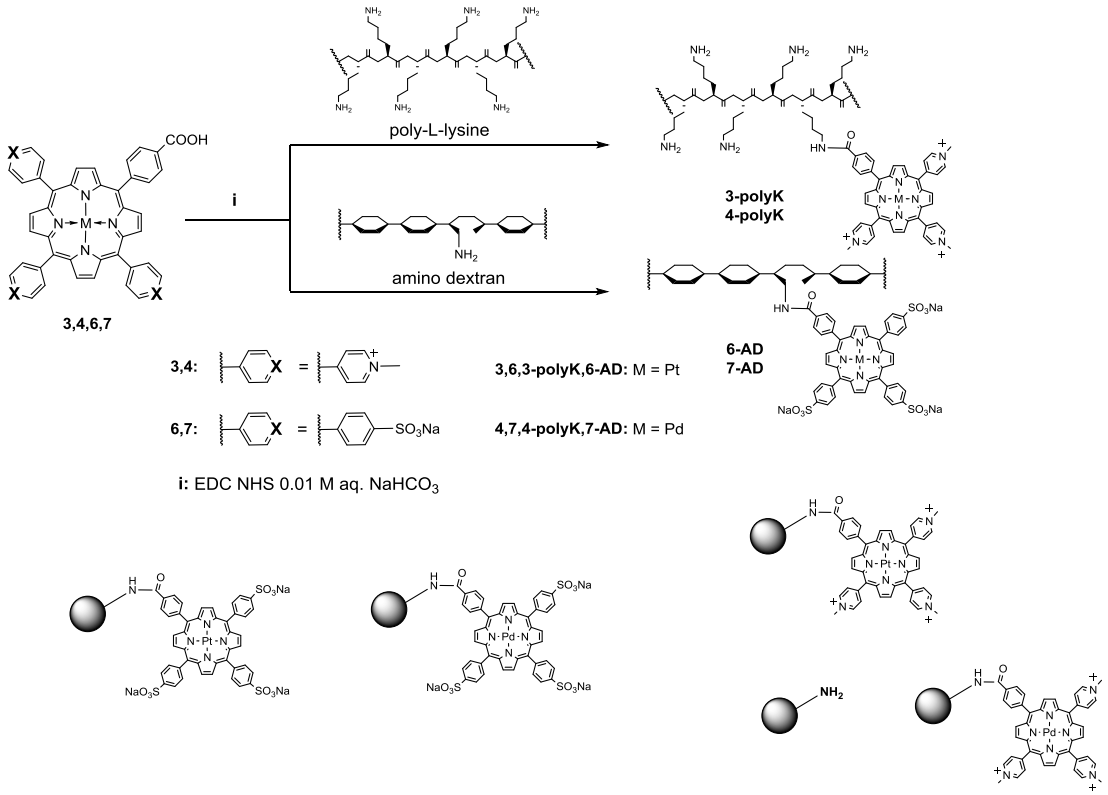
Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information



General procedure for the conjugation of porphyrins to amino-functionalised substrates.

Conjugate 3-poly-L-Lys: A solution of porphyrin **3** (3 mg, 4.0 x 10^{-3} mmol) in deionised water was treated with EDC (2 mg, 1.0 x 10^{-2} mmol) and NHS (2 mg, 1.7 x 10^{-2} mmol) and it was allowed to stand at room temperature for 30 minutes. The solution was then added to a solution of poly-L-lysine (30000-70000 MW) in 0.01 M aqueous $NaHCO_3$ (20 mL). The resulting mixture was shielded from light and shaken for 8 hours on a rotating shaker. The desired conjugate was purified by gel filtration. Methanol was added to the eluate, and the conjugate was recovered by filtration through membrane and dried *in vacuo*. The desired conjugate was obtained as a light orange-red solid. (42 mg, 84 % recovery). Estimated loading: 398 nmol/mg; UV/vis: (H_2O) λ (%): 401 (100), 517 (13.5), 552 (8.0)

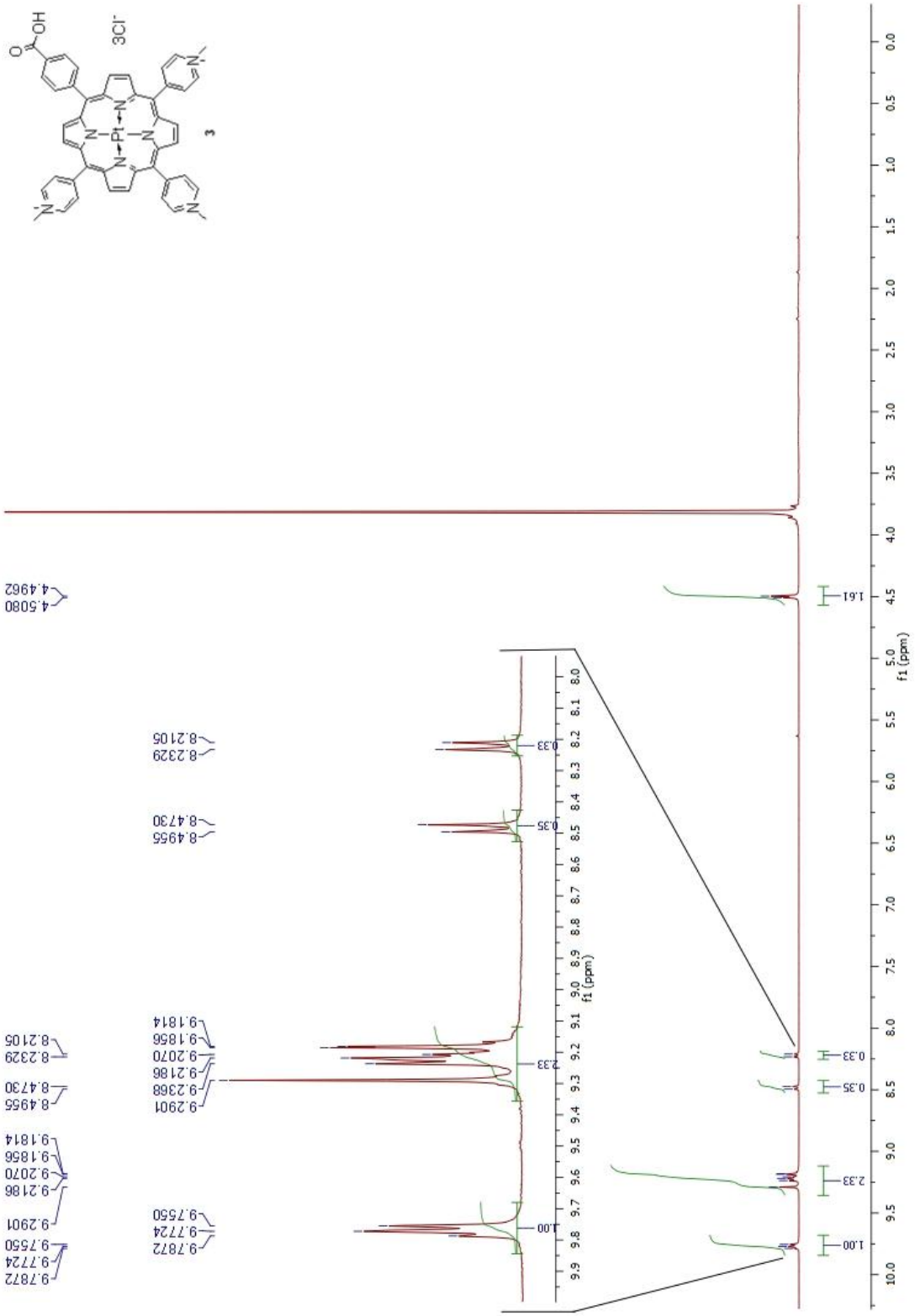
Conjugate 4-poly-L-Lys: The conjugated nanospecies were obtained following the general procedure, using porphyrin **4** (3 mg, 3.0 x 10^{-3} mmol). The desired conjugate was obtained as a light red solid. (38 mg, 76 % recovery). Estimated loading: 263 nmol/mg; UV/vis: (H_2O) λ (%): 416 (100), 530 (10.0), 568 (3.5).

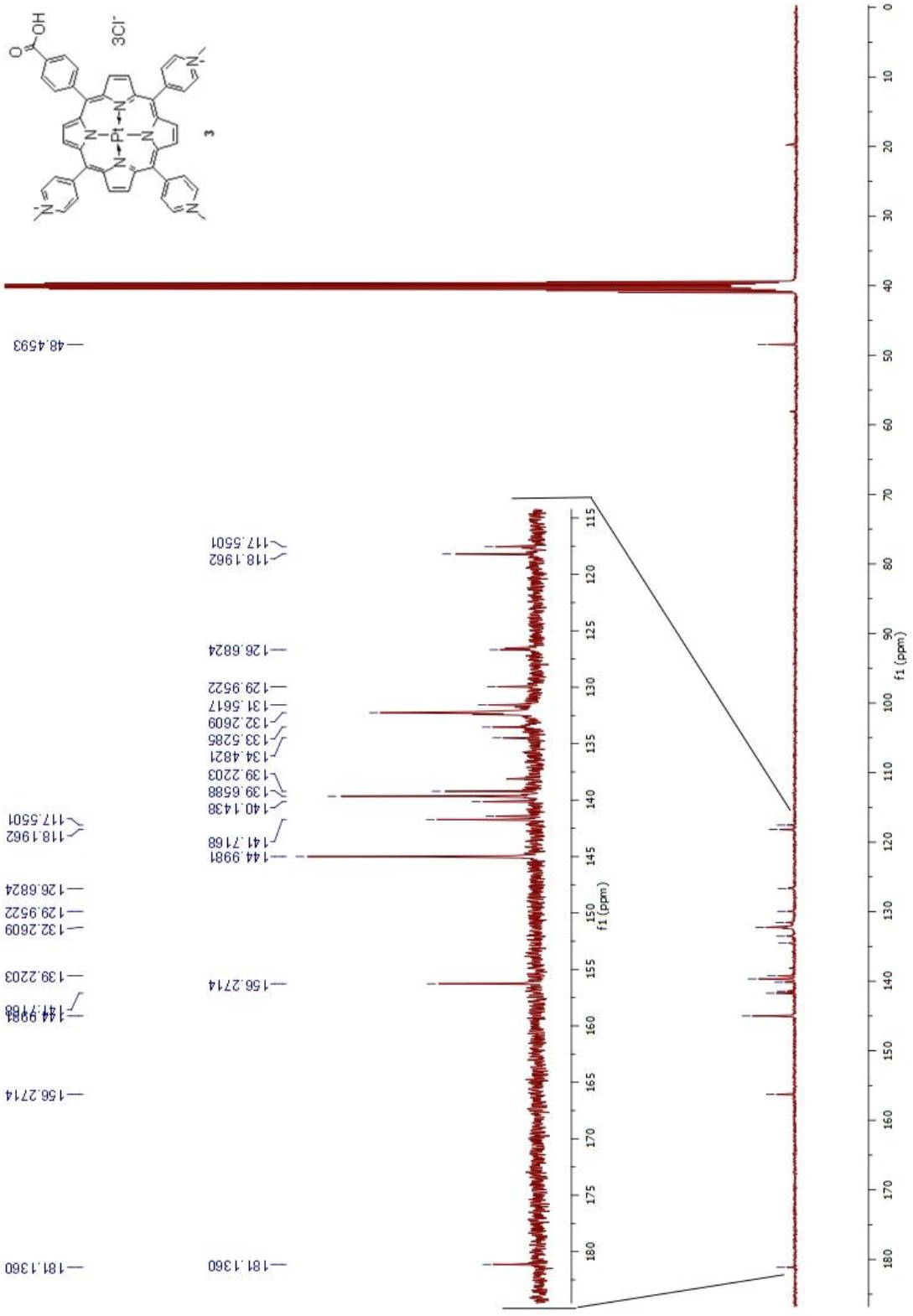
Conjugate 6-aminodextran: The desired conjugate was obtained following the general procedure, using aminodextran (10000 MW, 100 mg) and porphyrin **6** (4 mg, 3.4 x 10^{-3} mmol). The desired conjugate was obtained as a dark red solid. (72 mg, 72 % recovery). Estimated loading: 21.2 nmol/mg; UV/vis: (H_2O) λ (%): 397 (100), 513 (11.1), 549 (3.6).

Conjugate 7-aminodextran: The conjugated nanospecies were obtained following the general procedure, using aminodextran (10000 MW, 100 mg) and porphyrin **7** (4 mg, 3.7 x

10^{-3} mmol). The desired conjugate was obtained as a brownish red solid. (81 mg, 81 % recovery). Estimated loading: 17.8 nmol/mg; UV/vis: (H_2O) λ (%): 408 (100), 527 (10), 561 (1.3).

Spectra


3Cl⁻
3
4.5080
4.4962
8.2105
8.2329
8.4730
8.4955
9.1814
9.1856
9.2070
9.2186
9.2368
9.2901
9.7872
9.7724
9.7550
1.61
0.33
0.35
2.33
1.00
f1 (ppm)


3Cl-
3
48.4593
117.5501
118.1962
126.6824
129.9522
131.5617
132.2609
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139.2203
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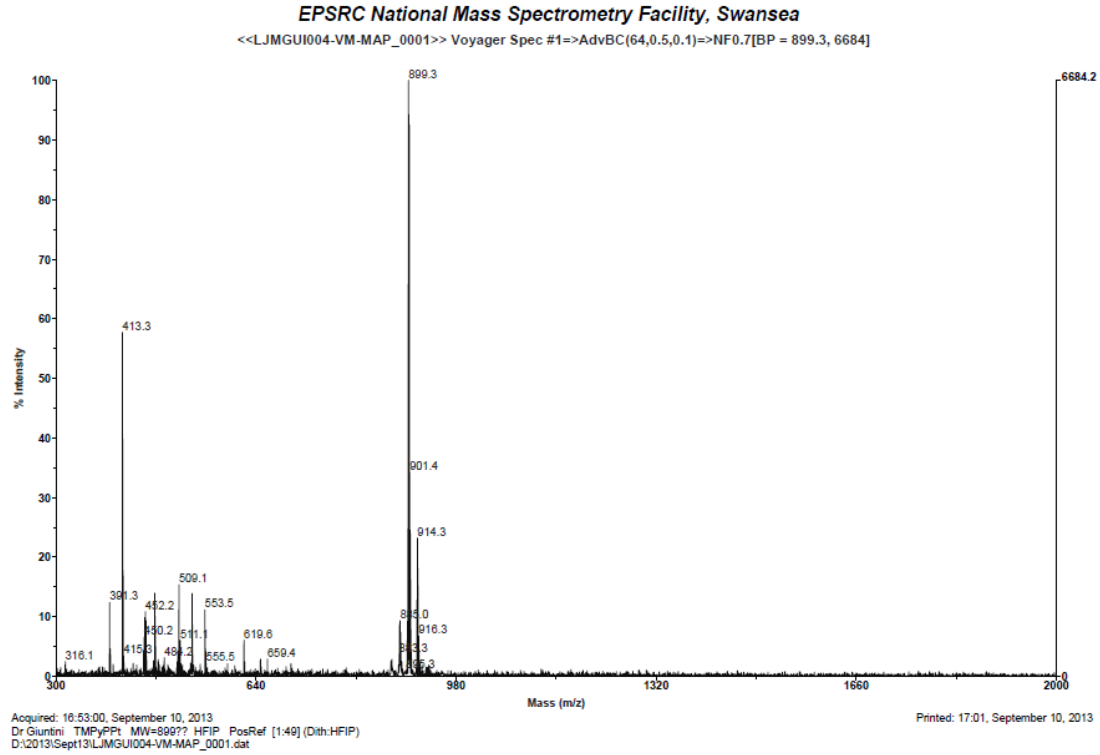
156.2714
181.1360
f1 (ppm)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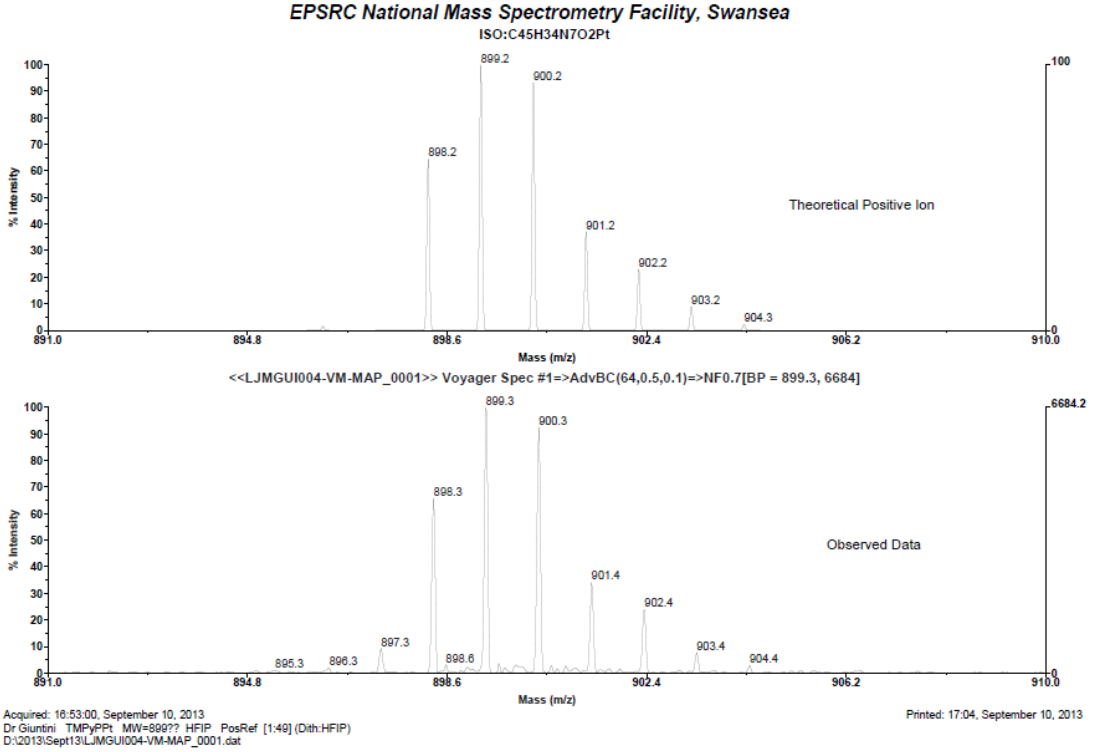
Mass (m/z)
899.3
6684.2
413.3
901.4
914.3
509.1
391.3
452.2
553.5
916.3
619.6
316.1
659.4
Acquired: 16:53:00, September 10, 2013
Dr Giuntini TMPyPPt MW=899?? HFIP PosRef [1:49] (Dith:HFIP)
D:\2013\Sept13\LJMGUI004-VM-MAP_0001.dat
Printed: 17:01, September 10, 2013


EPSRC National Mass Spectrometry Facility, Swansea
ISO:C45H34N7O2Pt
% Intensity
Mass (m/z)
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900.2
898.2
901.2
902.2
903.2
904.3
Theoretical Positive Ion
<<LJMGUI004-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>NF0.7[BP = 899.3, 6684]
899.3
6684.2
900.3
898.3
901.4
902.4
897.3
903.4
895.3
896.3
898.6
904.4
Observed Data
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Dr Giuntini TMPyPPt MW=899?? HFIP PosRef [1:49] (Dith:HFIP)
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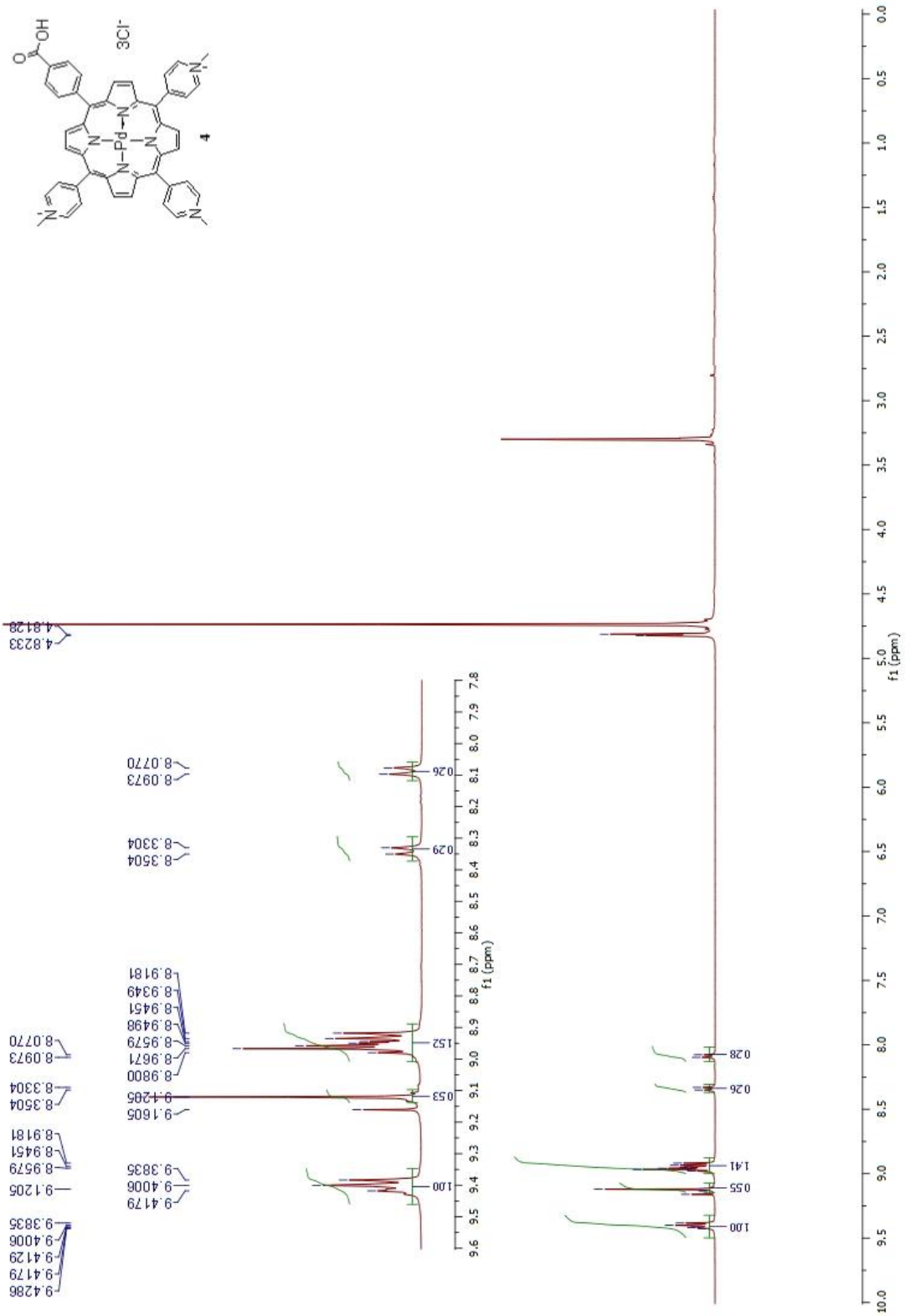
3Cl-
4
4.8233
4.8128
8.0770
8.0973
8.3304
8.3504
8.9181
8.9349
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8.9498
8.9579
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8.9800
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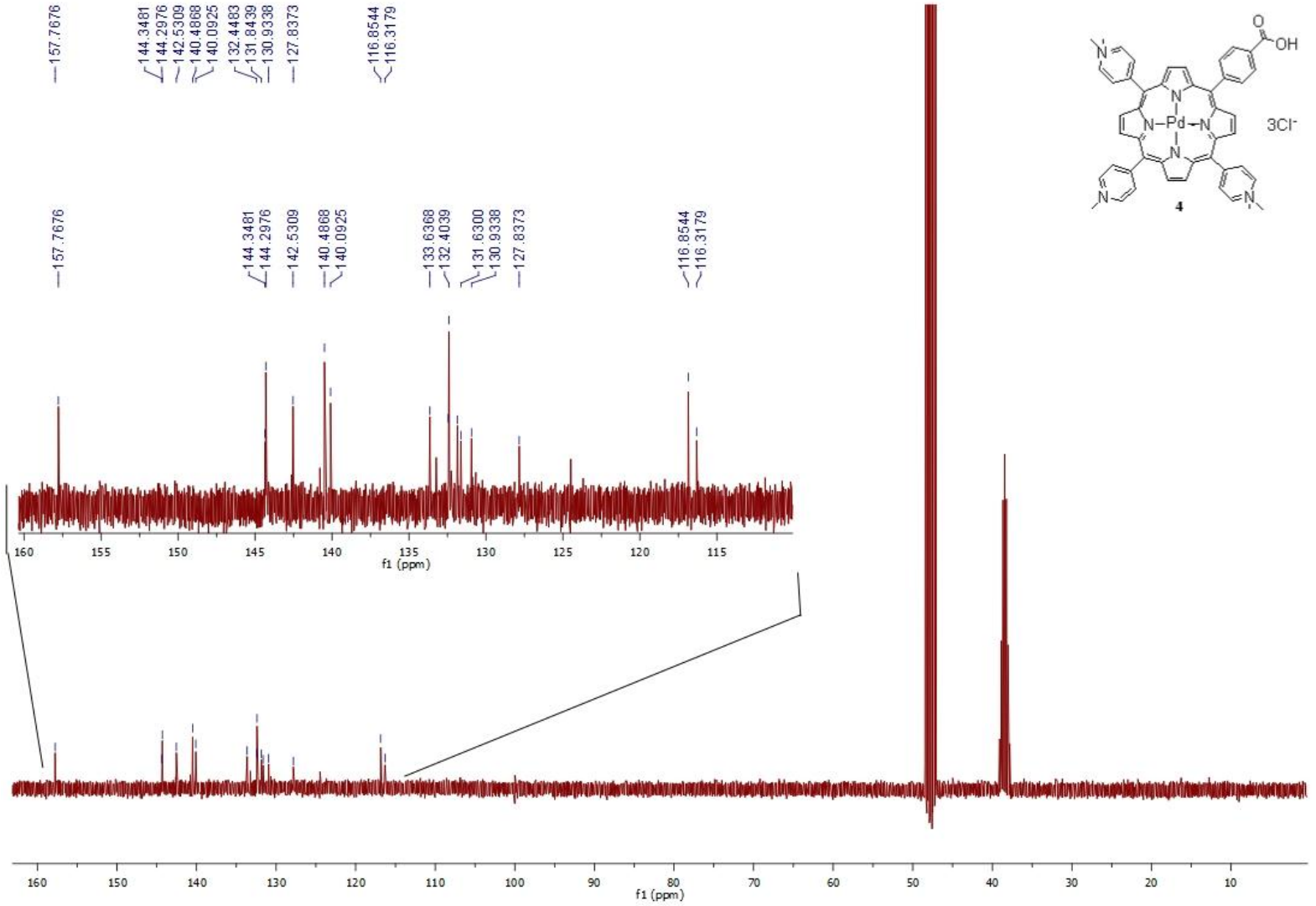
9.1605
9.3835
9.4006
9.4179
9.4286
f1 (ppm)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144.2976
142.5309
140.4868
140.0925
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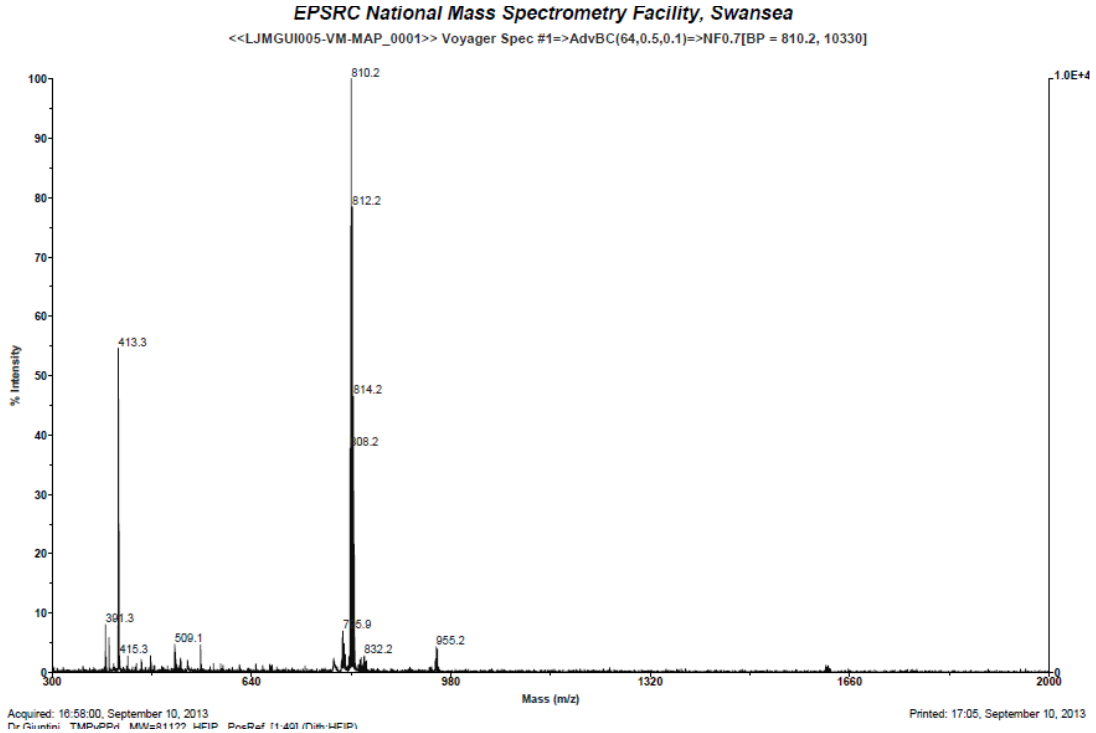
116.3179
133.6368
132.4039
131.6300
130.9338
f1 (ppm)
OH
3Cl-
Pd
4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<<LJMGUI005-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>NF0.7[BP = 810.2, 10330]
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Mass (m/z)
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413.3
814.2
808.2
391.3
415.3
509.1
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832.2
955.2
1.0E+4
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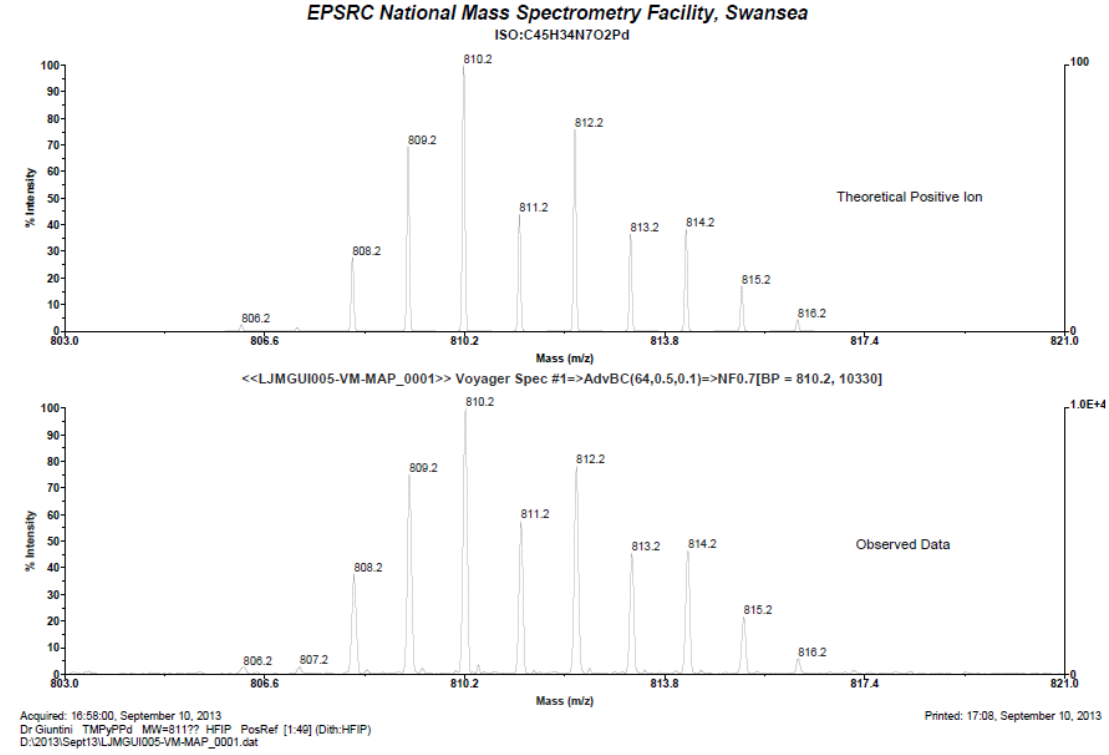
EPSRC National Mass Spectrometry Facility, Swansea
ISO:C45H34N7O2Pd
% Intensity
Mass (m/z)
Theoretical Positive Ion
810.2
809.2
812.2
811.2
813.2
814.2
808.2
815.2
806.2
816.2
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Observed Data
807.2
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Printed: 17:08, September 10, 2013
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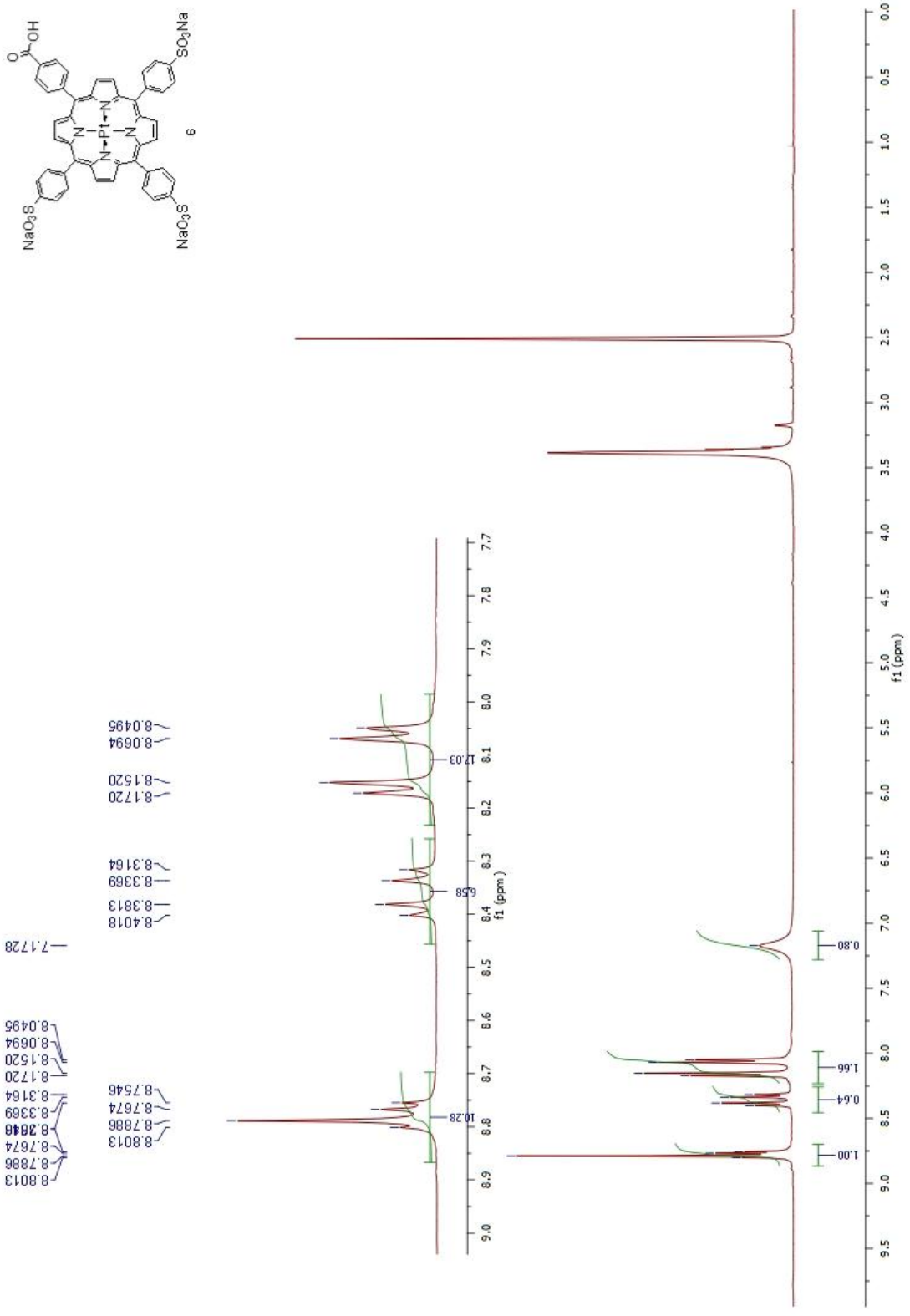
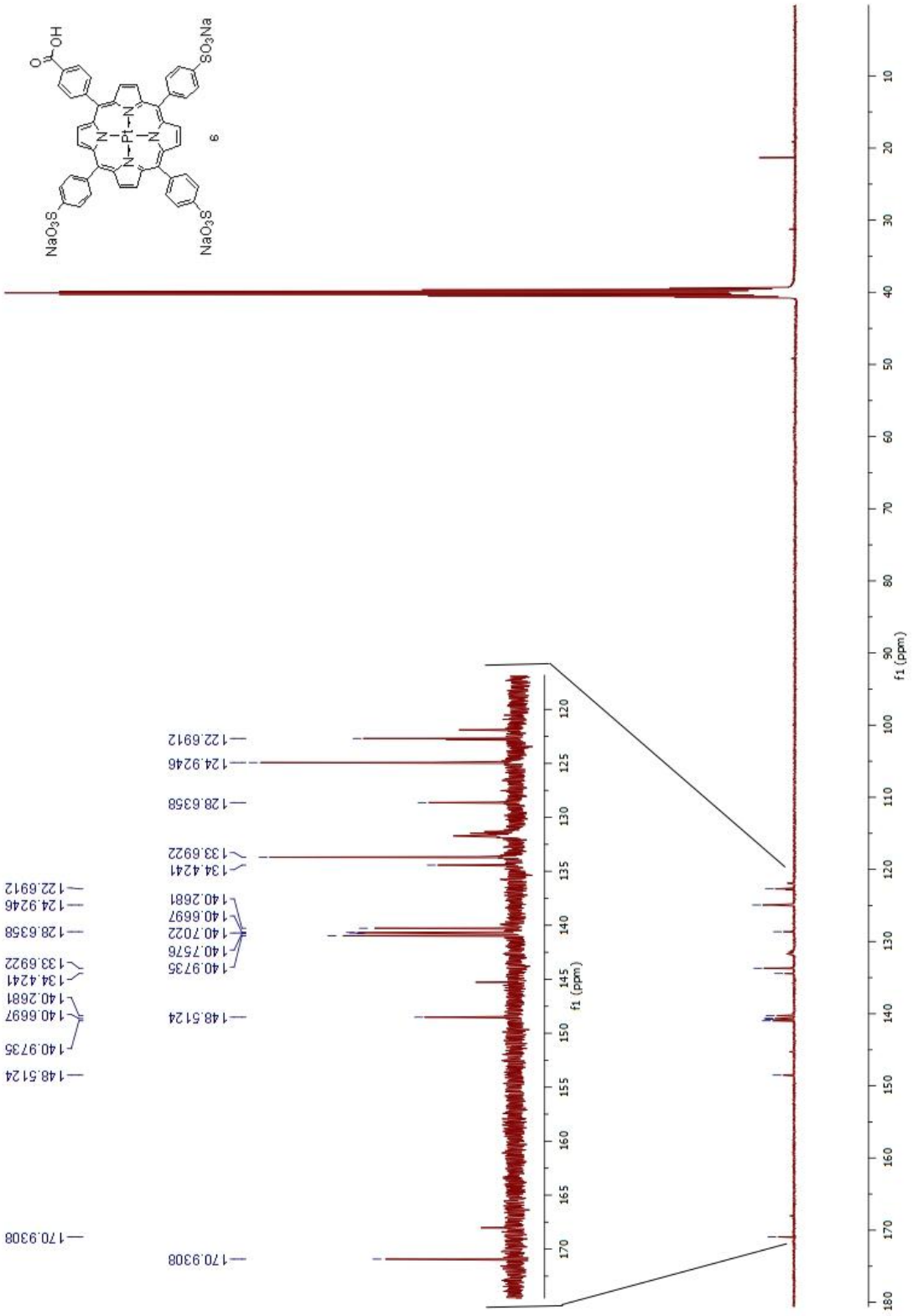

HO
O
SO3Na
NaO3S
NaO3S
Pt
9
8.8013
8.7886
8.7674
8.3369
8.3164
8.1720
8.1520
8.0694
8.0495
7.1728
8.4018
8.3813
8.3369
8.3164
8.1720
8.1520
8.0694
8.0495
8.8013
8.7886
8.7674
8.7546
f1 (ppm)
10.28
6.58
12.03
0.80
1.66
0.64
1.00
f1 (ppm)


OH
O
SO3Na
NaO3S
NaO3S
Pt
N
9
122.6912
124.9246
128.6358
133.6922
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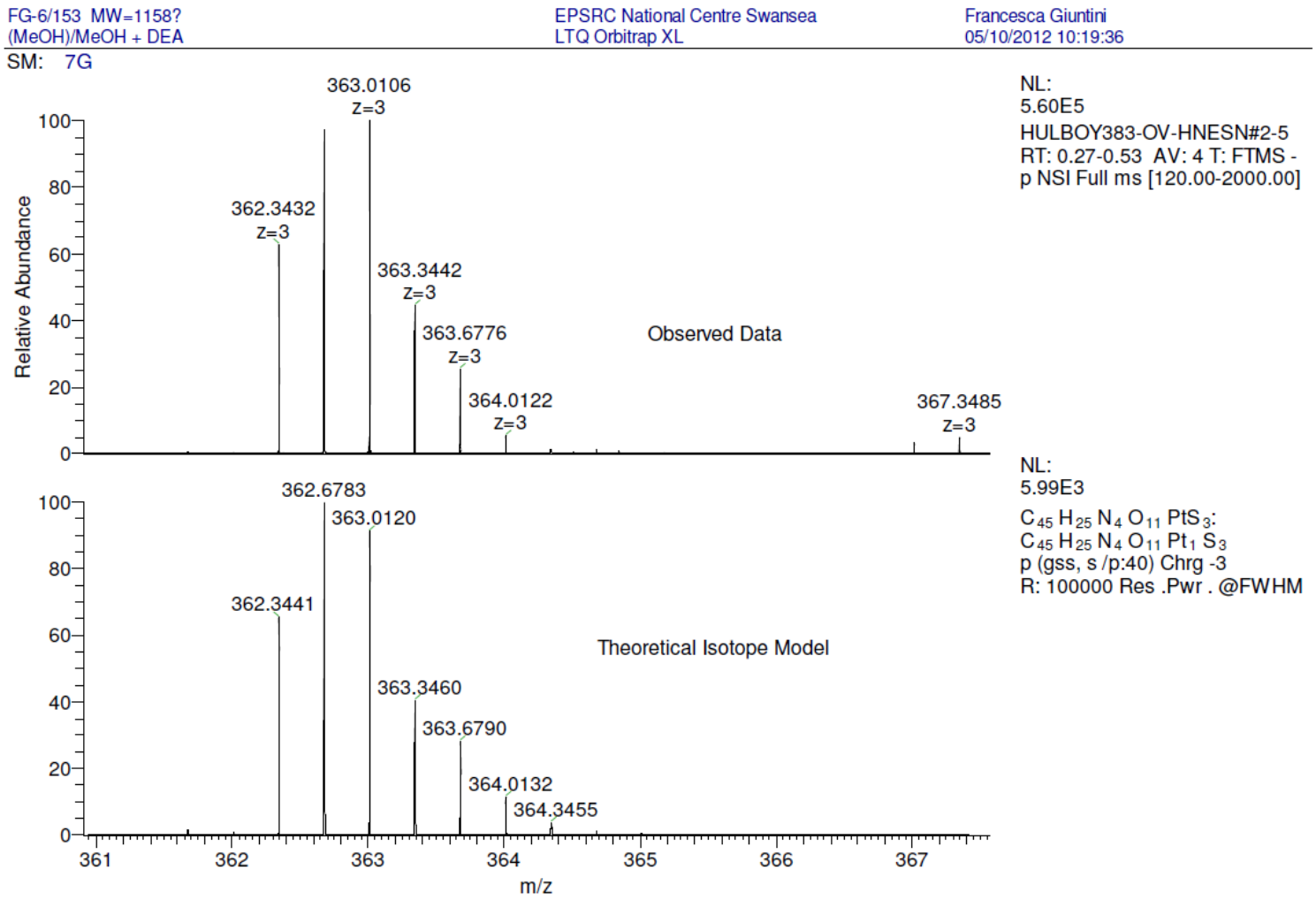
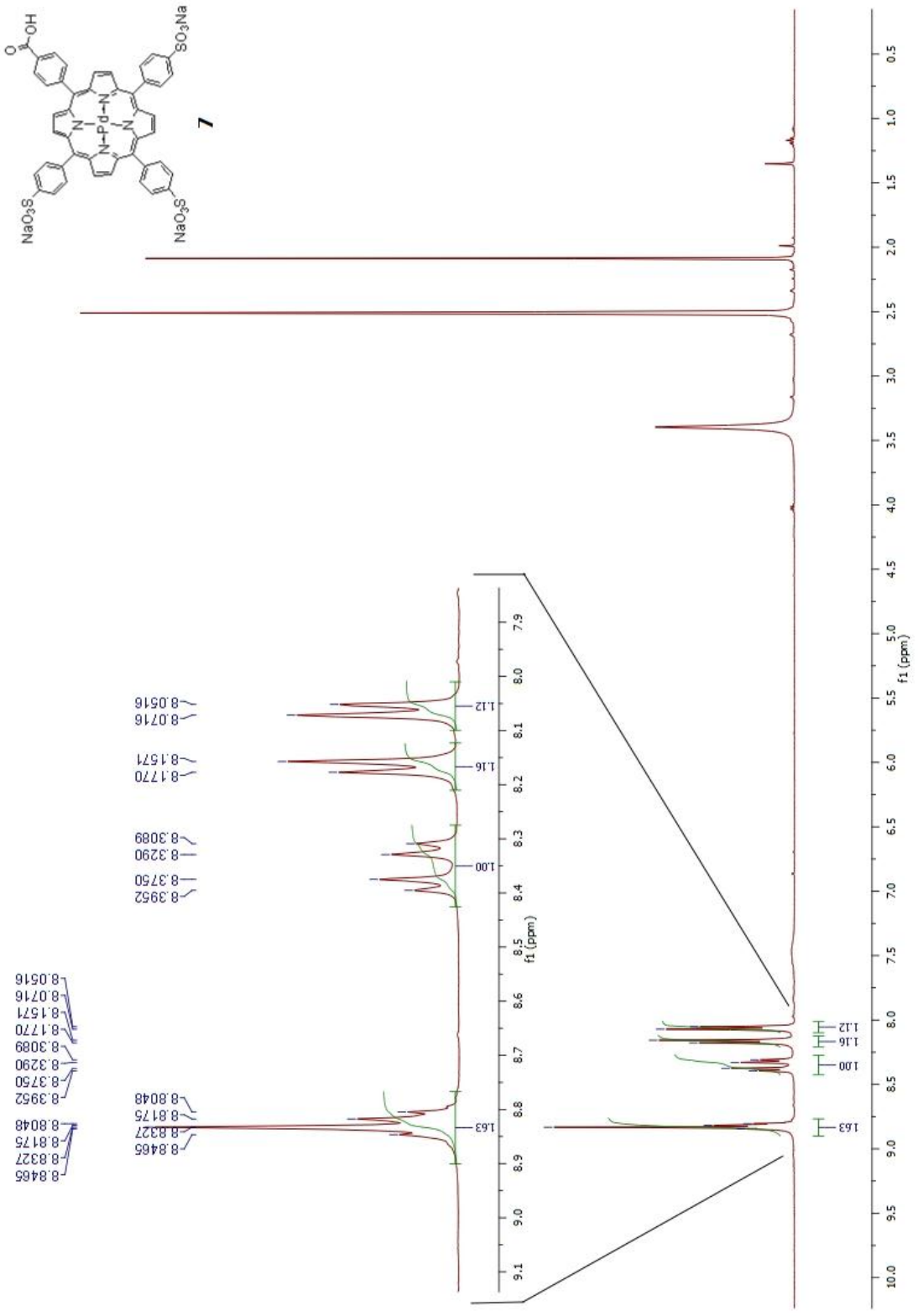
140.2681
140.6697
140.7022
140.7576
140.9735
148.5124
170.9308
f1 (ppm)


FG-6/153 MW=1158?
(MeOH)/MeOH + DEA
EPSRC National Centre Swansea
LTQ Orbitrap XL
Francesca Giuntini
05/10/2012 10:19:36
SM: 7G
363.0106
z=3
362.3432
z=3
363.3442
z=3
363.6776
z=3
364.0122
z=3
367.3485
z=3
Observed Data
NL:
5.60E5
HULBOY383-OV-HNESN#2-5
RT: 0.27-0.53 AV: 4 T: FTMS -
p NSI Full ms [120.00-2000.00]
Relative Abundance
362.6783
363.0120
362.3441
363.3460
363.6790
364.0132
364.3455
Theoretical Isotope Model
NL:
5.99E3
C45 H25 N4 O11 PtS3:
C45 H25 N4 O11 Pt1 S3
p (gss, s /p:40) Chrg -3
R: 100000 Res .Pwr . @FWHM
m/z


7
NaO3S
SO3Na
NaO3S
O
OH
N
Pd
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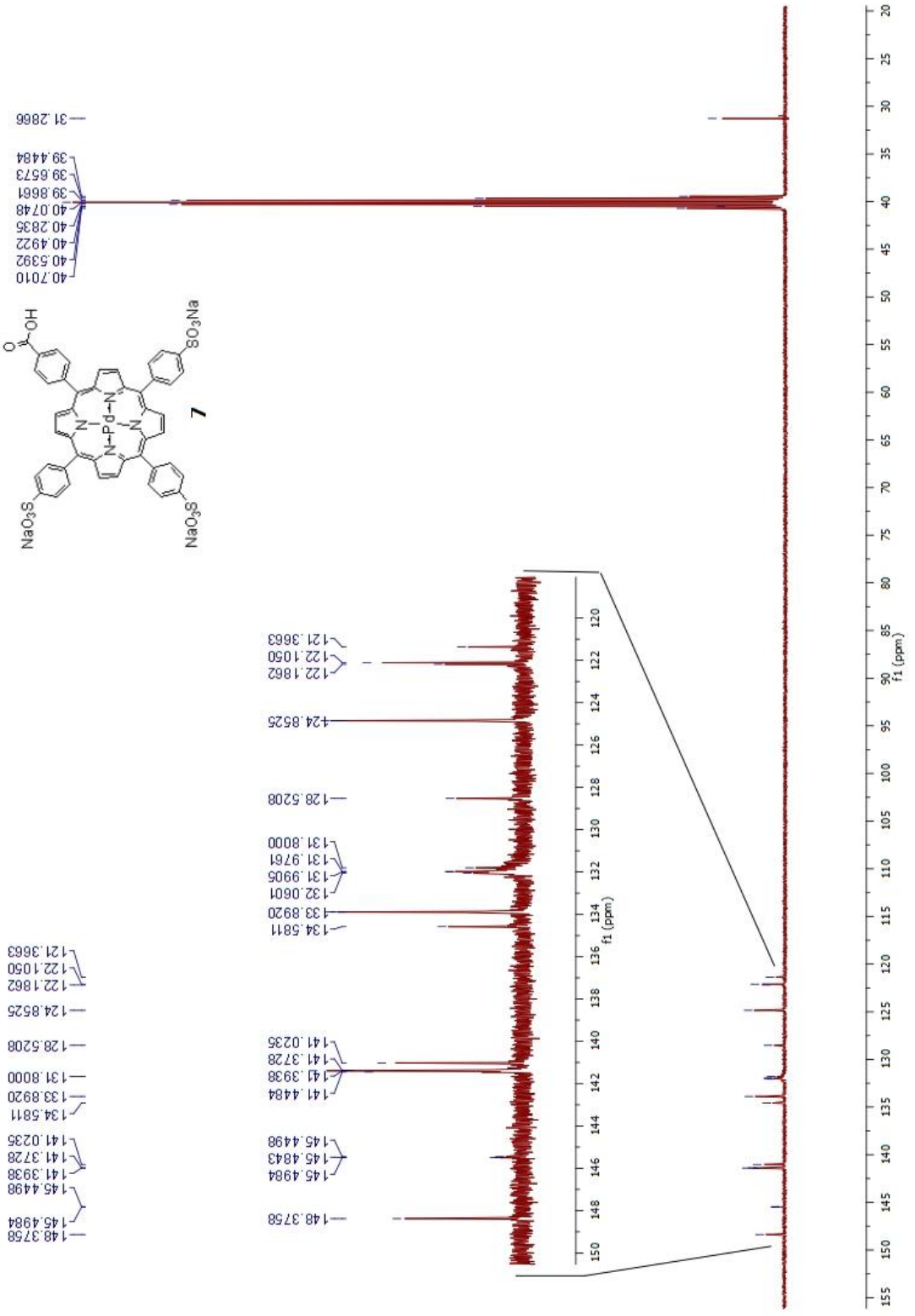
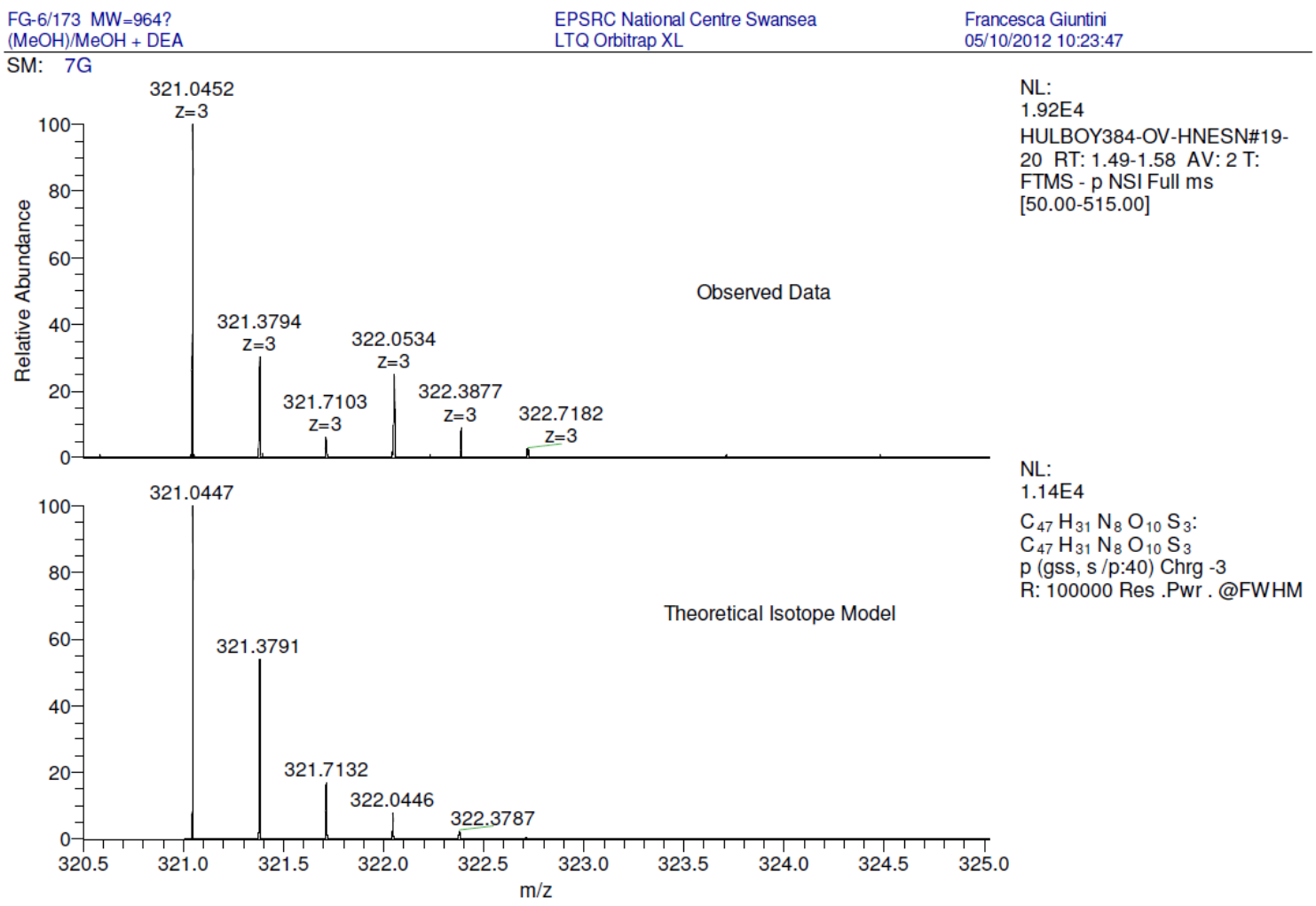
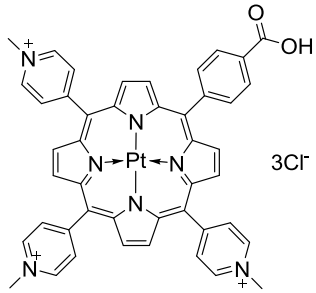
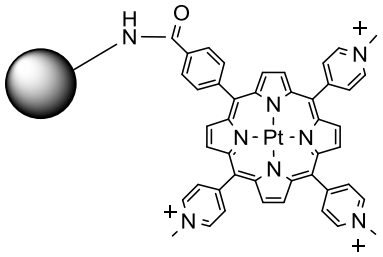
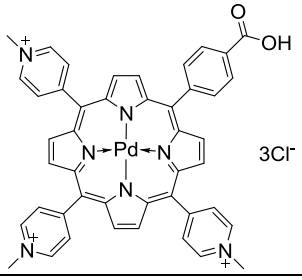
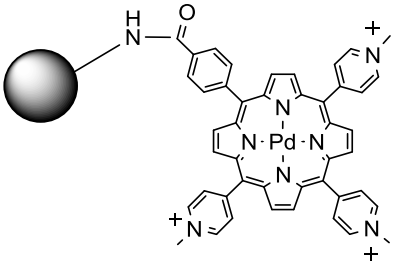
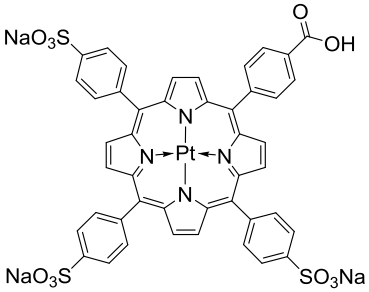
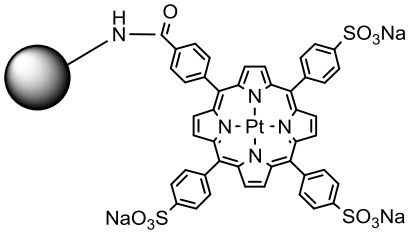
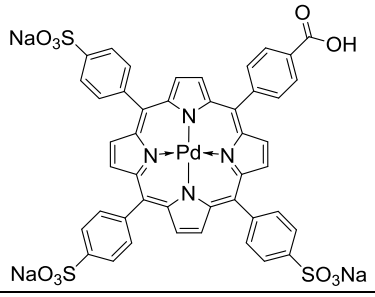
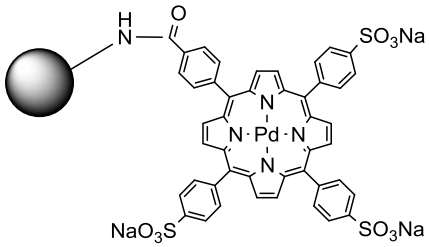
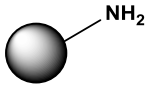
8.8327
8.8175
8.8048
8.3952
8.3750
8.3290
8.3089
8.1770
8.1571
8.0716
8.0516
1.63
1.00
1.16
1.12
f1 (ppm)


31.2866
39.4484
39.6573
39.8661
40.0748
40.2835
40.4922
40.5392
40.7010
HO
O
SO3Na
NaO3S
NaO3S
Pd
N
7
121.3663
122.1050
122.1862
124.8525
128.5208
131.8000
131.9761
131.9905
132.0601
133.8920
134.5811
141.0235
141.3728
141.3938
141.4484
145.4498
145.4843
145.4984
148.3758
f1 (ppm)

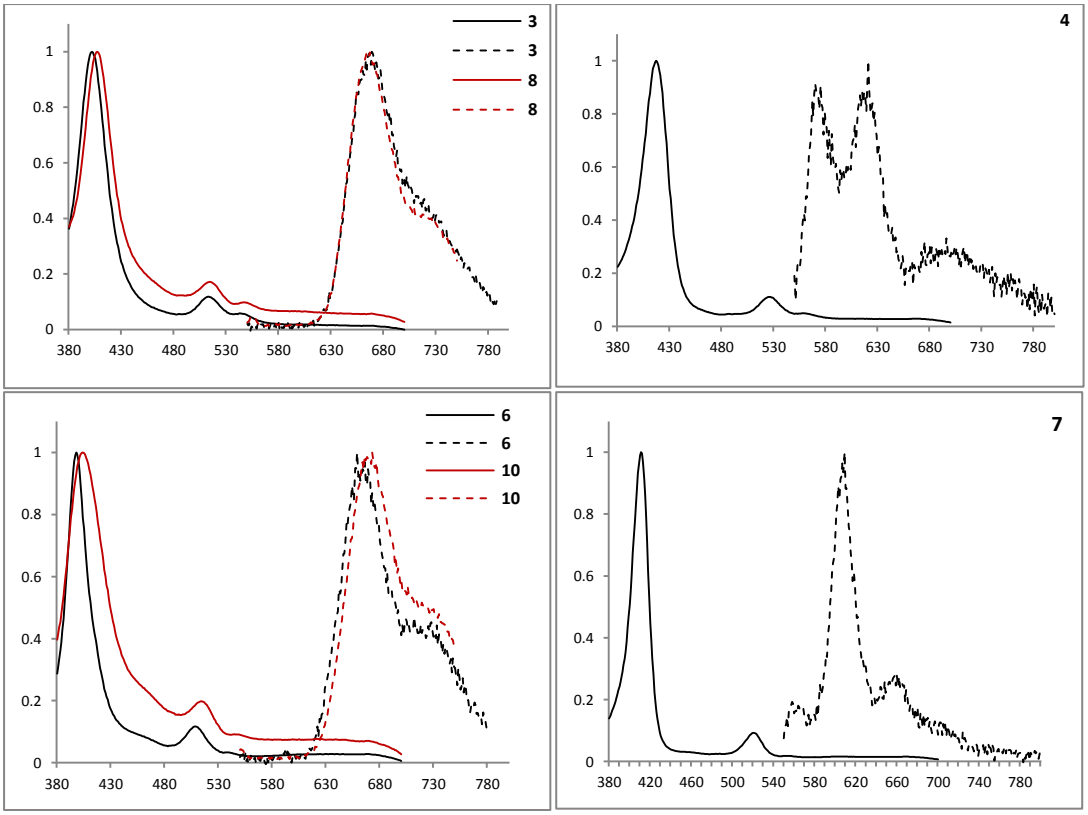

FG-6/173 MW=964?
(MeOH)/MeOH + DEA
EPSRC National Centre Swansea
LTQ Orbitrap XL
Francesca Giuntini
05/10/2012 10:23:47
SM: 7G
321.0452
z=3
321.3794
z=3
321.7103
z=3
322.0534
z=3
322.3877
z=3
322.7182
z=3
Observed Data
NL:
1.92E4
HULBOY384-OV-HNESN#19-20 RT: 1.49-1.58 AV: 2 T: FTMS - p NSI Full ms [50.00-515.00]
Relative Abundance
321.0447
321.3791
321.7132
322.0446
322.3787
Theoretical Isotope Model
NL:
1.14E4
C47 H31 N8 O10 S3:
C47 H31 N8 O10 S3
p (gss, s /p:40) Chrg -3
R: 100000 Res .Pwr . @FWHM
m/z

Structures of the porphyrins and nanoconjugates

Porphyrins	Nanoconjugates
3 	**8** 
4 	**9** 
6 	**10** 
7 	**11** 
 amino-functionalised polyacrylamide nanoparticle	

Absorption and emission spectra of porphyrins and nanoconjugates

The graphs depicted below represent the absorption (solid lines) and the emission (dashed lines) of the porphyrins (black lines) and the nanoconjugates (dark red lines), as the intensity (normalised arbitrary units) versus wavelength (nanometers).



O_2 calibrations in time-resolved domain

- The samples were held in a four-sided quartz cuvette equipped with a degassing bulb.
- Prior to measurements the sample was completely degassed by a series of freeze-pump-thaw cycles.
- Once degassed the concentration of oxygen in the sample cell was adjusted by back-filling the cell with a known pressure of air, and according to Henry's Law, $[O_2] \propto p_{air}$.
- Phosphorescence lifetime and intensity measurements (in correspondence of the emission λ_{max}) were performed at six oxygen concentrations within the 0 - 0.27 M range.
- Phosphorescence lifetimes were recorded using a time-correlated photon counting spectrometer. The samples were excited using the output of a pulsed nitrogen laser (VSL-337i OEM), which provided a 10Hz pulse train of pulse duration < 5 ns at 337 nm, with a pulse energy of ca. 5 μJ. Emission was collected at 90° to the excitation source and the emission wavelength was selected using a monochromator (Bentham TM300) and the selected light detected using a red-sensitive photon counting photomultiplier module (Hamamatsu H10682-1). The arrival times of multiple photons were recorded from each laser shot using a multi-channel scaler, and the data from a minimum of 10,000 laser shots was acquired to furnish the emission decay.

- Example of calibration: porphyrin **3**

M	p_{air} (mmHg)	pO_2 (mmHg)[a]	$[O_2]$ (M)[b]	I_{em}	$1/I_{em}$	τ (s)	1 / τ
1	1.94	0.41	6.89×10^{-07}	1.00	1.00	1.03×10^{-05}	$9.71 \times 10^{+05}$
2	102.99	21.63	3.66×10^{-05}	0.49	2.03	6.04×10^{-06}	$1.66 \times 10^{+05}$
3	283.09	59.45	1.01×10^{-04}	0.24	4.14	2.74×10^{-06}	$3.65 \times 10^{+05}$
4	452.99	95.13	1.61×10^{-04}	0.17	5.85	2.09×10^{-06}	$4.78 \times 10^{+05}$
5	588.90	123.67	2.09×10^{-04}	0.15	6.63	1.56×10^{-06}	$6.41 \times 10^{+05}$
6	760.00	159.60	2.70×10^{-04}	0.10	9.65	1.15×10^{-06}	$8.70 \times 10^{+05}$

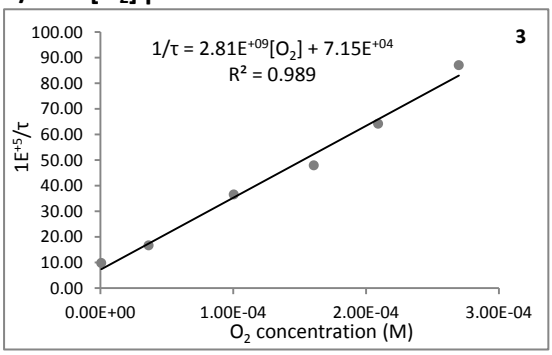
M = measurement point
p_{air} = air pressure in the sample cell (in mmHg)
pO_2 = oxygen pressure in sample cell (in mmHg)
$[O_2]$ = molar concentration of oxygen in the sample cell
I_{em} = intensity of phosphorescence measured at the emission λ_{max} (670 nm for **3**)
τ = triplet lifetime (in seconds)
[a]:
pO_2 (mmHg)= p_{air} (mmHg)x 0.21
[b]:

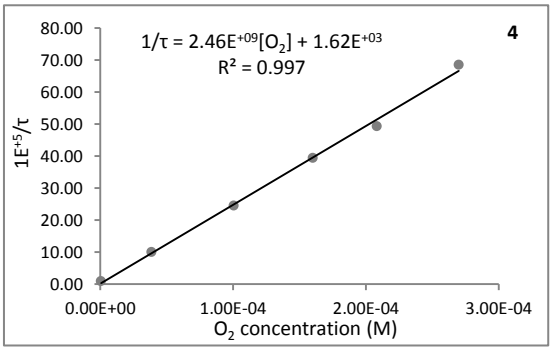
$$[O_2](M)=\frac{pO_2\ mmHg}{(760\ mmHg\ atm^{-1})x(757\ atm\ M^{-1})}$$

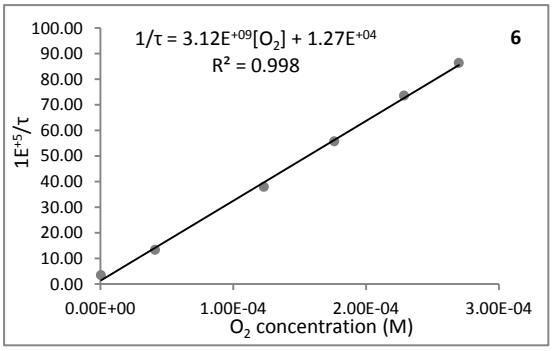
0.21: molar fraction of oxygen in air
760 mmHg atm^{-1}: conversion factor from Torr to atm
757 $atmM^{-1}$: Henry's law constant for oxygen in water at 25 °C

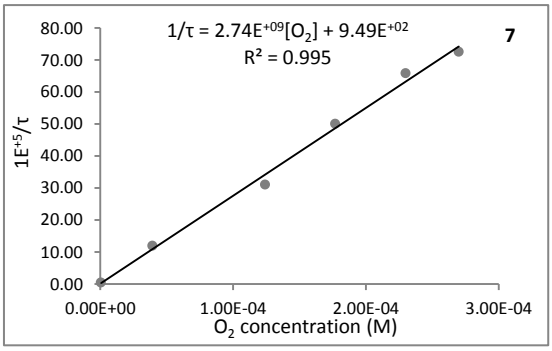
- The values (1/τ) or (1/I) were plotted against the oxygen concentration. The k_q values were obtained from the corresponding linear regression equations ($1/\tau = k_q[O_2] + 1/\tau_0$) or ($1/I = k_q[O_2] + 1/I_0$).

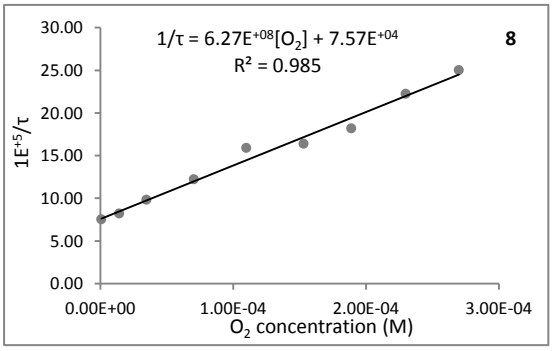
1/τ vs. [O_2] plots

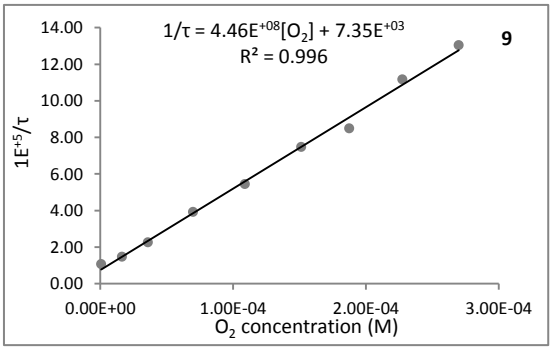


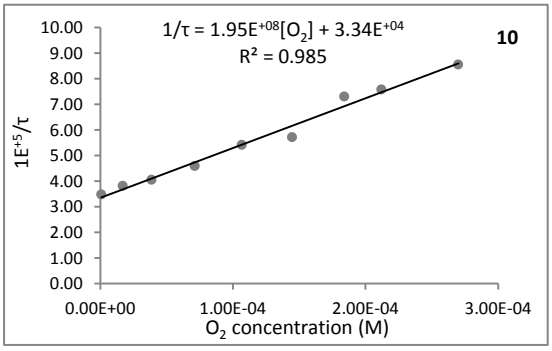


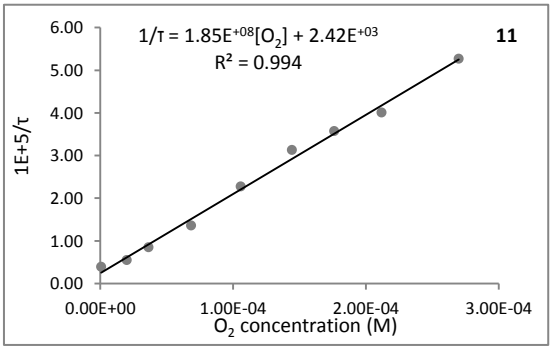




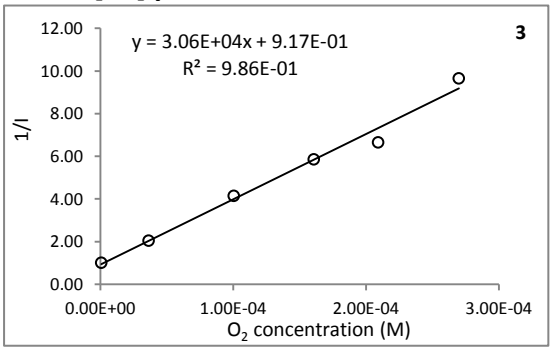


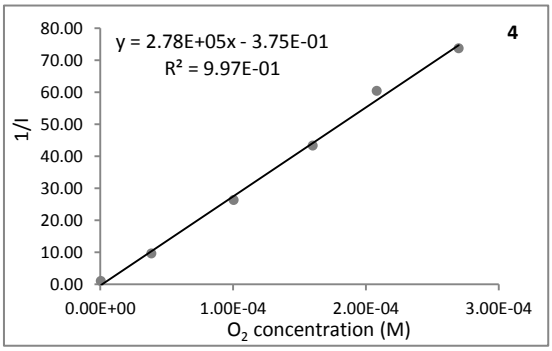


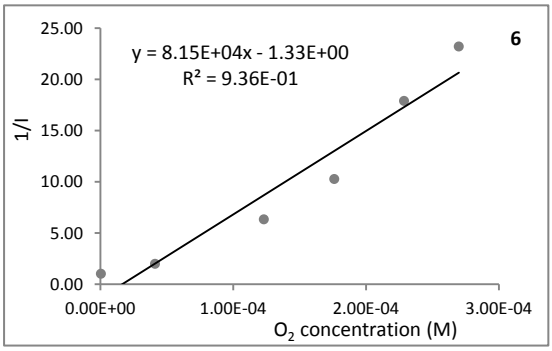


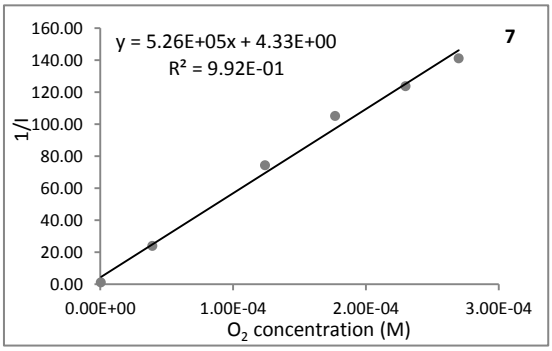


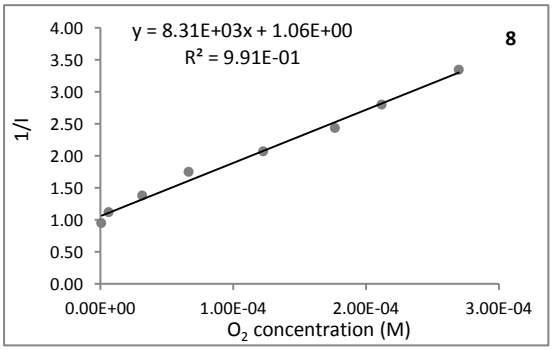
1/I vs. [O_2] plots

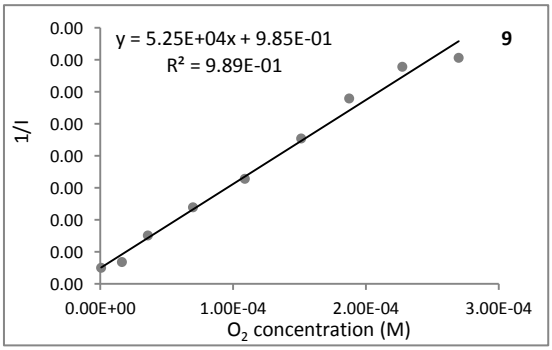


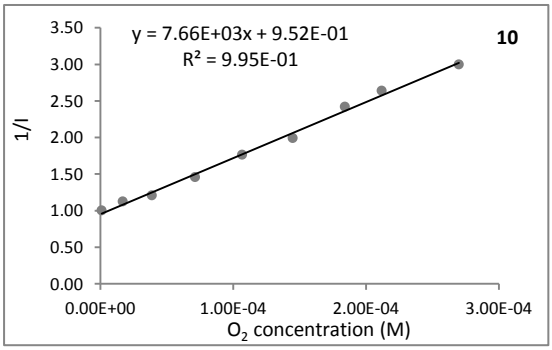


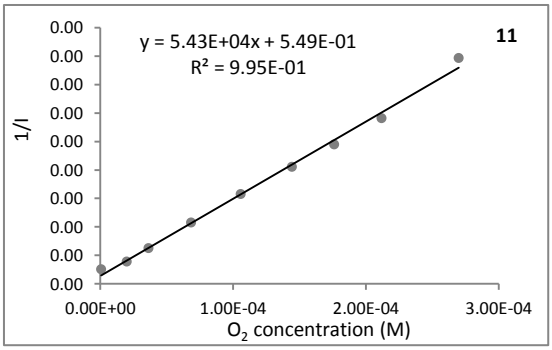




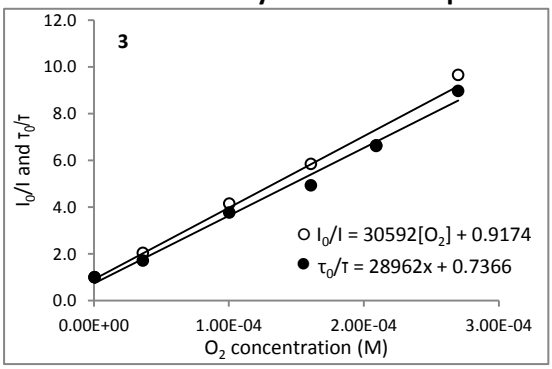


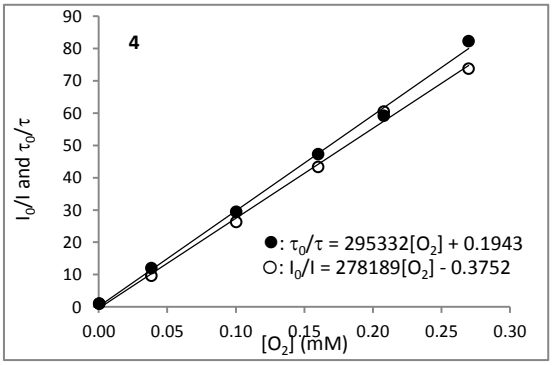


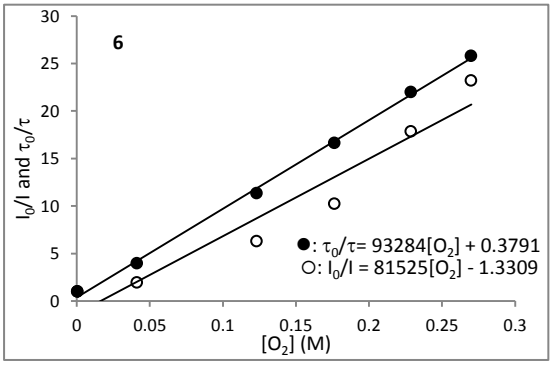


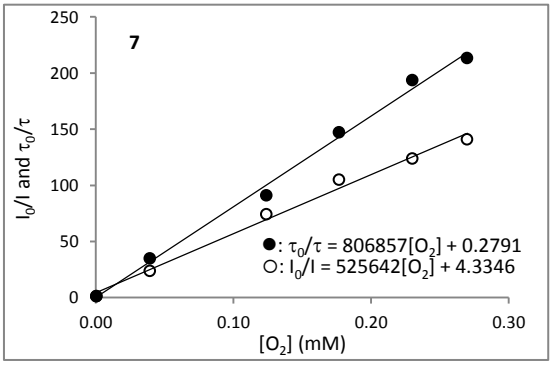


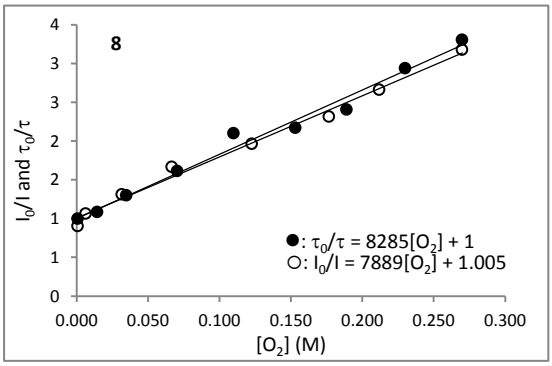
Lifetime and intensity Stern-Volmer plots

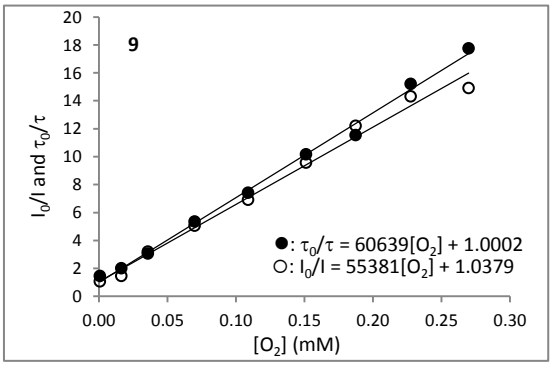


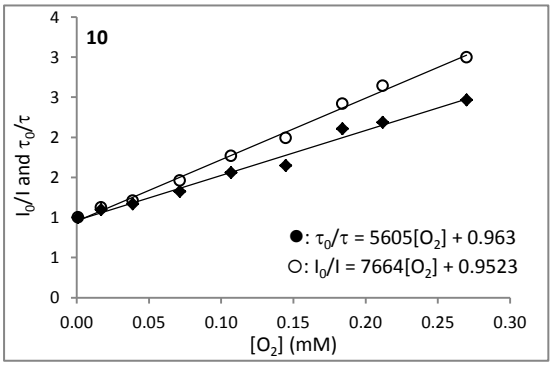


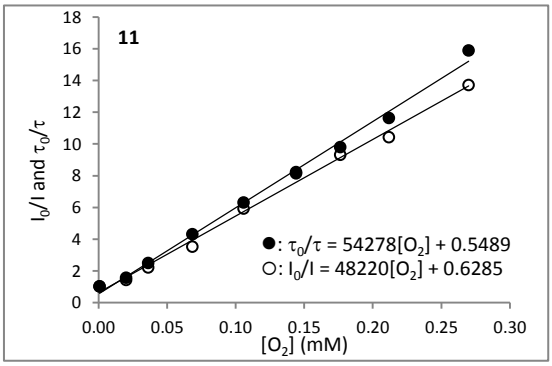












Spectrum of the diode lamp used for the photostability experiments