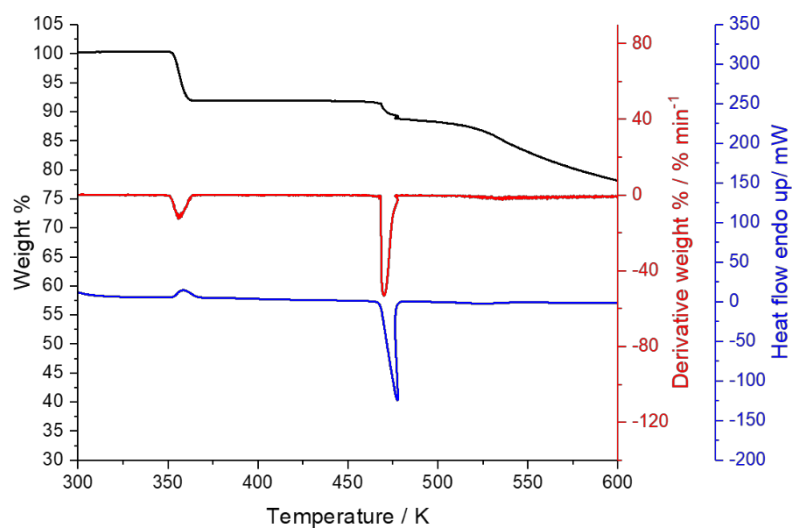


Figure S4. TGA analysis (black) of $1^{\text{Pr}}\cdot\text{MeCN}$ at 300 – 600 K with a heating rate of 10 K min^{-1} . The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue. ^{††}

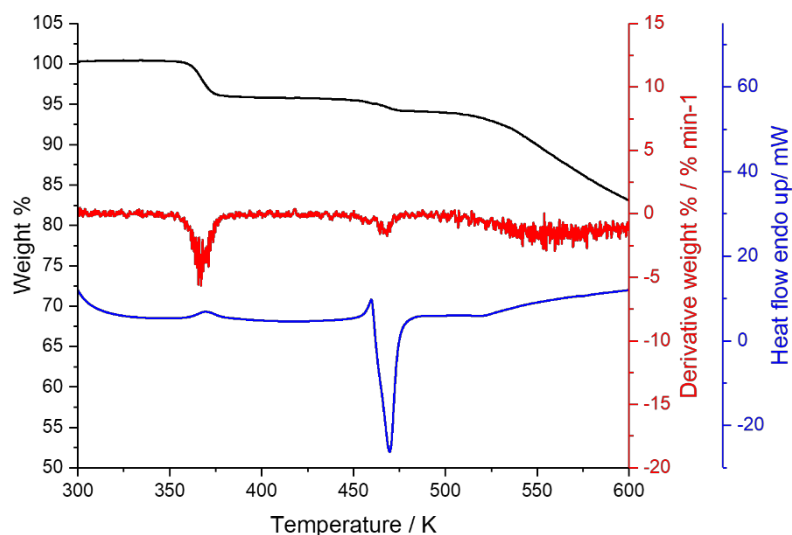


Figure S5. TGA analysis (black) of $1^{\text{Bu}} \cdot 0.5\text{MeCN}$ at 300 – 600 K with a heating rate of 10 K min^{-1} . The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue.

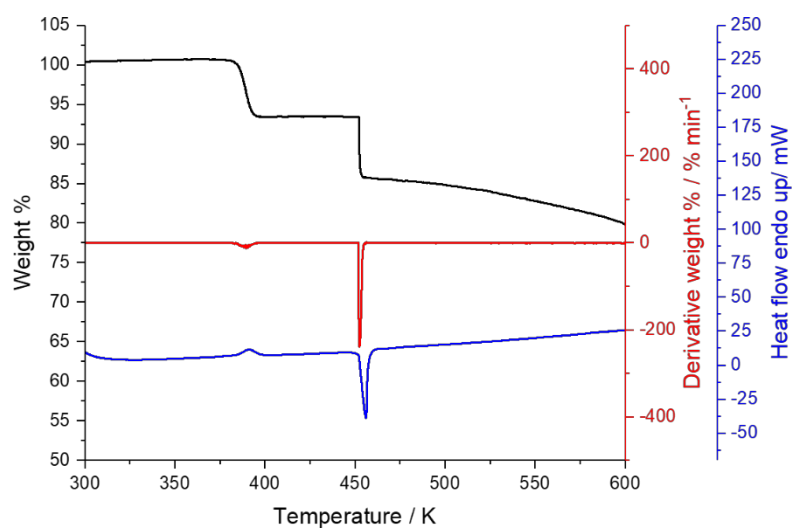


Figure S6. TGA analysis (black) of $2^{\text{Et}} \cdot \text{MeCN}$ at 300 – 600 K with a heating rate of 10 K min^{-1} . The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue. ††

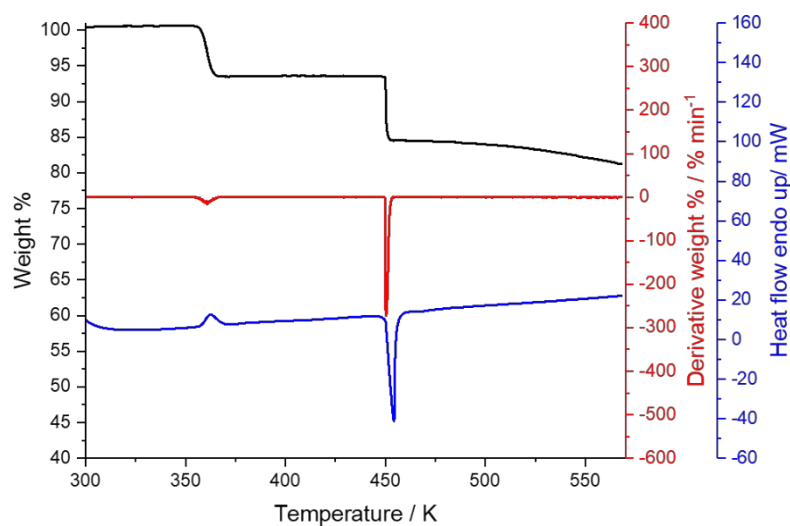


Figure S7. TGA analysis (black) of $2^{\text{Pr}}\cdot\text{MeCN}$ at 300 – 600 K with a heating rate of 10 K min^{-1} . The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue. ^{††}

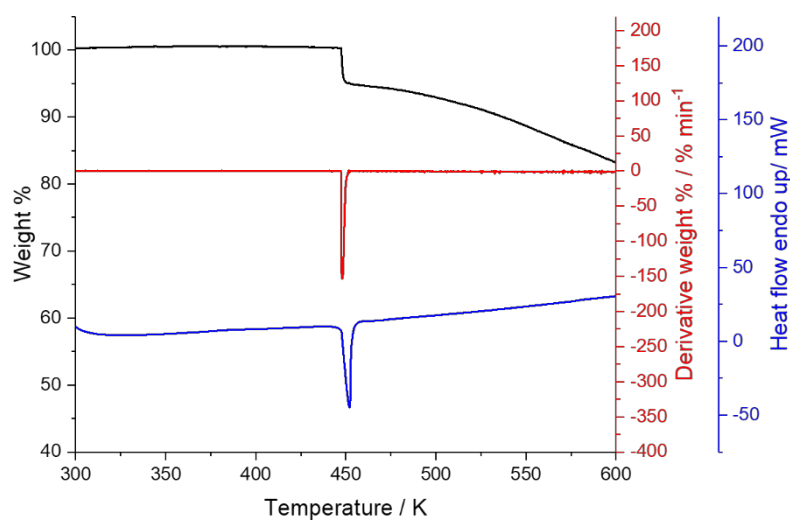


Figure S8. TGA analysis (black) of 2^{Bu} at 300 – 600 K with a heating rate of 10 K min^{-1} . The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue. ^{††}

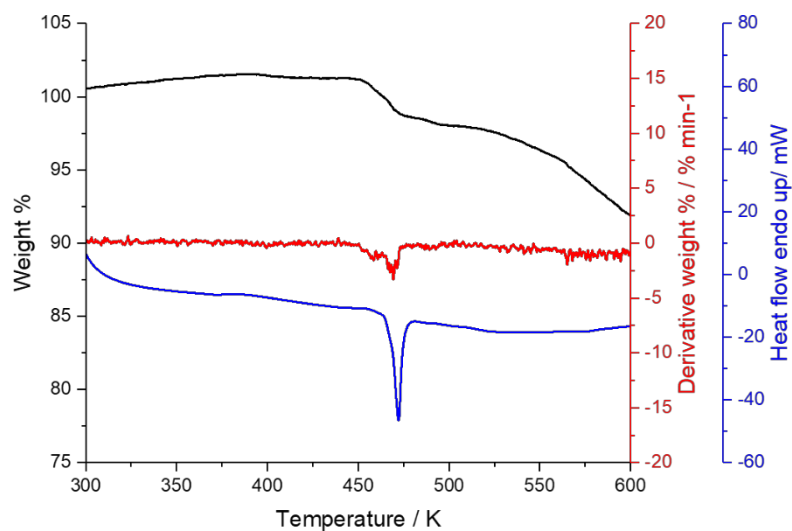


Figure S9. TGA analysis (black) of **1^{Pr}** at 300 – 600 K with a heating rate of 10 K min⁻¹. The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue.

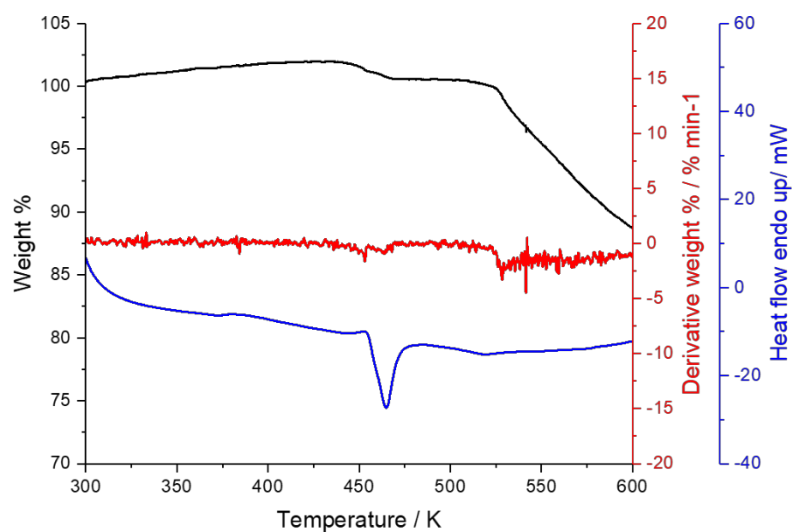


Figure S10. TGA analysis (black) of **1^{Bu}** at 300 – 600 K with a heating rate of 10 K min⁻¹. The derivative TG curve (red) shows %-weight loss per minute, whereas the heat flow curve is given in blue.

Variable temperature single crystal and powder X-ray crystallography

High temperature X-ray data collection. High temperature crystallography (> 273 K) was performed on crystals mounted on glass fibers using a high temperature Wacker silicone paste that may give rise to spurious diffraction peaks (epoxy was found to be too reactive with these systems). In the case of **1^{Pr}**, **1^{Bu}**, and **2^{Bu}**, several peaks attributed to the paste were excluded from data refinements. In the case of **1^{Pr}** and **2^{Bu}** the crystals were comparatively small and poorly crystalline compared to **1^{Bu}**, which led to weak or diffuse data at high angles.

Disorder. The use of restraints DFIX, DANG, and ISOR, and the EADP constraint were needed to model the disordered *N*-butyl chains and/or solvent molecules in **IV** (**E = S; R = Bu**), **1^{Bu}**, and **1^{Bu}·0.5MeCN** because of a combination of poor crystallinity, weak data, high temperature data collection, and/or unresolved twinning effects. A standard DFIX of 1.5 Å was used for all single C–C bonds and occasionally DANG were needed to restrain the C–C–C angles of the *N*-butyl chains. The atom occupancies were refined freely and were constrained to their proximate fractional occupancies only when necessary. ISOR restraint and the EADP constraint were necessary, especially for high temperature data, where large anisotropy and small partial occupancies (*ca.* 0.33) of the carbon atoms were encountered. In the two independent data sets obtained for **1^{Bu}·0.5MeCN**, both positional disorder of the solvent molecules, pyridinium ring, and *N*-butyl chains were refined. To avoid over parameterization, especially in the case of **1^{Bu}·0.5MeCN**, it was refined as a single-component, thus only the most important components of the disorder were modelled to demonstrate the connectivity and crystal packing effects of the structure. The high degree of disorder gives rise to the large $\Delta\rho_{\max}/\Delta\rho_{\min}$ ($\text{e} \cdot \text{\AA}^{-3}$) found in both data sets that are likely associated with unresolved disorder of the DTDA ring (the heaviest atom, *i.e.* sulfur, in this salt). The combination of weak data, disorder, and twinning leads to high values of R_{int} and goodness-of-fit on F_2 .

Twinning. In all cases, several attempts were made to grow better quality crystals, but in our hands, this was unsuccessful and the non-merohedral twinning or multicrystalline behavior of the crystals were persistent in **IV** (**E = S; R = Pr**), **IV** (**E = Se; R = Et, Bu**), **2^{Bu}**, and **1^{Bu}·0.5MeCN**. All data sets were processed as two-component twins using the twin/multicrystal function of CrysAlis^{PRO} (v. 39.46). For **IV** (**E = S; R = Pr**), **IV** (**E = Se; R = Et**), and **2^{Bu}**, the unindexed peaks were less than 13 % of the total reflections. While the percentage of unindexed peaks were significantly higher for **IV** (**E = Se; R = Bu**) and **1^{Bu}·0.5MeCN**, 23 and 43 % of the total, respectively, and the use of additional twin components (multicrystal) did not lead to improvements in the data reduction as a third component accounted for less than 5 % of the total reflections.

For **1^{Bu}·0.5MeCN**, only very small needle-like crystals were obtained and the non-merohedral twinning was persistent across multiple crystal growth attempts. Two separate data sets were recorded and identical connectivity and crystal packing was established for each set. For one dataset, the indexing and refinement of a two-component twin was performed in CrysAlis^{PRO} (v. 39.46). Different mask size (0.5 – 1.5) were tested in attempts to improve deconvolution of the peaks of the two twin components. All data sets were processed with 3D profile fitting using smart back-ground correction (using a frame range of $n = 3$) as the data was weak, especially at high angles. In the second data set of **1^{Bu}·0.5MeCN**, the indexing and refinement was performed as a single component (*ca.* 60 % of reflections) since there was no additional components that were indexed to more than 5 % of all reflections. An improvement of I/σ and R_{int} were obtained, however, the data completeness to 0.83 Å resolution was low (*ca.* 87 %) because of the very weak or absent reflections at high angles (Figures A2 and A3, Appendix 1). Overall, the combination of small crystal size and poor crystallinity contributes to the poor quality data obtained for both data sets of **1^{Bu}·0.5MeCN** (Table A1 and Figures A1–A4, Appendix 1).

In both datasets, the solvent MeCN could be located from the electron density map and was found to be disordered over at least two positions. It did not interact strongly with the DTDA ring as found in related solvates (see main text). The pyridinium rings and *N*-butyl chains were also disordered in both data sets. We note that the Pawley refinement of the unit cell parameters of the bulk phase of **1^{Bu}·0.5MeCN** is consistent with the single crystal X-ray diffraction data, suggesting the absence of noticeable proportions of additional impurity phases. Moreover, the analytical EA and TGA data are also consistent with the stoichiometry of one DTDA and one TCNQ per one-half of MeCN solvent molecule, as established by single crystal X-ray diffraction.

Comments on Single Crystal X-ray Crystallographic Data.

IV. The A- and/or B-alerts given below are common for all the triflate salts of **IV**. These short electrostatic interactions between the DTDA/DSDA radical-cation and the triflate anion are typical for these salts but are currently not recognized by Platon.

IV (E = S; R = Et):

Alert level B

PLAT430_ALERT_2_B Short Inter D...A Contact S2 ..01 . 2.82 Ang.
 x,y,z = 1_555 Check

IV (E = Se; R = Et):

Alert level A

PLAT430_ALERT_2_A Short Inter D...A Contact Se2 ..01 . 2.87 Ang.
1+x, y, z = 1_655 Check

IV (E = S; R = Pr):

Alert level A

PLAT430_ALERT_2_A Short Inter D...A Contact S2 ..01 . 2.81 Ang.
-1+x, y, z = 1_455 Check

Alert level B

PLAT430_ALERT_2_B Short Inter D...A Contact S1 ..01 . 2.87 Ang.
-1+x, y, z = 1_455 Check

IV (E = Se; R = Pr): No alert given in the CheckCIF as the shortest Se---O interaction is ≥ 2.9 Å.

IV (E = S; R = Bu):

Alert level A

PLAT430_ALERT_2_A Short Inter D...A Contact S1 ..01 . 2.75 Ang.
x, y, z = 1_555 Check

Alert level B

PLAT430_ALERT_2_B Short Inter D...A Contact S2 ..01 . 2.88 Ang.
x, y, z = 1_555 Check

IV (E = S; R = Bu):

Alert level A

PLAT430_ALERT_2_A Short Inter D...A Contact Se2 ..01 . 2.87 Ang.
-1+x, y, z = 1_455 Check

1^{Et}·EtCN and **1^{Pr}·MeCN**. The B-alerts given below are due to short intermolecular interactions between the electronegative nitrogen atom of the R–CN (R = Et, Me) fragment of the solvent and the electropositive region of the electrostatic potential surface (σ -hole) located at the centroid of the S–S bond of the DTDA radical-cation.⁵

1^{Et}·EtCN:

Alert level B

PLAT430_ALERT_2_B Short Inter D...A Contact S2 ..N8 . 2.89 Ang.
-1+x, y, z = 1_455 Check


1^{Pr}·MeCN:

Alert level B

PLAT430_ALERT_2_B Short Inter D...A Contact S1 ..N8 . 2.90 Ang.
1+x, y, z = 1_655 Check

1^{Bu}. The B-alert given below is due to short intermolecular interactions between the electronegative nitrogen atom of the R–CN (R = Et, Me) fragment of the solvent and the electropositive region of the electrostatic potential surface (σ -hole) located at the centroid of the S–S bond of the DTDA radical-cation.⁵


1^{Bu}:

 **Alert level B**

PLAT430_ALERT_2_B Short Inter D...A Contact S2 ..N4 . 2.87 Ang.
x, y, z = 1_555 Check

1^{Bu}·0.5MeCN, two component twin. The individual B-alerts are given below with their responses. Full details and discussion of the disorder, twinning, and overall weak data are given above and in Appendix 1, below.

1^{Bu}·0.5MeCN:

 **Alert level B**

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 36% Check

Author Response: Overall, the data is weak, and all the tested crystals were invariably twinned/multi-crystals.

PLAT082_ALERT_2_B High R1 Value 0.16 Report

Author Response: The high R_1 value is a result of poor quality data and the considerable disorder of the *N*-butyl-substituents and solvent molecules that could not be fully modelled because further refinement of the disorder using a meaningful scheme failed. The model demonstrates the connectivity of the molecules and the major components of the disordered alkyl chains and the solvent. The solvent MeCN was found from electron density maps and was modelled over two positions with partial (0.50) occupancy to show that it does occupy space between the alkyl chains and the heterocyclic rings and is likely disordered over several positions.

PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) 0.44 Report

Author Response: This can be assigned to poor quality data, combined with twinning and disorder effects in the chemical species.

PLAT097_ALERT_2_B Large Reported Max. (Positive) Residual Density 2.88 eA-3


Author Response: This can be assigned to disorder or twinning, as the positive residual density appears to be systematic and consistent with the position and metrics (*ca.* 2 Å) of the heavy sulfur atoms (S–S bond) of the DTDA rings.

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds 0.02232 Ang.

Author Response: The low bond precision is due to poor quality data.


1^{Bu}·0.5MeCN, single component. The individual A- and B-alerts are given below with their responses. Full details and discussion of the disorder, twinning, and overall weak data are given above and in Appendix 1, below.

1^{Bu}·0.5MeCN:

 **Alert level A**

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.865 Why?

Author Response: The poor crystallinity and weak or absence of diffraction at high angles results in lower data resolution and completeness of data.

 **Alert level B**

PLAT082_ALERT_2_B High R1 Value 0.16 Report

Author Response: The high R_1 value is a result of poor quality data and the considerable disorder of the *N*-butyl-substituents, pyridinium rings, and solvent molecules that could not be fully modelled because further refinement of the disorder using a meaningful scheme failed. The model demonstrates the connectivity of the molecules and the major components of the disordered alkyl chains and the solvent.

PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) 0.45 Report

Author Response: This can be assigned to poor quality data, combined with twinning and disorder effects in the chemical species.

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds 0.01413 Ang.

Author Response: The low bond precision is due to poor quality data.

Table S6. Crystallographic data for HT-1^{Pr}, LT-1^{Bu}, and HT-1^{Bu}.

Compound	HT-1 ^{Pr}	LT-1 ^{Bu}	HT-1 ^{Bu}
CCDC Code	2181988	2181986	2181989
Formula	C ₂₁ H ₁₅ N ₇ S ₂	C ₂₂ H ₁₇ N ₇ S ₂	C ₂₂ H ₁₇ N ₇ S ₂
Molecular weight (g·mol ⁻¹)	429.52	443.54	443.54
<i>T</i> (K)	370.00(10)	120.00(10)	370.00(10)
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	8.5769(13)	6.8439(3)	7.0368(2)
<i>b</i> (Å)	8.6659(10)	11.1768(5)	11.0204(5)
<i>c</i> (Å)	14.2670(10)	14.2752(7)	14.6680(3)
α (°)	79.378(7)	93.617(4)	95.102(3)
β (°)	83.874(8)	90.731(4)	90.443(2)
γ (°)	83.814(10)	106.931(4)	105.997(3)
<i>V</i> (Å ³)	1032.1(2)	1041.99(9)	1088.48(6)
<i>Z</i>	2	2	2
ρ_{calc} (g·cm ⁻³)	1.382	1.414	1.353
μ (mm ⁻¹)	2.529	0.281	2.414
<i>F</i> (000)	444.0	460.0	460.0
Crystal size (mm ³)	0.109 × 0.093 × 0.03	0.253 × 0.197 × 0.045	0.222 × 0.194 × 0.075
Radiation (Å)	Cu K α (λ = 1.54184)	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)
2 θ range for data collection (°)	6.328 to 134.766	4.928 to 57.918	6.052 to 144.858
Reflections collected	5803	17696	15984
Independent reflections	3671	4920	4231
	[<i>R</i> _{int} = 0.1302, <i>R</i> _{sigma} = 0.1326]	[<i>R</i> _{int} = 0.0279, <i>R</i> _{sigma} = 0.0234]	[<i>R</i> _{int} = 0.0242, <i>R</i> _{sigma} = 0.0172]
Data/restraints/parameters	3671/0/272	4920/0/281	4231/25/283
Goodness-of-fit on <i>F</i> ²	1.040	1.170	1.053
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1130, <i>wR</i> ₂ = 0.2594	<i>R</i> ₁ = 0.0720, <i>wR</i> ₂ = 0.1941	<i>R</i> ₁ = 0.0650, <i>wR</i> ₂ = 0.1880
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1598, <i>wR</i> ₂ = 0.3183	<i>R</i> ₁ = 0.0746, <i>wR</i> ₂ = 0.1952	<i>R</i> ₁ = 0.0715, <i>wR</i> ₂ = 0.1967
Largest diff. peak/hole / e Å ⁻³	0.79/−0.76	0.69/−0.51	0.51/−0.76

^a Value for *R*_{int} is determined for the major component of the twin refinement.

Table S7. Refined unit cell parameters of **1^{Pr}** and **1^{Bu}·0.5MeCN** determined by Pawley analysis of bulk powder (PXR) along with the corresponding single crystal data values (SCXR).

Parameters	1 ^{Pr}			1 ^{Bu} ·0.5MeCN	
	SCXR	SCXR	PXR	SCXR	PXR
<i>T</i> (K)	120	370	293	120	293
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	8.4212(5)	8.5769(12)	8.549(3)	13.442(3)	13.578(3)
<i>b</i> (Å)	8.4510(5)	8.6659(10)	8.569(2)	13.464(3)	13.533(5)
<i>c</i> (Å)	14.1533(8)	14.2670(10)	14.242(4)	13.959(5)	14.080(6)
α (°)	84.671(5)	79.378(7)	79.603(1)	92.94(2)	93.032(2)
β (°)	80.088(5)	83.874(8)	84.131(2)	107.47(3)	107.570(3)
γ (°)	85.166(4)	83.814(10)	84.217(1)	111.98(2)	112.206(6)
<i>V</i> (Å ³)	985.54	1032.08	1017.10	2196.1	2242.40
<i>R</i> _p ^a			0.0359		0.0449
<i>R</i> _{wp} ^a			0.0494		0.0607
<i>R</i> ₁	0.0528	0.1130		0.1607	
<i>wR</i> ₂	0.1726	0.3183		0.3905	
Goodness-of-fit			1.4988		1.0901

^a *R*_p and *R*_{wp} indicate *R*-profile and weighted *R*-profile factors from Pawley analyses, respectively.

Table S8. Refined unit cell parameters of **1^{Pr}·MeCN**, **1^{Bu}** and **2^{Bu}** determined by Pawley analysis of bulk powder (PXRD) along with the corresponding single crystal data values (SCXRD).

Parameters	1^{Pr}·MeCN		1^{Bu}		2^{Bu}	
	SCXRD	PXRD	SCXRD	PXRD	SCXRD	PXRD
<i>T</i> (K)	120	293	370	293	120	293
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	8.8121(5)	8.837(8)	7.0368(2)	6.846(2)	6.8562(4)	6.963(2)
<i>b</i> (Å)	10.8960(6)	10.877(9)	11.0204(5)	11.018(3)	11.2499(12)	11.182(4)
<i>c</i> (Å)	11.7291(6)	11.87(1)	14.6680(3)	14.653(9)	14.3107(8)	14.617(5)
α (°)	98.130(4)	98.773(7)	95.102(3)	94.810(9)	94.006(7)	94.789(2)
β (°)	92.145(4)	92.343(6)	90.443(2)	89.84(1)	90.362(5)	90.370(2)
γ (°)	97.591(5)	97.050(8)	105.997(3)	106.334(6)	106.853(7)	106.346(3)
<i>V</i> (Å ³)	1103.29	1117.44	1088.48	1056.71	1053.41	1087.72
<i>R</i> _p ^a		0.0450		0.0326		0.0340
<i>R</i> _{wp} ^a		0.0764		0.0483		0.0341
<i>R</i> ₁	0.0387		0.0570		0.0757	
<i>wR</i> ₂	0.0946		0.1692		0.2176	
Goodness-of-fit		1.6728		3.43748		1.4164

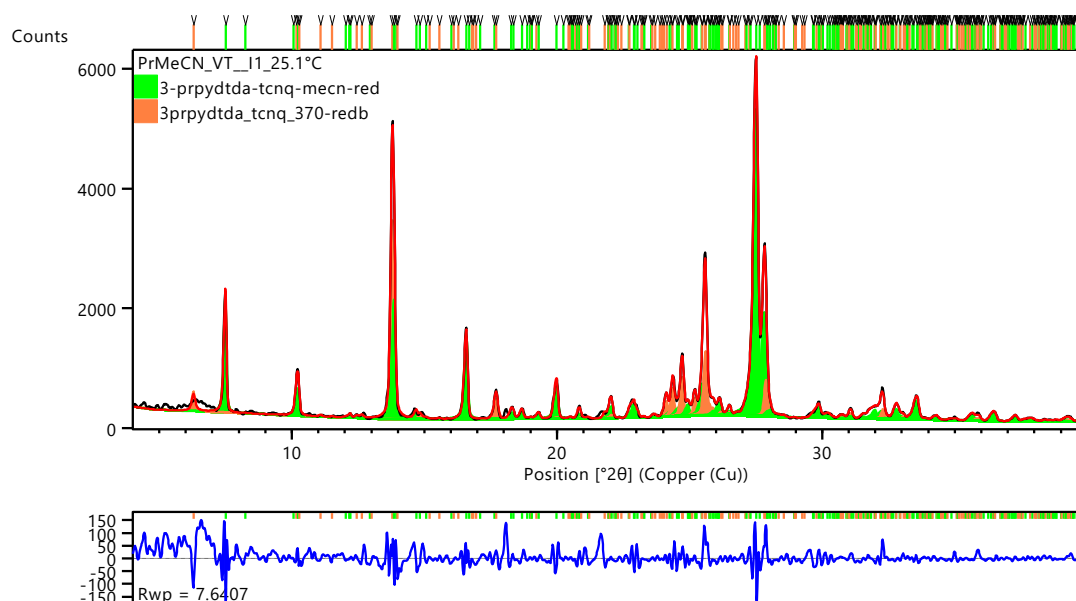


Figure S11. Pawley refinement plot of $1^{\text{Pr}}\cdot\text{MeCN}$ at 298 K from variable temperature powder X-ray measurement. Experimental pattern is shown in black and refined profile in red. Green colored bars on top correspond to characteristic Bragg peak positions of the assigned phase and orange bars indicate peak positions of residual desolvated phase 1^{Pr} . The difference plot of experimental vs. refined profile is shown below in blue.

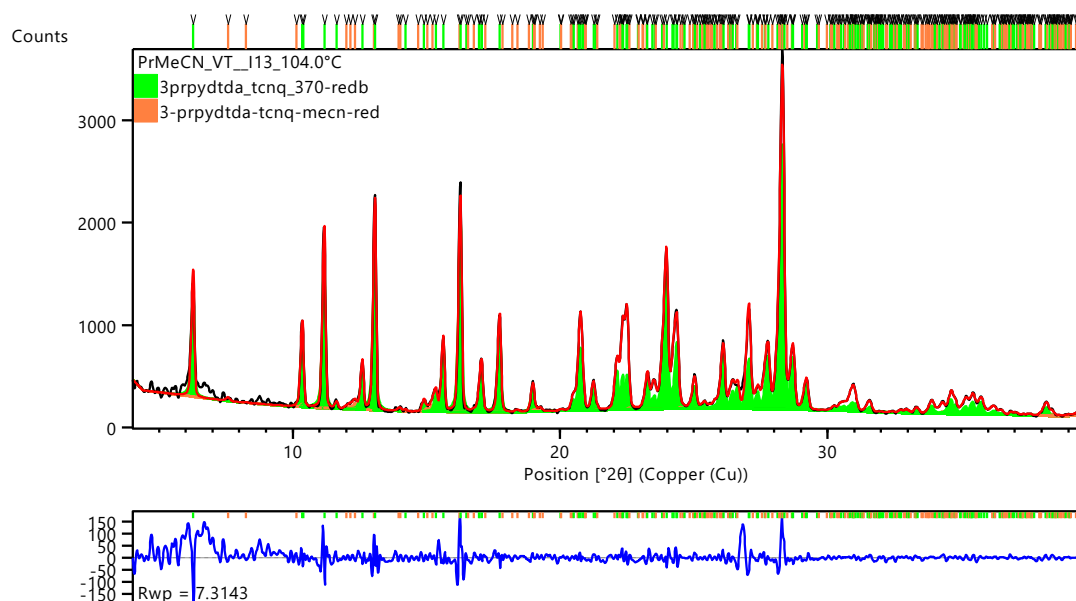


Figure S12. Pawley refinement plot of 1^{Pr} at 377 K from variable temperature powder X-ray measurement. Experimental pattern is shown in black and refined profile in red. Green colored bars on top correspond to characteristic Bragg peak positions of the assigned phase and orange bars indicate peak positions of residual solvated phase $1^{\text{Pr}}\cdot\text{MeCN}$. The difference plot of experimental vs. refined profile is shown below in blue.

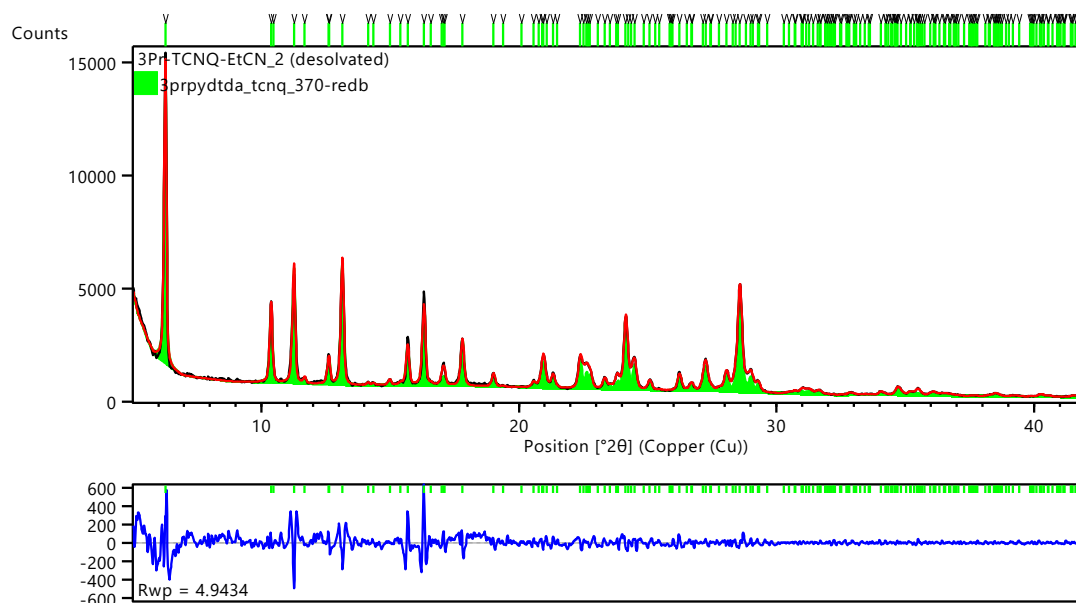


Figure S13. Pawley refinement plot of **1^{Pr}**. Experimental pattern is shown in black and refined profile in red. Green colored bars on top correspond to characteristic Bragg peak positions of the assigned phase. The difference plot of experimental vs. refined profile is shown below in blue.

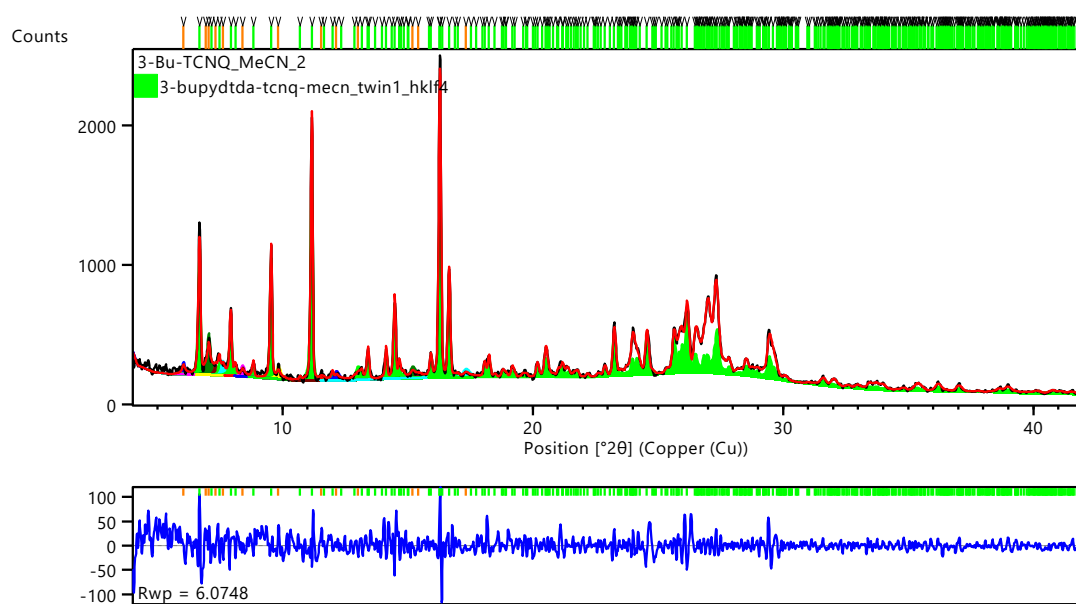


Figure S14. Pawley refinement plot of **1^{Bu}-0.5MeCN**. Experimental pattern is shown in black and refined profile in red. Green colored bars on top correspond to characteristic Bragg peak positions of the assigned phase. A few orange bars indicate peak positions of residual impurity phase. The difference plot of experimental vs. refined profile is shown below in blue.

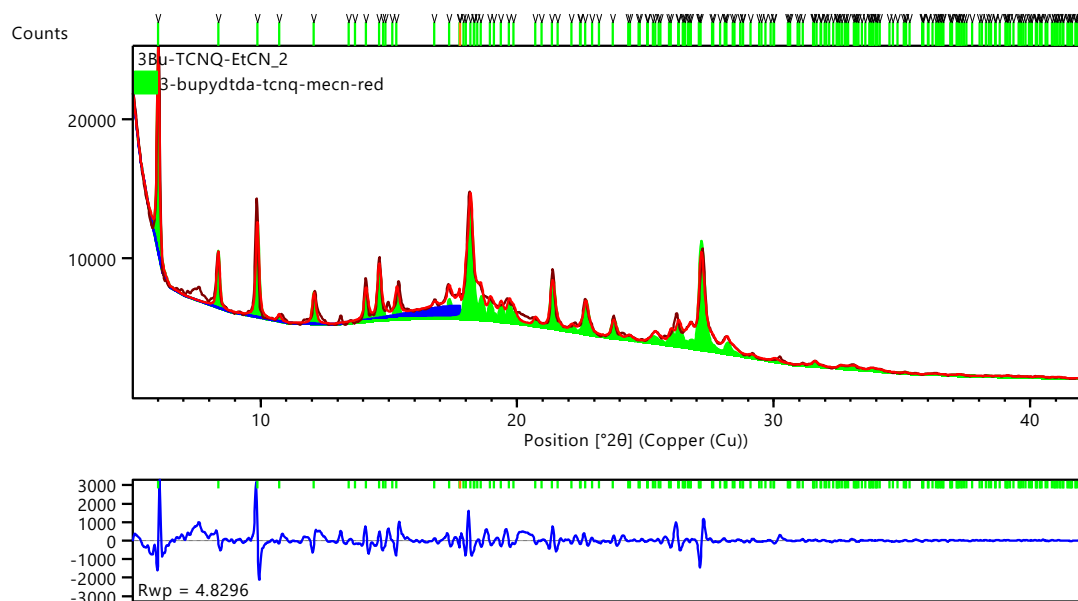


Figure S15. Pawley refinement plot of **1^{Bu}**. Experimental pattern is shown in black and refined profile in red. Green colored bars on top correspond to characteristic Bragg peak positions of the assigned phase. The difference plot of experimental vs. refined profile is shown below in blue.

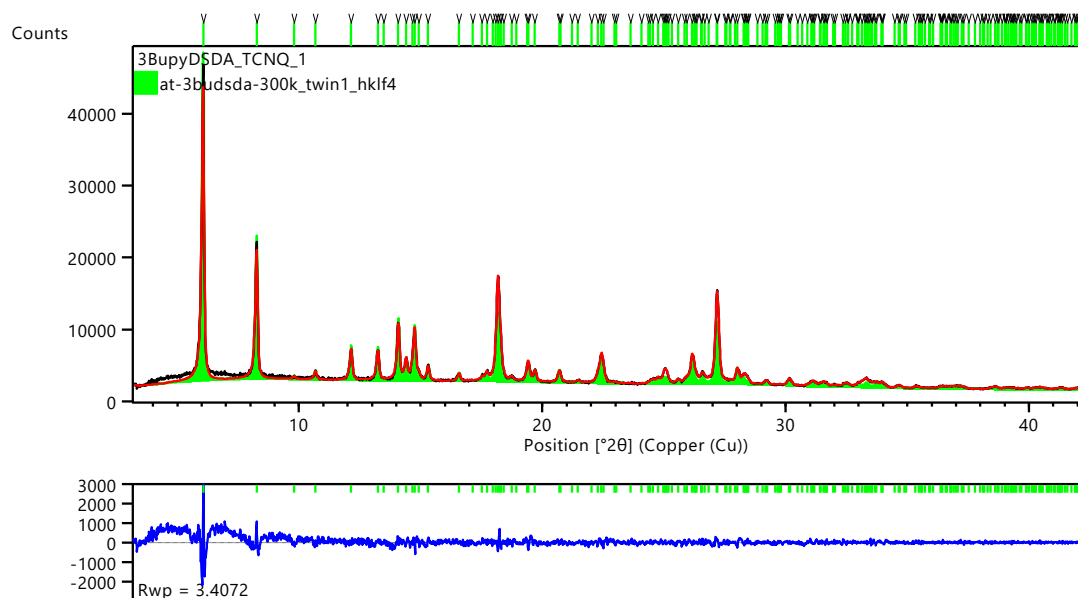


Figure S16. Pawley refinement plot of **2^{Bu}**. Experimental pattern is shown in black and refined profile in red. Green colored bars on top correspond to characteristic Bragg peak positions of the assigned phase. The difference plot of experimental vs. refined profile is shown below in blue.

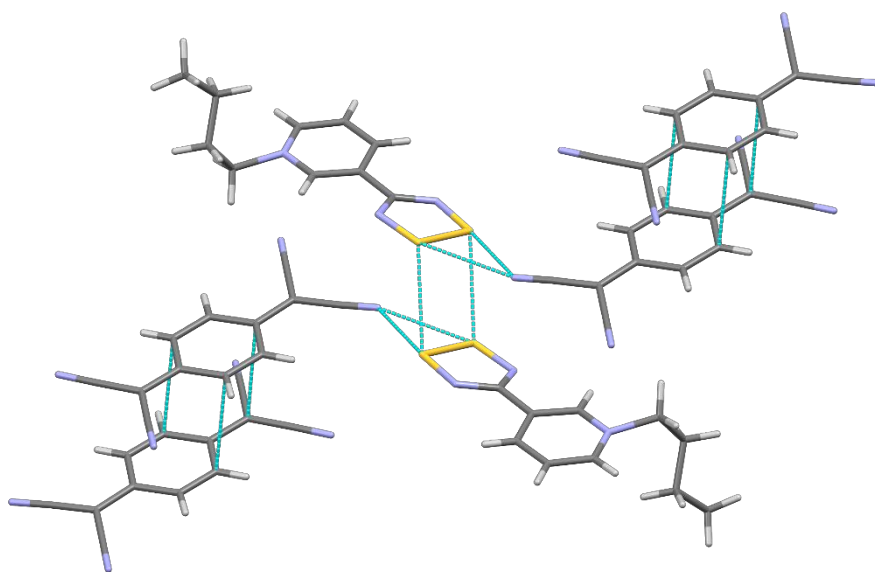


Figure S17. View of intermolecular S...N, S...S, and C...C contacts (blue) found between *trans*-antirafacial dimers of DTDA radical-cations and non-eclipsed dimers of TCNQ anion-radicals in **1^{Bu}** at 370 K.

Density functional theory calculations

All calculations were performed with the Gaussian 16 suite of programs.⁶

Table S9. Energies (a.u.) of singlet and triplet (in parenthesis) state DTDA and TCNQ dimers calculated using the geometries they adopt in the crystal structures of low (LT) and high temperature (HT) structures of **1^{Pr}** and **1^{Bu}**.

Compound	DTDA...DTDA		TCNQ...TCNQ	
	PBE1PBE	LC- ω hPBE	PBE1PBE	LC- ω hPBE
LT- 1^{Pr}	-2618.61379786 (-2618.60181287)	-2619.07529858 (-2619.06823790)	-1356.29832417 (-1356.29371070)	-1356.75104265 (-1356.74784725)
HT- 1^{Pr}	-2618.59820441 (-2618.58990620)	-2619.06042189 (-2619.05557450)	-1356.29516048 (-1356.29340322)	-1356.74562957 (-1356.74435876)
LT- 1^{Bu}	-2697.18361146 (-2697.16975869)	-2697.69510665 (-2697.68697353)	-1356.29888312 (-1356.29163808)	-1356.75031909 (-1356.74538781)
HT- 1^{Bu}	-2697.14701796 (-2697.13818688)	-2697.66450243 (-2697.65934129)	-1356.29617172 (-1356.29179977)	-1356.75296754 (-1356.75002669)

Appendix 1

Table A1. Comparison of crystallographic data for two-independent data sets collected for **1^{Bu}·0.5MeCN** and refined as a two-component twin and as a single component.

Compound	1^{Bu}·0.5MeCN twin ^a	1^{Bu}·0.5MeCN single component ^b
CCDC Code	2182780	2207551
Formula	C ₄₆ H ₃₇ N ₁₅ S ₄	C ₄₆ H ₃₇ N ₁₅ S ₄
Molecular weight (g·mol ⁻¹)	928.14	928.14
<i>T</i> (K)	120.00(10)	120.00(10)
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	13.442(3)	13.4272(3)
<i>b</i> (Å)	13.464(3)	13.468(3)
<i>c</i> (Å)	13.959(5)	13.922(5)
α (°)	92.94(2)	93.021(17)
β (°)	107.47(3)	107.522(15)
γ (°)	111.98(2)	112.055(15)
<i>V</i> (Å ³)	2196.1(11)	2185.6(8)
<i>Z</i>	2	2
ρ_{calc} (g·cm ⁻³)	1.401	1.410
μ (mm ⁻¹)	2.426	2.437
<i>F</i> (000)	964.0	964.0
Crystal size (mm ³)	0.215 × 0.042 × 0.015	0.197 × 0.031 × 0.021
Radiation (Å)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for data collection (°)	6.754 to 137.994	6.778 to 137.982
Reflections collected	11545	9623
Independent reflections	11545 [<i>R</i> _{int} = 0.2257 ^c , <i>R</i> _{sigma} = 0.1951]	6978 [<i>R</i> _{int} = 0.0603, <i>R</i> _{sigma} = 0.1402]
Data/restraints/parameters	11545/236/492	6978/136/571
Goodness-of-fit on <i>F</i> ²	1.109	1.294
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1615 <i>wR</i> ₂ = 0.3889	<i>R</i> ₁ = 0.1569 <i>wR</i> ₂ = 0.3997
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.2663 <i>wR</i> ₂ = 0.4363	<i>R</i> ₁ = 0.2092 <i>wR</i> ₂ = 0.4483
Largest diff. peak/hole / e Å ⁻³	2.88/−0.88	1.57/−0.81

^a For the purpose of comparison, the crystal data for **1^{Bu}·0.5MeCN** from Table 1 has been reproduced. This data set was refined as a two-component twin.

^b A second, independent, data set for **1^{Bu}·0.5MeCN** has been collected and refined as a single component. See Figures A2–A4.

^c Value for *R*_{int} is determined for the major component of the twin refinement.

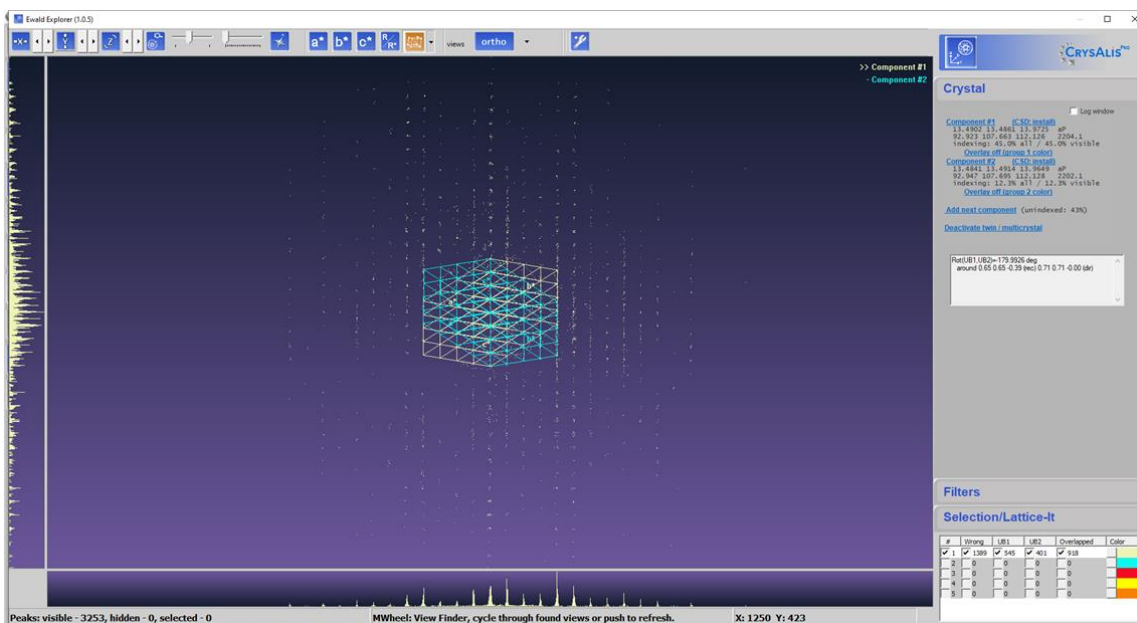


Figure A1. View of the orthogonal projection of peaks in reciprocal space of the two-component twin refinement of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$. Major component is given in white while the minor component is given in bright blue.

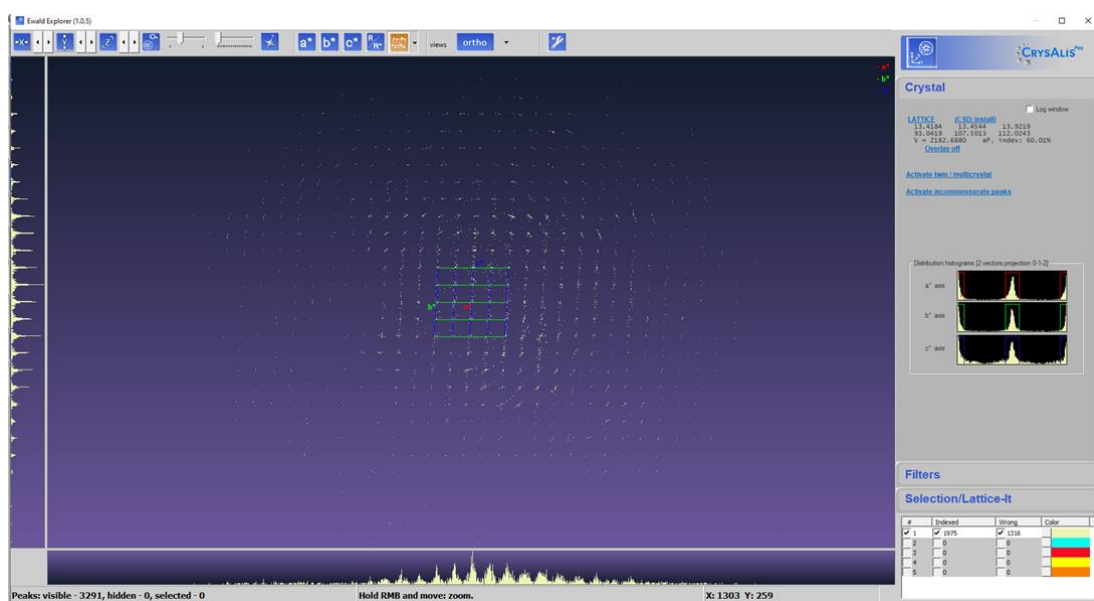


Figure A2. View of the orthogonal projection of peaks in reciprocal space of the single component refinement of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$.

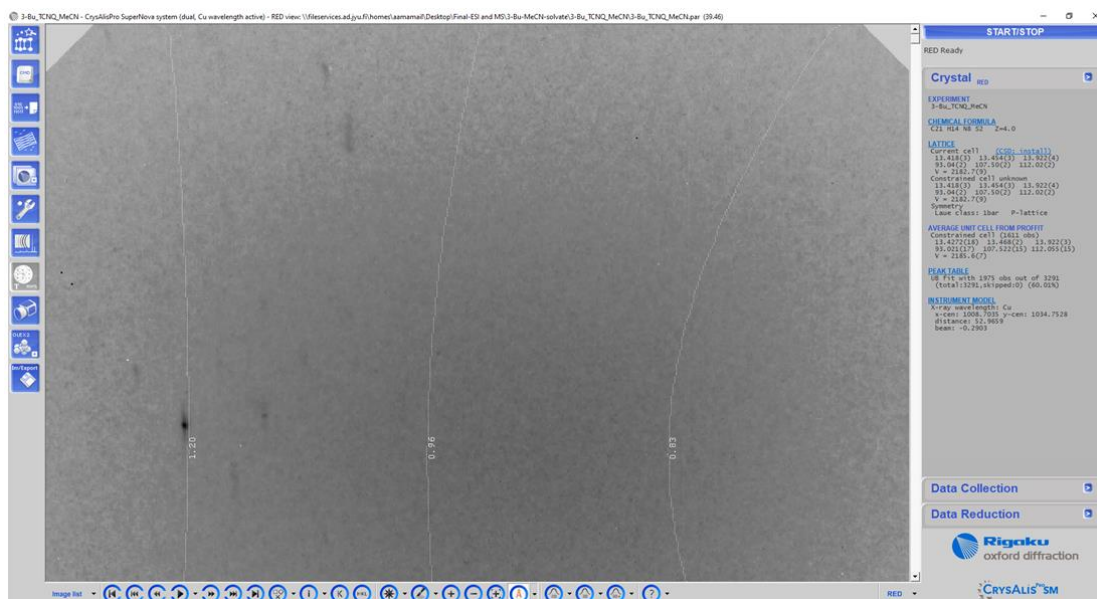


Figure A3. Visualization of a single high angle frame (at 2k) in CrysAlisPro (39.46) from the single component data set of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$ with an overlay of resolution rings given in white. Note both the weak and diffuse peaks beyond 1.20 Å resolution and the absence of defined peaks beyond 0.96 Å.

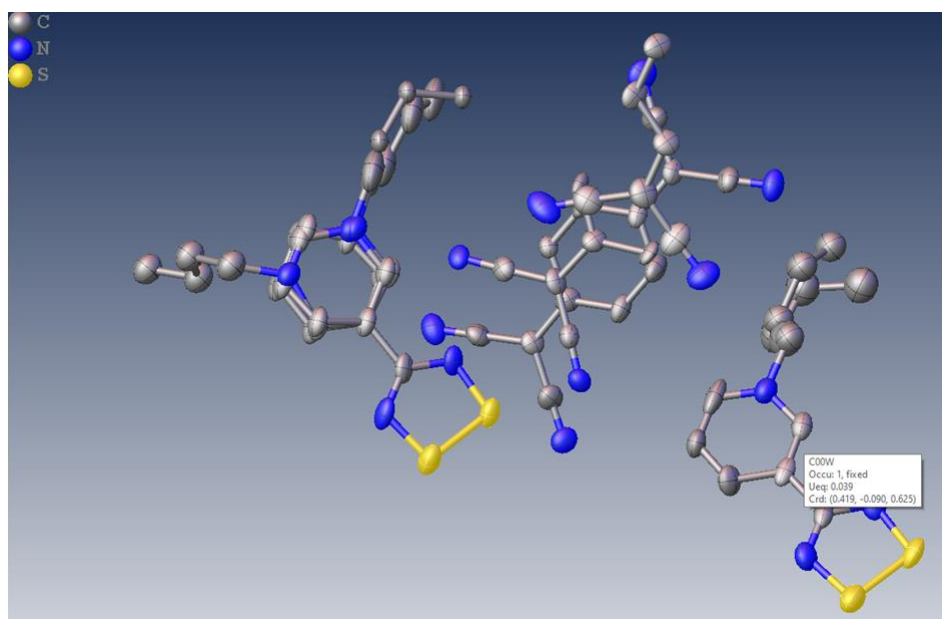


Figure A4. Representative view of the refined disorder of *N*-butyl chains and pyridinium rings from the single component data set of $1^{\text{Bu}}\cdot 0.5\text{MeCN}$ prepared using Olex2 (v 1.2). Hydrogen atoms and disordered solvent molecules are omitted for clarity.

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