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# **Supporting Information**

# Introducing a Pyrazole/Imidazole Based Hybrid Cyclophane: Hydrogen Bond Sensor and Binucleating Ligand Precursor

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## 1. General remarks

Chemicals were purchased from commercial suppliers and used without further purification if not stated otherwise. Anhydrous acetonitrile and dichloromethane were obtained from an MBraun solvent purification system, degassed by freeze-pump-thaw technique and stored over molecular sieves.

Liquid NMR spectra were recorded on a Bruker Avance DPX 400 and a Bruker DRX 400. Chemical shifts are given in parts per million (ppm) and the spectra were referenced by using the residual solvent shift as internal standards (dimethyl sulfoxide- $d_6$ , <sup>1</sup>H NMR  $\delta$  2.50, <sup>13</sup>C NMR  $\delta$  39.52; acetonitrile- $d_3$ , <sup>1</sup>H NMR  $\delta$  1.94, <sup>13</sup>C NMR  $\delta$  118.26; chloroform-d, <sup>1</sup>H NMR  $\delta$  7.26, <sup>13</sup>C NMR  $\delta$  77.16). MS-ESI analyses were performed on a Thermo Scientific LCQ/Fleet spectrometer by Thermo Fisher Scientific. Elemental analyses were obtained from the microanalytical laboratory of the Technical University of Munich.

### 2. Experimental details

Syntheses were performed under air in non-dried solvents if not stated otherwise. Sodium imidazolide, 3,5-bis(hydroxymethyl)pyrazole hydrochloride (**1-OH**), 3,5-bis(chloromethyl)-pyrazolium chloride (**1-CI**), 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (**2-CI**) and methylene-bis(trifluoromethane-sulfonate) were synthesized according to literature procedures.<sup>1</sup>

### 3,5-Bis(bromomethyl)-pyrazolium bromide (1-Br)

Under inert atmosphere **1-OH** (3.00 g, 18.23 mmol, 1 equiv.) and thionyl bromide (18.9 g, 7.1 mL, 91.14 mmol, 5 equiv.) were placed in a Schlenk flask equipped with a pressure valve at 0 °C with vigorous stirring. After 30 min the cooling bath was removed and the mixture was allowed to slowly reach room temperature. After additional 2 h of stirring at room temperature the dark red solution was heated to 40 °C for 30 min. After cooling to room temperature 100 mL diethyl ether were added to precipitate an off-white solid. The precipitate was washed with diethyl ether until the filtrate was completely colorless. After drying *in vacuo* **1-Br** was obtained as a white powder in a yield of 4.21 g (12.36 mmol, 70 %). <sup>1</sup>H NMR (400.13 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 12.19 (br s, 2H, *H*<sub>NH</sub>), 6.39 (s, 1H, *H*<sub>CCHC</sub>), 4.61 (s, 4H, *H*<sub>CH2</sub>). <sup>13</sup>C{<sup>1</sup>H}</sup> NMR (100.62 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 144.4, 105.7, 24.3. MS-ESI (m/z): 254.69 (**1-Br**–Br<sup>-</sup>)<sup>+</sup>. Elemental analysis (%) calcd: C 17.94, H 2.08, N 8.37; found: C 17.89, H 2.08, N 8.15.

#### 3,5-Bis(bromomethyl)-1-(tetrahydropyran-2-yl)-1H-pyrazole (2-Br)<sup>1</sup>

**1-Br** (4.10 g, 12.36 mmol, 1 equiv.) was suspended in 150 mL dry dichloromethane under inert atmosphere. Subsequently, 3,4-dihydro-2*H*-pyran (3.35 mL, 3.12 g, 37.07 mmol, 3 equiv.) was added and the mixture was stirred at room temperature for 16 h. To the brownish mixture a solution of 8 g NaHCO<sub>3</sub> in 150 mL water was added. The phases were separated and the aqueous phase was extracted with dichloromethane (2x 100 mL). The combined organic phase was dried over MgSO<sub>4</sub>, filtered and evaporated *in vacuo*. After purification of the crude product by flash chromatography (hexane/Et<sub>2</sub>O = 9:1) and drying *in vacuo* **2-Br** was obtained as a white solid in a yield of 2.95 g (8.43 mmol, 69 %). DC:  $R_f$  = 0.63 (pentane/Et<sub>2</sub>O = 1:1, [UV, CAM]). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, 298 K): δ (ppm) = 6.40 (s, 1H,  $H_{CCHC}$ ), 5.44 (dd, <sup>3</sup>*J* = 9.51/2.72 Hz,1H,  $H_{thp}$ ), 4.57 (d, <sup>2</sup>*J* = 11.73 Hz, 1H,  $H_{CH2}$ ), 4.50 (d, <sup>2</sup>*J* = 11.73 Hz, 1H,  $H_{CH2}$ ), 4.46 (d, <sup>2</sup>*J* = 11.03 Hz, 1H,  $H_{cH2}$ ), 4.42 (d, <sup>2</sup>*J* = 11.03 Hz, 1H,  $H_{cH2}$ ), 4.02 (d, <sup>2</sup>*J* = 11.19 Hz, 1H,  $H_{thp}$ ), 3.69 (dt, <sup>2.3</sup>*J* = 11.19/2.96 Hz, 1H,  $H_{thp}$ ), 2.45-2.34 (m, 1H,  $H_{thp}$ ), 2.15-1.98 (m, 2H,  $H_{thp}$ ), 1.78-1.50 (m, 3H,  $H_{thp}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 298 K): δ (ppm) = 148.4, 139.9, 108.0, 85.2, 67.9, 29.4, 25.2, 25.0, 22.5, 20.1. ESI-MS (m/z): 254.95 (**2**-thp+H<sup>+</sup>)<sup>+</sup>, 338.62 (**2**+H<sup>+</sup>)<sup>+</sup>.

<sup>&</sup>lt;sup>1</sup> The compound was synthesized before via a different approach (J. C. Röder, F. Meyer, M. Konrad, S. Sandhöfner, E. Kaifer, H. Pritzkow, Eur. J. Org. Chem. 2001, 4479-4487.)

### 3,5-Bis(imidazol-1-ylmethyl)-1-(tetrahydropyran-2-yl)-1H-pyrazole (3)

### Procedure A:

Under inert atmosphere a Schlenk tube was charged with sodium imidazolide (2.13 g, 26.60 mmol, 2.2 equiv.) and a solution of **2-Cl** (3.00 g, 12.09 mmol, 1 equiv.) in 50 mL dry acetonitrile was added under vigorous stirring. The resulting suspension was allowed to warm to room temperature overnight and filtered through a pad of Celite. The solution was concentrated to dryness, the crude product dissolved in 50 mL dichloromethane and extracted with water (2x 50 mL). The aqueous extract was washed with 50 mL dichloromethane and the combined organic phase was dried over MgSO<sub>4</sub>, filtered and concentrated to dryness. After drying *in vacuo* **3** was obtained as a white solid in a yield of 3.77 g (12.09 mmol, quant.).

### Procedure B:

Under inert atmosphere a Schlenk tube was charged with sodium imidazolide (1.12 g, 14.02 mmol, 2.2 equiv.) and cooled to 0 °C. A solution of **2-Br** (2.23 g, 6.37 mmol, 1 equiv.) in 40 mL dry acetonitrile was added under vigorous stirring. The resulting suspension was allowed to warm to room temperature overnight and filtered through a pad of Celite. The solution was concentrated to dryness, the crude product dissolved in 50 mL dichloromethane and extracted with water (2x 50 mL). The aqueous extract was washed with 50 mL dichloromethane and the combined organic phase was dried over MgSO<sub>4</sub>, filtered and concentrated to dryness. After drying *in vacuo* **3** was obtained as a white solid in a yield of 1.99 g (6.37 mmol, quant.). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  (ppm) = 7.52 (*virt.* t, <sup>4</sup>*J* = 1.11 Hz, 1H, *H*<sub>NCHN</sub>), 7.49 (*virt.* t, <sup>4</sup>*J* = 1.12 Hz, 1H, *H*<sub>NCHN</sub>), 7.07 (*virt.* t, 1H, <sup>3,4</sup>*J* = 1.11 Hz, 1H, *H*<sub>NCHC</sub>), 7.04 (*virt.* t, <sup>3,4</sup>*J* = 1.12 Hz, 1H, *H*<sub>NCHC</sub>), 6.87 (*virt.* t, <sup>3,4</sup>*J* = 1.32 Hz, 1H, *H*<sub>NCHC</sub>), 5.96 (s, 1H, *H*<sub>CCHC</sub>), 5.23 (d, <sup>2</sup>*J* = 15.88 Hz, 1H, *H*<sub>CH2</sub>), 5.16 (d, <sup>2</sup>*J* = 15.88 Hz, 1H, *H*<sub>Hp</sub>), 2.09-1.89 (m, 2H, *H*<sub>thp</sub>), 5.05 (*virt.* d, <sup>4</sup>*J* = 0.73 Hz, 2H, *H*<sub>CH2</sub>), 3.99-3.92 (m, 1H, *H*<sub>thp</sub>), 3.62-3.54 (m, 1H, *H*<sub>thp</sub>), 2.27-2.13 (m, 1H, *H*<sub>thp</sub>), 2.09-1.89 (m, 2H, *H*<sub>thp</sub>), 1.68-1.52 (m, 3H, *H*<sub>thp</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  (ppm) = 147.3, 139.4, 137.4, 137.3, 130.2, 129.8, 119.3, 119.1, 106.5, 86.0, 67.6, 44.7, 41.8, 29.4, 24.9, 22.1. ESI-MS (m/z): 156.94 (**3**+2H<sup>+</sup>)<sup>2+</sup>, 313.11 (**3**+H<sup>+</sup>)<sup>+</sup>, 624.78 (2x **3**+H<sup>+</sup>)<sup>+</sup>. Elemental analysis (%) calcd: C 61.52, H 6.45, N 26.90; found: C 61.39, H 6.44, N 26.55.

#### Calix[4]imidazolium[2]pyrazole tetrakis(trifluormethansulfonate) (4-OTf)

Under inert atmosphere a 1 L Schlenk flask was charged with **3** (1.13 g, 3.62 mmol, 1 equiv.) and 500 mL dry acetonitrile were added. The clear solution was cooled to -40 °C and subsequently a solution of methylene bistriflate (1.13 g, 3.62 mmol, 1 equiv.) in 50 mL dry acetonitrile was added with vigorous stirring over the course of 45 min. The resulting mixture was allowed to warm to room temperature overnight with stirring and the solvent removed *in vacuo*. The residue was redissolved in 30 mL ethanol and filtered. The filtrate was treated with 1.5 mL of a 1:1 mixture of trifluoromethanesulfonic anhydride and water and stirred at room temperature for 30 min. Diethyl ether (150 mL) was added to precipitate a white solid that was washed with diethyl ether (2x 20 mL) and acetone (2x 20 mL). After drying *in vacuo* **4-OTf** was obtained as a white solid in a yield of 1.27 g (1.16 mmol, 64 %). <sup>1</sup>H NMR (400.13 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 13.32 (s, 4H, *H*<sub>NH</sub>), 9.38 (s, 4H, *H*<sub>NCHN</sub>), 8.00 (s, 4H, *H*<sub>NCHC</sub>), 7.81 (s, 4H, *H*<sub>NCHC</sub>), 6.62 (s, 4H, *H*<sub>CH2</sub>), 6.46 (s, 2H, *H*<sub>CCHC</sub>), 5.51 (s, 8H, *H*<sub>CH2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 145.2 (br), 137.7, 123.2, 122.8, 120.6 (q, <sup>1</sup>*J*<sub>C-F</sub> = 322 Hz), 105.9, 58.1, 46.2 (br), 43.1 (br). Elemental analysis (%) calcd: C 31.14, H 2.52, N 15.57, S 11.88; found: C 31.42, H 2.64, N 15.23, S 11.91. ESI-MS (m/z): 211.12 (**4-OTf**-3OTf<sup>-</sup>)<sup>3+</sup>, 391.26 (**4-OTf**-2OTf<sup>-</sup>)<sup>2+</sup>, 931.01 (**4-OTf**-OTf<sup>-</sup>)<sup>+</sup>.

### Calix[4]imidazolium[2]pyrazole tetrakis(hexafluorophosphate) (4-PF<sub>6</sub>)

To a solution of **4-OTf** (1.27 g, 1.16 mmol, 1 equiv.) in 4 mL water was added NH<sub>4</sub>OH(aq) (25 %, 1 mL) at room temperature. The mixture was stirred for 15 min at room temperature and subsequently added to a solution of NH<sub>4</sub>PF<sub>6</sub> (839 mg, 5.15 mmol, 5 equiv.) in 5 mL water. The resulting suspension was stirred at room temperature for 30 min and filtered. The residue was washed with water (2x 10 mL), redissolved in a minimum of acetonitrile and precipitated with diethyl ether. After washing with diethyl ether (2x 10 mL) and drying *in vacuo*, **4-PF**<sub>6</sub> was obtained as a white solid in a yield of 1.03 g (0.94 mmol, 81 %). One equivalent of MeCN was found to remain in the sample. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 13.33 (s, 2H, *H*<sub>NH</sub>), 9.41 (s, 4H, *H*<sub>NCHN</sub>), 8.00 (d, <sup>3</sup>*J* = 2.12 Hz, 4H, *H*<sub>NCHC</sub>), 7.79 (d, <sup>3</sup>*J* = 2.12 Hz, 4H, *H*<sub>NCHC</sub>), 6.63 (s, 4H, *H*<sub>CH2</sub>), 6.45 (s, 2H, *H*<sub>CCHC</sub>), 5.51 (s, 8H, *H*<sub>CH2</sub>), 2.07 (s, 3H, *H*<sub>MeCN</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 141.1 (br), 137.8, 123.2, 122.8, 118.1 (MeCN), 105.3, 58.1, 44.9 (br), 1.2 (MeCN). <sup>31</sup>P NMR (161.98 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  (ppm) = 144.2. Elemental analysis (%) calcd for **4-PF**<sub>6</sub> · MeCN: C 28.25, H 2.83, N 16.47; found: C 28.06, H 2.87, N 16.21. ESI-MS (m/z): 241.04 (**4-PF**<sub>6</sub>-2H<sup>+</sup>-4PF<sub>6</sub><sup>-</sup>)<sup>2+</sup>, 314.18 (**4-PF**<sub>6</sub>-H<sup>+</sup>-3PF<sub>6</sub><sup>-</sup>)<sup>2+</sup>, 373.09 (**4-PF**<sub>6</sub>-2PF<sub>6</sub><sup>-</sup>)<sup>2+</sup>, 773.03 (**4-PF**<sub>6</sub>-H<sup>+</sup>-2PF<sub>6</sub><sup>-</sup>)<sup>+</sup>, 918.91 (**4-PF**<sub>6</sub>-3PF<sub>6</sub><sup>-</sup>)<sup>+</sup>.

### (Calix[4]imidazolylidene[2]pyrazolato)dinickel(II) bis(hexafluorophosphate) (5-PF<sub>6</sub>)

To a mixture of **4-PF**<sub>6</sub> · **MeCN** (92 mg, 0.083 mmol, 1 equiv.), bis(triphenylphosphine)nickel(II) chloride (109 mg, 0.167 mmol, 2 equiv.) and caesium carbonate (275 mg, 0,830 mmol, 10 equiv.) 5 mL dry acetonitrile were added under inert atmosphere and the resulting suspension was stirred at 70 °C for 16 h. The suspension was allowed to cool to room temperature and was concentrated to approximately 2 mL. Subsequently, 10 mL of water were added to precipitate a yellow solid which was isolated by centrifugation and washed three times with water. The residue was dissolved in acetonitrile, filtered and diethyl ether was added to the solution to precipitate a solid that was washed with diethyl ether three times. The crude product was purified by fractional precipitation (MeCN, Et<sub>2</sub>O). After drying *in vacuo* **5-PF**<sub>6</sub> was obtained as pale yellow solid in a yield of 48 mg (0.054 mmol, 65 %). <sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  (ppm) = 7.34 (d, <sup>3</sup>*J* = 1.98 Hz, 4H, *H*<sub>NCHC</sub>), 7.24 (d, <sup>3</sup>*J* = 1.98 Hz, 4H, *H*<sub>NCHC</sub>), 6.45 (s, 2H, *H*<sub>CCHC</sub>), 6.12 (d, <sup>2</sup>*J* = 12.85 Hz, 2H, *H*<sub>CH2</sub>), 6.07 (d, <sup>2</sup>*J* = 12.85 Hz, 2H, *H*<sub>CH2</sub>), 5.29 (d, <sup>2</sup>*J* = 15.58 Hz, 4H, *H*<sub>CH2</sub>), 5.24 (d, <sup>2</sup>*J* = 15.58 Hz, 4H, *H*<sub>CH2</sub>). <sup>13</sup>C{<sup>1</sup>H</sup>} NMR (100.62 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  (ppm) = 159.8, 146.0, 122.8, 122.3, 105.6, 62.3, 47.2. <sup>31</sup>P NMR (161.98 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  (ppm) = -144.6. Elemental analysis (%) calcd for **5-PF**<sub>6</sub> · 0.5 Et<sub>2</sub>O: C 33.84, H 2.95, N 18.21; found: C 34.05, H 2.96, N 18.04. ESI-MS (m/z): 297.38 (**5-PF**<sub>6</sub>-2PF<sub>6</sub><sup>-</sup>)<sup>2+</sup>, 739.25 (**5-PF**<sub>6</sub>-PF<sub>6</sub><sup>-</sup>)<sup>+</sup>.

# 3. NMR spectra of compound 1-Br



Figure 1: <sup>1</sup>H NMR spectrum of 1-Br in DMSO-d<sub>6</sub> at 400.13 MHz. 1-Br slowly decomposes in DMSO solution.



**Figure 2:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **1-Br** in DMSO-d<sub>6</sub> at 100.62 MHz. **1-Br** slowly decomposes in DMSO solution (the decomposition products are marked by \*).

# 4. NMR spectra of compound 3



Figure 3: <sup>1</sup>H NMR spectrum of 3 in CDCl<sub>3</sub> at 400.13 MHz.



Figure 4:  ${}^{13}C{}^{1}H$  NMR spectrum of 3 in CDCl<sub>3</sub> at 100.62 MHz.

# 5. NMR spectra of compound 4-OTf



**Figure 5:** <sup>1</sup>H NMR spectrum of **4-OTf** in DMSO- $d_6$  at 400.13 MHz.



**Figure 6:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4-OTf** in DMSO- $d_6$  at 100.62 MHz. The broad signals at 145.2, 46.2 and 43.1 ppm were assigned by 2D HSQC and 2D HMBC NMR spectroscopy (*vide infra*).

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**Figure 7:** 2D HSQC NMR spectrum of **4-OTf** in DMSO- $d_6$  (only relevant area). The spectrum proves the existence of carbon resonances at 43 and 46 ppm which are too broad to be resolved in the respective 1D <sup>13</sup>C NMR spectrum.



**Figure 8:** 2D HMBC NMR spectrum of **4-OTf** in DMSO- $d_6$  (only relevant area). The spectrum proves the existence of a carbon resonance at 145 ppm which is too broad to be resolved in the respective 1D <sup>13</sup>C NMR spectrum.

# 6. NMR spectra of compound 4-PF<sub>6</sub>



**Figure 9:** <sup>1</sup>H NMR spectrum of **4-PF**<sub>6</sub> in DMSO- $d_6$  at 400.13 MHz. One equivalent of MeCN is present that is not removable *in vacuo*. H<sub>NH</sub> is not visible due to a fast exchange with residual water in the sample.



**Figure 10:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4-PF**<sub>6</sub> in DMSO- $d_6$  at 100.62 MHz. The signal at 141.3 ppm was identified by 2D HMBC spectroscopy (*vide infra*).



**Figure 11:** 2D HSQC NMR spectrum of **4-PF**<sub>6</sub> in DMSO- $d_6$  (only relevant area).



**Figure 12:** 2D HMBC NMR spectrum of  $4-PF_6$  in DMSO- $d_6$  (only relevant area). The spectrum proves the existence of a carbon resonance at 141 ppm which is too broad to be resolved in the respective 1D <sup>13</sup>C NMR spectrum.

# 7. NMR spectra of compound $5-PF_6$



Figure 13: <sup>1</sup>H NMR spectrum of 5-PF<sub>6</sub> in CD<sub>3</sub>CN at 400.13 MHz.



Figure 14: Variable temperature <sup>1</sup>H NMR spectrum of **5-PF**<sub>6</sub> in CD<sub>3</sub>CN at 100.62MHz (only relevant area).



Figure 15:  ${}^{13}C{}^{1}H$  NMR spectrum of 5-PF<sub>6</sub> in CD<sub>3</sub>CN at 100.62 MHz.

## 8. Crystallographic details

### General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II,  $\kappa$ -CCD), a rotating anode (Bruker AXS, FR591) with MoK<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å) (Compound **4-OTf, 4-PF**<sub>6</sub>), or a fine-focussed sealed tube respectively (Compound **5-PF**<sub>6</sub>), and a graphite monochromator by using the APEX II software package.<sup>1</sup> The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.<sup>2</sup> Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.<sup>2</sup> Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the APEX 2 software<sup>1</sup> in conjunction with SHELXL-2014<sup>3</sup> and SHELXLE<sup>4</sup>. Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and U<sub>iso(H)</sub> = 1.5·U<sub>eq(C)</sub>. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and U<sub>iso(H)</sub> = 1.2·U<sub>eq(C)</sub>. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\Delta w (F_o^2-F_c^2)^2$  with SHELXL-97<sup>5</sup> weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.<sup>6</sup> Images of the crystal structures were generated by PLATON.<sup>7</sup>

### Special:

**4-OTf:** The unit cell contains two water molecules close to a special position which have been treated as a diffuse contribution to the overall scattering without specific atom positions by PLATON/SQUEEZE.<sup>7</sup> Geometrical restraints have been applied for disordered OTf<sup>-</sup> anions (see CIF).

4-PF<sub>6</sub>: Geometrical restraints have been applied for disordered PF<sub>6</sub><sup>-</sup> anions (see CIF).

**5-PF<sub>6</sub>:** Geometrical restraints have been applied for disordered PF<sub>6</sub><sup>-</sup> anions (see CIF).

### References:

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- 7 Spek, A. L. "PLATON", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

## 8.1 Compound 4-OTf (CCDC 1057574)



Figure 163: Asymmetric unit of the crystal structure of 4-OTf. ADPs are given at the 50% probability level.

A clear colourless fragment-like specimen of  $C_{28}H_{28}F_{12}N_{12}O_{12}S_4$ , approximate dimensions 0.214 mm x 0.296 mm x 0.498 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a MONTEL mirror monochromator and a Mo FR591 rotating anode ( $\lambda = 0.71073$  Å).

A total of 3974 frames were collected. The total exposure time was 11.04 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 56097 reflections to a maximum  $\theta$  angle of 25.35° (0.83 Å resolution), of which 8270 were independent (average redundancy 6.783, completeness = 99.9%, R<sub>int</sub> = 5.98%) and 7024 (84.93%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $\underline{a} = 18.437(7)$  Å,  $\underline{b} = 12.746(3)$  Å,  $\underline{c} = 21.166(6)$  Å,  $\beta = 114.813(18)^\circ$ , volume = 4514.(3) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 210 reflections above  $20 \sigma(I)$  with  $4.007^\circ < 20 < 44.82^\circ$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.688. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8520 and 0.9320.

The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 787 variables converged at R1 = 4.87%, for the observed data and wR2 = 13.00% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.863 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.479 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.066 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.648 g/cm<sup>3</sup> and F(000), 2280 e<sup>-</sup>.

**Table 1.** Sample and crystal data for AltPh21 AP6289-123.

Identification code	AltPh21 AP6289-123			
Chemical formula	$C_{28}H_{28}F_{12}N_{12}O_{12}S_4$			
Formula weight	1080.84			
Temperature	123(2) K			
Wavelength	0.71073 Å			
Crystal size	0.214 x 0.296 x 0.498 mm			
Crystal habit	clear colourless fragment			
Crystal system	monoclinic			
Unit cell dimensions	a = 18.437(7) Å	α = 90°		
	b = 12.746(3) Å	$\beta = 114.813(18)^{\circ}$		
	c = 21.166(6) Å	γ = 90°		
Volume	4514.(3) Å <sup>3</sup>			
Z	4			
Density (calculated)	1.648 g/cm <sup>3</sup>			
Absorption coefficient	0.332 mm <sup>-1</sup>			
F(000)	2280			

Table 2. Data collection and structure refiner	nent for AltPh21 AP628	39-123.		
Diffractometer	Bruker Kappa APEX II CCD			
Radiation source	FR591 rotating anode	e, Mo		
Theta range for data collection	1.92 to 25.35°			
Index ranges	-25<=h<=25, -15<=k<	=15, -22<=l<=21		
Reflections collected	56097			
Independent reflections	8270 [R(int) = 0.0598	]		
Coverage of independent reflections	99.9%			
Absorption correction	multi-scan			
Max. and min. transmission	0.9320 and 0.8520			
Refinement method	Full-matrix least-squares on F <sup>2</sup>			
Refinement program	SHELXL-2014 (Sheldrick, 2014)			
Function minimized	$\Sigma w(F_0^2 - F_c^2)^2$			
Data / restraints / parameters	8270 / 266 / 787			
Goodness-of-fit on F <sup>2</sup>	1.033			
$\Delta/\sigma_{max}$	0.001			
Final R indices	7024 data; I>2σ(I)	R1 = 0.0487, wR2 = 0.1226		
	all data	R1 = 0.0577, wR2 = 0.1300		
Weighting scheme	w=1/[ $\sigma^2(F_o^2)$ +(0.0563P) <sup>2</sup> +6.3127P] where P=( $F_o^2$ +2 $F_c^2$ )/3			
Largest diff. peak and hole	0.863 and -0.479 eÅ-	3		
R.M.S. deviation from mean	0.066 eÅ <sup>-3</sup>			

## 8.2 Compound **4-PF**<sub>6</sub> (CCDC 1057575)



Figure 174: Asymmetric unit of the crystal structure of 4-PF<sub>6</sub>. ADPs are given at the 50% probability level.

A clear colourless fragment-like specimen of C<sub>30</sub>H<sub>37</sub>F<sub>24</sub>N<sub>15</sub>P<sub>4</sub>, approximate dimensions 0.140 mm x 0.239 mm x 0.302 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a MONTEL mirror monochromator and a Mo FR591 rotating anode ( $\lambda = 0.71073$  Å).

A total of 2557 frames were collected. The total exposure time was 21.31 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 105935 reflections to a maximum θ angle of 25.36° (0.83 Å resolution), of which 4306 were independent (average redundancy 24.602, completeness = 99.8%,  $R_{int}$  = 4.62%) and 3733 (86.69%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $\underline{a}$  = 17.748(2) Å,  $\underline{b}$  = 14.432(2) Å,  $\underline{c} = 17.585(2)$  Å, volume = 4504.2(11) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9980 reflections above 20  $\sigma(I)$  with  $4.632^{\circ} < 2\theta < 49.59^{\circ}$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.927. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9110 and 0.9570.

The final anisotropic full-matrix least-squares refinement on  $F^2$  with 418 variables converged at R1 = 4.84%, for the observed data and wR2 = 13.60% for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 0.596 e<sup>-</sup> /Å<sup>3</sup> and the largest hole was -0.576 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.069 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.751 g/cm<sup>3</sup> and F(000), 2392 e<sup>-</sup>.

Table 3. Sample and crystal data for AltPh24 AP6302-123.

Identification code	AltPh24 AP6302-123			
Chemical formula	$C_{30}H_{37}F_{24}N_{15}P_4$			
Formula weight	1187.62			
Temperature	123(2) K			
Wavelength	0.71073 Å			
Crystal size	0.140 x 0.239 x 0.302 mm			
Crystal habit	clear colourless fragment	clear colourless fragment		
Crystal system	orthorhombic	orthorhombic		
Space group	P n m a			
Unit cell dimensions	a = 17.748(2) Å	α = 90°		
	b = 14.432(2) Å	β = 90°		
	c = 17.585(2) Å	γ = 90°		
Volume	4504.2(11) Å <sup>3</sup>			
Z	4			
Density (calculated)	1.751 g/cm <sup>3</sup>			
Absorption coefficient	0.314 mm <sup>-1</sup>			
F(000)	2392			

Table 4. Data collection and structure refinem	ent for AltPh24 AP630	2-123.	
Diffractometer	Bruker Kappa APEX II	CCD	
Radiation source	FR591 rotating anode	, Mo	
Theta range for data collection	1.63 to 25.36°		
Index ranges	-21<=h<=21, -17<=k<	=17, -21<=l<=21	
Reflections collected	105935		
Independent reflections	4306 [R(int) = 0.0462]		
Coverage of independent reflections	99.8%		
Absorption correction	multi-scan		
Max. and min. transmission	0.9570 and 0.9110		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Refinement program	SHELXL-2014 (Sheldrick, 2014)		
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$		
Data / restraints / parameters	4306 / 148 / 418		
Goodness-of-fit on F <sup>2</sup>	1.057		
$\Delta / \sigma_{max}$	0.013		
Final R indices	3733 data; I>2σ(I)	R1 = 0.0484, wR2 = 0.1300	
	all data	R1 = 0.0558, wR2 = 0.1360	
Weighting scheme	w=1/ $[\sigma^2(F_o^2)+(0.0609)]$ where P= $(F_o^2+2F_c^2)/3$	P) <sup>2</sup> +8.9144P]	
Largest diff. peak and hole	0.596 and -0.576 eÅ <sup>-3</sup>		
R.M.S. deviation from mean	0.069 eÅ <sup>-3</sup>		



Figure 185: Packing diagram of  $4-PF_6$  showing interactions to neighboring cations and  $PF_6^-$  anions.

## 8.3 Compound 5-PF<sub>6</sub> (CCDC 1057576)



Figure 196: Asymmetric unit of the crystal structure of 5-PF<sub>6</sub>. ADPs are given at the 50% probability level.

A clear colourless fragment-like specimen of  $C_{27}H_{29}F_{12}N_{13}Ni_2OP_2$ , approximate dimensions 0.321 mm x 0.335 mm x 0.341 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo fine-focus tube ( $\lambda = 0.71073$  Å).

A total of 4228 frames were collected. The total exposure time was 11.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 120413 reflections to a maximum  $\theta$  angle of 25.38° (0.83 Å resolution), of which 12603 were independent (average redundancy 9.554, completeness = 99.7%, R<sub>int</sub> = 11.11%, R<sub>sig</sub> = 6.69%) and 8369 (66.40%) were greater than  $2\sigma(F^2)$ . The final cell constants of <u>a</u> = 16.9279(10) Å, <u>b</u> = 14.4946(8) Å, <u>c</u> = 28.0590(15) Å,  $\beta$  = 93.054(4)°, volume = 6874.9(7) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 6373 reflections above 20  $\sigma(I)$  with 4.823° < 2 $\theta$  < 47.29°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.880. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6680 and 0.6820.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P 1 21/n 1, with Z = 8 for the formula unit,  $C_{27}H_{29}F_{12}N_{13}Ni_2OP_2$ . The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 1095 variables converged at R1 = 4.70%, for the observed data and wR2 = 11.79% for all data. The goodness-of-fit was 1.038. The largest peak in the final difference electron density synthesis was 0.753 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.596 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.093 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.853 g/cm<sup>3</sup> and F(000), 3872 e<sup>-</sup>.

Identification code	AltPh18			
Chemical formula	$C_{27}H_{29}F_{12}N_{13}Ni_2OP_2$			
Formula weight	958.99			
Temperature	123(2) К			
Wavelength	0.71073 Å			
Crystal size	0.321 x 0.335 x 0.341 mm			
Crystal habit	clear colourless fragment			
Crystal system	monoclinic			
Space group	P 1 21/n 1			
Unit cell dimensions	a = 16.9279(10) Å	α = 90°		
	b = 14.4946(8) Å	$\beta=93.054(4)^\circ$		
	c = 28.0590(15) Å	γ = 90°		
Volume	6874.9(7) Å <sup>3</sup>			
Z	8			
Density (calculated)	1.853 g/cm <sup>3</sup>			
Absorption coefficient	1.303 mm <sup>-1</sup>			
F(000)	3872			

Table 5. Sample and crystal data for AltPh18.

Table 6. Data collection and structure r	efinement for AltPh18.				
Diffractometer	Bruker Kappa APEX II CCD				
Radiation source	fine-focus tube, Mo				
Theta range for data collection	1.37 to 25.38°				
Index ranges	-20<=h<=20, -17<=k<=17	, -33<=l<=33			
Reflections collected	120413	20413			
Independent reflections	12603 [R(int) = 0.1111]				
Coverage of independent reflections	99.7%				
Absorption correction	multi-scan				
Max. and min. transmission	0.6820 and 0.6680				
Structure solution technique	direct methods				
Structure solution program	SHELXS-97 (Sheldrick, 2008)				
Refinement method	Full-matrix least-squares on F <sup>2</sup>				
Refinement program	SHELXL-97 (Sheldrick, 2008) and SHELXLE (Huebschle. 2011				
Function minimized	$\Sigma w(F_0^2 - F_c^2)^2$				
Data / restraints / parameters	12603 / 21 / 1095				
Goodness-of-fit on F <sup>2</sup>	1.038				
$\Delta/\sigma_{max}$	0.001				
Final R indices	8369 data; I>2σ(I)	R1 = 0.0470, wR2 = 0.1007			
	all data	R1 = 0.0850, wR2 = 0.1179			
Weighting scheme	w=1/[ $\sigma^2$ (F <sub>o</sub> <sup>2</sup> )+(0.0333P) <sup>2</sup> +9.8331P] where P=(F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3				
Largest diff. peak and hole	0.753 and -0.596 eÅ <sup>-3</sup>				
R.M.S. deviation from mean	0.093 eÅ <sup>-3</sup>				

# 9. Hirshfeld surface analysis<sup>2</sup>

4-OTf (2 independent molecules in the asymmetric unit)





H…O (34.3%)

H…F (20.1%)

N…H (4.5%)











H…all (79.4%)





2.4 d.

2.0









28

# **4-PF**<sub>6</sub>



# H…all (77.0%)

2.4 de

2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6

w

H…F (49.4%)





d,

2.2

1.6





N…H (6.0%)



# 29

## 10. Computational details

Quantum chemical calculations were performed using the Gaussian09 software package.<sup>3</sup> The functional  $\omega$ B97xD as well as the basis sets 6-311++G\*\* and LANL2DZ were employed as implemented in this software package. Single point frequency calculations were performed using the coordinates as determined by x-ray crystallography. For the visualization of the structures the program *ChemCraft* (Version 1.8) by G. A. Zhurko was used.



G [kcal/mol] = -995595.586353

Ν	0.259700000	1.376200000	-3.333100000	N	0.855900000	1.338000000	4.113100000
Ν	-0.855900000	-1.338000000	-4.113100000	N	1.872400000	-3.855900000	0.466400000
Ν	-1.872400000	3.855900000	-0.466400000	N	1.729900000	-3.790900000	-1.657700000
Ν	-1.729900000	3.790900000	1.657700000	N	0.177200000	-3.058200000	-3.351100000
Ν	-0.177200000	3.058200000	3.351100000	N	-0.099900000	-2.464400000	2.594700000
Ν	0.099900000	2.464400000	-2.594700000	Н	-0.745500000	-2.836500000	2.124800000
Н	0.745500000	2.836500000	-2.124800000	C	-1.145700000	-3.246800000	-3.086400000
С	1.145700000	3.246800000	3.086400000	Н	-1.534100000	-3.994800000	-2.646700000
Н	1.534100000	3.994800000	2.646700000	С	1.795500000	2.179000000	3.564800000
С	-1.795500000	-2.179000000	-3.564800000	Н	2.732500000	2.028600000	3.531200000
Н	-2.732500000	-2.028600000	-3.531200000	С	1.135900000	0.039500000	4.766400000
С	-1.135900000	-0.039500000	-4.766400000	Н	2.069000000	0.039500000	5.098700000
Н	-2.069000000	-0.039500000	-5.098700000	Н	0.535900000	-0.065000000	5.546900000
Н	-0.535900000	0.065000000	-5.546900000	С	1.861100000	-2.087200000	3.449000000
С	-1.861100000	2.087200000	-3.449000000	Н	2.778200000	-2.140700000	3.683900000
Н	-2.778200000	2.140700000	-3.683900000	С	1.545100000	-4.163000000	1.886400000
С	-1.545100000	4.163000000	-1.886400000	Н	2.329700000	-4.580900000	2.321100000
Н	-2.329700000	4.580900000	-2.321100000	Н	0.797300000	-4.811600000	1.916600000
Н	-0.797300000	4.811600000	-1.916600000	С	1.156100000	-4.234300000	-0.560600000
С	-1.156100000	4.234300000	0.560600000	Н	0.357600000	-4.745300000	-0.522000000
Н	-0.357600000	4.745300000	0.522000000	С	1.231300000	-4.013900000	-3.010900000
С	-1.231300000	4.013900000	3.010900000	Н	1.977700000	-3.923400000	-3.655400000
Н	-1.977700000	3.923400000	3.655400000	Н	0.874800000	-4.935200000	-3.081400000
Н	-0.874800000	4.935200000	3.081400000	С	2.882000000	-3.110400000	-1.320800000
С	-2.882000000	3.110400000	1.320800000	Н	3.495100000	-2.691200000	-1.915000000
Н	-3.495100000	2.691200000	1.915000000	С	2.960300000	-3.164000000	0.028500000
С	-2.960300000	3.164000000	-0.028500000	Н	3.645200000	-2.788100000	0.569000000
Н	-3.645200000	2.788100000	-0.569000000	С	0.343400000	-1.880800000	-3.962500000
С	-0.343400000	1.880800000	3.962500000	Н	1.170400000	-1.502300000	-4.237800000
Н	-1.170400000	1.502300000	4.237800000	С	0.948100000	-1.126400000	3.848400000
С	-0.948100000	1.126400000	-3.848400000	C	1.161300000	-2.941000000	2.643400000
С	-1.161300000	2.941000000	-2.643400000				
Ν	-0.259700000	-1.376200000	3.333100000				



G [kcal/mol] = -995567.0729439

С	1.012846000	3.797831000	1.184606000	C	2.388558000	4.108559000	0.682248000
Ν	-0.484020000	3.189110000	2.539970000	Н	2.978683000	4.306829000	1.451929000
Н	-0.873244000	2.896231000	3.272901000	Н	2.351467000	4.916660000	0.111429000
Ν	-3.034211000	2.683640000	0.090080000	C	1.012451000	-3.797869000	1.184614000
Ν	0.845063000	3.371341000	2.429657000	N	-0.484352000	-3.189090000	2.539978000
Ν	-3.063939000	1.197440000	-1.468054000	Н	-0.873546000	-2.896169000	3.272908000
Ν	3.148483000	1.205917000	-1.304658000	Ν	-3.034490000	-2.683360000	0.090086000
Ν	2.965582000	2.988028000	-0.097561000	N	0.844712000	-3.371359000	2.429665000
С	-2.679593000	0.000119000	-2.208499000	Ν	-3.064064000	-1.197160000	-1.468051000
Н	-3.123260000	0.000241000	-3.093436000	N	3.148357000	-1.206183000	-1.304655000
Н	-1.700479000	0.00068000	-2.354701000	N	2.965271000	-2.988372000	-0.097554000
С	-2.424569000	1.609208000	-0.378225000	С	-2.424736000	-1.608892000	-0.378221000
Н	-1.656397000	1.198868000	0.001322000	Н	-1.656522000	-1.198632000	0.001325000
С	2.300050000	1.971262000	-0.621264000	С	2.299845000	-1.971538000	-0.621260000
Н	1.368192000	1.813110000	-0.525363000	Н	1.368004000	-1.813290000	-0.525359000
С	-0.215806000	3.896794000	0.500666000	С	-0.216212000	-3.896706000	0.500674000
Н	-0.361926000	4.176000000	-0.395596000	Н	-0.362360000	-4.175900000	-0.395587000
С	4.302755000	2.874758000	-0.456405000	С	4.302457000	-2.875242000	-0.456399000
Н	5.004121000	3.469622000	-0.218117000	Н	5.003760000	-3.470078000	-0.218109000
С	4.416783000	1.757951000	-1.208800000	С	4.416600000	-1.758449000	-1.208796000
Н	5.213453000	1.416509000	-1.597664000	Н	5.213306000	-1.417091000	-1.597661000
С	-2.644425000	3.374221000	1.335203000	С	-2.644776000	-3.373979000	1.335211000
Н	-3.053638000	4.275442000	1.356245000	Н	-3.054082000	-4.275158000	1.356255000
Н	-2.980531000	2.865639000	2.115283000	Н	-2.980829000	-2.865261000	2.115290000
С	-4.128189000	2.044395000	-1.707113000	С	-4.128401000	-2.044005000	-1.707108000
Н	-4.752986000	1.983026000	-2.420038000	Н	-4.753192000	-1.982474000	-2.420034000
С	-4.108131000	2.976895000	-0.730600000	С	-4.108441000	-2.976505000	-0.730593000
Н	-4.717100000	3.698627000	-0.626880000	Н	-4.717484000	-3.698173000	-0.626872000
С	2.776987000	-0.000165000	-2.029795000	С	-1.155787000	-3.498256000	1.422245000
н	1.798917000	-0.000114000	-2.183315000	С	2.388130000	-4.108741000	0.682257000
н	3.223893000	-0.000189000	-2.913163000	Н	2.978235000	-4.307071000	1.451939000
С	-1.155423000	3.498344000	1.422238000	Н	2.350956000	-4.916840000	0.111440000

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