

Metal-free reduction of the greenhouse gas sulfur hexafluoride, formation of SF₅ containing ion pairs and the application in fluorinations

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A protocol for the fast and selective two-electron reduction of the potent greenhouse gas sulfur hexafluoride (SF₆) by organic electron donors at ambient temperature has been developed. The reaction yields solid ion pairs consisting of donor dications and SF₅-anions which can be effectively used in fluorination reactions.

Introduction

Sulphur hexafluoride is a non-flammable, odourless and colourless gas of high density.¹ The unique physical and chemical properties of SF₆ makes it suitable in specialized electrical equipment, commercial products as well as in scientific and industrial processes. Due to its great arc-quenching ability, almost 80% of all SF₆ produced is used as insulator and fire suppression agent in high-voltage circuit breakers.² Another application of SF₆ consists in its use as a blanketing, sound- and thermo-insulating agent in industry³ and as a contrast agent for ultrasound imaging in medicine.⁴ Furthermore, sulphur hexafluoride is applied in the determination of ventilation efficiency as well as in environmental modeling.⁵

However, despite the mentioned applications, SF₆ is a potent greenhouse gas included to Kyoto Protocol.^{6,7} According to the World Meteorological Organization, the atmospheric lifetime of SF₆ is ca 3200 years and its global warming potential is 22450 times higher than that of CO₂.⁸ Therefore, beside the necessity to control the level of SF₆ emissions and development of more efficient trapping techniques,⁹ a methodology to decompose this gas is on demand. Thus, since 1980s several reports on the SF₆ activation followed by the total reduction to compounds containing futile sulfides and fluorides have been published.

Such procedures generally require harsher conditions or/and elemental alkali metals.¹⁰ Polycrystalline silicon, tin oxide and organic polymer layers react with sulphur hexafluoride at high temperature.¹¹ More recently, protocols for the SF₆-activation under milder conditions were reported. These methods require transition metals as catalyst or reducing agent and the products of SF₆-decomposition are fluorides, sulfides or/and silicon and phosphorus fluoro-derivatives.^{12a-f} In addition, the reduction with tetrakis(dimethylamino)ethylene under UV-light irradiation is described.¹³

Results and Discussion

Based on our interest in developing metal-free reactions, we wondered whether purely organic molecules without UV irradiation would be able either to decompose this greenhouse gas at room temperature or to selectively activate it in an efficient manner, allowing simultaneous use of the reduction products in fluorination procedures. In particular, we were also interested in the preparation of the SF₅⁻ anion¹⁴ from sulphur hexafluoride which would potentially allow the formation of SF₅ containing organic molecules which are of considerable interest as well.¹⁵ Taking into account that strong reducing agents react with SF₆ we became interested in the use of organic electron donors.

Organic electron donors¹⁶ are easily accessible in multigram scale and redox reactions can be performed in regular organic solvents with common laboratory glassware. Hence, 2,2'-bipyridyl based organic electron donors **1a**,^{16c} **1b** and a member of viologens,¹⁷ octyl-4,4'-bipyridine **1c** (Figure 1) were chosen as reducing agents. Next to the 2,2'- and 4,4'-bipyridine derivatives we were also interested in evaluating other electron donors including TMBI (Tetramethylbisimidazolidine) **1d**¹⁸ and TDAE (Tetrakis-dimethylaminoethylene) **1e**.¹⁹

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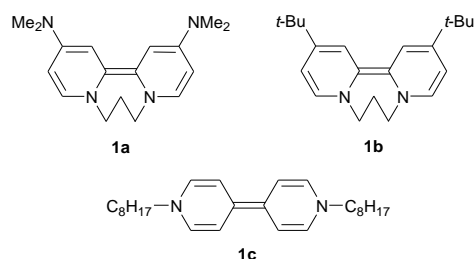
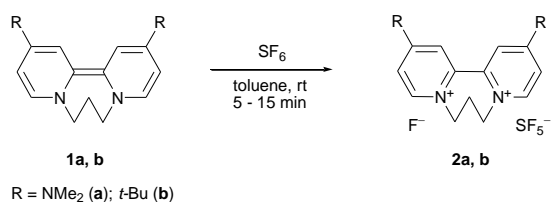


Figure 1 Selected donors **1a-c** for the SF₆-activation.

Interestingly, exposure of **1a** and **1b** in n-hexane or toluene to SF₆ at ambient temperature led to an immediate colour change. The deep-purple colour of the starting material disappeared completely within minutes and formation of a brown microcrystalline precipitate was observed (**2a** and **2b**, Scheme 1).



Scheme 1 Reduction of SF₆ by organic electron donors.

The *in situ* ¹⁹F{¹H} NMR analysis of the supernatant solution showed, except of the residual SF₆, no fluorine containing materials. Subsequently, the solution was filtered off and the solvent was removed to dryness; however, no residue was obtained. The isolated products **2a** and **2b** were found to be poorly soluble in most common organic solvents. The ¹H- and ¹³C NMR spectra, recorded in acetonitrile-d₃, DMSO-d₆ and DMF-d₇, revealed products **2a** and **2b** as the reaction is driven by restoration of aromaticity and formation of the corresponding 2,2'-bipyridinium dications **1a**²⁺ and **1b**²⁺. Ambient temperature ¹⁹F NMR spectra showed signals of F⁻ along with the signals of the solvent decomposition by anhydrous fluoride anion (e.g. DF₂⁻). The ¹⁹F NMR spectra of the salts **2a** and **2b** in acetonitrile-d₃ and DMF-d₇ recorded at -30 °C revealed two broad singlets at δ = +60.5 ppm and δ = -142.8 ppm, respectively (Figure 2, top). These data are in an excellent agreement with the previously described signals of SF₅⁻ and F⁻ anions in acetonitrile-d₃. Low temperature ¹⁹F NMR measurement performed in liquid SO₂ with 1,2-difluorobenzene as an internal standard (δ = -138.8 ppm) gave rise to the signal of fluoride (δ = -140 ppm) and a singlet signal at δ = +72.2 ppm corresponding to thionyl fluoride SOF₂.²⁰ This result may be rationalized by the decomposition of SF₅⁻ to SF₄ and F⁻, and the following reaction of SF₄ with SO₂. Upon evaporation of sulphur dioxide and addition of acetonitrile-d₃

the ¹⁹F NMR spectrum (See SI) at 298 K shows the absence of SOF₂ and formation of SO₂F⁻.²¹ In order to establish the identity of the composition in solution and in bulk, solid state ¹⁹F-NMR spectroscopy analysis of **2b** was performed (Figure 2, bottom). The spectrum gives rise to two broad singlet signals appearing at positions identical to those found in solution (δ = +60.2 ppm SF₅⁻; δ = -150 ppm F⁻). Noteworthy, the intensity of the signal at δ = +60.2 ppm decays upon time, thus with 25 kHz rotational speed at ambient temperature after 24 h about 60% of the peak intensity vanished, whereas at 40 °C the signal disappeared completely after 12 h. These results are explained by the thermal instability of the SF₅⁻ anion.

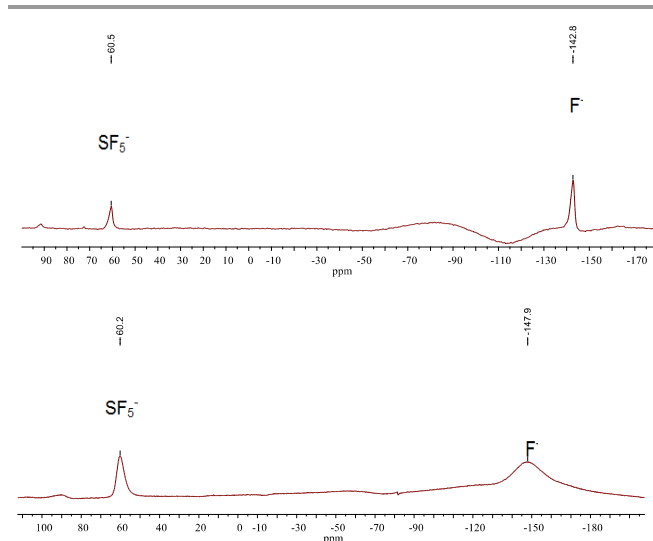


Figure 2 top) The ¹⁹F NMR spectrum of the **2b** [bis-(t-Bu)Py(propylene)]²⁺F⁻; SF₅⁻ in acetonitrile-d₃ at -30 °C; bottom) The solid state ¹⁹F NMR spectrum of **2b** [bis-(t-Bu)Py(propylene)]²⁺F⁻; SF₅⁻ at a spinning rate of 30 kHz.

Previously, IR and Raman spectra of salts containing SF₅⁻ have been reported. Yet, no Raman spectra for **2a, b** samples could be measured due to intensive fluorescence. However, IR spectroscopy provided us with an additional evidence for the presence of SF₅⁻ anions. The SF₅⁻ anion in CsSF₅ adopts a square-pyramidal geometry^{14d} of C_{4v} symmetry, giving rise to three characteristic absorbance maxima in the IR spectrum at 795, 525 and 469 cm⁻¹. These data are in excellent agreement with our results (Figure 3).

Diocetylviologen (C₈V) **1c** also reacted with SF₆ to give a blue-green paramagnetic microcrystalline precipitate. However, only one signal of fluoride-anions (δ = -160 ppm) and no evidences for SF₅⁻-anion in the ¹⁹F NMR spectra was observed. Taking into consideration the colour of the product and its paramagnetivity we assume that incomplete oxidation of viologen occurred and the corresponding radical cation C₈V^{•+} was formed.^{17a} Further experiments with other electron donors, such as TMBI **1d** and TADE **1e** did not show any reaction.

In order to understand the correlation between the activity of the organic electron donors toward SF₆ activation and their redox potential compounds **1a-e** were subjected to cyclic voltammetry (CV) studies. The results are presented in Table 1.

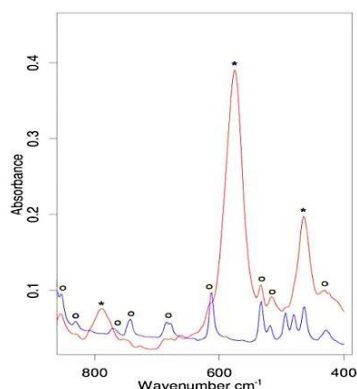


Figure 3 The IR spectra of **2b** (upper line) and **[1b]2Br⁻** (See SI) (bottom line). Bands attributed to the {bis(*t*-Bu)Py(propylene)}²⁺ dication and to the SF₅⁻ anion are denoted with (o) and (*), respectively.

Table 1 RedOx-potentials (vs SCE) of donors **1a-e** measured by CV.

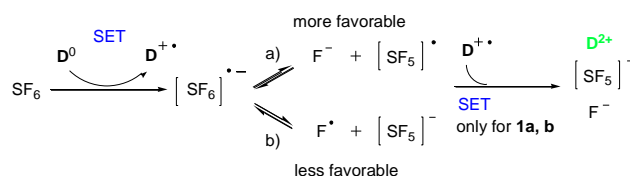
Organic Electron Donor	E ¹ _{1/2} (V)	E ² _{1/2} (V)	Reaction with SF ₆
1a	-1.12	-	observed
1b	-0.98	-0.71	observed
C ₈ V (1c)	-0.81	-0.37	observed
TMBI (1d)	-0.67	-	not observed
TDAE (1e)	-0.78; -0.62 ⁱ⁾	-0.46 ⁱⁱ⁾	not observed

All measurements were done in acetonitrile vs Ag/Ag⁺(CH₃CN)-couple quasi-reference electrode with ferrocene (E_{redOx} = 0.073 V) as an internal standard. The values are recalculated and stated versus Saturated Calomel Electrode (vs SCE); i) two anodic peaks; ii) one cathodic peak.

Starting with donor **1a** we carried out the measurements in acetonitrile and Ag/Ag⁺ reference electrode (for details see SI). According to literature data,^{16c} **1a** shows one reversible two-electron oxidation wave with E_{1/2} = -1.23 V vs SCE in DMF due to similarity of E_{RedOx} for each SET-process. The same behaviour was observed for **1a** in acetonitrile and redox potential was determined with E_{1/2} = -1.12 V vs SCE. The donor **1b** had not been measured before and two reversible one-electron waves were obtained with E¹_{1/2} = -0.98 V and E²_{1/2} = -0.71 V vs SCE. Following this observation, we also measured redox-potentials of dioctylviologen **1c**, (E¹_{1/2} = -0.81 V; E²_{1/2} = -0.37 V vs SCE); TMBI **1d** (E¹_{1/2} = -0.67 V vs SCE) and TDAE **1e** (two anodic peaks (E¹_{pa} = -0.78 V; E²_{pa} = -0.62 V vs SCE) and one cathodic (E_{pc} = -0.46 V vs SCE) were observed. From these results, we conclude that the electron donor need to have a redox potential of about E_{1/2} = -0.8 V vs SCE in order to activate SF₆.

The oxidation path of the electron donors is known and it proceeds through SET-processes *via* formation of a radical cation. However, so far, mechanistic investigations of SF₆ reduction are rare and were mainly performed in a gaseous phase or with solvated electrons.²² Based on these studies and our observations we propose the following mechanism for the

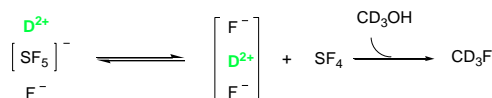
sulphur hexafluoride reduction: SET from the electron donor D to SF₆ results in formation of the donor radical-cation and SF₆^{-•}-radical-anion couple (Scheme 2). The dissociation pathway of the resulting anion-radical SF₆^{-•} is not clear and can lead either to fluorine-radical and SF₅⁻ anion (path **b**) or fluoride-anion and SF₅^{-•}-radical (path **a**). However, the latter is considered to be more favourable.



Scheme 2 Proposed mechanism for the SF₆ reduction. D – organic e-donor.

The fact that viologen C₈V is not forming the SF₅⁻ anion product can be rationalized by the value of its redox-potentials (Table 1). The first E_{redOx} is sufficient to activate SF₆ but the second one is too low for the reduction of the SF₅-radical. Notably, E²_{1/2} is sufficient for the reduction of fluorine-radicals²³ and C₈V should give a SF₅-anion containing product in case of path **b**. However, this is not observed, supporting the notion that path **a** is more probable. Finally, after the second SET from D⁺ (for **1a, b**) an ion pair consisting of a dication, a F⁻ and SF₅⁻ anion [D²⁺][F⁻, SF₅⁻] is formed, which can be detected.

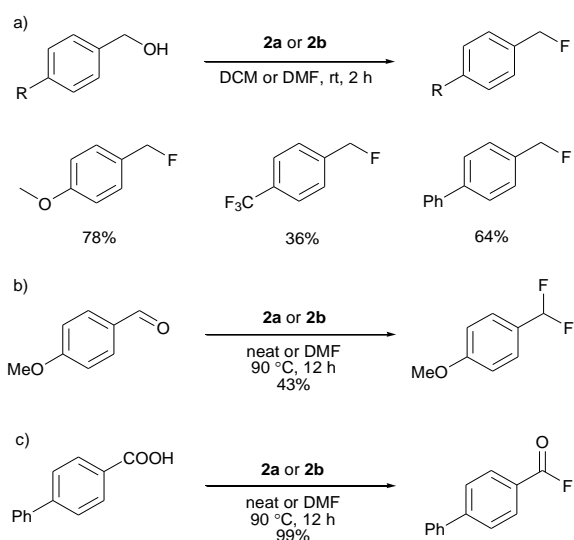
During our NMR studies, we recorded ¹⁹F-NMR spectra of **2a** and **2b** in methanol-d₄. Interestingly, we observed a septet signal which was assigned to the formation of CD₃F (δ = -276.0 ppm, sept, J²(D,F) = 7.1 Hz) (Scheme 3).²⁴



Scheme 3 Organic electron donor mediated deoxyfluorination.

This result can be explained by a decay of the formed [D²⁺][F⁻, SF₅⁻] ion pair in solution and the formation of [D²⁺][2F⁻] and sulphur tetrafluoride (SF₄) which is known as deoxy-fluorinating reagent.²⁵

Given that salts [D²⁺][F⁻, SF₅⁻] can be considered as solid, safe and easy to handle storage of SF₄, we decided to evaluate this new procedure by applying the method to the fluorination of benzyl alcohols, aldehydes and carboxylic acids. Our proof-of-concept studies are shown in Scheme 4. Generally, the reaction occurred with all three substrate classes and provided the benzyl fluorides from the corresponding alcohols (Scheme 4a), aryl-difluoromethanes from benzyl aldehyde (Scheme 4b) and acid fluoride from the carboxylic acid (Scheme 4c).²⁶



Scheme 4 Deoxyfluorination of benzylic alcohols, aldehydes and carboxylic acids with **2a** and **2b**.

Conclusions

In summary, we report the use of organic electron donors for the activation of the greenhouse gas, sulphur hexafluoride. Bipyridine-based organic electron donors were found to react fast and selectively with SF₆ at ambient temperature in non-polar aprotic solvents within minutes to yield solid ion pairs consisting of donor dications [D²⁺], fluoride [F⁻] and [SF₅⁻] anions. The presence of the SF₅⁻ anion was confirmed by NMR- and IR-spectroscopy analysis. The salts can be isolated and also be applied as fluorinating reagents. This was demonstrated by the deoxyfluorination of alcohols, aldehydes as well as carboxylic acids. Thus, SF₆ is a readily available and stable precursor for the otherwise more difficult to handle deoxyfluorinating reagent, sulphur tetrafluoride. Given the simplicity of the procedure it can be used for both, the decomposition of one of the most potent greenhouse gases and at the same time the generation of a powerful fluorinating reagent. Further applications of this metal-free activation of SF₆ as well as demonstration to reuse and recycle the electron donors are currently part of our further research.

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Notes and references

- 1 NIOSH Pocket Guide to Chemical Hazards, No 0576, <http://www.cdc.gov/niosh/npg/npgd0576.html>.

- 2 (a) F. Jakob and N. Perjanik in *Sulfur Hexafluoride, A Unique Dielectric*, Analytical ChemTech International, Inc.; (b) L. G. Christophorou, J. K. Olthoff and R. J. V. Brun, *IEEE Elect. Insul. Mag.*, 1997, **13**, 20; (c) H. Okubo and A. Beroual, *IEEE Elect. Insul. Mag.*, 2011, **27**, 34; (d) G. P. Gambaretto, P. Rinaldo and M. Palato, *US3479286 (A)*, 1969; (e) J. Gibson and B. Colton, *US8524105 (B2)*, 2013.
- 3 (a) S. P. Cashion, N. J. Ricketts and P. C. Hayes, *J. Light Met.*, 2002, **2**, 37; (b) S. Bartos, C. Laush, J. Scharfenberg, R. Kantamaneni, *J. Cleaner. Prod.*, 2007, **15**, 979; (c) U. Rapoport, *US2015065788 (A1)*, 2015.
- 4 (a) Y. Barak, J. W. Heroman and S. Schaal, *Clin. Ophthalmol.*, 2013, **7**, 423; (b) K. Maggon, *Drugs Fut.*, 1994, **19**, 1101; (c) G. P. Bezante, N. Girardi, S. Agosti and A. Barsotti, *Eur. J. Echocardiogr.*, 2006, **7**, S2; (d) N. Flor, F. S. Ardanelli, S. Serantoni, F. Brovelli and G. P. Cornalba, *Acta Radiol.*, 2006, **46**, 543.
- 5 (a) J. A. Mosovsky, *Am. Ind. Hyg. Assoc.*, 1995, **56**, 44; (b) M. Maiss, L. P. Steele, R. J. Francey, P. J. Fraser, R. L. Langenfelds, N. B. A. Trivett and I. Levin, *Atmos. Environ.*, 1996, **30**, 1621; (c) G. R. Davison, *Appl. Geochem.*, 2002, **17**, 1361; (d) M. H. Deighton, S. Richard, O. Williams, M. C. Hannah, R. J. Eckard, T. M. Boland, W. J. Wales and P. J. Moate, *Anim. Feed Sci. Tech.*, 2014, **197**, 47.
- 6 J. T. Houghton, L. G. Meira-Filho, B. A. Callander, N. Harris, A. Kattenberg and K. Maskell in *Climate Change 1995 - The Science of Climate Change*, Cambridge University Press, New York, 1996, 121.
- 7 (a) G. P. Stiller, T. von Clarmann, M. Hoepfner, N. Glatthor, U. Grabowski, S. Kellmann, A. Kleinert, A. Linden, M. Milz, T. Reddmann, T. Steck, H. Fischer, B. Funke, M. L. Puerzas and A. Engel, *Atmos. Chem. Phys.*, 2008, **8**, 677; (b) P. Forster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. W. Fahey, J. Haywood, J. Lean, D. C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. V. Dorland in *Changes in Atmospheric Constituents and Radiative Forcing in Climate Change. Fourth Assessment Report of the IPCC*. Cambridge University Press, 2007.
- 8 (a) Scientific Assessment of Ozone Depletion, *WMO, Geneva, Switzerland* 2003; (b) A. A. Lindley and A. McCulloch, *J. Fluorine Chem.*, 2005, **126**, 1457; (c) M. Maiss and C. A. M. Brenninkmeijer, *Environ. Sci. Technol.*, 1998, **32**, 3077.
- 9 (a) M. Pittroff, T. Schwarze, H.-J. Belt and P. Barthelemy, *CA2341246 (A1)*, 2000; (b) I. Senkovska, E. Barea, J. A. R. Navarro and S. Kaskel, *Micropor. Mesopor. Mat.*, 2012, **156**, 115; (c) I. A. Riddell, M. M. J. Smulders, J. K. Clegg and J. R. Nitschke, *Chem. Commun.*, 2011, **47**, 457.
- 10 (a) J. R. Case and F. Nyman, *Nature*, 1962, **193**, 473; (b) M. Weidenbruch, A. Schäfer and R. Rankers, *J. Organomet. Chem.*, 1980, **195**, 171; (c) A. A. Opalovsky and E. U. Lobkov, *J. Fluorine Chem.*, 1973, **2**, 349; (d) A. P. Hagen, D. J. Jones and S. R. Ruttman, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1217; (e) J. Pola, P. Engst and M. Horak, *Collect. Czech. Chem. Comm.*, 1979, **44**, 2092; (f) F. Pepi, A. Ricci, M. D. Stefano, M. Rosi and G. D'Arcangelo, *J. Phys. Chem. A*, 2002, **106**, 9261; (g) D. Kashiwagi, A. Takai, T. Takubo, K. Nagaoka, T. Inoue and Y. Takita, *Ind. Eng. Chem. Res.*, 2009, **48**, 632; (h) J. Zhang, J. Z. Zhou, Q. Liu, G. Qian and Z. P. Xu, *Environ. Sci. Technol.*, 2013, **47**, 6493; (i) H. C. Cowen, F. Riding and E. Warhurst, *J. Chem. Soc.*, 1953, 4168; (j) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1964, **3**, 1198.
- 11 (a) C. Wyse, R. Torres, T. Barnes, M. Scott, M. Young, X. Li and T. Gesser, *Photovoltaic Specialists Conference (PVSC)*, 2009, *34th IEEE*, 2435; (b) P. S. Das, B. Adhikari and S. Maiti, *J. Polym. Sci. Pol. Chem.*, 1994, **32**, 39; (c) T. Syau, B. J. Baliga and R. W. Hamaker, *J. Electrochem. Soc.*, 1991, **138**, 3076; (d) F. D. M. Nobre, P. J. Tatschand and S. A. Moskhalev, *Conference (IMOC)*, 2009 SBMO/IEEE MTT-S International;

- (e) A. M. Nunes, S. A. Moshkalev, P. J. Tatsch and A. M. Daltrin, *J. Integr. Circuits Syst.*, 2007, **2**, 74; (f) M. P. Garrity, T. W. Peterson and J. F. O'Hanlon, *J. Vac. Sci. Technol. A*, 1996, **14**, 550.
- 12 (a) B. G. Harvey, A. M. Arif, A. Gloeckner and R. D. Ernst, *Organometallics*, 2007, **26**, 2872; (b) R. Basta, B. G. Harvey, A. M. Arif and R. D. Ernst, *J. Am. Chem. Soc.*, 2005, **127**, 11924; (c) P. Holze, B. Horn, C. Limberg, C. Matlachowski and S. Mebs, *Angew. Chem. Int. Ed.*, 2014, **53**, 2750; (d) L. Zámostná, T. Braun and B. Braun, *Angew. Chem. Int. Ed.*, 2014, **53**, 2745; (e) L. Zámostná and T. Braun, *Angew. Chem. Int. Ed.*, 2015, **54**, 10650; (f) T. A. McTeague and T. F. Jamison, *Angew. Chem. Int. Ed.*, 2016, **55**, 15072.
- 13 a) D. Sevenard, P. Kirsch, A. A. Kolomeitsev, G.-V. Rösenthaller, DE 10220901 A1, **2003**; b) D. Sevenard, P. Kirsch, A. A. Kolomeitsev, G.-V. Rösenthaller (Merck), DE 10321114 A1, **2003**; c) D. Sevenard, P. Kirsch, A. A. Kolomeitsev, G.-V. Rösenthaller, DE 10321112 A1, **2004**.
- 14 (a) R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, 1963, **25**, 1097; (b) L. F. Drullinger and J. E. Griffiths, *Spectrochim. Acta A*, 1971, **27A**, 1793; (c) K. O. Christe, E. C. Curtis, C. J. Schack and D. Pilipovich, *Inorg. Chem.*, 1972, **11**, 1679; (d) J. Bittner, J. Fuchs and K. Seppelt, *Z. Anorg. Allg. Chem.*, 1988, **557**, 182; (e) M. Clark, C. J. Kellen-Yuen, K. D. Robinson, H. Zhang, Z. Y. Yang, K. V. Madappat, J. W. Fuller, J. L. Atwood and J. S. Thrasher, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 809; (f) J. T. Goettel, N. Kostiuik and M. Gerken, *Angew. Chem. Int. Ed.*, 2013, **52**, 8037.
- 15 For a comprehensive review see: P. R. Savoie and J. T. Welch, *Chem. Rev.*, 2015, **115**, 1130.
- 16 For selected reviews and examples, see: (a) J. Broggi, T. Terme and P. Vanelle, *Angew. Chem. Int. Ed.*, 2014, **53**, 384; (b) J. Murphy, *J. Org. Chem.*, 2014, **79**, 3731; (c) J. Garnier, A. R. Kennedy, L. E. A. Berlouis, J. A. Murphy and T. A. Turner, *Beilstein J. Org. Chem.*, 2010, **6**, No. 73; (d) J. Garnier, D. W. Thomson, S.-Z. Zhou, P. I. Jolly, L. E. A. Berlouis and J. A. Murphy, *Beilstein J. Org. Chem.*, 2012, **8**, 994; (e) S. S. Hanson, N. A. Richard and C. A. Dyker, *Chem. Eur. J.*, 2015, **21**, 8052; (f) S. S. Hanson, E. Doni, K. T. Traboulee, G. Coulthard, J. A. Murphy and C. A. Dyker, *Angew. Chem. Int. Ed.*, 2015, **54**, 11236; (g) S. O'Sullivan, E. Doni, T. Tuttle and J. A. Murphy, *Angew. Chem. Int. Ed.*, 2014, **53**, 474.
- 17 (a) P. M. S. Monk in *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*, Wiley, Chichester, 1998; (b) M. Mohammad, *J. Org. Chem.*, 1987, **52**, 2779; (c) M. Kuroboshi, A. Kuwano and H. Tanaka, *Electrochem.*, 2008, **76**, 862; (d) M. Kuroboshi, R. Kobayashi, T. Nakagawa and H. Tanaka, *Synlett*, 2009, **1**, 85; (e) S. Durben and T. Baumgartner, *Angew. Chem. Int. Ed.*, 2011, **50**, 7948; (f) M. Kuroboshi, T. Yamamoto and H. Tanaka, *Synlett*, 2013, **24**, 197; (g) M. Kuroboshi, T. Shiba and H. Tanaka, *Tetrahedron Lett.*, 2013, **54**, 3666; (h) C. Reus, M. Stolar, J. Vanderkley, J. Nebauer and T. Baumgartner, *J. Am. Chem. Soc.*, 2015, **137**, 11710.
- 18 (a) H. E. Winberg, J. E. Carnahan, D. D. Coffman and M. Brown, *J. Am. Chem. Soc.*, 1965, **87**, 2055; (b) M. F. Lappert, T. R. Martin and G. M. McLaughl, *J. Chem. Soc. Chem. Comm.*, 1980, **13**, 635; (c) M. K. Denk, A. Thadani, K. Hatano and A. J. Lough, *Angew. Chem. Int. Ed.*, 1997, **36**, 2607.
- 19 For selected articles on the utilization of TDAE, see: (a) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, 1964, **86**, 2101; for a review, see: (b) M. Médebielle and W. R. Dolbier Jr., *J. Fluorine Chem.*, 2008, **129**, 930.
- 20 T. S. Cameron, R. J. Deeth, I. Dionne, H. Du, H. Donald, B. Jenkins, I. Krossing, J. Passmore and H. K. Roobottom, *Inorg. Chem.*, 2000, **39**, 5614.
- 21 N. Kuhn, H. Bohnen, J. Fahl, D. Bläser and R. Boese, *Chem. Ber.*, 1996, **129**, 1579.
- 22 (a) R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, 1951, **19**, 534; (b) A. J. Ahearn and N. B. Nannay, *J. Chem. Phys.*, 1953, **21**, 119; (c) G. E. Streit, *J. Chem. Phys.*, 1982, **77**, 826; (d) E. C. M. Chen, L.-R. Shuie, E. D. D'sa, C. F. Batten and W. E. Wentworth, *J. Chem. Phys.*, 1988, **88**, 4711; (e) F. Li-Aravena and M. Saporoschenko, *J. Chem. Phys.*, 1993, **98**, 8888; (f) R. E. Weston Jr., *J. Phys. Chem.*, 1995, **99**, 13150; (g) A. Rosa, F. Brüning, S. V. K. Kumar and E. Illenberger, *Chem. Phys. Lett.*, 2004, **391**, 361; (h) K. Haygarth and D. M. Bartels, *J. Phys. Chem. A*, 2010, **114**, 7479; (i) A. Akhgarnusch, R. F. Höckendorf and M. K. Beyer, *J. Phys. Chem.*, 2015, **119**, 9978; (j) J. Troe, T. M. Miller and A. A. Viggiano, *J. Chem. Phys.*, 2012, **136**, 121102.
- 23 For example E_{redOx} for Selectfluor™, known as a radical fluorinating reagent, is $E = +0.2$ V vs SCE; M. Rueda-Becerril, O. Mahé, M. Drouin, M. B. Majewski, J. G. West, M. O. Wolf, G. M. Sammis and J.-F. Paquin, *J. Am. Chem. Soc.*, 2014, **136**, 2637.
- 24 K. Jackowski, M. Kubiszewski and W. Makulski, *J. Mol. Struct.*, 2002, **614**, 267.
- 25 C.-L. Wang, *J. Org. React.* **1985**, *34*, 319.
- 26 In addition, a one-pot approach has also been tested. Exposure of the electron donor **1a** and **1b** solutions in an aprotic solvent to SF₆ via balloon, with subsequent addition of benzyl alcohol led to the formation of the corresponding benzyl fluoride.