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Supporting Information

Robust Optical Oxygen Sensors based on Polymer-bound NIR-emitting Platinum(II) Benzoporphyrins

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Table S 1. Amounts of the monomers for the synthesis of 4-vinylphenylboronic acid-styrene copolymers with different amount of 4-vinylphenylboronic acid (compounds **4**) and actual Ph-B$(OH)_2$ content in the resulted polymers as determined by atomic spectroscopy.

Polymer	**Styrene**		**4-Vinylboronic acid**			**Actual Ph-B$(OH)_2$ content**
Abbreviation	**m [g]**	**n [mol]**	**m [mg]**	**n [mmol]**	**mol %**	**mol %**
PS0.05	20	0.192	14.20	$9.60*10^{-5}$	0.05	0.05
PS0.1	20	0.192	28.40	$1.92*10^{-4}$	0.1	0.07
PS0.25	5	0.048	18.0	$1.20*10^{-4}$	0.25	0.20
PS1	5	0.048	71.0	0.48	1	1.55

Table S 2. Amount of the components used for grafting $PtTPTBPBr_4$ (**3a**) to various 4-vinylphenylboronic acid-styrene copolymers (compounds **4**)

Polymer				**$PtTPTBPBr_4$**			**Yield**	**Dye content**
Used Polymer	**m [g]**	**n [mol]**	**eq**	**m [mg]**	**n [mmol]**	**eq**	**[%]**	**[% wt]**
PS0.05	1.313	0.0126	1000	10	$7.56*10^{-3}$	1.2	56	0.33
PS0.1	0.656	0.0063	1000	10	$7.56*10^{-3}$	1.2	50	0.63
PS0.25	0.535	0.0051	1000	20	$1.51*10^{-2}$	3.0	84	1.82
PS1	0.158	0.0015	1000	20	$1.51*10^{-2}$	10	71	6.92

Table S 3. GPC-Data of 4-vinylphenylboronic acid-styrene copolymers before and after the reaction with $PtTPTBPBr_4$

	Molecular Weight Distribution before grafting $PtTPTBPBr_4$				**Molecular Weight Distribution after grafting $PtTPTBPBr_4$**			
Polymer	**Mn [g/mol]**	**Mw [g/mol]**	**Mz [g/mol]**	**PDI**	**Mn [g/mol]**	**Mw [g/mol]**	**Mz [g/mol]**	**PDI**
PS0.05	59900	181600	494700	3.03	54100	168000	505000	3.11
PS0.1	99700	404000	1218000	4.05	119000	457800	1321000	3.85
PS0.25	58100	244100	828000	4.20	62000	251000	721800	4.05
PS1	25500	46700	74200	1.83	39800	92500	187900	2.32

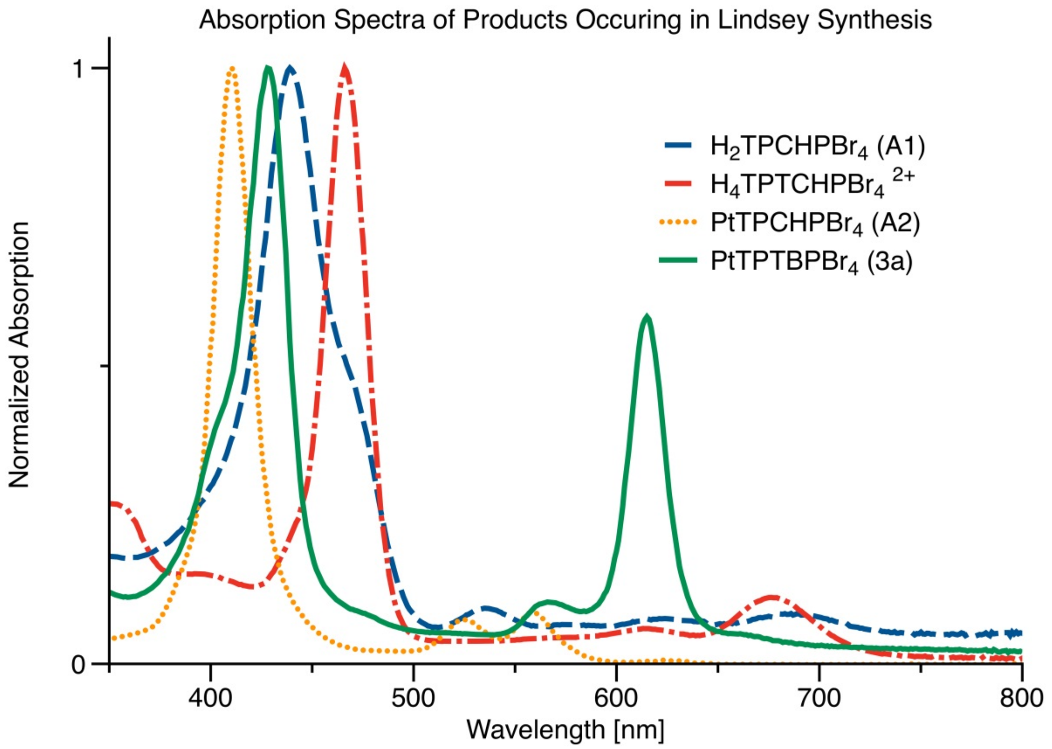


Figure S 1. Normalized absorption spectra (in acetone) of the intermediates and products in the Lindsey Synthesis.

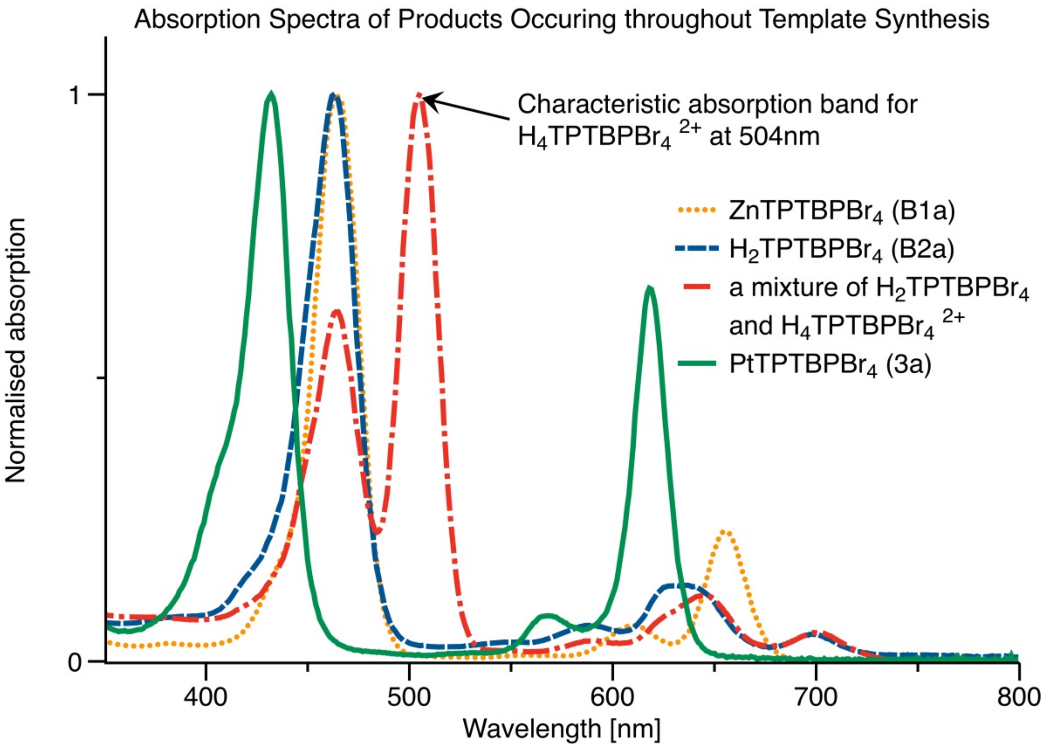


Figure S 2. Normalized absorption spectra (in dichloromethane) of the intermediates and products in the modified Template Synthesis.

Zn-5-(4-bromophenyl)-10,15,20-tri(phenyl)-tetrabenzoporhyrin (ZnTPTBPBr, B1b)

Zn-4-bromophenylaetate (8.00 g, 16.23 mmol), phenylacetic acid (11.03 g, 81.06 mmol) and 1,2-dicyanobenzene (8.31 g, 64.80 mmol) were mixed and homogenized using a mortar. The solid mixture was split into equal portions of roughly 700 mg, placed into 2.5 ml Supelco® vials and compressed. The vials were sealed with a metal screw cap, placed into a pre-heated metal block at 140 °C. The reagents were heated to a temperature of 280 °C and left to react for 40 minutes while stirring and subsequently left to cool. The melt in each vial was dissolved in acetone to a volume of 300 ml. The raw product was precipitated in a mixture of EtOH/H_2O/sat. $NaHCO_3$ (1000/200/50, v/v/v). The product was further purified by Al_2O_3 column chromatography (eluent: DCM + 2 % THF) and a silica-gel column (eluent: DCM). Yield: 977 mg, 6 %. UV–Vis (DCM): $\lambda_{max,}$ nm (rel. int.): 462 (1.00), 607 (0.06), 651 (0.18).

5-(4-bromophenyl)-10,15,20-tri(phenyl)-tetrabenzoporhyrin (H_2TPTBPBr, B2b)

ZnTPTBPBr (250 mg, 0.261 mmol) was dissolved in 500 ml of DCM and 50 ml of concentrated HCl was slowly added. The protonated ligand could be observed via UV-Vis spectrum at its characteristic band at 501 nm in acetone. The mixture was extracted with H_2O/sat. $NaHCO_3$ (500/50, v/v) until no protonated ligand could be observed. The product was dried over Na_2SO_4 and the solvent was removed. Yield: 180 mg, 77 %. UV–Vis (acetone): λ_{max}, nm (rel. int.): 460 (1.00), 584 (0.05), 627 (0.12), 696 (0.04).

Pt(II)-5-(4-bromophenyl)-10,15,20-tri(phenyl)-tetrabenzoporhyrin (PtTPTBPBr, 3b)

The free ligand (180 mg, 0.201 mmol) was dissolved in 200 ml TMB. The solution was heated to reflux at 170 °C. N_2 was bubbled through the reaction mixture. $Pt(C_6H_5CN)Cl_2$ (152.2 mg, 0.322 mmol) was added in small pre-dissolved portions (0.4 eq in TMB) over 2 hours. The reaction was monitored via absorption spectroscopy. After cooling, the product centrifuged and the solvent removed using rotary evaporation. The crude product was purified on an Al_2O_3 column (eluent: CH/DCM, 2/1, v/v). The product was dissolved in a small volume acetone and precipitated in a five-fold volume hexane and dried at 60°C. Yield: 105 mg, 48 %. ^{1}H NMR (300 MHz, Chloroform-d) δ 8.29 – 7.81 (m, 19H), 7.33 – 7.03 (m, 16H). MALDI-TOF: m/z: [M^+] calc for $C_{60}H_{35}N_4Pt$, 1086.169; found, 1086.2. UV–Vis (acetone): λ_{max}, nm (rel. int.): 428 (1.00), 563 (0.05), 613 (0.58).

Compound **A2** **PtTPCHPBr$_4$** Ionisation: **MALDI/Dith**

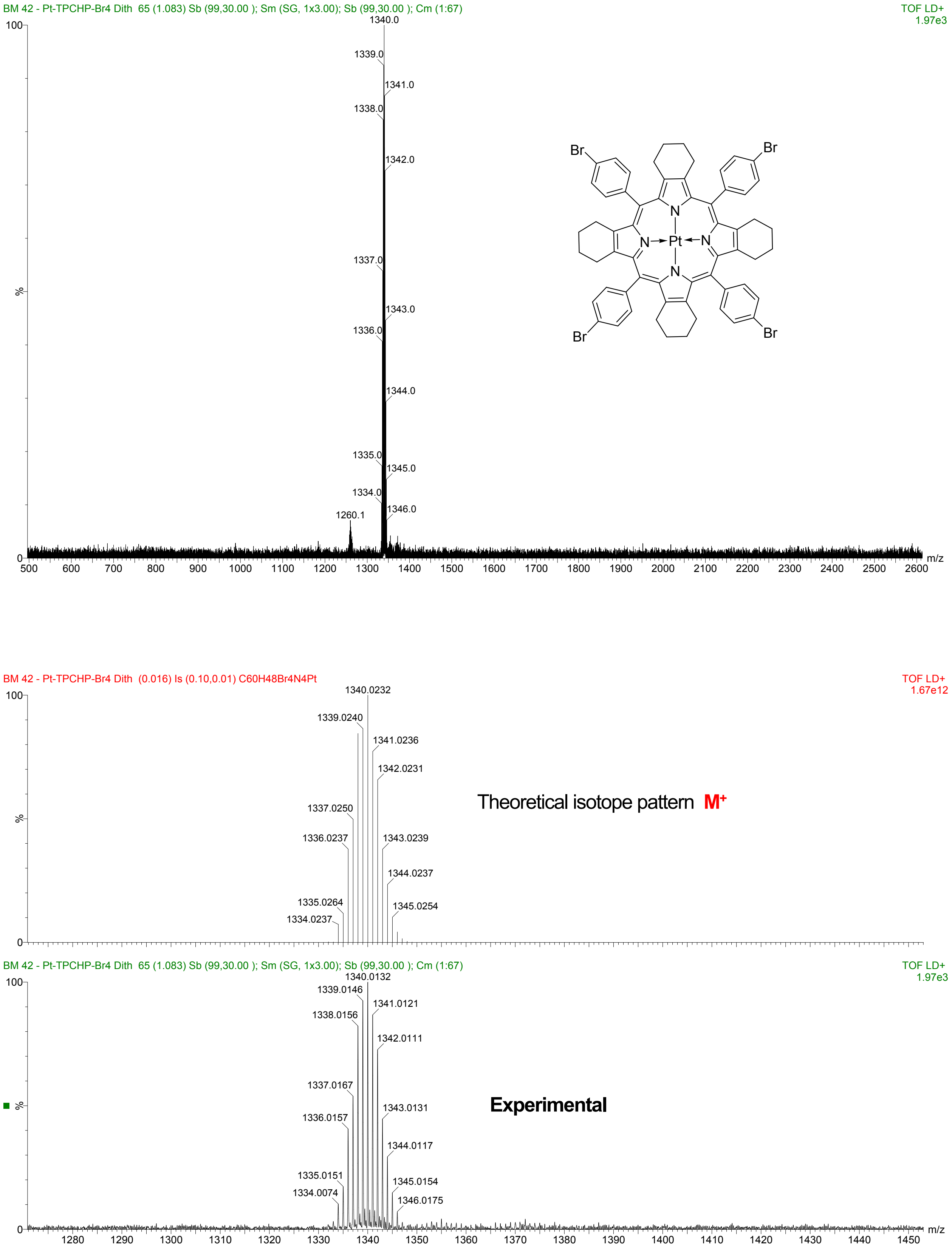
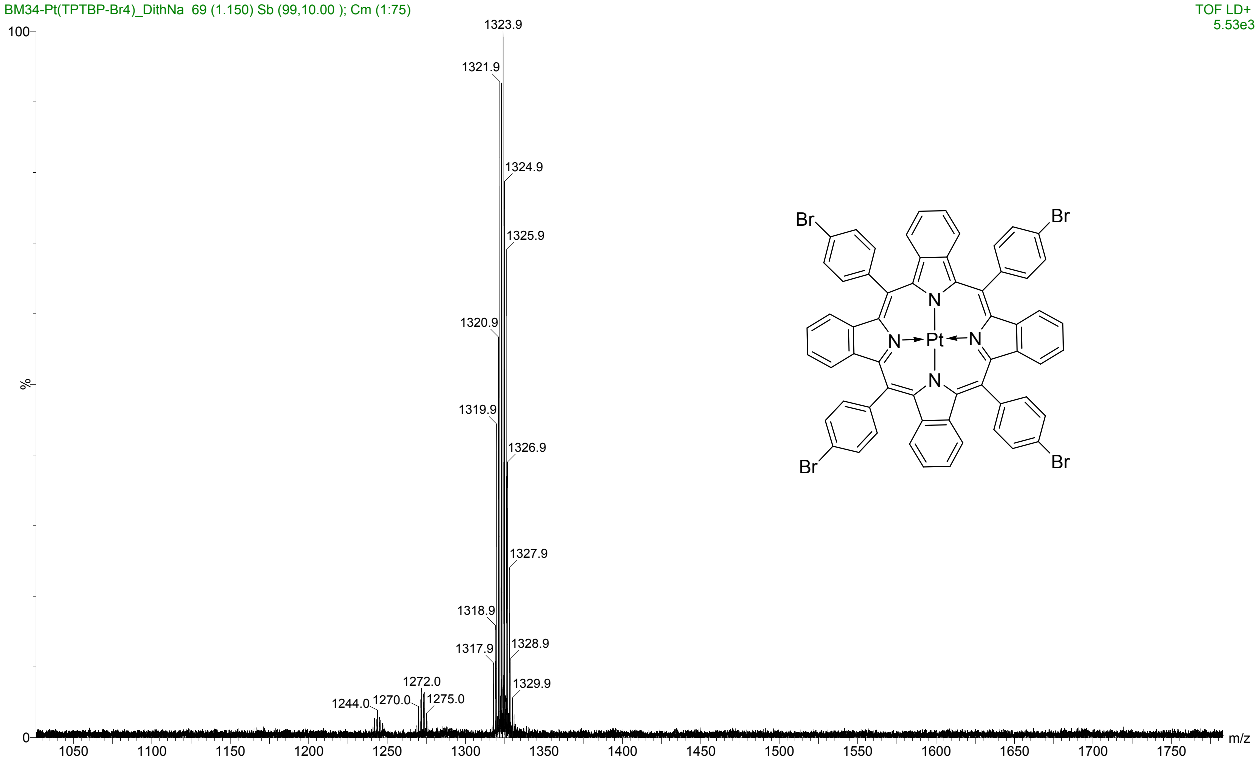


Figure S 3. Mass spectrum (MALDI) of PtTPCHPBr$_4$.

Compound **3a PtTPTBPBr$_4$** Ionisation: **MALDI/Dith**



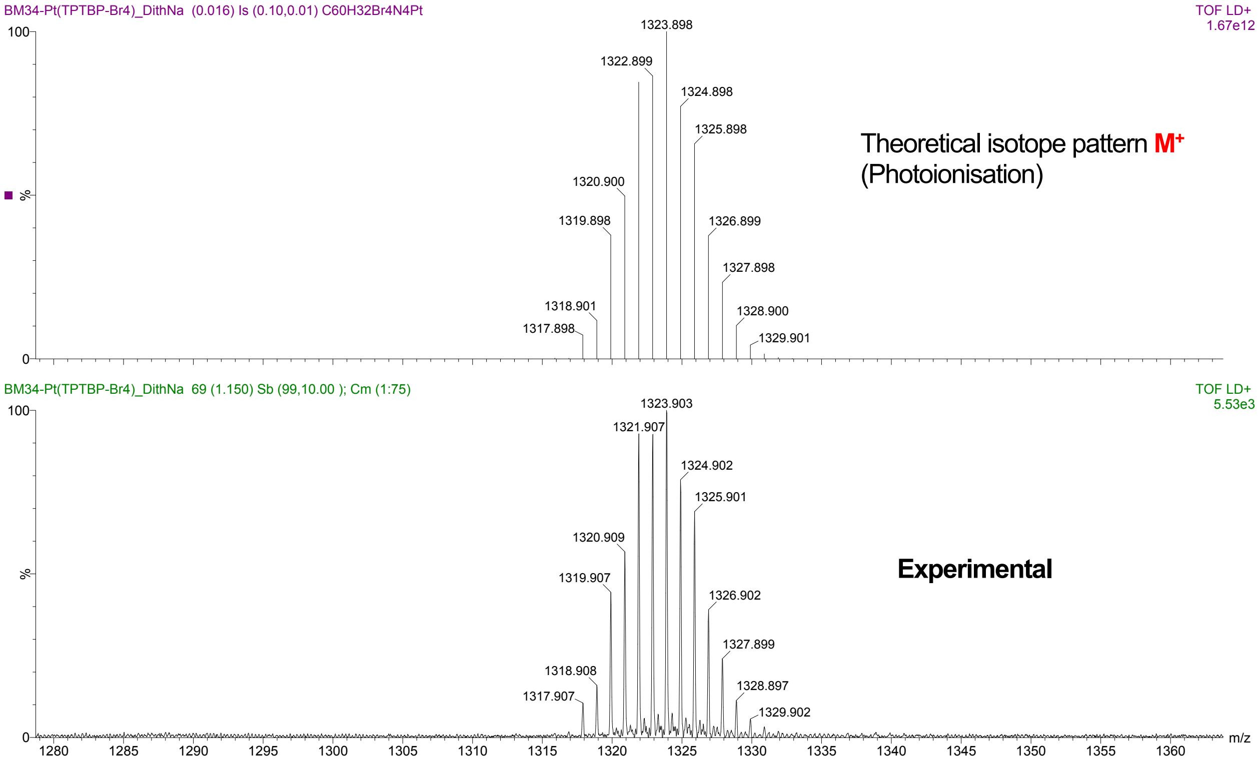


Figure S 4. Mass spectrum (MALDI) of PtTPTBPBr$_4$ obtained via Lindsey method.

Compound **3a PtTPTBPBr$_4$** Ionisation: **MALDI**

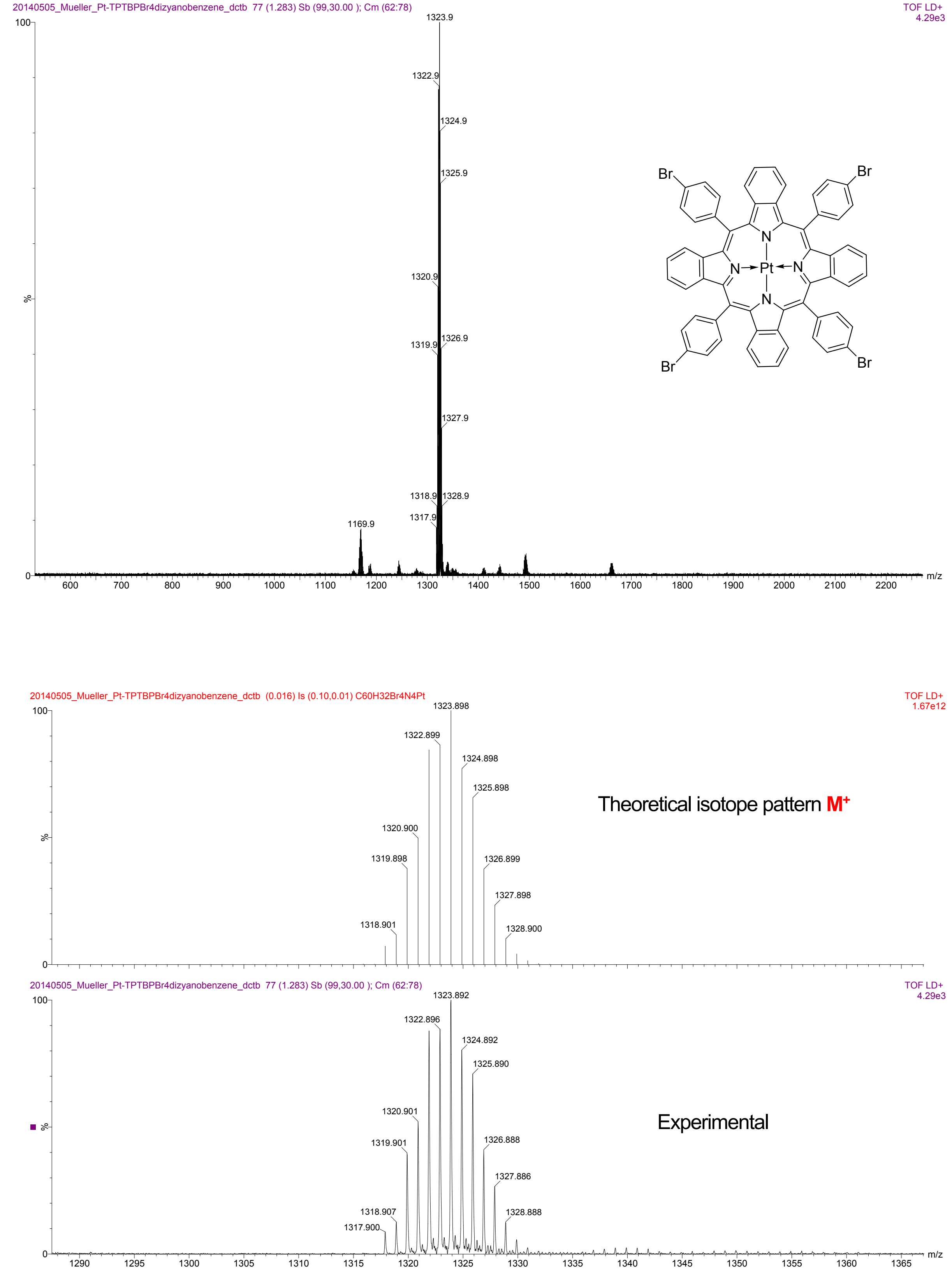


Figure S 5. Mass spectrum (MALDI) of PtTPTBPBr$_4$ obtained via Template method.

Compound **3b PtTPTBPBr** Ionisation: **MALDI/DCTB**

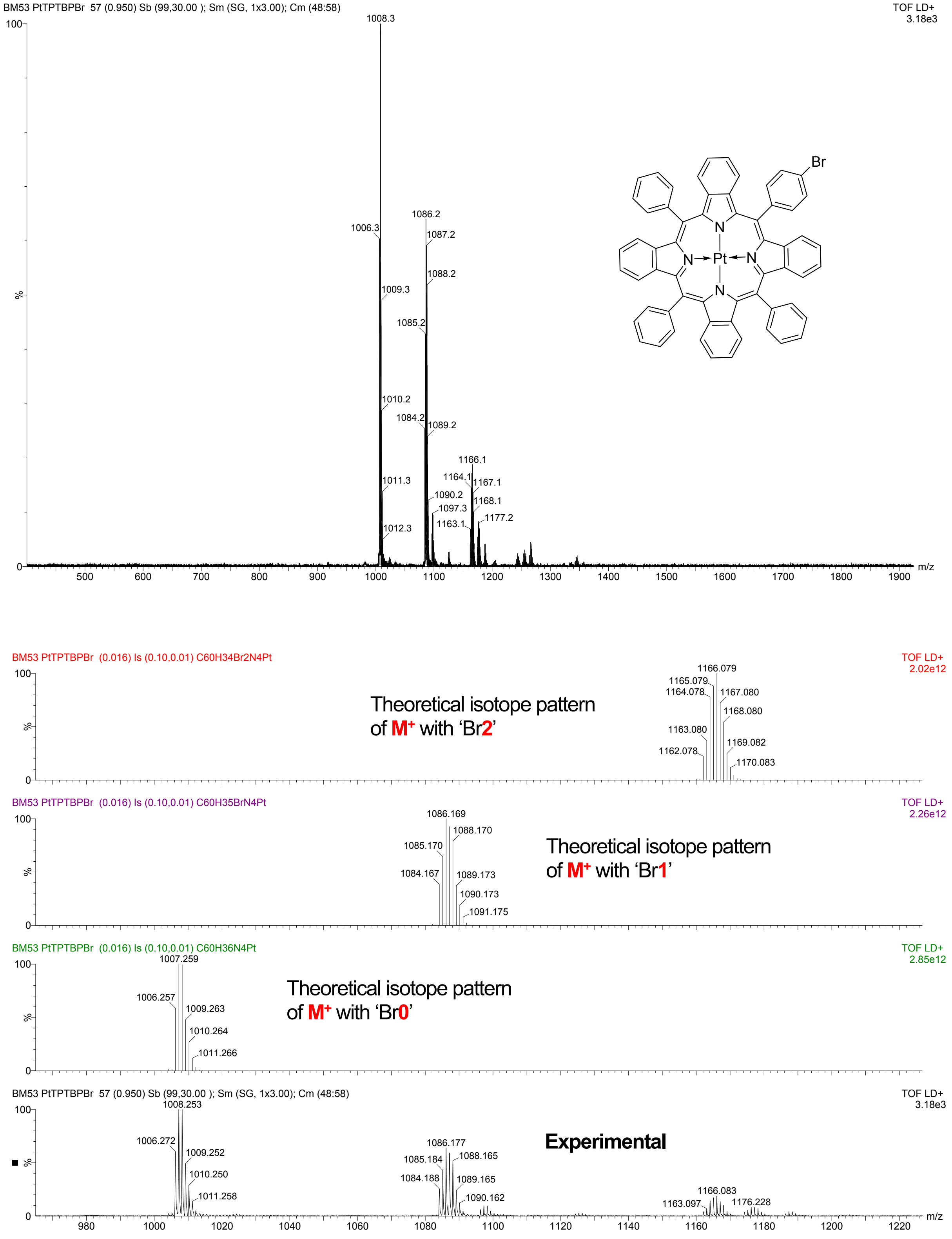


Figure S 6. Mass spectrum (MALDI) of PtTPTBPBr obtained via template method. The spectrum indicates presence of nonsubstituted PtTPTBP and dibromo-subsituted porpyhrin.

Compound **5 PtTPTBPStyr** Ionisation: **MALDI / DCTB**

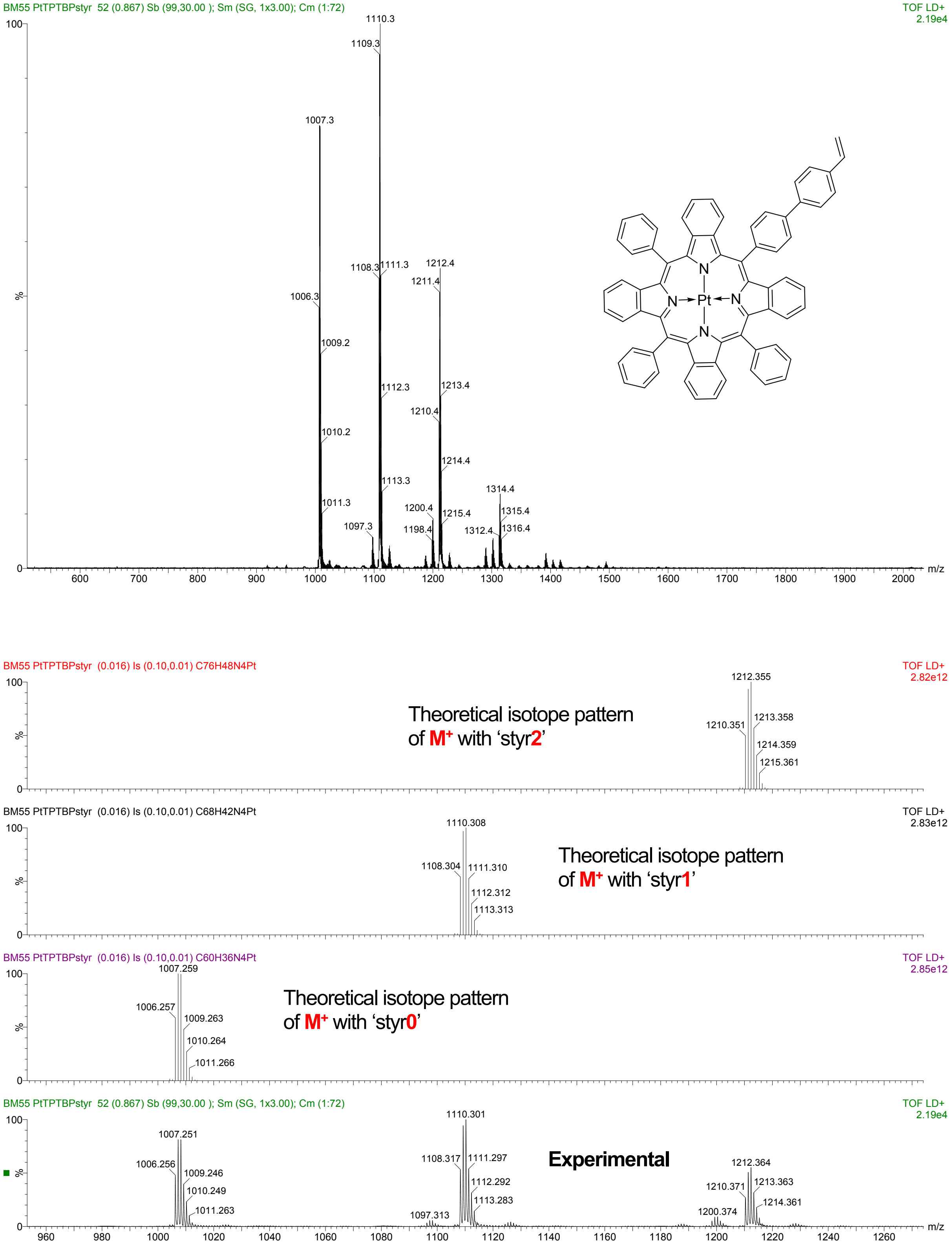


Figure S 7. Mass spectrum (MALDI) of PtTPTBPBStyr. The spectrum indicates presence of nonsubstituted PtTPTBP and the Pt(II) porpyhrin bearing two styryl groups.

$$\frac{\tau_0}{\tau} = \frac{1}{\dfrac{f}{1+K_{SV1}\cdot pO_2} + \dfrac{1-f}{1+K_{SV2}\cdot pO_2}} \qquad (1)$$

Equation 1. This equation is adapted from so called “two site model” and is used to fit the lifetime plots. K_{SV1} and K_{SV2} are the Stern-Volmer constants for the first and the second site, respectively, and f is the distribution coefficient for the first site. Note that the equating is physically meaningful only for the luminescence intensity plots, but nevertheless almost ideally describes the lifetime plots as well.

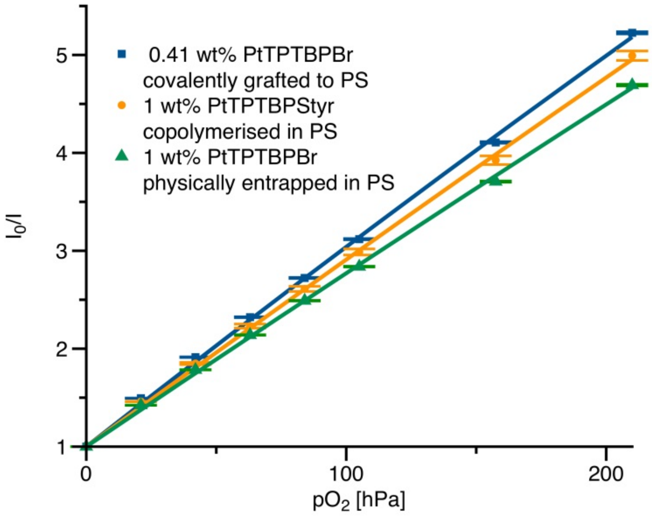


Figure S 8. Stern-Volmer plots (luminescence intensity) for polystyrene-based sensing materials.