Electronic Supplementary Information

Electrospray ionisation mass spectrometry – Bruker Microtof II settings:
Endplate Offset: 400 V, 85 nA
Capillary: 4000V, 131 nA
Nebulizer: 2.0 bar
Dry Gas: 8.0 L/min
Dry Temperature: 180 °C
Capillary Exit: 175 V
Skimmer 1: 50.0 V
Hexapole 1: 23.0 V
Hexapole RF: 550.0 Vpp
Skimmer 2: 23.0V

Fig S. 1. GEPASI – User-defined parameters

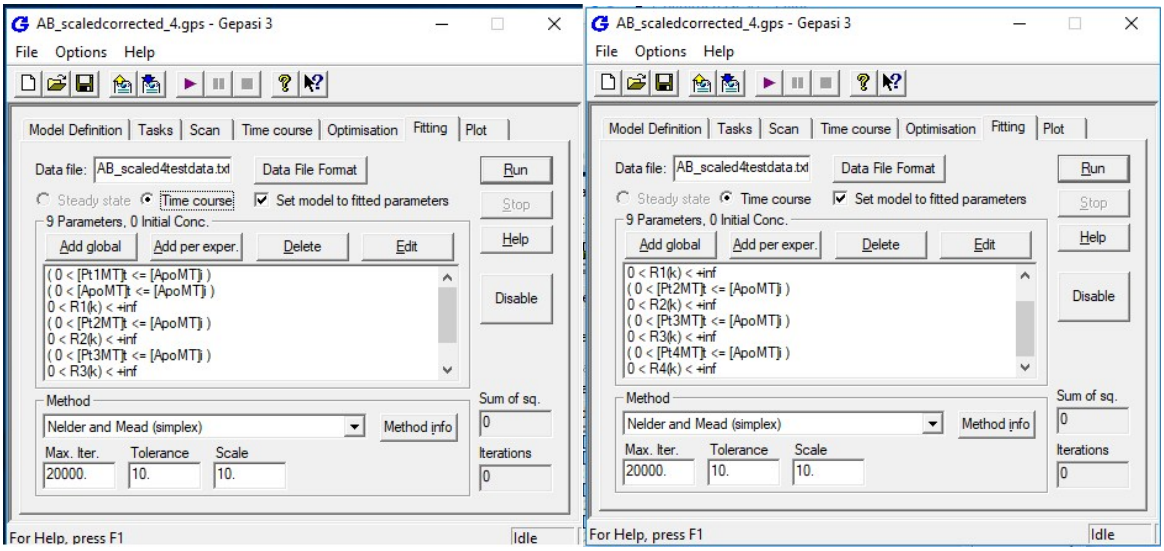


Fig S. 2. Experimental Mass Spectral Data

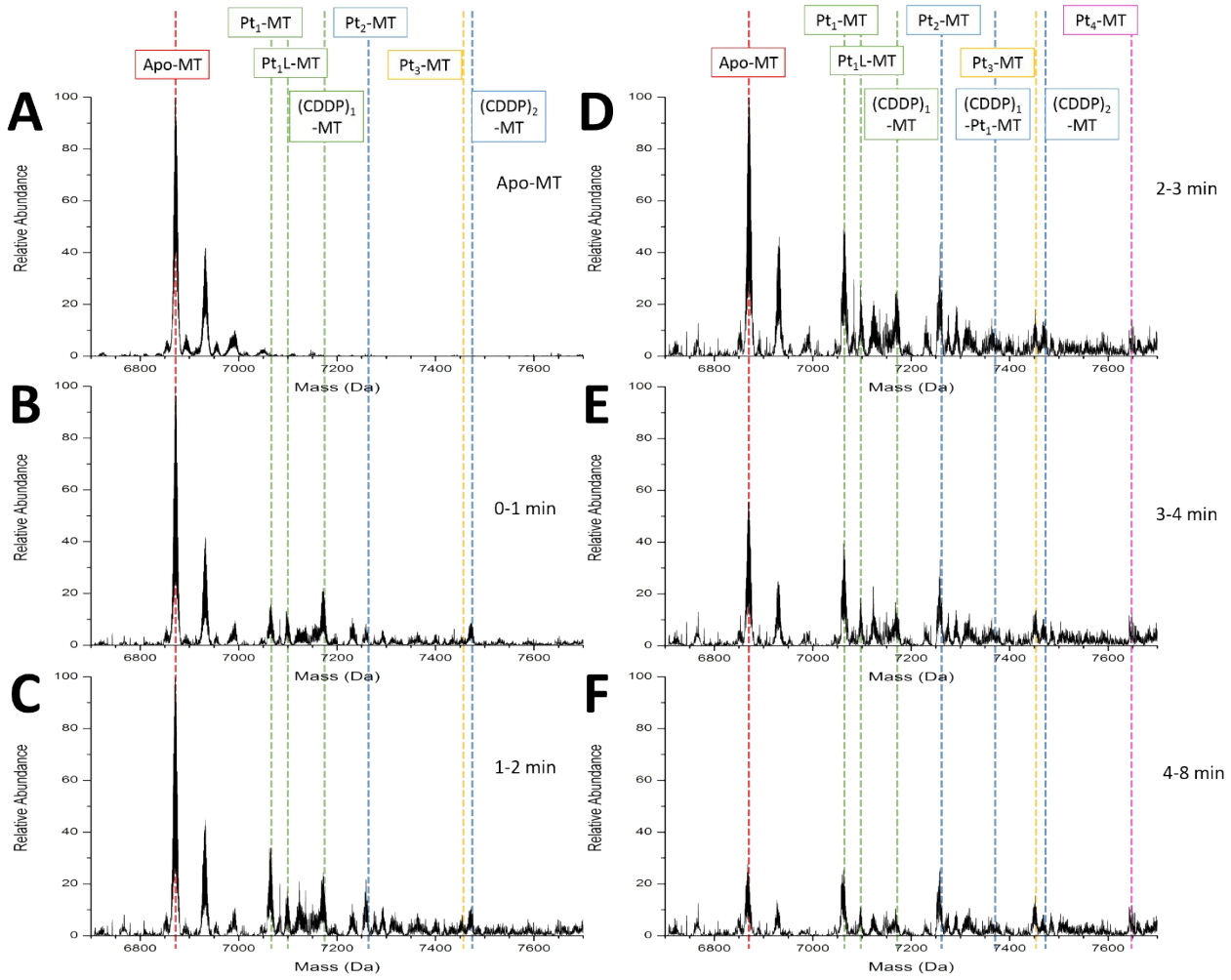


Figure 1 ESI Mass Spectra following the reaction of cisplatin with apo-MT1a. The apo peak is highlighted by the red dashed line. Platinated species are coloured according to the number of Pt(II) atoms contained, with its associated partially ligated (Pt_xL-MT) or fully ligated ($(CDDP)_x$-MT) species sharing the same colour. MT bound to Pt_1 represented with green dashed lines. MT bound to Pt_2 represented with blue dashed lines. MT bound to Pt_3 represented with yellow dashed lines. MT bound to Pt_4 represented with pink dashed lines.

Table S. 1.

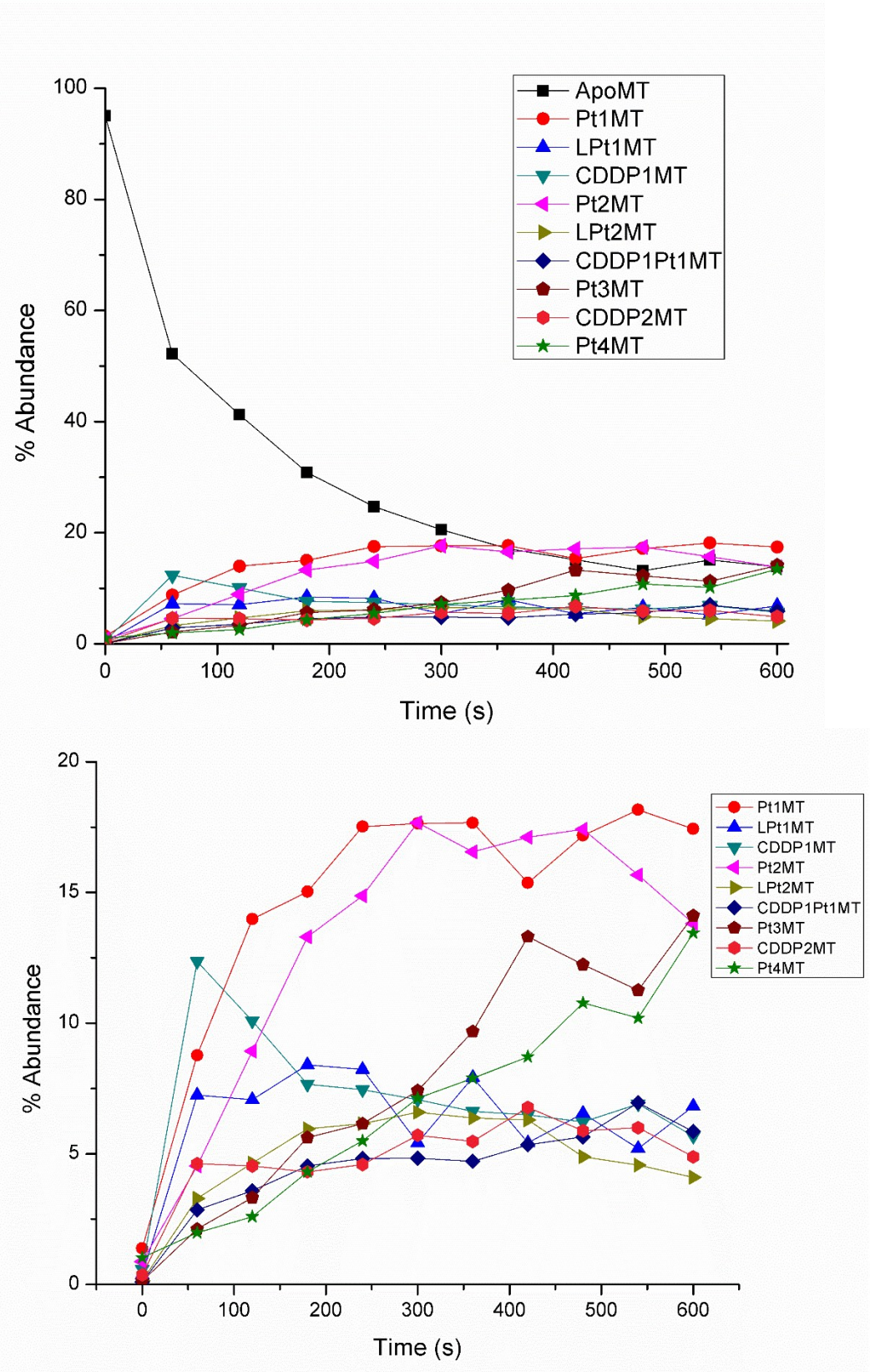
SPECIES	Experimental mass (Da)	Theoretical Mass (Da)
apoMT	6868.8*	6875.1 (Expasy/Uniprot)**
Pt_1MT	7062.8	7070.2
†LPt_1MT	7096.8	-
$CDDP_1MT$	7167.8	7175.1
Pt_2MT	7258.7	7265.1
†LPt_2MT	7290.8	-
$CDDP_1Pt_1MT$	7363.68	7370.1
Pt_3MT	7453.7	7460.1
$CDDP_2MT$	7470.7	7475.1
Pt_4MT	7648.5	7655.1

*the experimental species are all systematically lighter by 6.3 Da

**theoretical mass taken from Expasy/Uniprot

†exact composition of L is undefined

Fig S. 3. Experimental Individual Species Abundance Data



```
**********************************
*      Gepasi version 3.30       *
*    Intel Pentium executable    *
* Thursday, 18 January 2018, 17:32 *
**********************************
AB_Build_CisplatinMT
STRUCTURAL ANALYSIS
Rank of the stoichiometry matrix: 6
key for step (column) numbers:
 0 - R1
 1 - R2
 2 - R3
 3 - R4

REDUCED STOICHIOMETRY MATRIX
          0   1   2   3
       ------------------
ApoMT     | -1   0   0   0
CDDP      |  0  -1  -1  -1
Pt1MT     |  0   0   1   1
Pt2MT     |  0   0   0   1

INVERSE OF THE REDUCTION MATRIX

          0   1   2   3   4   5
       --------------------------
ApoMT     |  1.0   0.0   0.0   0.0   0.0   0.0
CDDP      |  1.0   1.0   0.0   0.0   0.0   0.0
Pt1MT     | -1.0   1.0   1.0   0.0   0.0   0.0
Pt2MT     | -0.0  -1.0  -2.0   1.0   0.0   0.0
Pt3MT     | -0.0  -0.0   1.0  -2.0   1.0   0.0
Pt4MT     | -0.0  -0.0   0.0   1.0   0.0   1.0

CONSERVATION RELATIONSHIPS
  4.0*ApoMT - CDDP + 3.0*Pt1MT + 2.0*Pt2MT + Pt3MT  = 0.0001
- 3.0*ApoMT + CDDP - 2.0*Pt1MT - Pt2MT + Pt4MT  = -5.42101e-020

ELEMENTARY MODES


PARAMETER FITTING
method: Nelder and Mead (simplex)
      Max. Iter. = 20000
      Tolerance = 10
```

Scale = 10

iterations = 1
simulations = 26
time = 2.806 s
speed = 9.26586 simulation/s

BEST SOLUTION:

Sum of squares = 3.76137e-010
Std. deviation = 7.33034e-006
RMS error = 5.84759e-006

Parameter	Value	Std.Deviation	
R1(k)	34.17	2.194	(6.42%)
R2(k)	22.7	1.466	(6.46%)
R3(k)	14.12	1.543	(10.92%)
R4(k)	27.15	5.827	(21.46%)

Covariances

R1(k)	1			
R2(k)	0.1899	1		
R3(k)	0.2829	0.3841	1	
R4(k)	0.09443	0.1142	0.09923	1

KINETIC PARAMETERS
R1 (Mass action (irreversible))
k = 3.4168e+001
R2 (Mass action (irreversible))
k = 2.2698e+001
R3 (Mass action (irreversible))
k = 1.4122e+001
R4 (Mass action (irreversible))
k = 2.7153e+001

COMPARTMENTS
V(compartment) = 1.0000e+000

RESULTS OF INTEGRATION (after 6.00e+002 s)
[ApoMT] initial = 1.000000e-004 uM, final = 4.068998e-006 uM
[CDDP] initial = 3.000000e-004 uM, final = 8.194357e-005 uM
[Pt1MT] initial = 0.000000e+000 uM, final = 2.338770e-005 uM

[Pt2MT] initial = 0.000000e+000 uM, final = 3.985484e-005 uM
[Pt3MT] initial = 0.000000e+000 uM, final = 1.579481e-005 uM
[Pt4MT] initial = 0.000000e+000 uM, final = 1.689366e-005 uM
J(R1) = 1.139259e-008 uM*L/s
J(R2) = 4.349945e-008 uM*L/s
J(R3) = 4.612169e-008 uM*L/s
J(R4) = 3.514334e-008 uM*L/s