Al(III)-NTA-Fluoride: A Simple Model System for Al–F Binding with Interesting Thermodynamics

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Table S1. Experimental parameters of the crystal structure of $[Al(NTA)(H_2O)_2]\cdot 2H_2O$

Parameter	$[Al(NTA)(H_2O)_2]\cdot 2H_2O$
Formula	$C_6H_{14}AlNO_{10}$
M_r	287.16
Habit	plate
Colour	colourless
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.9061(6)
b (Å)	14.6917(7)
c (Å)	13.8670(6)
b (°)	95.546(2)
U, Å^3	2414.3(2)
Z	8
D_{calc}, g cm^{-3}	1.580
m, mm^{-1}	1.982
Unique refl.	4740
Obsd. refl. ($I>2s(I)$)	4268
$R(I>2s(I))$	0.0307
R'(all)	0.0351
$wR(I>2s(I))$	0.0797
wR'(all)	0.0823

Table S2. Coordination geometry of the independent complex units found in the crystal structure of $[Al(NTA)(H_2O)_2]\cdot 2H_2O$

Compound	Molecule 1	Molecule 2	Minimized geometry [a]
	Distance (Å)		
Al–N1	2.055(1)	2.100(1)	2.09
Al–O11	1.879(1)	1.900(1)	1.85
Al–O21	1.885(1)	1.854(1)	1.84
Al–O31	1.897(1)	1.885(1)	1.85
Al–O1w	1.822(1)	1.838(1)	1.93
Al–O2w	1.889(1)	1.882(1)	2.01
	Angle (°)		
N1–Al–O11	83.73(5)	81.26(5)	83.7
N1–Al–O21	85.53(5)	85.05(5)	87.1
N1–Al–O31	81.51(5)	82.37(5)	83.9
N1–Al–O1w	173.09(5)	175.50(5)	173.0
N1–Al–O2w	95.44(5)	93.04(5)	100.0
O11–Al–O21	91.15(5)	90.77(5)	97.6
O11–Al–O31	163.93(5)	162.07(5)	160.0
O11–Al–O1w	96.76(5)	101.01(5)	97.7
O11–Al–O2w	87.38(5)	85.14(5)	83.5
O21–Al–O31	93.99(5)	95.05(5)	97.3
O21–Al–O1w	87.57(5)	91.02(5)	85.9
O21–Al–O2w	178.14(5)	175.72(5)	172.9
O31–Al–O1w	98.66(5)	95.84(5)	96.6
O31–Al–O2w	87.72(5)	88.49(5)	83.4
O1w–Al–O2w	91.47(5)	91.03(5)	87.0

[a] B3LYP/def2-TZVP/PCM geometry

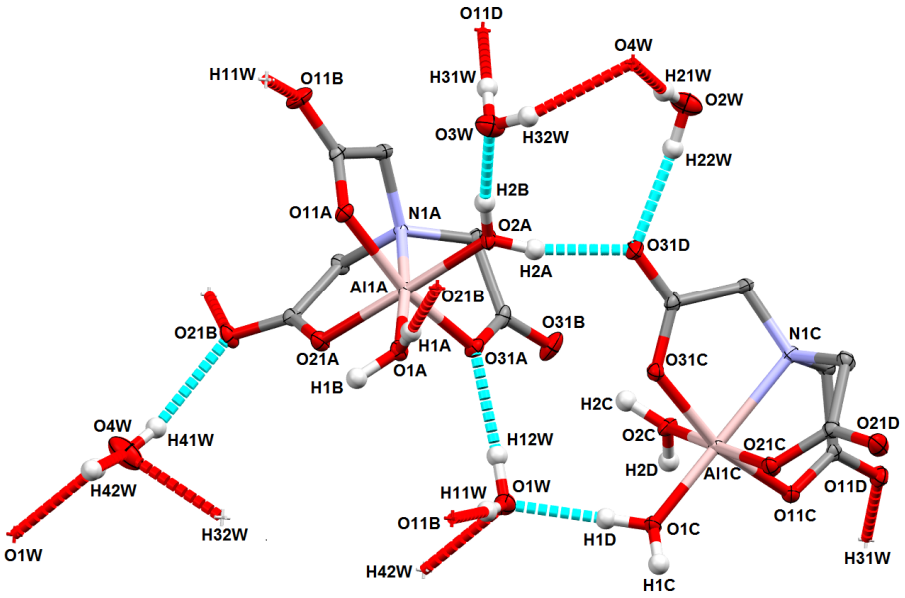


Figure S1. Hydrogen-bond system found in the crystal structure of $[Al(NTA)(H_2O)_2]\cdot 2H_2O$; Carbon-bound hydrogen atoms are omitted for clarity.

Table S3. Parameters of intermolecular hydrogen bonds found in the crystal structure of $[Al(NTA)(H_2O)_2]\cdot 2H_2O$

D–H	*d*(D–H) (Å)	*d*(H···A) (Å)	<DHA (°)	*d*(D···A) (Å)	A [symmetry code]
O1A–H1A	0.82(3)	1.75(3)	177(3)	2.565(2)	O21B [x, –y+3/2, z–1/2]
O1A–H1B	0.91(3)	1.68(3)	175(3)	2.592(2)	O11D [x–1, y, z]
O2A–H2A	0.85(3)	1.78(3)	167(3)	2.612(2)	O31D
O2A–H2B	0.87(3)	1.76(3)	172(2)	2.623(2)	O3W
O1C–H1C	0.90(3)	1.70(3)	164(3)	2.579(2)	O21D [–x+1, –y+2, –z+1]
O1C–H1D	0.85(3)	1.82(3)	179(2)	2.664(2)	O1W
O2C–H2C	0.88(3)	1.71(3)	170(2)	2.580(2)	O31B
O2C–H2D	0.86(3)	1.69(3)	177(3)	2.554(2)	O2W [–x+1, y+1/2, –z+3/2]
O1W–H11W	0.85(3)	1.85(3)	175(2)	2.701(2)	O11B [–x, y+1/2, –z+3/2]
O1W–H12W	0.89(3)	2.00(2)	177(2)	2.883(2)	O31A
O2W–H21W	0.86(3)	1.90(3)	169(3)	2.740(2)	O4W [–x, y–1/2, –z+3/2]
O2W–H22W	0.85(3)	1.98(3)	176(3)	2.829(2)	O31D
O3W–H31W	0.85(3)	2.00(3)	158(3)	2.809(2)	O11D [–x+1, y–1/2, –z+3/2]
O3W–H32W	0.86(3)	2.20(3)	159(3)	3.011(2)	O4W [–x, y–1/2, –z+3/2]
O4W–H41W	0.83(3)	2.13(3)	158(3)	2.915(2)	O21B
O4W–H42W	0.85(3)	2.09(3)	160(3)	2.900(2)	O1W [–x, –y+2, –z+2]

Table S4. Overall protonation and stepwise dissociation constants of H_3NTA (I = 0.1 M NMe_4Cl, 25 °C)

Species	logβ	pK_a	pK_a [a]
$(HL)^{2-}$	9.65(1)	9.65	9.84
$(H_2L)^{-}$	12.10(1)	2.45	2.52
(H_3L)	14.00(1)	1.90	1.81

[a] Ref. 1

Table S5. Overall stability constants and stepwise protonation constants of Al^{III} complexes with H_3NTA (I = 0.1M NMe_4Cl, 25 °C)

Species	logβ	log$K$	log$K$ [a]
[Al(NTA)]	11.99(1)	11.99	12.0
$[Al(NTA)(OH)]^{-}$	6.61(1)	5.38	5.09
$[Al(NTA)(OH)_2]^{2-}$	–1.84(1)	8.46	8.28

[a] Ref. 1

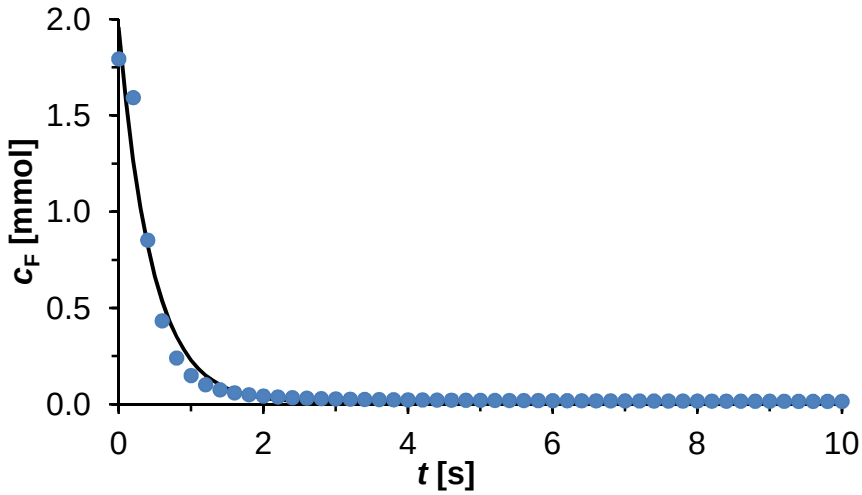


Figure S2. Kinetics of fluoride binding (pH = 7, c_F = 2.0 mM, $c_{Al(NTA)}$ = 20 mM, 25 °C)

[1] A. E. Martell and R. M. Smith, *Critical Stability Constants*; Plenum Press: New York, 1974–1989, vol. 1–6; NIST Standard Reference Database 46 (Critically Selected Stability Constants of Metal Complexes), version 5.0, 1994.

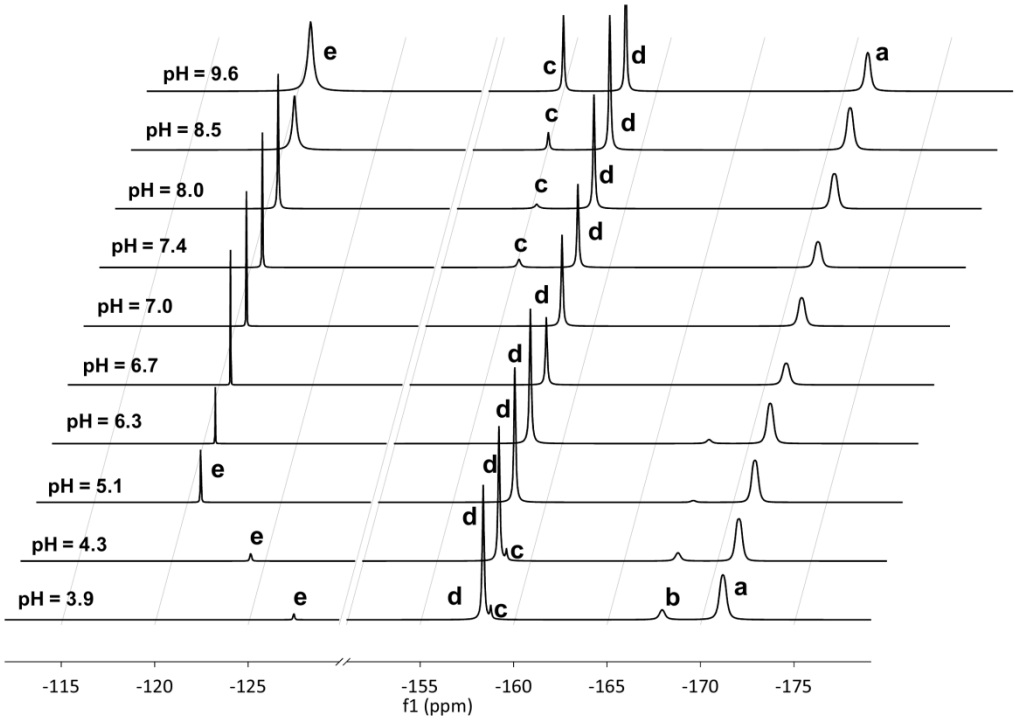


Figure S3. ^{19}F NMR spectra of the [Al(NTA)]–F^- mixture at a 1:2 molar ratio as a function of pH (25 °C, c_F = 25 mM); difluorido complex (a, d), *trans*F-monofluorido complex (b), *cis*F-monofluorido complex (c), free fluoride (e)

Table S6. Calculated chemical shifts (in ppm) of ^{19}F nuclei of the $[Al(NTA)(F)_2]^{2-}$ complex at different levels using the B3LYP/def2-TZVP/PCM geometry

	Def2-TZVP		IGLO-II		IGLO-III		IGLO-III + sec. ref.[a]	
	F_{trans}	F_{cis}	F_{trans}	F_{cis}	F_{trans}	F_{cis}	F_{trans}	F_{cis}
B3LYP	–213	–205	-	-	–230	–215	–181	–166
PBE0	–211	–201	-	-	–218	–202	–181	–166
BHandHLYP	–193	–184	–188	–180	–207	–193	–178	–164
Experimental values	–170	–157	–170	–157	–170	–157	–170	–157

[a] Secondary reference $[Al(H_2O)_5(F)]^{2+}$ was used to achieve better agreement with experiment.

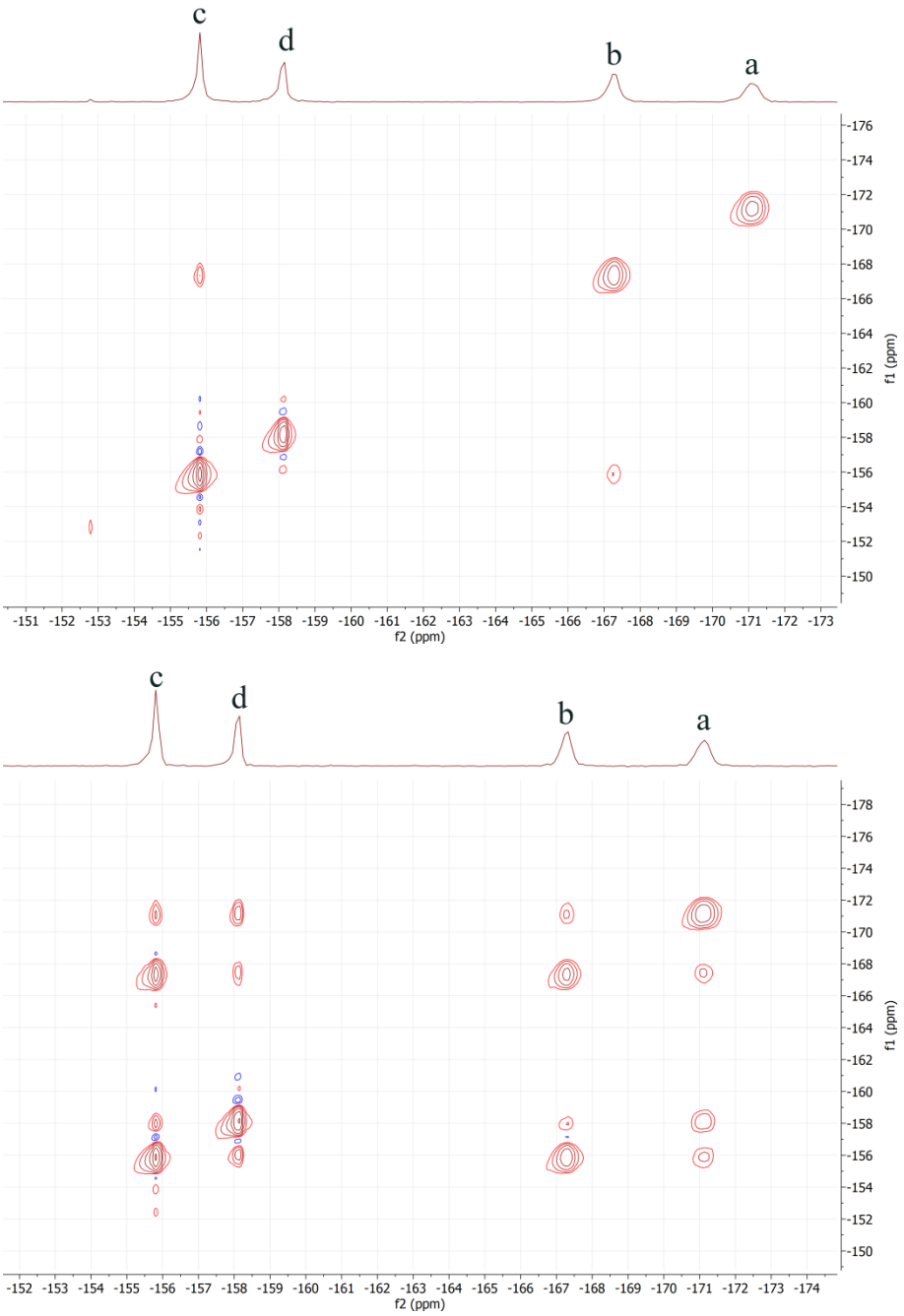


Figure S4. ^{19}F NMR EXSY spectra of the [Al(NTA)]–F^- system. The mixing times were 3 ms (top) and 300 ms (bottom) ($c_{[Al(NTA)]} = c_F$ = 25 mM, pH = 7.5, 25 °C). Difluorido complex (a, d), *trans*F-monofluorido complex (b), *cis*F-monofluorido complex (c)

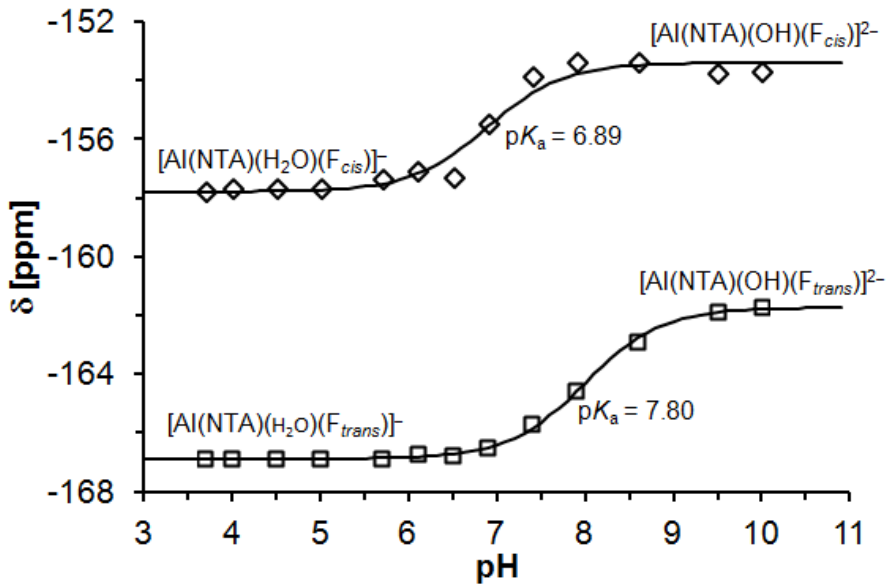
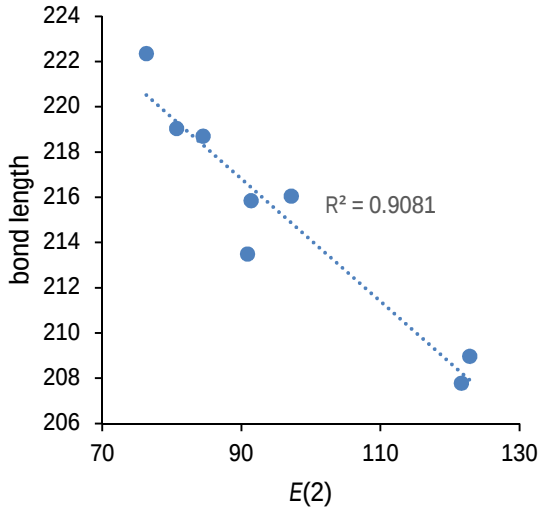


Figure S5. ^{19}F NMR chemical shifts of monofluorido species as function of pH (25 °C, c_F = 25 mM, $c_{Al(NTA)}$ = 25 mM); the lines represent the best fits.

Table S7. Calculated equilibrium constants of the formation of ternary complexes (25 °C)

Equilibrium	log*K*
$[Al(NTA)(H_2O)_2] + F^- \leftrightarrow [Al(NTA)(H_2O)(\textit{cis}F)] + H_2O$	4.9 ± 0.3
$[Al(NTA)(H_2O)_2] + F^- \leftrightarrow [Al(NTA)(H_2O)(\textit{trans}F)] + H_2O$	5.1 ± 0.3
$[Al(NTA)(H_2O)_2] + 2\ F^- \leftrightarrow [Al(NTA)(F)_2] + 2\ H_2O$	9.5 ± 0.5

A



B

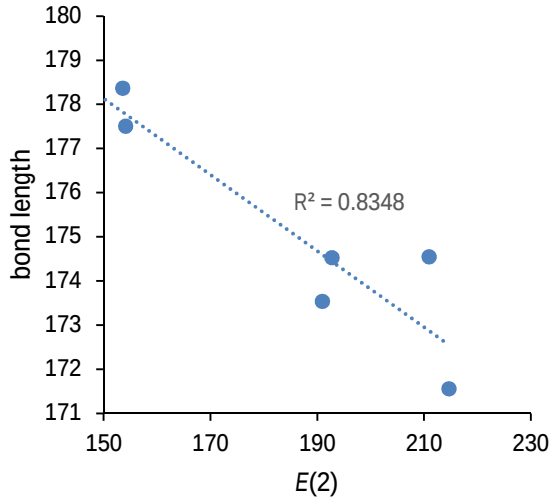


Figure S6. Correlation between calculated bond length, in pm, and stabilization energies, in kcal/mol, for nitrogen atoms (A) and fluorine atoms (B)

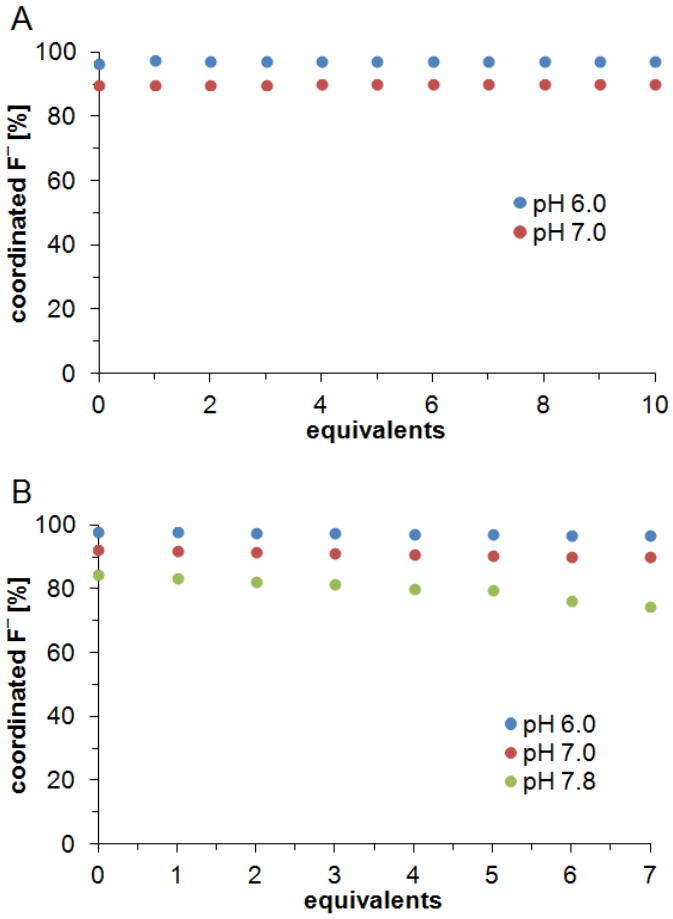


Figure S7. Stability of the Al-H_3NTA-F^- ternary complexes (c_F = $c_{[Al(NTA)]}$ = 2.0 mM) as function of added acetate (A) or carbonate (B)

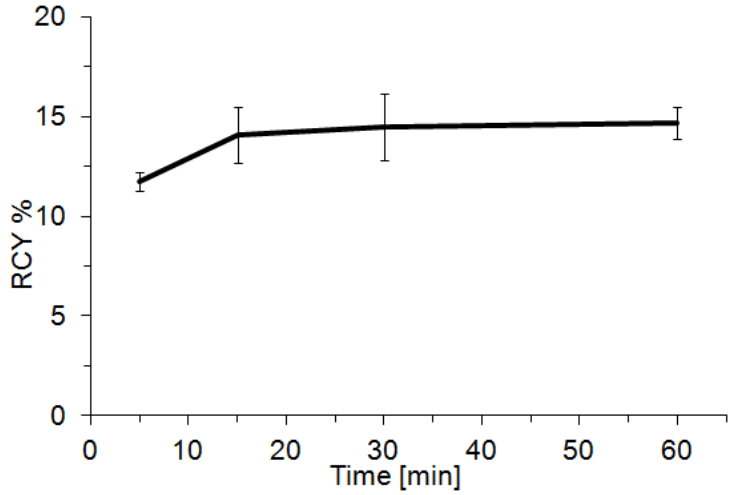


Figure S8. Radiochemical yield of [Al(NTA)] labelling with [^{18}F]F^{-} as function of time ($c_{[Al(NTA)]}$ = 10 mM, 20 MBq, pH 4.5, 95 °C).