Supporting Information

Tetracationic Imidazoliumyl-Substituted Phosphorus-Sulfur Heterocycles from a Cationic Organophosphorus Sulfide

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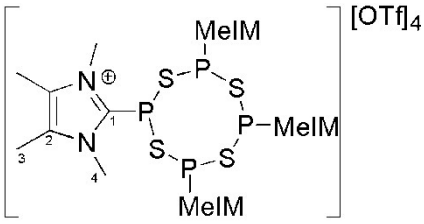
S1. Experimental Details

General Remarks:

All manipulations were performed in a Glovebox MB Unilab produced by MBraun or using standard Schlenk technique[1] under an inert atmosphere of purified Argon (purchased from Westfalen AG). Dry, oxygen-free solvents (drying agents in brackets; [CaH_2]: CH_2Cl_2, C_6H_5F, 1,2-$C_6H_4F_2$, [sodium]: pentane, *n*-hexane, [sodium/benzophenone]: Et_2O) were employed. Deuterated benzene (C_6D_6) was purchased from Sigma-Aldrich and distilled from sodium prior to use. Deuterated dichloromethane and acetonitrile (CD_2Cl_2, CD_3CN ampoule) were purchased from Sigma-Aldrich and stored over molecular sieves for at least 2 d prior to use. Reagents $(Me_3Si)_2S$ and DMAP were purchased from Sigma Aldrich and distilled or sublimed prior to use. Compounds **3a,b[OTf]** were prepared according to literature known procedures.[2] All glassware was oven-dried at temperatures above 180°C prior to use. NMR spectra (including variable temperature and 2D-EXSY NMR spectra) of compounds were measured on a Bruker AVANCE III HD Nanobay (^{1}H (400.13 MHz), ^{13}C (100.61 MHz), ^{31}P (161.98 MHz), ^{19}F (376.46 MHz)) at 300 K. ^{31}P{/} EXSY spectra were recorded at 335 K with a pulse sequence from the Bruker pulse library NOESYPH, 90°–t_1–90°–t_m–90°–*acqu*, in the phase sensitive TPPI mode. A total of 256 scans per FID of 2K data points were used per time increment. All ^{13}C NMR spectra were exclusively recorded with composite pulse decoupling. Assignments of the carbon atoms in the ^{13}C spectra were performed via indirect deduction from the cross-peaks in 2D correlation experiments (HMBC; HSQC). Chemical shifts were referenced to δ_{TMS} = 0.00 ppm (^{1}H, ^{13}C) and $\delta_{H3PO4(85\%)}$ = 0.00 ppm (^{31}P, externally). Chemical shifts (δ) are reported in ppm. Coupling constants (*J*) are reported in Hz. Absolute values are reported except for coupling constants derived by means of line shape iteration (*vide infra*). Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY, PP-COSY) when necessary. Melting points were recorded on an electrothermal melting point apparatus (Barnstead Electrothermal IA9100) in sealed capillaries under Argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperatures using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong and vs = very strong. Elemental analysis of compound

15[OTf] was performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster, Germany. Elemental analyses of compounds **9a,b[OTf]$_4$** were performed on a vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme GmbH.

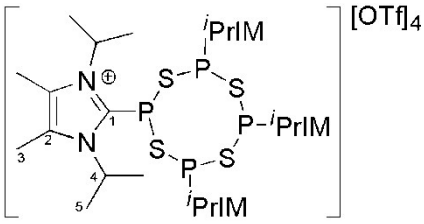
S1.1 Preparation of 9a[OTf]$_4$



$(Me_3Si)_2S$ (1.35 mL, 1.14 g, 6.4 mmol) was added dropwise to a suspension of **3a**[OTf] (2.39 g, 6.4 mmol) in fluorobenzene (10 mL). The suspension was stirred for 5 h at ambient temperature. All volatiles were removed *in vacuo*. After recrystallization from acetonitrile/diethylether and filtration, **3a**[OTf]$_4$ was obtained as colorless solid. Single crystals suitable for X-Ray structure determination were obtained *via* slow diffusion of diethylether into a saturated solution of **3a**[OTf]$_4$ in acetonitrile;

Yield: 2.02 g (6.0 mmol, 94%); **mp**.: 104 – 106 °C; **Raman (100 mW, r.t., in cm^{-1})**: ν = 2968(25), 2935(42), 2863(96), 2233(16), 2088(43), 2032(23), 1626(45), 1479(28), 1451(56), 1406(62), 1384(59), 1336(100), 1285(17), 1255(16), 1224(20), 1100(63), 1031(45), 982(22), 771(21), 755(28), 667(15), 640(15), 600(38), 571(30), 543(42), 500(43), 404(19), 349(33), 314(28), 267(21), 218(26); **IR (ATR, r.t., in cm^{-1})**: ν = 1624(vw), 1491(vw), 1443(w), 1406(vw), 1381(vw), 1335(vw), 1274(vw), 1252(m), 1220(vw), 1157(vw), 1141(vw), 1027(s), 948(vw), 854(w), 770(vw), 753(vw), 668(vw), 634(vs), 571(w), 515(w), 503(vw), 448(m); **^{1}H NMR (CD_2Cl_2, 300 K,** δ in **ppm)**: δ = 2.26 (24H, s, C3−H), 4.02 (24H, s, C4−H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K,** δ in **ppm)**: δ = 9.5 (s, C4), 36.0 (s, C3), 128.8 (q, $^1J_{CF}$ = 321.0 Hz, −CF_3), 132.8 (s, C2), 138.4 (s, C1); **^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K,** δ in **ppm)**: δ = 47.9 (s); **^{19}F NMR (CD_2Cl_2, 300 K,** δ in **ppm)**: δ = −79.5 (s); **elemental analysis**: $C_{32}H_{48}F_{12}N_8O_{12}P_4S_8$ (1345.13): calcd.: N 8.3, C 28.6, H 3.6, S 19.1, found: N 8.0, C 28.4, H 3.5, S 18.5.

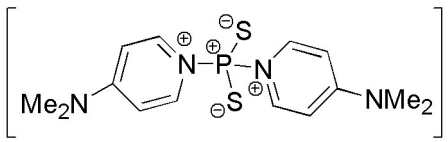
S1.2 Preparation of 9b[OTf]$_4$



$(Me_3Si)_2S$ (3.57 mL, 3.02 g, 16.8 mmol) was added dropwise to a suspension of **3b**[OTf] (7.20 g, 16.8 mmol) in fluorobenzene (20 mL). The suspension was stirred for 5 h at ambient temperature. All volatiles were removed *in vacuo*. After recrystallization from acetonitrile/diethylether and filtration, **9b**[OTf]$_4$ was obtained as colorless solid;

Yield: 6.05 g (15.4 mmol, 92%); **mp**.: decomposition T > 245 °C; **Raman (100 mW, r.t., in cm^{-1})**: ν = 2990(69), 2946(100), 2881(26), 2742(14), 2448(21), 2419(32), 2041(9), 1615(38), 1449(58), 1431(65), 1404(44), 1380(43), 1349(16), 1288(64), 1260(18), 1231(17), 1191(16), 1154(21), 1137(19), 1092(13), 1027(58), 954(18), 931(18), 886(30), 796(22), 759(34), 676(86), 580(27), 544(17), 457(21), 405(12), 348(23), 316(31), 284(26), 269(30); **IR (ATR, r.t., in cm^{-1})**: ν = 2987(vw), 1612(vw), 1400(vw), 1378(vw), 1302(vw), 1266(s), 1219(m), 1138(m), 1112(vw), 1090(vw), 1029(vs), 943(vw), 929(vw), 901(vw), 793(vw), 751(w), 675(w), 634(vs); **^{1}H NMR (CD$_3$CN, 300 K, in ppm)**: δ = 1.69 (48H, d, $^{3}J_{HH}$ = 6.91 Hz, C5−H), 2.39 (24H, s, C3−H), 5.24 (8H, s (br.), C4−H); **^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm)**: δ = 10.8 (s, C3), 21.9 (s, C5), 55.9 (s, C4), 122.1 (q, $^{1}J_{CF}$ = 321.6 Hz, −CF$_3$), 134.4 (s, C2), 137.9 (s, C1); **^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm)**: δ = 50.4 (s); **^{19}F NMR (CD$_3$CN, 300 K, in ppm)**: δ = −79.1 (s, −CF$_3$); **elemental analysis**: $C_{48}H_{80}F_{12}N_8O_{12}P_4S_8$ (1568.24): calcd.: N 7.1, C 36.7, H 5.1, S 16.3, found: N 7.1, C 36.6, H 5.4, S 16.1.

S1.3 Reaction of 9a,b[OTf]$_4$ with DMAP and preparation of 14[OTf]



9a,b[OTf]$_4$ (0.09 mmol) and 4 eq. of DMAP (46 mg, 0.38 mmol) were combined in a schlenk flask and MeCN (10 mL) was added. The reaction mixture was stirred for 7 d at ambient temperature. The slow addition of diethylether afforded **14**[OTf] as yellow, crystalline powder.

Yield: not determined; **mp**.: 99 – 101 °C; **Raman (50 mW, r.t., in cm^{-1})**: ν = 3104(27), 3091(27), 3132(18), 2977(24), 2937(60), 2901(27), 2864(18), 2823(24), 1636(48), 1585(81), 1479(24), 1442(24), 1422(24), 1405(24), 1339(9), 1312(15), 1228(30), 1046(54), 1030(75), 975(18), 945(60), 769(87), 753(33), 654(27), 613(72), 584(27), 573(24), 552(57), 499(24), 466(30), 369(36), 347(33), 312(42), 299(36), 250(42), 210(72); **IR (ATR, r.t., in cm^{-1})**: ν = 3089 (vw), 1646 (vw), 1629(m), 1583 (vw), 1571 (vw), 1505 (w), 1435 (vw), 1401 (w), 1313 (w), 1272 (vw), 1258 (m), 1219 (s), 1148 (vs), 1050 (w), 1028 (w), 1012 (vw), 826 (m), 803 (vw), 753 (vs), 717 (vw), 690 (vw), 652 (w), 635 (m); **^{1}H NMR (CD$_3$CN, 300 K, in ppm)**: δ = 3.23 (12H, s, C4–H), 6.84 (4H, d, C2–H); 8.88 (4H, t, C1–H); **^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm)**: δ = 40.1 (s, C4), 107.54 (s, C2), 121.0 (q, $^{1}J_{CF}$ = 320.9 Hz, CF$_3$), 139.1 (s, C1), 154.6 (s, C3); **^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm)**: δ = 96.2 (s); **^{19}F{^{1}H} NMR (CD$_3$CN,**

300 K, in ppm): δ = –79.4 (s, $–CF_3$); **elemental analysis**: $C_{16}H_{20}F_6N_4O_6PS_4$ (636.99): calcd.: N 11.5, C 36.9, H 4.1, found: N 11.3, C 36.9, H 4.1.

Representative NMR Spectra of the reaction mixtures are depicted in Figures S1-S3. Derivatives **12a,b**[OTf] were identified by their characteristic $^{31}P\{^1H\}$ chemical shift but not isolated from the reaction mixtures.

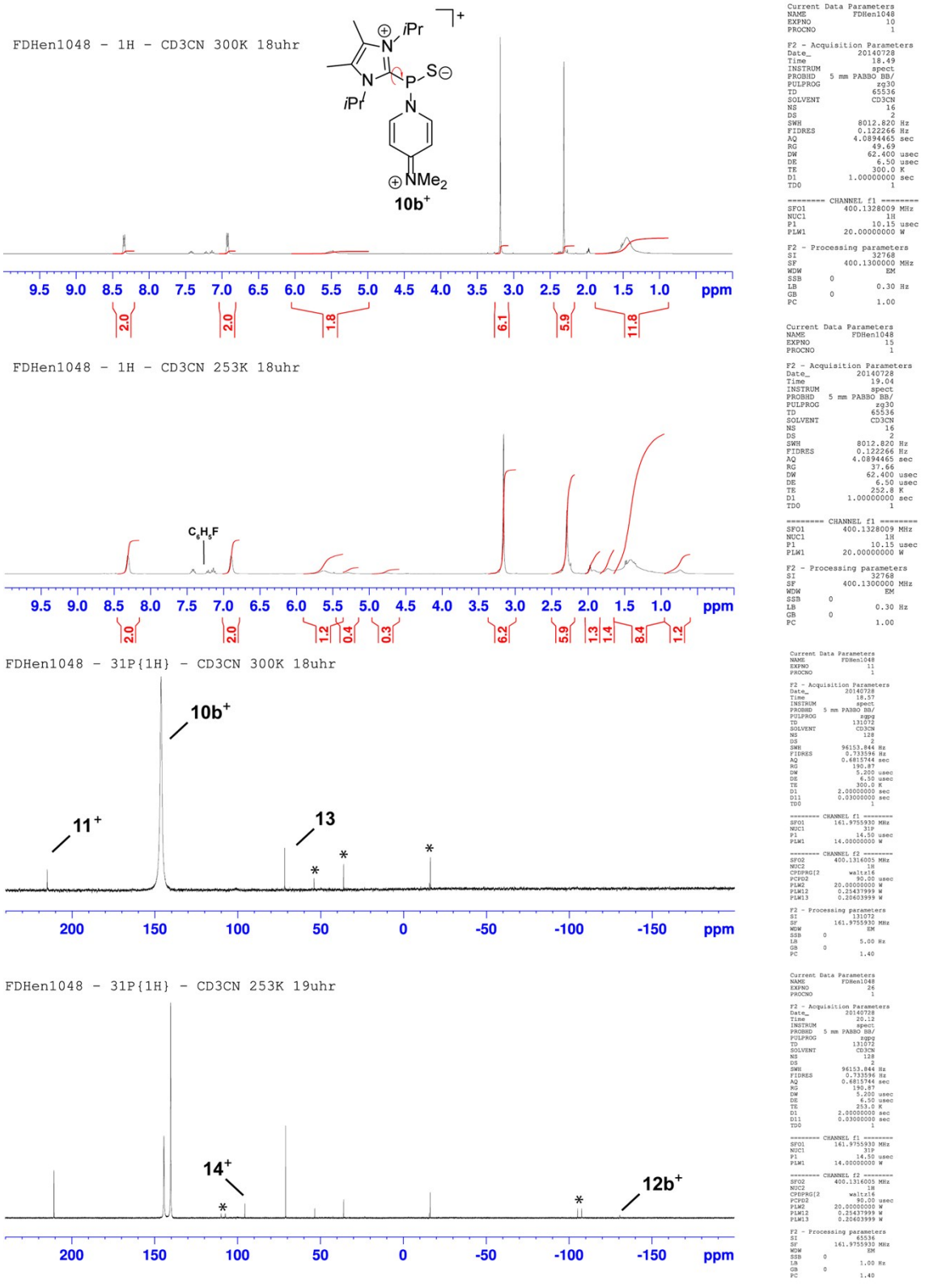


Fig. S1. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture of **9b**$[OTf]_4$with 4 eq. DMAP after 10 min (first three spectra) and 1h (last spectrum) (acetonitrile/C_6D_6-capillary, 300 and 253 K, for details see spectrum); * indicates small amounts of an unidentified side-product; traces of C_6H_5F can be observed in the ^{1}H NMR spectra.

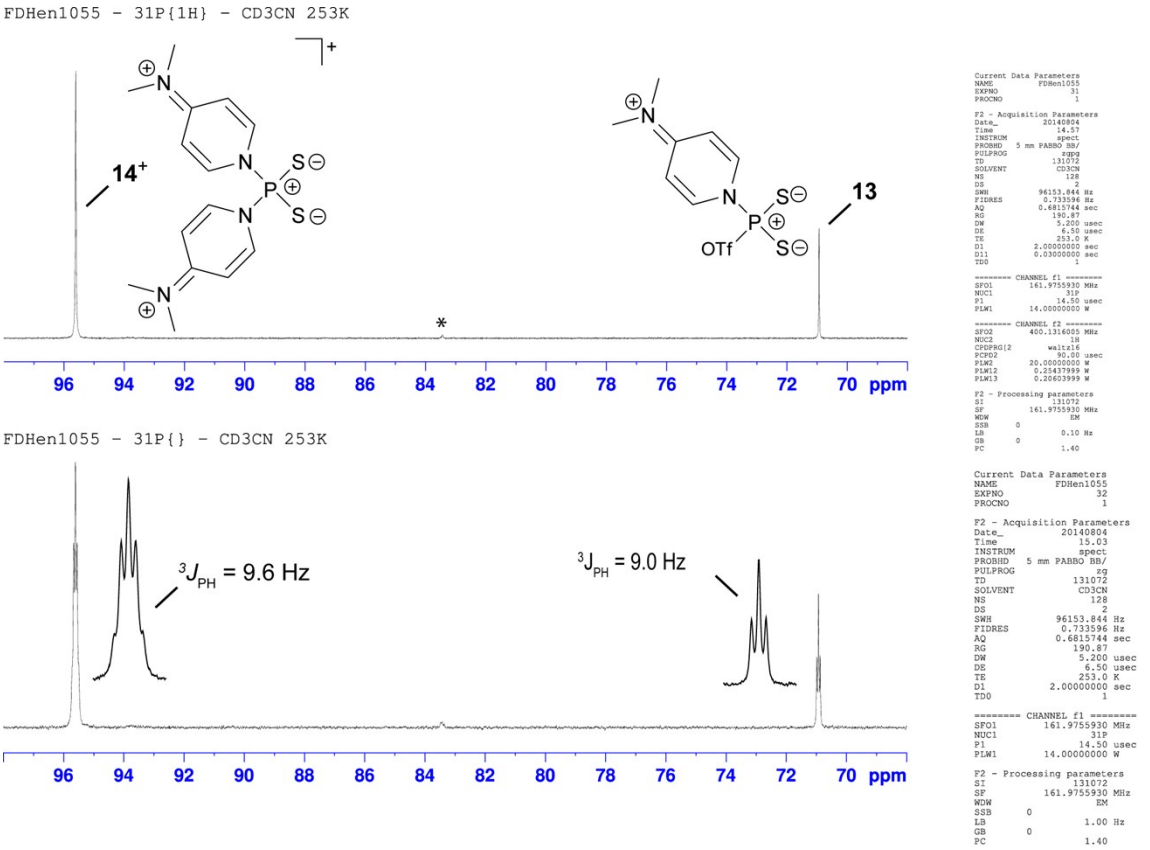


Fig. S2. $^{31}P\{\backslash\}$ NMR and $^{31}P\{^{1}H\}$ NMR spectra of the equilibrium mixture of compound **13** and cation **14**$^{+}$ (acetonitrile/C_6D_6-capillary, 253 K); * indicates small amounts of an unidentified side-product.

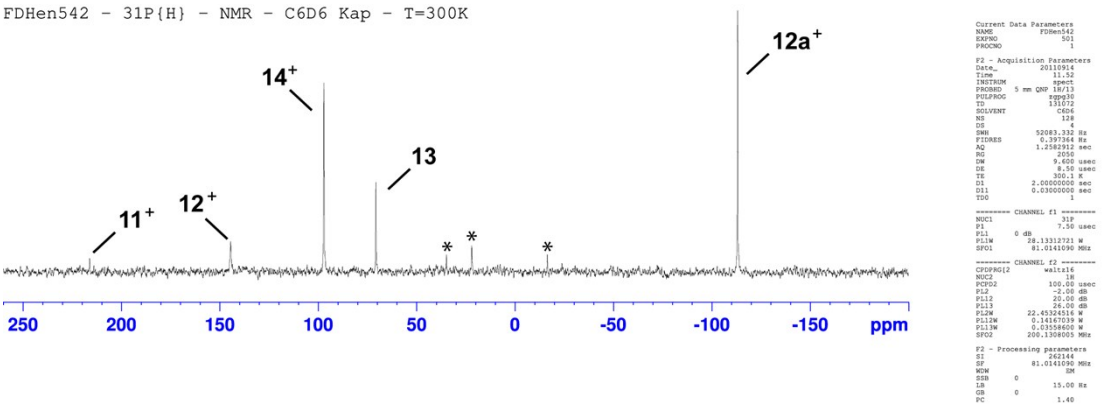


Fig. S3. $^{31}P\{\backslash\}$ NMR spectrum of the reaction mixture of **9a**$[OTf]_4$with 4 eq. DMAP after 12 h (acetonitrile/C_6D_6-capillary, 300 K); * indicates small amounts of an unidentified side-product.

S2 Crystallographic Details

Single crystals were coated with Paratone-N oil, mounted using a glass fiber pin and frozen in the cold nitrogen stream of the goniometer. The datasets were either collected with a Bruker AXS APEX II CCD equipped with a rotation anode or a fine focussed sealed tube at 153(1) K using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) with a scan width of 0.3°. Data reduction was done using the Bruker SMART[3] software package. Data were corrected for absorption effects using the SADABS routine (empirical multi-scan method). Data of **9b**$[OTf]_4$ were processed and corrected by CrysAlis Pro software.[4] Structure solutions were found with the SHELXS package using the direct method and were refined with SHELXL[5] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were generated with idealized geometries and isotropically refined using a riding model. Triflate anions tend to be disordered in general unless a significant interaction of one of the oxygen atoms to a Lewis acidic atom is present. In most cases these disorders resulted in the observation of residual density near the triflate anions which was smaller than 1 in magnitude.

Molecular structures were drawn using the ORTEP software.[6] Packing diagrams were generated using the software Diamond 4.[7]

14[OTf] was found to crystallize in two different polymorphs in the space groups $P2_1/m$ and P-1, respectively. In the monoclinic structure the N1-P1-N1 angle at 95.17(9)° is slightly smaller compared to N1-P1-N3 (96.77(8)°) in the triclinic structure, whereas all bond lengths are almost equal. The most prominent difference in the packing is the orientation of the triflate anion in the groove between the DMAP residues as shown in Fig. S4. Both structures are built of layers of strings consisting of antiparallel oriented cations showing offset π-stacking interactions of about 3.5 Å (Fig. S5). The strings are separated by alternately oriented triflate anions.

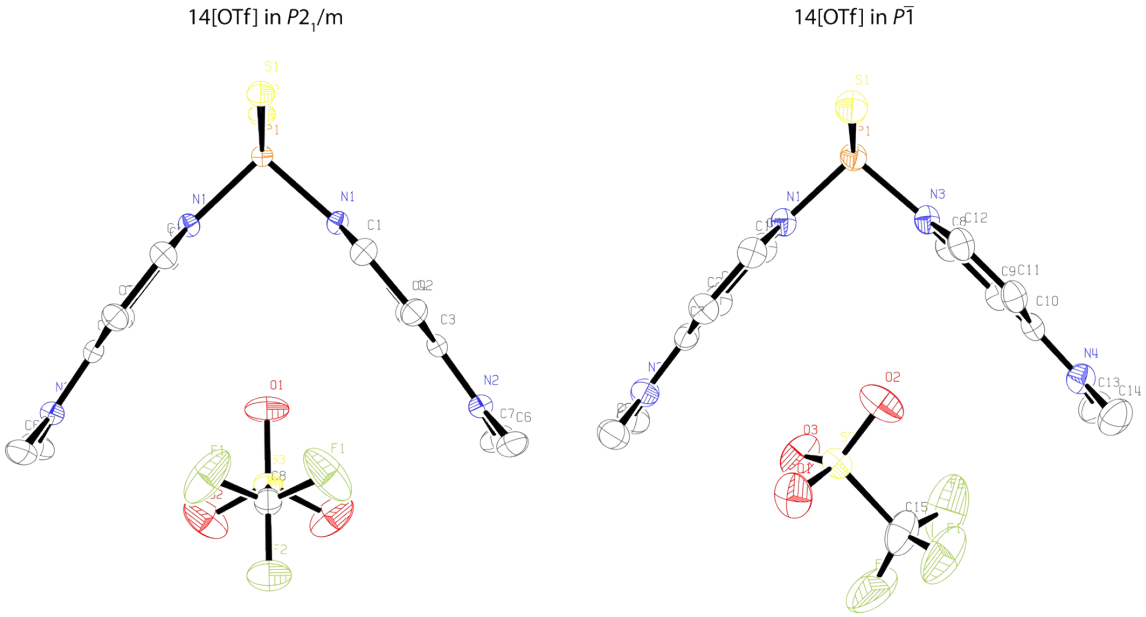


Fig. S4. Depiction of the cation **14**$^{+}$ along the molecules σ_v with different orientation of the counter ion. Ellipsoids drawn at 50 % probability. Hydrogen atoms omitted for clarity.

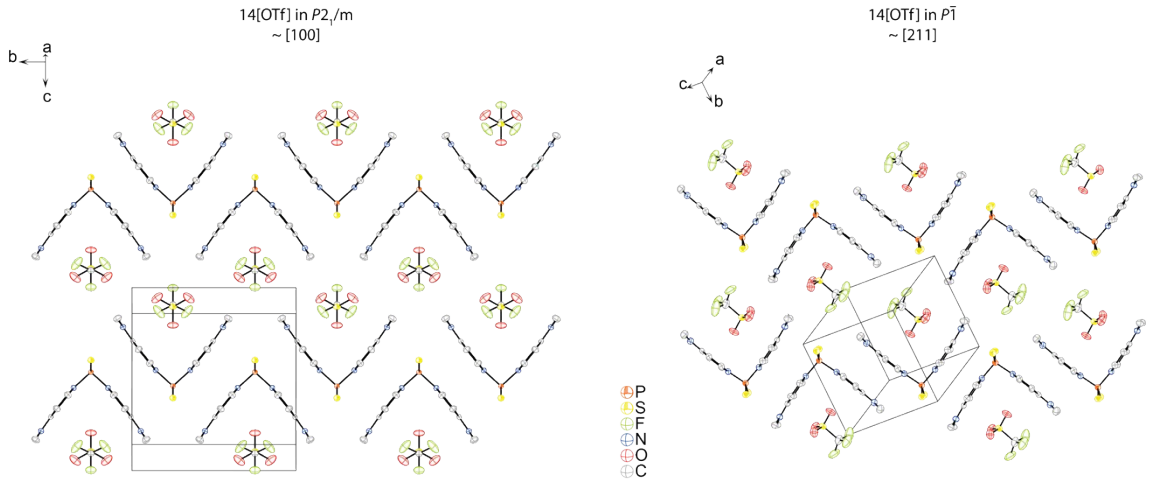


Fig. S5. Packing diagrams of the two polymorphs of **14**[OTf] along approximate directions [100] and [211] showing similar layers of antiparallel oriented cations. Ellipsoids drawn at 50 % probability. Hydrogen atoms omitted for clarity.

9b$[OTf]_4$ crystallizes in the acentric space group *I*4. However, disorder of the tetracation makes it look like being centric in space group *I*4/m. The structure model was refined with disorder on both, the cation and the triflate anion. To achieve convergence SIMU and SADI restraints were applied on the anion and the imidazoliumyl moiety. Furthermore the solvent molecule present in the structure could not be localized in the void and was therefore treated by the SQUEEZEroutine.[8] The molecular structure of cation **9b**$^{4+}$ is depicted in S6.

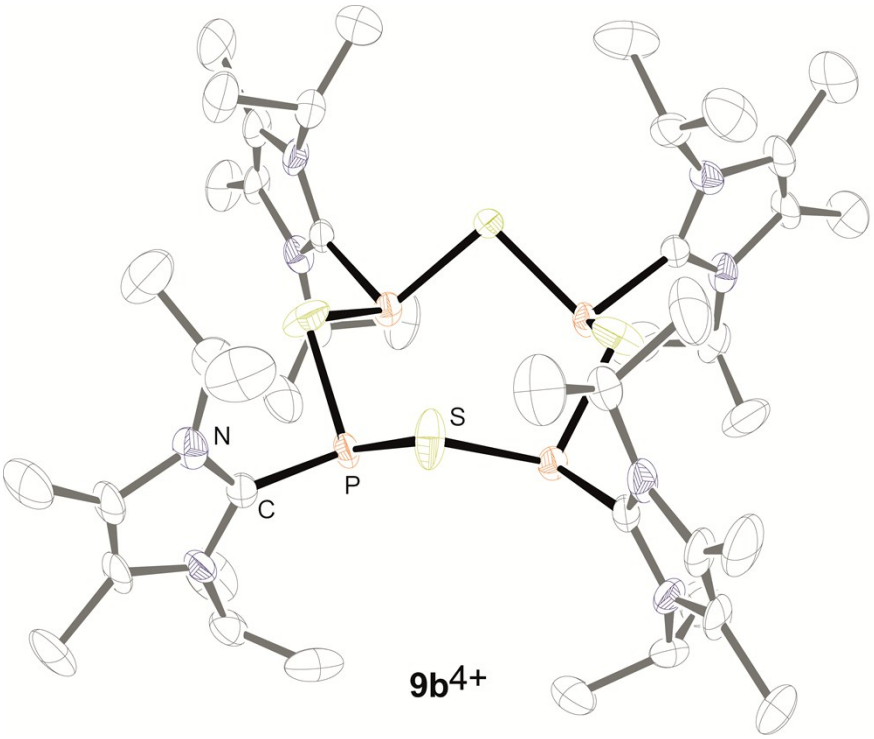


Fig. S6. Molecular structure of tetracation **9b**$^{4+}$ in **9b**[OTf]$_4$. All hydrogen atoms and triflate anions are omitted for clarity.

S2.1 Crystallographic Data of 9a,b[OTf]$_4$ and 14[OTf].

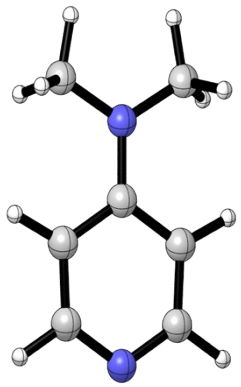
	9a[OTf]$_4$·3MeCN	**9b**[OTf]$_4$	**14**[OTf]	**14**[OTf]
formula	$C_{38}H_{57}F_{12}N_{11}O_{12}P_4S_8$	$C_{48}H_{80}F_{12}N_8O_{12}P_4S_8$	$C_{15}H_{20}F_3N_4O_3PS_3$	$C_{15}H_{20}F_3N_4O_3PS_3$
M_r in g mol^{-1}	1468.31	1569.56	488.50	488.50
dimension in mm^3	0.26x0.07x0.06	0.04x0.04x0.11	0.14x0.07x0.03	0.33x0.23x0.19
color, habit	colorless, plate	Colorless, block	yellow, block	yellow, block
crystal system	triclinic	tetragonal	triclinic	monoclinic
Space group	*P*-1	*I*4	*P*-1	$P2_1/m$
a in Å	9.1184(7)	17.5055(4)	8.3991(6)	6.5855(4)
b in Å	13.928(1)	17.5055(4)	10.1015(7)	12.5308(6)
c in Å	25.501(2)	13.3734(6)	13.5475(9)	12.4698(7)
α in °	101.117(1)	90	69.158(1)	90
β in °	91.826(1)	90	78.162(1)	91.568(2)
γ in °	94.621(1)	90	84.594(1)	90
V in Å^3	3163.8(4)	4098.2(3)	1051.1(1)	1028.64(10)
Z	2	2	2	2
T in K	153(1)	153(1)	153(1)	153(1)
ρ_c in g cm^{-3}	1.541	1.272	1.544	1.577
F(000)	1508	1632	504	504
λ, Å	0.71073 (MoK$_\alpha$)	0.71073 (MoK$_\alpha$)	0.71073 (MoK$_\alpha$)	0.71073 (MoK$_\alpha$)
μ in mm^{-1}	0.480	0.374	0.480	0.490
absorption correction	SADABS	Multi-scan	SADABS	SADABS
reflections collected	32464	18047	10111	8389
reflections unique	15043	5071	4929	2607
R_{int}	0.0340	0.0226	0.0241	0.0158
R_σ	0.0520	0.0264	0.0388	0.0189
reflection obs. [I>4σ(I)]	11173	4006	3819	2345
residual density in e Å^{-3}	1.374, -0.821	1.052, -0.282	0.528, -0.342	1.10, -0.40
Parameters	785	378	266	144
GOOF	1.038	1.097	1.029	1.061
R_1 [I>4σ(I)]	0.0456	0.0623	0.0412	0.0369
wR_2 (all data)	0.1207	0.1761	0.1064	0.1055
CCDC	1424341	1426199	1424343	1424342

S3 Computational chemistry

All quantum mechanical calculations have been performed, using Orca 3.0.2.[9] Geometries and energies were calculated applying the B3LYP hybrid DFT functional and the def2-SVP basis set of Weigend and co-workers.[10] To correct the DFT results towards potential dispersive non-covalent interactions the third version of Grimmes atom-pair wise dispersion correction with Becke-Johnson damping (D3BJ) was applied.[11] The Gibbs free enthalpy was derived from the electronic energy based on a subsequent frequency calculation, which additionally confirmed the stationary point as a minimum. Molecules where visualized using CYLview[12] and raytraced by POV-Ray.[13]

S3.1 Cartesian coordinates and graphical representations of DMAP, $9a^+$, $10a^+$, 14^+ and $12a^+$

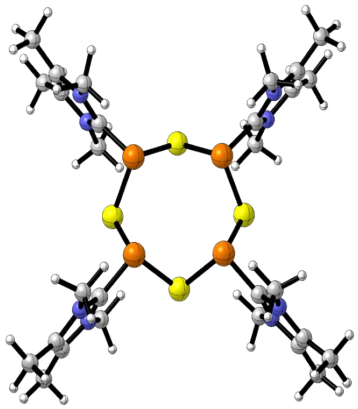
S3.1.1 DMAP



C	-2.55200023262138	0.58098151574043	-0.00472886513175
C	-1.38151018415295	-0.20422897235113	0.13773628948497
C	-1.48910127770322	-1.59272205580034	0.15775319194056
N	-2.63657999982301	-2.27023664086728	0.05267710074329
C	-3.74213278276306	-1.53062958763072	-0.07962085501052
C	-3.76744766875607	-0.13847055315103	-0.11413909891139
N	-2.51085737793609	1.95355316400909	-0.03458494682302
C	-3.73882380615543	2.71138434780190	-0.15816474649638
C	-1.24358533207442	2.64135039497302	0.10146043370181
H	-0.39726573812088	0.25243219928248	0.23366144206287
H	-0.57706374945262	-2.19277229791378	0.26792184248125
H	-4.68834818900358	-2.07963736448631	-0.16598074045719
H	-4.72367906171986	0.37118974578975	-0.22659360271057
H	-3.50598548828554	3.78411721727666	-0.16578923123098
H	-4.43231673946796	2.51921621537843	0.68176238205848
H	-4.27731409939270	2.47657244914121	-1.09495371745378
H	-0.53527693380484	2.36276456154034	-0.70017001721472

H	-0.75343502690694	2.42524511601876	1.06958699006423
H	-1.40874182685946	3.72496751624852	0.04216611290286

S 3.1.2 9a^{4+}



C	5.49049695714655	3.69853393146780	8.79915852112079
C	3.46768575164941	4.07957105132932	9.69888818820244
C	4.39752413807460	4.82562467991288	10.40802852963586
C	1.99489784651419	3.95873903500036	9.87034147130436
C	4.21931771334764	5.74616160937779	11.56367480615870
C	3.51670132239212	2.49599481786026	7.77029559876366
C	6.87076972021276	5.17786070316955	10.31767282679910
C	8.62643805697586	-1.16391085590457	8.67134338064912
C	8.14952608999452	-3.19650219236667	9.50037821995442
C	9.20886559276617	-2.67603459532949	10.22922395351684
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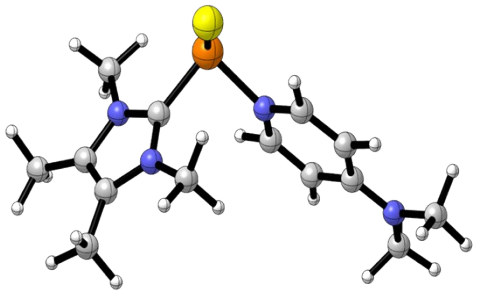

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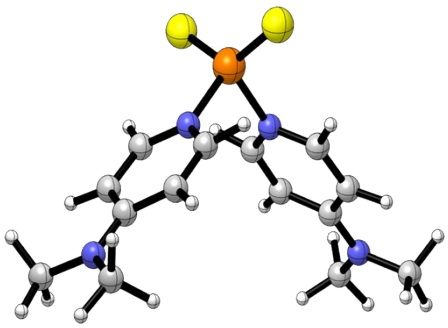

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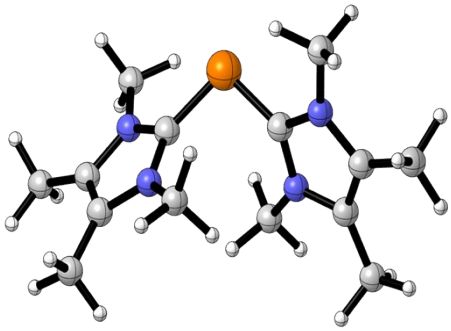

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