#### Electronic Supplementary Information

# Exploring transition metal fluoride chelates – synthesis, properties and prospects towards potential PET probes

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## Experimental details

The complexes were generally synthesised in atmospheric conditions unless otherwise stated. The known compounds are referenced where appropriate.  $[CrCl_3(thf)_3]$  was prepared by the literature method.<sup>51</sup> 2,2':6'2"-terpyridyl was obtained from Sigma-Aldrich and used as received. 1,4,7-Trimethyl-1,4,7-triazacyclononane was prepared according to a previously reported method.<sup>52</sup> Anhydrous  $[NMe_4]F$  was obtained by recrystallising the commercial sample (Aldrich) from <sup>i</sup>PrOH as described by Christe *et al.*<sup>53</sup> CH<sub>2</sub>Cl<sub>2</sub> and diethyl ether were dried prior to use by distillation from CaH<sub>2</sub> and sodium benzophenone ketyl, respectively. Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000-200 cm<sup>-1</sup>. <sup>1</sup>H, <sup>19</sup>F{<sup>1</sup>H} and <sup>59</sup>Co were recorded from H<sub>2</sub>O/D<sub>2</sub>O or MeOH/CD<sub>3</sub>OD solutions using a Bruker AV400 spectrometer and referenced to TMS *via* the residual solvent resonance, CFCl<sub>3</sub> and  $[Co(CN)_6]^{3-}$ , respectively. Microanalyses were undertaken by London Metropolitan University. UV-visible spectra were recorded in solution (H<sub>2</sub>O or MeCN) and as powdered solids, using the diffuse reflectance attachment, in a Perkin Elmer 750S spectrometer. Magnetic measurements were made on a Johnson Matthey magnetic balance.

**[CrCl<sub>3</sub>(Me<sub>3</sub>-tacn)].** Reaction carried out in anhydrous conditions using Schlenk and glove box techniques using a modification of the method reported.<sup>52</sup> [CrCl<sub>3</sub>(thf)<sub>3</sub>] (170 mg, 0.46 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> to give a purple solution, to which Me<sub>3</sub>-tacn (94 mg, 0.55 mmol) was added, resulting in a green solution. The reaction mixture was stirred at room temperature for 1 h. A green solid was filtered from the reaction mixture, washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 78 mg, 52 %. Required for C<sub>9</sub>H<sub>21</sub>Cl<sub>3</sub>CrN<sub>3</sub>: C, 32.8; H, 6.4; N, 12.8. Found: C, 32.6; H, 6.5; N, 12.6 %. IR (Nujol,  $v/cm^{-1}$ ): 340, 327 (Cr–Cl). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 14144, 15898, 21505, 38610, 45662.

 $[CrF_3(py)_3]$ ·3.5H<sub>2</sub>O. This was prepared by the literature method.<sup>S4</sup> Purple solid. Yield: 43 %. IR (Nujol, v/cm<sup>-1</sup>): 3391, 1659 (H<sub>2</sub>O), 571, 559 (Cr–F). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 14144, 17361, 21277, 26596, 31646, 38168, 45872. UV-vis 10<sup>-3</sup> M in water/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 18051 (95), 26385 (110), 28902 (136), 31546 (203).

[CrF<sub>3</sub>(terpy)]·4H<sub>2</sub>O. This was prepared by the literature method.<sup>20</sup> Purple solid. Yield: 92 %. Required for  $C_{15}H_{11}NCrF_3N_3\cdot4H_2O$ : C, 43.5; H, 4.6; N, 10.1. Found: C, 43.5; H, 4.2; N, 10.0 %. IR (Nujol, v/cm<sup>-1</sup>): 3370, 1664 (H<sub>2</sub>O), 552 (br, Cr–F). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 14104, 17361, 22573, 24213, 28329, 31348, 39063, 46296. UV-vis 10<sup>-3</sup> M in water/cm<sup>-1</sup> ( $\epsilon/M^{-1}$  cm<sup>-1</sup>): 14245 (45), 17921 (172), 22573 (118), 24213 (244), 25840 (443).

**[CrF<sub>3</sub>(Me<sub>3</sub>-tacn)]·3.5H<sub>2</sub>O.** This was prepared by the literature method.<sup>20</sup> Purple solid. Yield: 53 %. Required for C<sub>9</sub>H<sub>21</sub>NCrF<sub>3</sub>N<sub>3</sub>·3.5H<sub>2</sub>O: C, 31.5; H, 8.2; N, 12.2. Found: C, 30.8; H, 8.8; N, 13.2 %. A small amount of pyridinium salt by-product in the isolated product is the likely cause for the larger than normal variation between the experimental and calculated data. IR (Nujol, v/cm<sup>-1</sup>): 3376, 1662 (H<sub>2</sub>O), 541, 511 (Cr–F). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 14771, 17762, 24213. UV-vis 10<sup>-3</sup> M in water/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 14815 (8), 17986 (97), 24570 (43).

[MnF<sub>3</sub>(terpy)]·MeOH·3H<sub>2</sub>O. This was prepared by modifying the method reported,<sup>24</sup> using anhydrous conditions, Schlenk and glove box techniques. Terpy (115 mg, 0.49 mmol) was dissolved in methanol (6 mL) and MnF<sub>3</sub> (50 mg, 0.45 mmol) was added resulting in a brown

solution with a small amount of black precipitate. The reaction mixture was stirred at room temperature for 2 h, before filtering to remove the black solid (MnO<sub>2</sub>). Diethyl ether (20 mL) was added, yielding an orange precipitate. The solid was filtered and dried *in vacuo*. Yield: 81 mg, 52 %. Required for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>MnN<sub>3</sub>·MeOH·3H<sub>2</sub>O: C, 44.6; H, 4.9; N, 9.7. Found: C, 45.1; H, 4.8; N, 9.0 %. IR (Nujol, v/cm<sup>-1</sup>): 3410, 1640 (H<sub>2</sub>O), 597, 573 (Mn–F). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 298 K):  $\delta$  = 3.28 (s, OH), 2.15 (s, CH<sub>3</sub>OH). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 12739, 18315, 21978, 26316, 30864, 26738, 44843. UV-vis 10<sup>-3</sup> M in water/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 15552 (160), 18182 (172); UV-Vis 10<sup>-3</sup> M in MeCN/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 13793 (17), 18149 (24), 22883 (60).

**[MnF<sub>3</sub>(Me<sub>3</sub>-tacn)]·2H<sub>2</sub>O.** Reaction carried out in anhydrous conditions using Schlenk and glove box techniques. A solution of MnF<sub>3</sub> (91 mg, 0.55 mmol) in MeOH (10 mL) was added to a MeOH (5 mL) solution of Me<sub>3</sub>-tacn (94 mg, 0.55 mmol), forming a green solution. The reaction mixture was left stirring at room temperature for 22 h after which time the solution was a deep red colour. The solvent was removed *in vacuo* and the resulting red solid was washed with diethyl ether (10 mL) before being dried *in vacuo*. Yield: 121 mg, 78 %. Required for C<sub>9</sub>H<sub>21</sub>F<sub>3</sub>MnN<sub>3</sub>· 2H<sub>2</sub>O: C, 33.9; H, 7.9; N, 13.2. Found: C, 33.8; H, 7.7; N, 13.0 %. IR (Nujol, v/cm<sup>-1</sup>): 3438, 1664 (H<sub>2</sub>O), 585, 553 (Mn–F). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 19569, 33898, 39063, 46083. UV-vis  $10^{-3}$  M in water/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 20534 (169), 22222 (143), 23810 (130); UV-vis  $10^{-3}$  M in MeCN/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 18904 (292).  $\mu_{eff}$  = 4.94 BM (298 K). Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of a concentrated solution of the complex in water.

**[FeCl<sub>3</sub>(Me<sub>3</sub>-tacn)].** This was made via a modification of the literature method.<sup>S5</sup> FeCl<sub>3</sub> (60 mg, 0.36 mmol) was dissolved in diethyl ether (5 mL) forming a brown solution and a diethyl ether (3 mL) solution of Me<sub>3</sub>-tacn (0.07 mL, 0.36 mmol) was added. The mixture was stirred for 15 mins. and the yellow solid formed filtered, washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 112 mg, 92 %. Required for C<sub>9</sub>H<sub>21</sub>Cl<sub>3</sub>FeN<sub>3</sub>: C, 32.4; H 6.4; N 12.6. Found: C, 32.3; H, 6.4; N, 12.6 %. IR (Nujol, v/cm<sup>-1</sup>): 308, 298 (Fe-Cl). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 17857, 25316, 32787, 44053.

**[FeF<sub>3</sub>(terpy)]·2H<sub>2</sub>O.** FeF<sub>3</sub>·3H<sub>2</sub>O (72 mg, 0.43 mmol) was suspended n-BuOH (15 mL) and a solution of terpy (101 mg, 0.43 mmol) in n-BuOH (5 mL) was added. The mixture was heated to reflux for 4 h, resulting in a clear red/purple solution. The mixture was cooled to room temperature and the solvent was removed *in vacuo* giving a fine pink/purple powder, which was washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 79 mg, 52 %. Required for  $C_{15}H_{11}F_3FeN_3\cdot 2H_2O$ : C, 47.1; H 4.0; N 11.00. Found: C, 46.4; H, 4.2; N, 10.6 %. IR (Nujol, v/cm<sup>-1</sup>): 540, 517, 503 (Fe–F). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 16026, 17857, 20619, 30675, 40323, 45249. UV-vis 10<sup>-3</sup> M in water/cm<sup>-1</sup> ( $\epsilon/M^{-1}$  cm<sup>-1</sup>): 16155 (72), 18116 (366), 20284 (210). Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of a concentrated solution of the complex in water.

[FeF<sub>3</sub>(Me<sub>3</sub>-tacn)]·H<sub>2</sub>O. This was synthesised using a modification of the literature method.<sup>19</sup>

*Method 1:*  $FeF_3 \cdot 3H_2O$  (88 mg, 0.53 mmol) was suspended in n-BuOH (15 mL) and a solution of Me<sub>3</sub>-tacn (90 mg, 0.53 mmol) in n-BuOH (5 mL) was added. The mixture was heated to reflux for 4 h, resulting in a clear yellow solution. The mixture was cooled to room temperature and the solvent was removed *in vacuo* giving a pale yellow solid, which was washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 60 mg, 40 %. Required for C<sub>9</sub>H<sub>21</sub>F<sub>3</sub>FeN<sub>3</sub>·H<sub>2</sub>O: C, 35.8; H

7.7; N 13.9. Found: C, 35.6; H, 8.1; N, 13.1 %. IR (Nujol, v/cm<sup>-1</sup>): 3439, 1664 (H<sub>2</sub>O), 529, 512 (Fe–F). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 22222, 26455, 33223, 40161, 46083. UV-vis  $10^{-2}$  M in water/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 32573 (60).

*Method 2:* [FeCl<sub>3</sub>(Me<sub>3</sub>-tacn)] (45 mg, 0.13 mmol) was dissolved in MeCN (10 mL) giving a yellow solution, and a suspension of [Me<sub>4</sub>N]F (56 mg, 0.60 mmol) in MeCN (5 mL) was added. The mixture was heated to reflux for 4 h. The solvent was removed *in vacuo* giving a pale yellow/orange solid.  $CH_2Cl_2$  (4 mL) was added and the mixture was filtered to remove the excess [Me<sub>4</sub>N]F and [Me<sub>4</sub>N]Cl, giving a clear yellow solution. The solvent was then removed *in vacuo* giving a yellow solid. Yield: 16 mg, 42 %. Spectroscopically identical to the product obtained following method 1., except that a small amount of [Me<sub>4</sub>N]Cl precipitated with the product and having similar solubility properties, it proved difficult to remove. This has also been observed in an analogous system.<sup>13</sup> IR (Nujol, v/cm<sup>-1</sup>): 536, 525 (Fe-F).

*Method 3*: [FeCl<sub>3</sub>(Me<sub>3</sub>-tacn)] (50 mg, 0.15 mmol) was dissolved in MeCN (15 mL) giving a yellow solution, and a solution of KF (35 mg, 0.60 mmol) in H<sub>2</sub>O (8 mL) was added. The mixture was left stirring at room temperature for 30 mins. and the solvents were removed *in vacuo*. The product was dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> (4 mL), filtered to remove the excess KF, and the solvent removed *in vacuo* giving a pale yellow solid. Yield: 28 mg, 67%. IR (Nujol, v/cm<sup>-1</sup>): 3437, 1664 (H<sub>2</sub>O), 524, 509 (Fe-F).

**[FeF<sub>3</sub>(BnMe<sub>2</sub>-tacn)]·3.5H<sub>2</sub>O.** FeF<sub>3</sub>·3H<sub>2</sub>O (69 mg, 0.41 mmol) was suspended in n-BuOH (15 mL) and a solution of BnMe<sub>2</sub>-tacn (103 mg, 42 mmol) in n-BuOH (5 mL) was added. The mixture was heated to reflux for 30 mins., resulting in a clear yellow solution. The mixture was cooled to room temperature and the solvent removed *in vacuo* giving a pale yellow solid, which was washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 129 mg, 74%. Required for C<sub>15</sub>H<sub>25</sub>F<sub>3</sub>FeN<sub>3</sub>·3.5H<sub>2</sub>O: C, 42.6; H, 7.6; N, 9.9. Found: C, 42.8; H, 7.9; N, 10.1%. IR (Nujol, v/cm<sup>-1</sup>): 3391, 1650 (H<sub>2</sub>O), 537, 517 (Fe–F). ES<sup>+</sup> MS (MeCN/H<sub>2</sub>O): *m/z* = 383 ([FeF<sub>3</sub>(BnMe<sub>2</sub>-tacn)+Na]<sup>+</sup>) (35%), 341 ([FeF<sub>2</sub>(BnMe<sub>2</sub>-tacn)]<sup>+</sup>) (100%). Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of a concentrated solution of the complex in water.

**[CoCl<sub>3</sub>(Me<sub>3</sub>-tacn)]·3H<sub>2</sub>O.** CoCl<sub>2</sub>·6H<sub>2</sub>O (149 mg, 0.63 mmol) was suspended in MeOH (5 mL) and a solution of Me<sub>3</sub>-tacn (110 mg, 0.63 mmol) in MeOH (5mL) was added dropwise. The mixture turned brown and then black within 10 mins. LiCl (29 mg, 0.63 mmol) was added to the mixture. The reaction mixture was left stirring for 2 h at room temperature and the solvent removed *in vacuo* giving a pale pink solid. This solid was washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 220 mg, 90 %. Required for C<sub>9</sub>H<sub>21</sub>Cl<sub>3</sub>CoN<sub>3</sub>·3H<sub>2</sub>O: C, 27.7; H 7.0; N 10.8. Found: C, 27.5; H, 6.9; N, 10.8 %. IR (Nujol, v/cm<sup>-1</sup>): 3376, 1640 (H<sub>2</sub>O), 261, 245 (Co–Cl). <sup>1</sup>H NMR (D<sub>2</sub>O, 298 K):  $\delta$  = 3.01 (m, [6H], CH<sub>2</sub>), 2.90 (m, [6H], CH<sub>2</sub>), 2.70 (s, [9H], CH<sub>3</sub>). <sup>59</sup>Co NMR (D<sub>2</sub>O, 298 K):  $\delta$  = 10190 (br s, w<sub>1/2</sub> = 2760 Hz). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 13158, 17699, 18868, 27778, 39216, 46512.

**CoF<sub>3</sub>(terpy)]·MeOH·H<sub>2</sub>O.** CoF<sub>2</sub>·4H<sub>2</sub>O (150 mg, 0.89 mmol) was suspended in MeOH (5 mL) and a solution of terpy (222 mg, 0.98 mmol) in MeOH (5mL) was added dropwise. The reaction mixture turned deep orange/brown within 20 minutes. NaF (15 mg, 0.36 mmol) was added to the mixture. The reaction mixture was left stirring at room temperature for 90 mins., filtered and the solvent removed *in vacuo*, giving an orange solid. This solid was washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 243 mg, 76 %. Required for  $C_{15}H_{11}CoF_3N_3$ ·MeOH·H<sub>2</sub>O:

C, 48.1; H, 4.3; N, 10.5. Found: C, 48.1; H, 4.5; N, 10.7 %. IR (Nujol, v/cm<sup>-1</sup>): 3377, 1654 (H<sub>2</sub>O), 665, 651, 637 (Co–F). <sup>1</sup>H NMR (D<sub>2</sub>O, 298 K):  $\delta$  = 9.07 (s, [2H], Ar-CH<sub>2</sub>), 8.63 (d, [3H], Ar-CH<sub>2</sub>), 8.20 (t, [2H], Ar-CH<sub>2</sub>), 7.39 (t, [2H], Ar-CH<sub>2</sub>), 7.31 (d, [2H], Ar-CH<sub>2</sub>), 3.23 (s, CH<sub>3</sub>OH). <sup>19</sup>F{<sup>1</sup>H} NMR (D<sub>2</sub>O, 298 K):  $\delta$  = -116 (br s). <sup>59</sup>Co NMR (D<sub>2</sub>O, 298 K):  $\delta$  = 8179 (br s, w<sub>1/2</sub> = 36700 Hz). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 17291, 19531, 24631, 32223. UV-vis = 10<sup>-3</sup> M in water/cm<sup>-1</sup> ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 17857 (75), 19724 (228), 22371 (262).

**[CoF<sub>3</sub>(Me<sub>3</sub>-tacn)]·2H<sub>2</sub>O.** CoF<sub>2</sub>·4H<sub>2</sub>O (72 mg, 0.42 mmol) was suspended in MeOH (5 mL) and a solution of Me<sub>3</sub>-tacn (72 mg, 0.42 mmol) in MeOH (5mL) was added dropwise. The mixture turned brown and then black within 20 minutes. NaF (13 mg, 0.31 mmol) was added to the mixture. The reaction mixture was left stirring at room temperature for 2 h, filtered and the solvent was removed *in vacuo* giving a brown solid. This solid was washed with diethyl ether (10 mL) and dried *in vacuo*. Yield: 85 mg, 70 %. The solid turned purple overnight. Required for C<sub>9</sub>H<sub>21</sub>CoF<sub>3</sub>N<sub>3</sub>·2H<sub>2</sub>O: C, 33.4; H 7.8; N 13.0. Found: C, 33.2; H, 7.9; N, 12.9 %. IR (Nujol, v/cm<sup>-1</sup>): 3353, 1656 (H<sub>2</sub>O), 591, 574 (Co–F). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 298 K):  $\delta$  = 3.12 (m, [6H], CH<sub>2</sub>), 3.02 (m, [6H], CH<sub>2</sub>), 2.84 (s, [9H], CH<sub>3</sub>). <sup>19</sup>F<sup>1</sup>H<sup>1</sup> NMR (CD<sub>3</sub>OD, 298 K):  $\delta$  = -149 (br s). <sup>59</sup>Co NMR (CD<sub>3</sub>OD, 298 K):  $\delta$  = 9093 (br s, w<sub>1/2</sub> = 15600 Hz). UV-vis (diffuse reflectance)/cm<sup>-1</sup>: 12739, 17544, 19608, 26667, 39216, 45455. Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of a concentrated solution of the complex in water.

#### X-ray Experimental

Crystals of the complexes were grown as described in the Experimental section. Data was collected using a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ( $\lambda = 0.71073$  Å) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013 or SHELX-2014/7.<sup>56</sup> H atoms bonded to C were placed in calculated positions using the default C–H distance, and refined using a riding model. In [MnF<sub>3</sub>(Me<sub>3</sub>-tacn)]·4H<sub>2</sub>O and [CoF<sub>3</sub>(Me<sub>3</sub>-tacn)]·4H<sub>2</sub>O, the carbon atoms in the ring were disordered and were modelled with split occupancy factors. Details of the crystallographic parameters are given in Table S1. CCDC reference numbers in cif format are [MnF<sub>3</sub>(Me<sub>3</sub>-tacn)]·4H<sub>2</sub>O: 1860121; [FeF<sub>3</sub>(terpy)]·3H<sub>2</sub>O: 1860122; [CoF<sub>3</sub>(Me<sub>3</sub>-tacn)]·4H<sub>2</sub>O: 1860123; [FeF<sub>3</sub>(BnMe<sub>2</sub>-tacn)]·2H<sub>2</sub>O: 1897030.

# Crystallographic Information



Figure S1. View of the H-bonding (blue dotted lines) and  $\pi$ -stacking (grey dotted lines) in the X-ray crystal structure of [FeF<sub>3</sub>(terpy)]·3H<sub>2</sub>O.



Figure S2. View of the H-bonding (blue dotted lines) in the X-ray crystal structure of  $[CoF_3(Me_3-tacn)] \cdot 4H_2O$ .

Table 31. A-lay crystallographic parameters.	Table S1.	X-ray c	rystallogr	aphic	parameter	s.ª
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Compound	[MnF <sub>3</sub> (Me <sub>3</sub> tacn)]·4H <sub>2</sub> O	[FeF <sub>3</sub> (terpy)]·3H <sub>2</sub> O	[CoF <sub>3</sub> (Me <sub>3</sub> -tacn)]·4H <sub>2</sub> O	[FeF <sub>3</sub> (BnMe <sub>2</sub> -tacn)]·2H <sub>2</sub> O
Formula	$C_9H_{21}F_3MnN_3\cdot4(H_2O)$	C <sub>15</sub> H <sub>11</sub> F <sub>3</sub> FeN <sub>3</sub> ·3(H <sub>2</sub> O)	$C_9H_{21}CoF_3N_3\cdot 4(H_2O)$	$C_{15}H_{29}F_3FeN_3O_2$
М	355.55	400.16	359.03	396.26
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group (no.)	Pbca (61)	P2 <sub>1</sub> /c (14)	Pbca (61)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (19)
a /Å	8.9041(2)	8.6981(2)	8.74923(7)	9.5216(3)
b/Å	13.2669(3)	25.5075(5)	13.14407(11)	12.4903(4)
c /Å	26.9700(6)	25.5075(5)	26.2569(3)	29.8518(9)
α/°	90	90	90	90
β/°	90	102.155(2)	90	90
γ /°	90	90	90	90
<i>U</i> /Å <sup>3</sup>	3185.96(12)	1613.96(7)	3019.55(5)	3550.20(19)
Ζ	8	4	8	8
μ(Mo-K <sub>α</sub> ) /mm <sup>-1</sup>	0.875	0.987	1.186	0.892
F(000)	1505	820	1518	1672
Total number reflns	32812	34245	30727	74969
R <sub>int</sub>	0.058	0.027	0.025	0.082
Unique reflns	3124	3177	2973	6982
No. of params, restraints	254, 276	235, 0	253, 243	449, 0
GOF	1.410	1.062	1.380	1.070
$R_1, wR_2 [I > 2\sigma(I)]^{b}$	0.069, 0.116	0.021, 0.057	0.059, 0.143 0.030, 0.056	
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.066, 0.117	0.023, 0.058	0.059, 0.143 0.034, 0.057	

<sup>a</sup> Common items: T = 293 K; wavelength (Mo-K<sub>α</sub>) = 0.71073 Å;  $\theta$ (max) = 27.5°;

<sup>b</sup>  $R_1 = \Sigma ||Fo|-|Fc||/\Sigma |Fo|$ ;  $wR_2 = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w Fo^4]^{1/2}$ 

Additional Spectroscopic Information:



Figure S3. Comparison of the IR spectra of  $[CrCl_3(Me_3-tacn)]$  (black),  $[CrF_3(Me_3-tacn)]$  (blue) and the crude product from the halide exchange reaction using  $[CrCl_3(Me_3-tacn)] + 4 [Me_4N]F$  (red).



Figure S4. Neat UV-vis diffuse reflectance spectrum of [CrCl<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S5. IR spectrum (Nujol) of [CrCl<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S6. Neat UV-vis diffuse reflectance spectrum of  $[CrF_3(py)_3]$ .



Figure S7. IR spectrum (Nujol) of [CrF<sub>3</sub>(py)<sub>3</sub>].



Figure S8. Neat UV-vis diffuse reflectance spectrum of [CrF<sub>3</sub>(terpy)].



Figure S9. Solution UV-vis spectrum of the complex:  $10^{-3}$  in H<sub>2</sub>O of [CrF<sub>3</sub>(terpy)].



Figure S10. IR spectrum (Nujol) of  $[CrF_3(terpy)]$ .



Figure S11. UV-vis stability tests of [CrF<sub>3</sub>(terpy)].



Figure S12. Neat UV-vis diffuse reflectance spectrum of  $[CrF_3(Me_3-tacn)]$ .



Figure S13. . Solution UV-vis spectrum of the complex:  $10^{-3}$  in H<sub>2</sub>O of [CrF<sub>3</sub>(Me<sub>3</sub>-tacn)].







Figure S15. Neat UV-vis diffuse reflectance spectrum of [MnF<sub>3</sub>(terpy)].



Figure S16. Solution UV-vis spectrum of the complex:  $10^{-3}$  in H<sub>2</sub>O of [MnF<sub>3</sub>(terpy)].



Figure S17. Solution UV-vis spectrum of the complex:  $10^{-3}$  in MeCN of [MnF<sub>3</sub>(terpy)].



Figure S18. IR spectrum (Nujol) of [MnF<sub>3</sub>(terpy)].



Figure S19. Neat UV-vis diffuse reflectance spectrum of  $[MnF_3(Me_3-tacn)]$ .



Figure S20. Solution UV-vis spectrum of the complex:  $10^{-3}$  in H<sub>2</sub>O of [MnF<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S21. Solution UV-vis spectrum of the complex:  $10^{-3}$  in MeCN of [MnF<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S22. IR spectrum (Nujol) of [MnF<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S23. UV-vis stability tests of [MnF<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S24. Neat UV-vis diffuse reflectance spectrum of [FeCl<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S25. IR spectrum (Nujol) of [FeCl<sub>3</sub>(Me<sub>3</sub>-tacn)].



Figure S26. Neat UV-vis diffuse reflectance spectrum of [FeF<sub>3</sub>(terpy)].



Figure S27. Solution UV-vis spectrum of the complex:  $10^{-3}$  in H<sub>2</sub>O of [FeF<sub>3</sub>(terpy)].



Figure S28. IR spectrum (Nujol) of [FeF<sub>3</sub>(terpy)].

![](_page_23_Figure_0.jpeg)

Figure S29. UV-vis stability tests of [FeF<sub>3</sub>(terpy)].

![](_page_24_Figure_0.jpeg)

Figure S30. Neat UV-vis diffuse reflectance spectrum of [FeF<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_24_Figure_2.jpeg)

Figure S31. Solution UV-vis spectrum of the complex:  $10^{-2}$  in H<sub>2</sub>O of [FeF<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_25_Figure_0.jpeg)

![](_page_25_Figure_1.jpeg)

![](_page_25_Figure_2.jpeg)

Figure S33. UV-vis stability tests of [FeF<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_26_Figure_0.jpeg)

Figure S34. Neat UV-vis diffuse reflectance spectrum of [CoF<sub>3</sub>(terpy)].

![](_page_26_Figure_2.jpeg)

Figure S35. Solution UV-vis spectrum of the complex:  $10^{-3}$  in H<sub>2</sub>O of [CoF<sub>3</sub>(terpy)].

![](_page_27_Figure_0.jpeg)

Figure S37.  $^{19}F\{^{1}H\}$  NMR spectrum (D<sub>2</sub>O, 298 K) of [CoF<sub>3</sub>(terpy)].

![](_page_28_Figure_0.jpeg)

![](_page_28_Figure_1.jpeg)

Figure S39. IR spectrum (Nujol) of  $[CoF_3(terpy)]$ .

![](_page_29_Figure_0.jpeg)

Figure S40. Neat UV-vis diffuse reflectance spectrum of [CoF<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_29_Figure_2.jpeg)

Figure S41. <sup>19</sup>F<sup>{1</sup>H} NMR spectrum (MeOD, 298 K) of [CoF<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_30_Figure_0.jpeg)

Figure S43. IR spectrum (Nujol) of [CoF<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_31_Figure_0.jpeg)

Figure S44. Neat UV-vis diffuse reflectance spectrum of [CoCl<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_31_Figure_2.jpeg)

![](_page_32_Figure_0.jpeg)

Figure S46.  ${}^{59}$ Co NMR spectrum (D<sub>2</sub>O, 298 K) of [CoCl<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_32_Figure_2.jpeg)

Figure S47. IR spectrum (Nujol) of [CoCl<sub>3</sub>(Me<sub>3</sub>-tacn)].

![](_page_33_Figure_1.jpeg)

Figure S48. IR spectrum (Nujol) of [FeF<sub>3</sub>(BnMe<sub>2</sub>-tacn)].

![](_page_33_Figure_3.jpeg)

Figure S49. ES<sup>+</sup> mass spectrum of  $[FeF_3(BnMe_2-tacn)+Na]^+$  (left) and the predicted isotope pattern for  $[FeF_3(BnMe_2-tacn)+Na]^+$  (right).

![](_page_34_Figure_0.jpeg)

Figure S50. View of the H-bonding (blue dotted) in the X-ray crystal structure of [FeF<sub>3</sub>(BnMe<sub>2</sub>-tacn)]·2H<sub>2</sub>O.

### Radiofluorination experiments

![](_page_35_Figure_1.jpeg)

Figure S51. A: UV-HPLC chromatogram of reference standard compound  $[Fe^{19}F_3(BnMe_2-tacn)]$  (Rt = 6.67 min); B: Analytical radio-HPLC chromatograms of the crude product from reaction of  $[Fe^{19}F_3(BnMe_2-tacn)]$  (1 mg, 2360 nmol) with  $[^{18}F]F^-$  in 75:25 MeCN:target water at 80°C for 10 min. Peak 1: Rt = 2.18 min 48% ( $[^{18}F]F^-$ ). Peak 2: 6.83 min 52% ( $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$ ).

![](_page_35_Figure_3.jpeg)

Figure S52. Radio-chromatogram of the crude product from [FeF<sub>3</sub>(BnMe<sub>2</sub>-tacn)] (1 mg, 2360 nmol) in 25 % MeCN/H<sub>2</sub>O at 25 °C for 10 mins. Peak 1: Rt = 1.98 min 93 % ([<sup>18</sup>F]F<sup>-</sup>). Peak 2: Rt = 6.90 min 7 % ([Ga<sup>18</sup>F<sup>19</sup>F<sub>2</sub>(BnMe<sub>2</sub>tacn)]).

![](_page_36_Figure_0.jpeg)

Figure S53. Radio-HPLC chromatogram of the purified  $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$  from reaction of  $[FeF_3(BnMe_2-tacn)]$  (0.1 mg, 236 nmol) and  $[^{18}F]F^-$  in 75:25 MeCN:H<sub>2</sub>O at 80 °C for 10 minutes, purified through a HLB cartridge and formulated in 10:90 EtOH/HSA at t = 50 minutes. Peak 1: Rt = 2.42 min 5% ( $[^{18}F]F^-$ ). Peak 2: Rt = 7.00 min 95% ( $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$ ).

![](_page_36_Figure_2.jpeg)

Figure S54. Radio-HPLC chromatogram of the purified  $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$  from reaction of  $[FeF_3(BnMe_2-tacn)]$  (0.1 mg, 236 nmol) and  $[^{18}F]F^-$  in 75:25 MeCN:H<sub>2</sub>O at 80 °C for 10 minutes, purified through an HLB cartridge and formulated in 10:90 EtOH/HSA at t = 120 minutes. Peak 1: Rt = 2.56 min 10% ( $[^{18}F]F^-$ ). Peak 2: Rt = 6.84 min 90% ( $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$ ).

![](_page_37_Figure_0.jpeg)

Figure S55. Radio-HPLC chromatogram of the purified  $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$  from reaction of  $[FeF_3(BnMe_2-tacn)]$  (0.1 mg, 236 nmol) and  $[1^{18}F]F^-$  in 75:25 MeCN:H<sub>2</sub>O at 80 °C for 10 minutes, purified through an HLB cartridge and formulated in 10:90 EtOH/PBS at t = 30 minutes. Rt = 7.54 min >99% ( $[Fe^{18}F^{19}F_2(BnMe_2-tacn)]$ ).

![](_page_37_Figure_2.jpeg)

Figure S56. Radio-HPLC chromatogram of the purified [ $Fe^{18}F^{19}F_2(BnMe_2-tacn)$ ] from reaction of [ $FeF_3(BnMe_2-tacn)$ ] (0.1 mg, 236 nmol) and [ $^{18}F$ ]F<sup>-</sup> in 75:25 MeCN:H<sub>2</sub>O at 80 °C for 10 minutes, purified through an HLB cartridge and formulated in 10:90 EtOH/PBS at t = 170 minutes. Peak 1: Rt = 2.68 min 10% ([ $^{18}F$ ]F<sup>-</sup>). Peak 2: Rt = 6.83 min 90% ([ $Fe^{18}F^{19}F_2(BnMe_2-tacn)$ ]).

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