Enhancing Photoinduced Electron Transfer Efficiency of Fluorescent pH-probes with Halogenated Phenols

Daniel Aigner[a], Stefan A Freunberger[b], Martin Wilkening[b], Robert Saf[b], Sergey M Borisov[a] and Ingo Klimant[a]

[a]Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria

[b]Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria

Syntheses

3-Chloro-4-hydroxybenzylamine

4-Hydroxybenzylamine (300 mg, 2.44 mmol) was dissolved in a mixture of 1M hydrochloric acid in acetic acid (5 mL) and *N,N*-dimethylformamide (0.5 mL). Sulfuryl chloride (414 µL, 5.12 mmol) was added and the precipitate formed upon stirring (RT, 2 h) was separated by centrifugation, washed with acetic acid (3 x 5 mL) and methylene chloride and left to dry. The product (containing ≈ 6 % impurity) was used without further purification, yield 264 mg (69 %). ^{1}H NMR (300 MHz, CD_3OD, TMS): δ = 7.44 (d, 1H, J = 1.9 Hz, H(1)); 7.22 (dd, 1H, J_1 = 8.3 Hz, J_2 = 1.8 Hz, H(2); 6.97 (d, 1H, J = 8.4 Hz, H(1); 4.00 (s, 2H, H(4)).

5(6)-Carboxy-2',7'-dichlorofluorescein

Trimellitic anhydride (1g, 5.21 mmol) and 4-chlororesorcinol (1.51g, 10.4 mmol) were stirred in methanesulfonic acid (25 mL) at 145°C for 1 h. The mixture was allowed to cool to RT and water (400 ml) was added. The crude product was washed thoroughly with water (1.5 L), dried and used without further purification, yield 2.36 g (98 %).

*5(6)-(3-Chloro-4-hydroxy-benzylaminocarboxy)-2',7'-dichlorofluorescein (**1B**)*

(5,6)-Carboxy-2',7'-dichlorofluorescein (350 mg, 0.62 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (166 mg, 0.87 mmol) and *N*-hydroxysuccinimide (100 mg, 0.87 mmol) were stirred in dry *N,N*-dimethylformamide (5 ml) for 1.5 h at RT. To the solution of NHS ester obtained were added 3-chloro-4-hydroxybenzylamine (205 mg, 1.30 mmol) and ethyldiisoproylamine (301 µL, 1.73 mmol)). After 4 h, the crude product was precipitated and washed with water, dried and purified by column chromatography (silica gel, 40 – 63 µm), eluent methylene chloride / methanol / acetic acid 98 / 2 / 0.25. Eluate containing product was concentrated to 5 ml, precipitated and

washed with water (4 x 100 mL), drying yielded 211 mg (46 %). ^{1}H NMR (300 MHz, CD_3OD containing 0.02 M NH_3, TMS): δ = 8.49 (d, 0.5H, J = 1.3 Hz, H(5a)); 8.01 – 8.15 (m, 1.5H, H(4a,4b,5b)); 7.69 (d, 0.5H, J = 1.0 Hz, H(3b)); 7.33 – 7.39 (m, 1H, H(3a,7)); 7.30 (d, 0.5H, J = 1.8 Hz, H(7)); 7.16 – 7.22 (dd, 0.5H, J_1 = 8.2 Hz, J_2 = 2.0 Hz, H(9)); 7.11 (d, 2.5H, J = 1.6 Hz, H(2,9)); 6.82 – 6.93 (dd, 1H, J_1 = 8.3 Hz, J_2 = 14.2 Hz, H(8)); 6.60 (s, 2H, H(1)); 4.43 – 4.56 (d, 2H, H(6)). MALDI-TOF: m/z [MH^+] 584.0069 found, 584.0071 calcd.

*5(6)-(4-Methyl-1-piperazinylcarboxy)-2',7'-dichlorofluorescein (**1C**)*

After preparing the NHS ester as described for **1B**, *N*-methylpiperazine (175 µL, 1.58 mmol) and ethyldiisoproylamine (301 µL, 1.73 mmol)) were added and the mixture was stirred for 4 h. Repeated precipitation with n-hexane (6 x 5 mL) afforded an oily residue which was purified by column chromatography, eluent methylene chloride / methanol / concentrated aqueous HCl 85 / 15 / 0.375, yield 163 mg (39 %). ^{1}H NMR (300 MHz, CD_3OD containing 0.02 M NH_3, TMS): δ = 8.09 – 8.17 (s + d, 1H, H(5a,5b); 7.65 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.1 Hz, H(4a,4b)); 7.27 – 7.39 (2d, 1H, J_1 = 7.7 Hz, J_2 = 1.2 Hz, H(3a,3b)); 7.10 – 7.19 (2s, 2H, H(2)); 6.59 (s, 2H, H(1)); 7.10 – 7.19 (2s, 2H, H(2)); 3.5 – 3.9 (m, 4H, H(6)); 2.44 – 3.64 (m, 4H, H(7)); 2.28 – 2.39 (2s, 3H, H(8)). MALDI-TOF: m/z [MH^+] 527.0756 found, 527.0776 calcd.

*Sulforhodamine B-4'-(N-(3,5-dichloro-4-hydroxyphenyl))sulfonamide (**2A**)*

4-Amino-2,6-dichlorophenol (17 mg, 0.096 mmol) and triethylamine (13.8 µL, 0.010 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (0.3 mL), the mixture was cooled to 0°C and lissamine rhodamine B (50 mg, 0.087 mmol) was added. After stirring for 4h at 0°C and 12h at RT, the crude product was precipitated with n-hexane (6 x 5 mL) and purified by column chromatography, eluent methylene chloride / methanol 96 / 4 1, yield 28 mg (45 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$, TMS): δ = 10.43 (1H, s, H(9)); 10.20 (1H, s, H(8)); 8.43 (1H,

d, J = 1.7 Hz, H(4)); 7.72 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, H(5)); 7.43 (2H, d, J = 7.9 Hz, H(6)); 7.06 (2H, s, H(7)); 6.98 (2H, dd, J_1 = 9.5 Hz, J_2 = 1.8 Hz , H(2)); 6.93 (2H, d, J = 1.9 Hz, H(3)); 6.84 (2H, d, J = 9.3 Hz , H(1)); 3.63 (8H, q, J = 7.1 Hz , H(10)); 1.20 (12H, t, J = 6.9 Hz , H(11)). MALDI-TOF: m/z [MNa^+] 740.1034 found, 740.1035 calcd.

*Sulforhodamine B-4'-(N-(3-azapentane-1,5-diyl))sulfonamide (**2C**)*

N-Methylpiperazine (21.2 µL, 0.19 mmol) was dissolved in anhydrous *N,N*-dimethylformamide (0.3 ml), lissamine rhodamine B (50 mg, 0.087 mmol) was added. Reaction and work-up were carried out as described for **2a**. Column chromatography was performed, eluent methylene chloride / methanol / 25% aqueous ammonia 94.5 / 5 / 0.5, yield 23 mg (41 %). ^{1}H NMR (300 MHz, D_2O, 0.1% HCl conc., TMS): δ = 8.49 (1H, d, J = 1.5 Hz, H(4)); 8.14 (1H, broad d, J = 7.8 Hz, H(5)); 7.57 (1H, d, J = 7.6 Hz, H(6)); 6.95 (2H, d, J = 9.7 Hz, H(1)); 6.92 (2H, dd, J_1 = 10.0 Hz, J_2 = 1.2 Hz , H(2)); 6.84 (2H, d, J = 1.1 Hz, H(3)); 4.03 (2H, d, J = 12.6 Hz, H(7)); 3.64 – 3.73 (2H, d, J = 12.3 Hz, H(7)); 3.53 – 3.64 (8H, q, J = 7.1 Hz, H(10)); 3.33 (3H, d, J = 12.6 Hz, H(8)); 2.92 – 3.06 (5H, m, H(8,9)); 1.24 (12H, 7, J = 6.9 Hz, H(11)). MALDI-TOF: m/z [MH^+] 641.2493 found, 641.2468 calcd.

*1,4-Diketo-3-((4-[N-(3,5-dichloro-4-hydroxyphenyl)amino]sulfonyl)phenyl)-6-phenylpyrrolo[3,4-c]pyrrole (**3A**)*

The preparation of **3A** is described elsewhere[1].

*1,4-Diketo-3-((4-[N-(3-chloro-4-hydroxyphenyl)amino]sulfonyl)phenyl)-6-phenylpyrrolo[3,4-c]pyrrole (**3B**)*

The preparation of **3B** is described elsewhere[1].

*1,4-Diketo-3-((4-(4-methyl-1-piperazinyl)sulfonyl)phenyl)-6-phenylpyrrolo[3,4-c]pyrrole (**3C**)*

1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (500 mg, 1.73 mmol) was heated in chlorosulfuric acid (5 mL) to 60 °C. After 3 h, the mixture was allowed to cool to RT and added dropwise onto *N*-methylpiperazine (10 ml, 90.1 mmol, pre-cooled to 0°C). The product was precipitated with H_2O (100 ml), washed thoroughly with water (1.5 L), dried and purified by column chromatography, eluent ethyl acetate / ethanol / 25% aqueous ammonia 89 / 10 / 1, yield 51 mg (7 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$, TMS): δ = 11.50 (1H, broad s, H(9)); 8.45 – 8.7 (2H, broad, H(13)); 8.41 (2H, d, J = 8.4 Hz, H(2,3)); 8.25 – 8.35 (2H, 2d, J = 7.7 Hz, H(5,8)); 7.68 – 7.83 (4H, m, H(1,4,6,7)); 2.93 (4H, broad t, H(10)); 2.35 (4H, broad t, H(11)); 2.12 (3H, s, H(12)). MALDI-TOF: m/z [MH^+] 451.1405 found, 451.1440 calcd.

*N-(3,5-Dichloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tertracarboxylic bisimide (**4A**)*

1,6,7,12-Tetrachloroperylene-3,4:9,10-tetracarboxylic bisanhydride (3 g, 5.66 mmol) was dissolved in 1-methyl-2-pyrrolidone (200 mL) at 110 °C. 4-Amino-2,6-dichlorophenol (1.04 g, 5.84 mmol), 2,6-diisopropylaniline (1.2 mL, 6.37 mmol) and propionic acid (100 mL) were added, the mixture was flushed with nitrogen and stirred at 110 °C for 22 h. 5 % aqueous NaCl (800 mL) was added, the orange precipitate was filtered, washed with water, dried and purified by column chromatography, eluent methylene chloride / toluene 70 / 30, yield 1.18 g (25 %).^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.75 (4H, 2s, H(1)); 7.53 (1H, t, J = 7.7 Hz, H(3)); 7.39 (2H, d, J = 7.9 Hz, H(2)); 7.29 (2H, s, H(6)); 6.08 (1H, s, H(7)); 2.74 (2H, quint, J = 6.7 Hz, H(4)); 1.19 (12H, dd, J_1 = 6.9 Hz, J_2 = 3.6 Hz, H(5)). MALDI-TOF: m/z [M^+] 849.9963 found, 849.9949 calcd.

*N-(3-Chloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tertracarboxylic bisimide (**4B**)*

4B was prepared in the same way as **4A**, 4-Amino-2-chlorophenol (813 mg, 5.66 mmol) was used instead of the dichloro compound, yield 1.41 g (31 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.75 (4H, 2s, H(1)); 7.53 (1H, t, J = 7.8 Hz, H(3)); 7.39 (2H, d, J = 7.8 Hz, H(2)); 7.33 (1H, d, J = 2.3 Hz, H(6)); 7.22 (1H, d, J = n.m. due to $CHCl_3$, H(8)); 7.17 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.3 Hz, H(7)); 5.77 (1H, s, H(9)); 2.74 (2H, quint, J = 6.8 Hz, H(4)); 1.19 (12H, dd, J_1 = 6.6 Hz, J_2 = 3.6 Hz, H(5)). MALDI-TOF: m/z [M^+] 816.0355 found, 816.0340 calcd.

*N-(2,6-Diisopropylphenyl)-N'-(2-(dimethylamino)ethyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tertracarboxylic bisimide (**4D**)*

1,6,7,12-Tetrachloroperyl-2-pyrrolidone (200 ml) at 80 °C. The mixture was flushed with nitrogen and *N,N*-dimethylethylene diamine (0.65 ml, 5.89 mmol) was added. After 1 h, temperature was raised to 120°C, 2,6-diisopropylaniline (4.61 ml, 24.4 mmol) and propionic acid (70 mL) and the mixture was stirred for 20 h. 20 % aqueous NaCl (1 l) was added, the orange precipitate was filtered, washed with dilute aqueous $NaHCO_3$, dried and purified by column chromatography, eluent methylene chloride / methanol 50 / 1, yield 1.36 g (33 %).^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.71 (4H, 2s, H(1)); 7.52 (1H, t, J = 7.6 Hz, H(3)); 7.38 (2H, d, J = 7.7 Hz, H(2)); 4.41 (2H, t, J = 5.7 Hz, H(6)); 2.76 (4H, m, H(4,7)); 2.42 (6H, s, H(8)); 1.18 (12H, dd, J_1 = 3.7 Hz, J_2 = 3.2 Hz, H(5)). MALDI-TOF: m/z [M-H^+] 760.1169 found, 760.1125 calcd.

*N-(3,5-Dichloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tertracarboxylic bisimide (**5A**)*

A mixture of **4A** (70 mg, 0.082 mmol), 1-methyl-2-pyrrolidone (7 mL), phenol (77mg, 0.82 mmol) and potassium carbonate (91 mg, 0.66 mmol) was stirred at 110°C for 15 h. 50 mL of

20 % aqueous NaCl containing 0.7 M HCl were added, the purple precipitate was filtered, washed with water, dried and purified by column chromatography, eluent toluene / ethanol 99 / 1, yield 54 mg (61 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.24 (4H, 2s, H(1)); 7.44 (1H, t, J = 8.4 Hz, H(3)); 7.23 – 7.34 (10H, m, H(2,8)); 7.21 (2H, s, H(6)); 7.12 (4H, m, H(9)); 6.98 (8H, t, J = 6.5 Hz, H(7)); 6.11 (1H, s, H(10)); 2.71 (2H, quint, J = 6.4 Hz , H(4)); 1.14 (12H, d, J = 6.6 Hz, H(5)). MALDI-TOF: m/z [M^+] 1080.248 found, 1080.258 calcd.

*N-(3-Chloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tertracarboxylic bisimide (**5B**)*

5B was prepared in the same way as **5A**, **4B** (70 mg, 0.086 mmol) was used as starting material, yield 40 mg (45 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.24 (4H, 2s, H(1)); 7.44 (1H, t, J = 8.2 Hz, H(3)); 7.23 – 7.33 (11H, m, H(2,6,10)); 7.06 – 7.16 (6H, m, H(7,8,11)); 6.98 (4H, dd, J_1 = 5.1 Hz, J_2 = 7.5 Hz, H(9)); 5.73 (1H, s, H(12)); 2.71 (2H, quint, J = 6.3 Hz , H(4)); 1.12 (12H, d, J = 6.8 Hz, H(5)). MALDI-TOF: m/z [M-H^+] 1045.2913 found, 1045.2892 calcd.

*N-(2,6-Diisopropylphenyl)-N'-(2-(dimethylamino)ethyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tertracarboxylic bisimide (**5D**)*

A mixture of **4D** (800 mg, 1.05 mmol), 1-methyl-2-pyrrolidone (50 mL), phenol (950 mg, 10.1 mmol) and potassium carbonate (1.1 g, 7.96 mmol) was stirred at 110°C for 3.5 h. 50 mL of 15 % aqueous NaCl containing 0.3 M HCl were added, the purple precipitate was filtered, washed with dilute aqueous $NaHCO_3$, dried and purified by column chromatography, eluent methylene chloride / methanol 98 / 2, yield 681mg (65 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.21 (4H, 2s, H(1)); 7.42 (1H, t, J = 7.8 Hz, H(3)); 7.20 – 7.33 (10H, m, H(2,10)); 7.12 (4H, q, J = 7.8 Hz, H(11)); 6.96 (8H, q, J = 3.9 Hz, H(9)); 4.28 (2H, t, J = 6.8 Hz, H(6));

2.58 – 2.75 (4H, m, (4,7)); 2.34 (6H, s, H(8)); 1.12 (12H, d, J = 6.8 Hz, H(5)). MALDI-TOF: m/z [M-H^+] 990.3752 found, 990.3754 calcd.

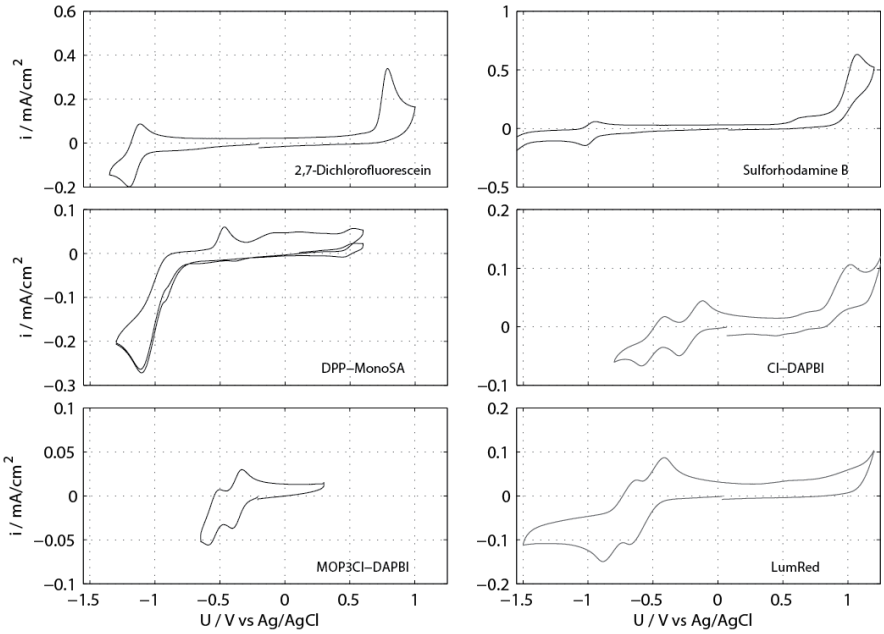
*N-(3,5-Dichloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1-(1-morpholinyl)-6,7,12-trichloroperylene-3,4:9,10-tertracarboxylic bisimide (**6A**)*

4A (175 mg, 0.24 mmol) was stirred in a mixture of morpholine (3 mL, 35 mmol) and 1-methyl-2-pyrrolidone (3 mL) at 40°C for 2 h. 50 ml 15 % aqueous NaCl containing 0.4 M HCl were added, the green precipitate was filtered, washed with water, dried and purified by column chromatography, eluent methylene chloride / methanol 50 / 1, yield 144 mg (75 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.73 (2H, s, H(1)); 8.59 (1H, s, H(1)); 8.54 (1H, s, H(1)); 7.53 (1H, t, J = 7.8 Hz, H(3)); 7.38 (2H, d, J = 7.7 Hz, H(2)); 7.30 (2H, s, H(6)); 6.08 (1H, s, H(11)); 4.07 – 4.32 (3H, m, H(7,10)); 3.95 (1H, t, J = 8.9 Hz, H(10)); 3.58 (1H, d, J = 11.4 Hz, H(9)); 3.37 (1H, t, J = 8.8 Hz, H(9)); 2.65 – 2.90 (3H, m, H(4,8)); 2.17 (1H, d, J = 13.7 Hz, H(8)); 1.19 (12H, dd, J_1 = 6.5 Hz, J_2 = 11.8 Hz, H(5)). MALDI-TOF: m/z [M-H^+] 900.0797 found, 900.0790 calcd.

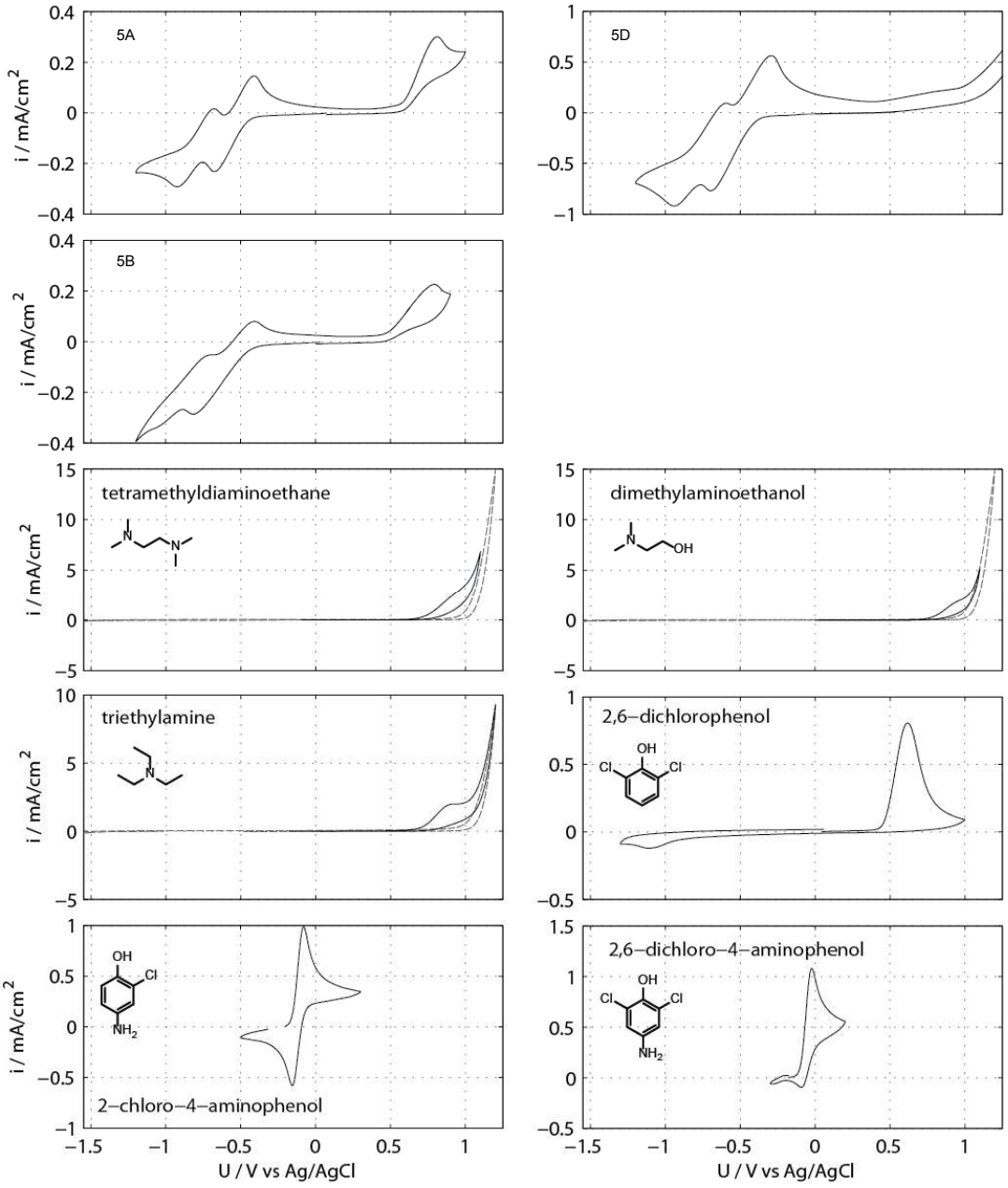
*N-(2,6-Diisopropylphenyl)-N'-(2-(dimethylamino)ethyl)-1-(1-morpholinyl)-6,7,12-trichloroperylene-3,4:9,10-tertracarboxylic bisimide (**6D**)*

6D was prepared in the same way as **6A**, **4D** (180 mg, 0.21 mmol) was used as starting material, eluent for column chromatography was methylene chloride / methanol 30 / 1, yield 132 mg (69 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.61 (2H, m, H(1)); 8.45 (2H, m, H(1)); 7.44 (1H, t, J = 7.8 Hz, H(3)); 7.30 (2H, d, J = 7.6 Hz, H(2)); 7.30 (2H, d, J = 7.6 Hz, H(2)); 4.32 (2H, m, H(6)); 3.95 – 4.25 (3H, m, H(9,12)); 3.84 (1H, m, H(12)); 3.53 (1H, t, J = 12.3 Hz, H(11)); 3.28 (1H, t, J = 8.4 Hz, H(11)); 2.55 – 2.95 (5H, m, H(4,7,10)); 2.31 (6H, 2d, H(8)); 2.06 (1H, t, J = 13.5 Hz, H(10)); 1.10 (12H, m, H(5)). MALDI-TOF: m/z [M-H^+] 809.0286 found, 809.0264 calcd.

Electrochemical measurements



Cyclic voltammograms of model compounds for fluorophores, denominated as stated in table 3 (main text). LumRed stands for LumogenRed (1,6,7,12-Tetraphenoxy-*N,N'*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tertracarboxylic bisimide), a model compound for **5A,B,D** for which a very similar first reduction potential (-0.55 V) was found. **5A,B,D** are shown in the following figure.

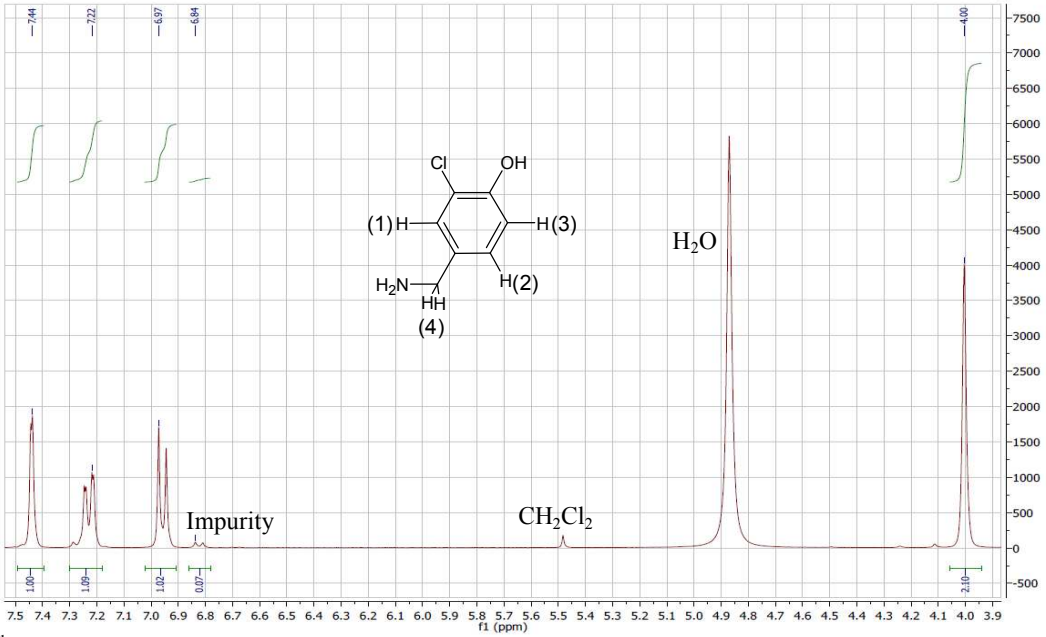


Cyclic voltammograms of model compounds for PET groups; in the curves for the amines, the dashed lines account for blank measurement (same solution without amine added).

NMR Spectroscopy and MALDI-TOF mass spectroscopy

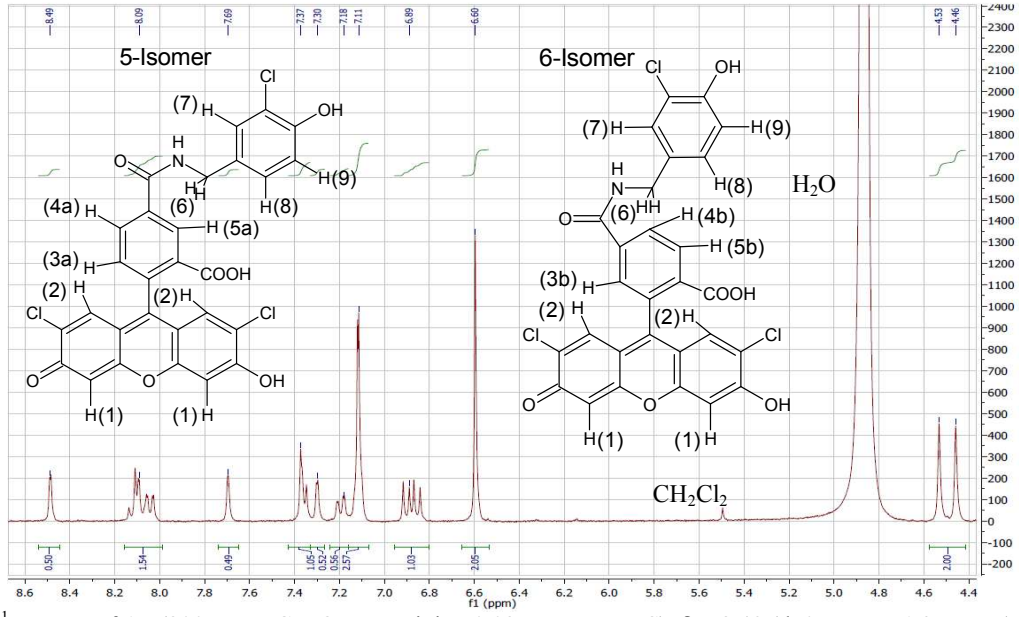
In MALDI-TOF, for the products **4-6 A-D**, in addition to $[MH]^+$ and $[MNa]^+$, M^+ $[M - H]^+$ and $[M - 2H]^+$ (products of photoionization) were detected.

3-Chloro-4-hydroxybenzylamine

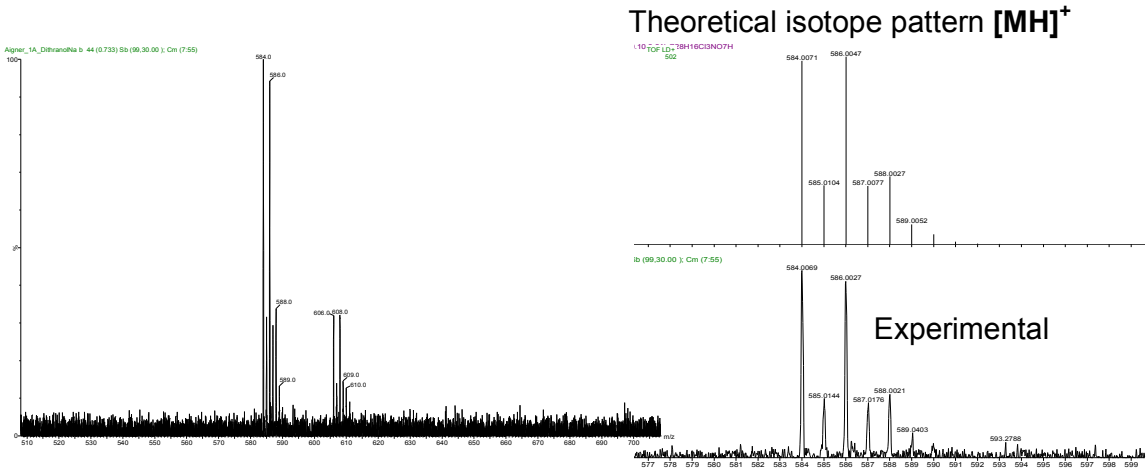


^{1}H NMR of 3-Chloro-4-hydroxybenzylamine (300 MHz, CD_3OD, TMS): δ = 7.44 (d, 1H, J = 1.9 Hz, H(1)); 7.22 (dd, 1H, J_1 = 8.3 Hz, J_2 = 1.8 Hz, H(2); 6.97 (d, 1H, J = 8.4 Hz, H(1); 4.00 (s, 2H, H(4)).

*5(6)-(3-Chloro-4-hydroxy-benzylaminocarboxy)-2',7'-dichlorofluorescein (**1B**)*

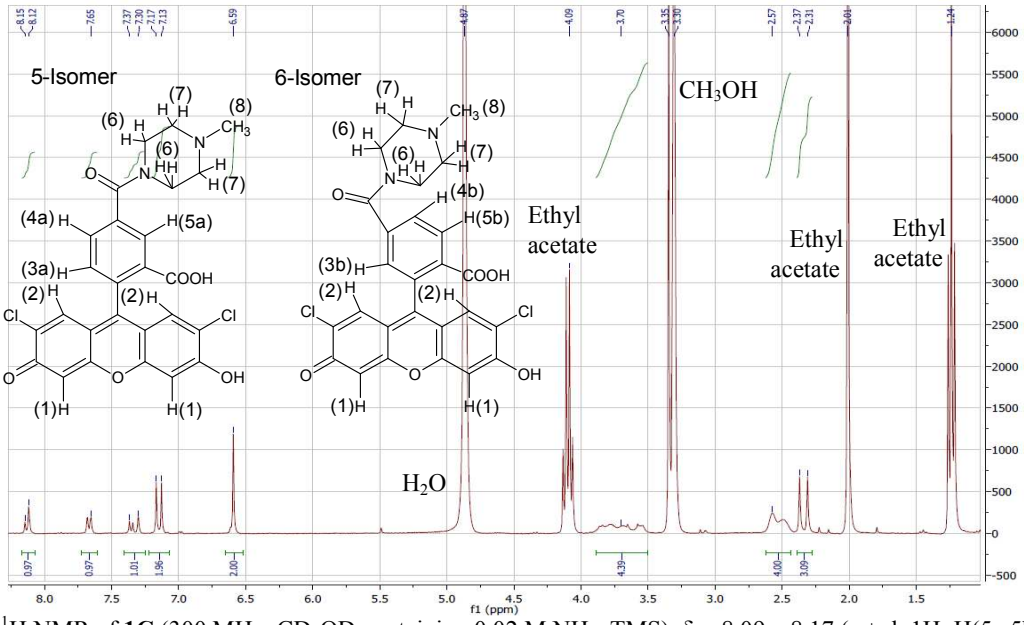


^{1}H NMR of **1B** (300 MHz, CD_3OD containing 0.02 M NH_3, TMS): δ = 8.49 (d, 0.5H, J = 1.3 Hz, H(5a)); 8.01 – 8.15 (m, 1.5H, H(4a,4b,5b)); 7.69 (d, 0.5H, J = 1.0 Hz, H(3b)); 7.33 – 7.39 (m, 1H, H(3a,7)); 7.30 (d, 0.5H, J = 1.8 Hz, H(7)); 7.16 – 7.22 (dd, 0.5H, J_1 = 8.2 Hz, J_2 = 2.0 Hz, H(9)); 7.11 (d, 2.5H, J = 1.6 Hz, H(2,9)); 6.82 – 6.93 (dd, 1H, J_1 = 8.3 Hz, J_2 = 14.2 Hz, H(8)); 6.60 (s, 2H, H(1)); 4.43 – 4.56 (d, 2H, H(6)).

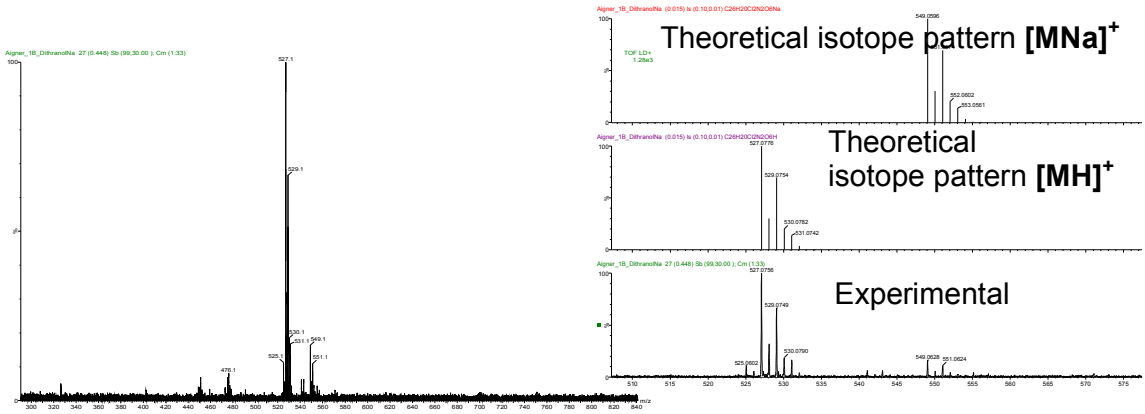


MALDI-TOF spectrum of **1B**

*5(6)-(4-Methyl-1-piperazinylcarboxy)-2',7'-dichlorofluorescein (**1C**)*

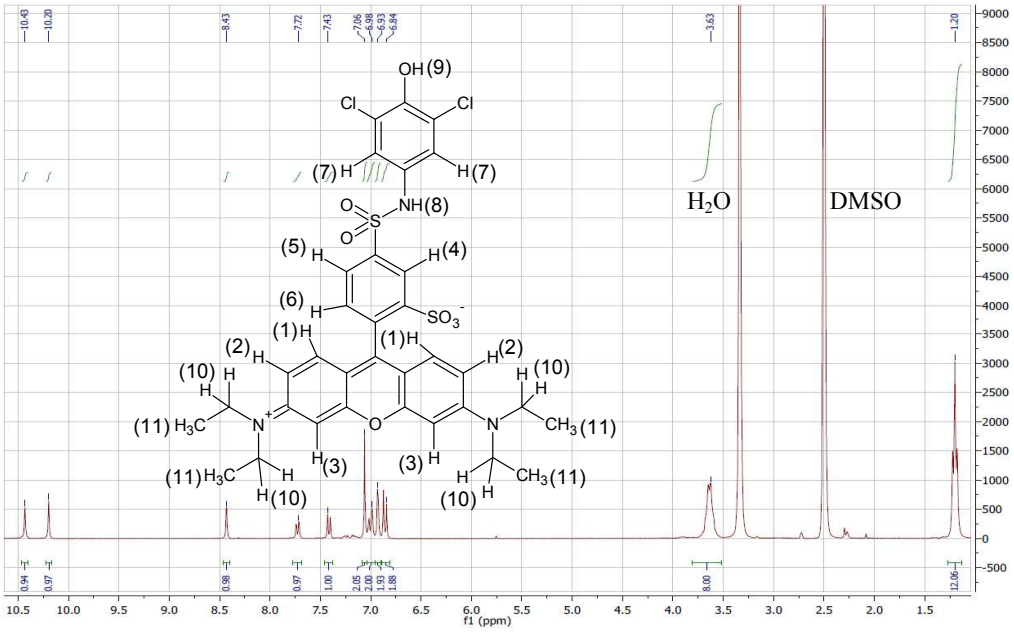


^{1}H NMR of **1C** (300 MHz, CD_3OD containing 0.02 M NH_3, TMS): δ = 8.09 – 8.17 (s + d, 1H, H(5a,5b); 7.65 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.1 Hz, H(4a,4b)); 7.27 – 7.39 (2d, 1H, J_1 = 7.7 Hz, J_2 = 1.2 Hz, H(3a,3b)); 7.10 – 7.19 (2s, 2H, H(2)); 6.59 (s, 2H, H(1)); 7.10 – 7.19 (2s, 2H, H(2)); 3.5 – 3.9 (m, 4H, H(6)); 2.44 – 3.64 (m, 4H, H(7)); 2.28 – 2.39 (2s, 3H, H(8)).

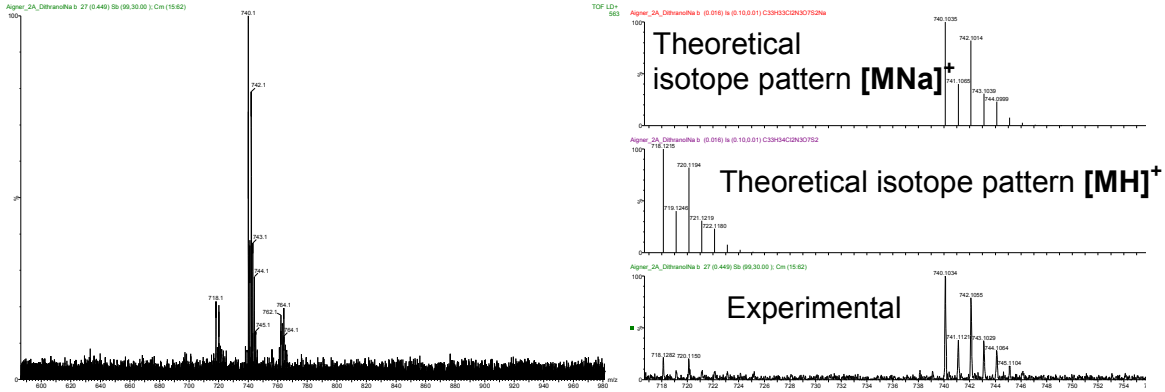


MALDI-TOF spectrum of **1C**

*Sulforhodamine B-4'-(N-(3,5-dichloro-4-hydroxyphenyl))sulfonamide (**2A**)*

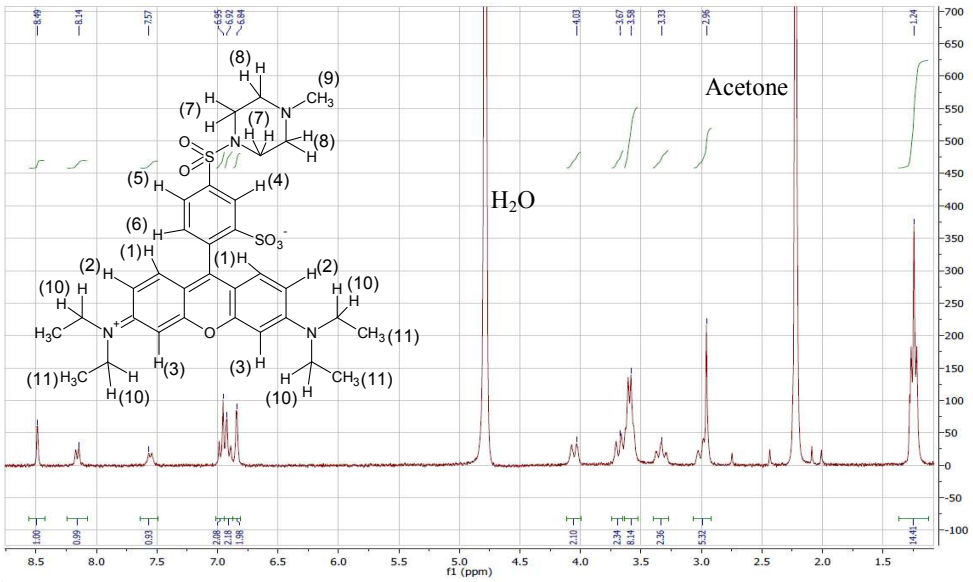


^{1}H NMR of **2A** (300 MHz, $(CD_3)_2SO$, TMS): δ = 10.43 (1H, s, H(9)); 10.20 (1H, s, H(8)); 8.43 (1H, d, J = 1.7 Hz, H(4)); 7.72 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, H(5)); 7.43 (2H, d, J = 7.9 Hz, H(6)); 7.06 (2H, s, H(7)); 6.98 (2H, dd, J_1 = 9.5 Hz, J_2 = 1.8 Hz , H(2)); 6.93 (2H, d, J = 1.9 Hz, H(3)); 6.84 (2H, d, J = 9.3 Hz , H(1)); 3.63 (8H, q, J = 7.1 Hz , H(10)); 1.20 (12H, t, J = 6.9 Hz, H(11)).

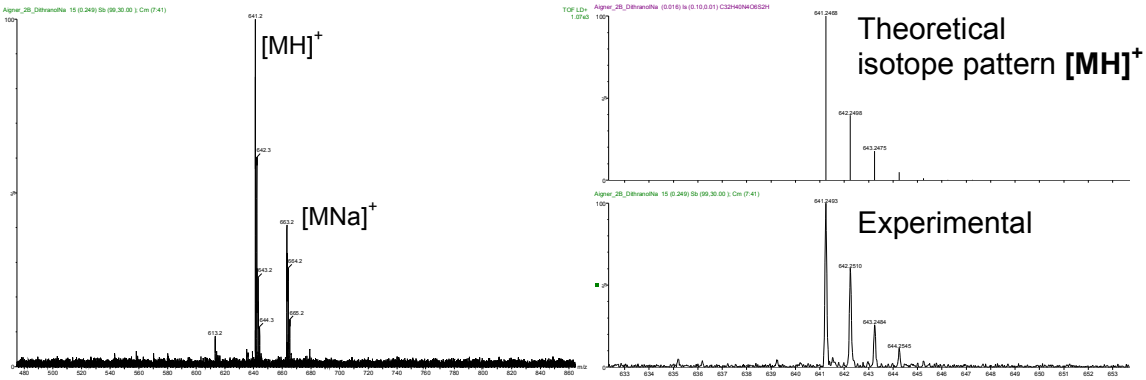


MALDI-TOF spectrum of **2A**

*Sulforhodamine B-4'-(N-(3-azapentane-1,5-diyl))sulfonamide (**2C**)*

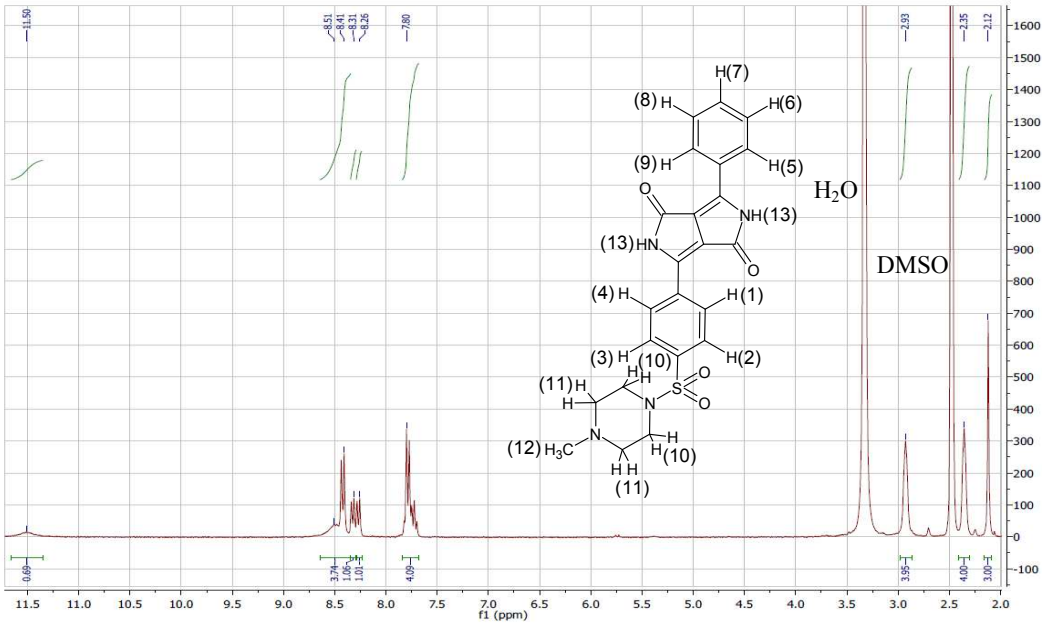


^{1}H NMR of **2C** (300 MHz, D_2O, 0.1% HCl conc., TMS): δ = 8.49 (1H, d, J = 1.5 Hz, H(4)); 8.14 (1H, broad d, J = 7.8 Hz, H(5)); 7.57 (1H, d, J = 7.6 Hz, H(6)); 6.95 (2H, d, J = 9.7 Hz, H(1)); 6.92 (2H, dd, J_1 = 10.0 Hz, J_2 = 1.2 Hz , H(2)); 6.84 (2H, d, J = 1.1 Hz, H(3)); 4.03 (2H, d, J = 12.6 Hz, H(7)); 3.64 – 3.73 (2H, d, J = 12.3 Hz, H(7)); 3.53 – 3.64 (8H, q, J = 7.1 Hz, H(10)); 3.33 (3H, d, J = 12.6 Hz, H(8)); 2.92 – 3.06 (5H, m, H(8,9)); 1.24 (12H, 7, J = 6.9 Hz, H(11)).

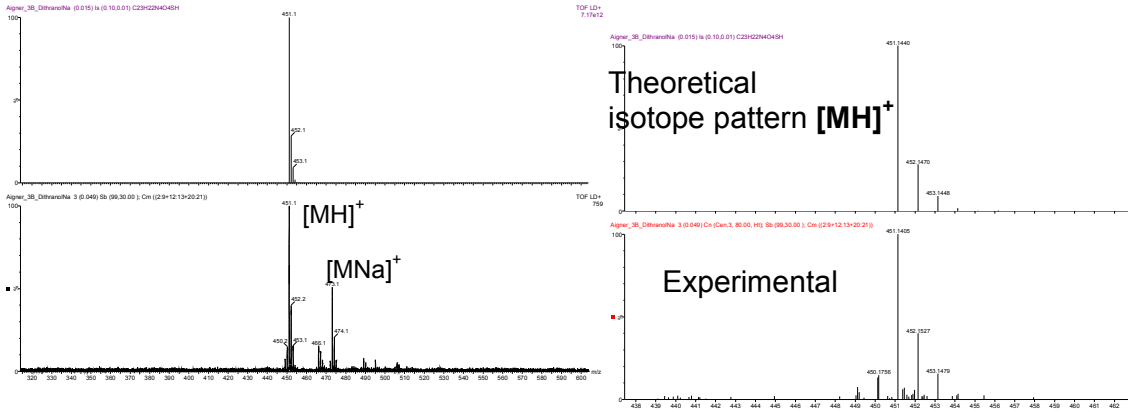


MALDI-TOF spectrum of **2C**

*1,4-Diketo-3-((4-(4-methyl-1-piperazinyl)sulfonyl)phenyl)-6-phenylpyrrolo[3,4-c]pyrrole (**3C**)*

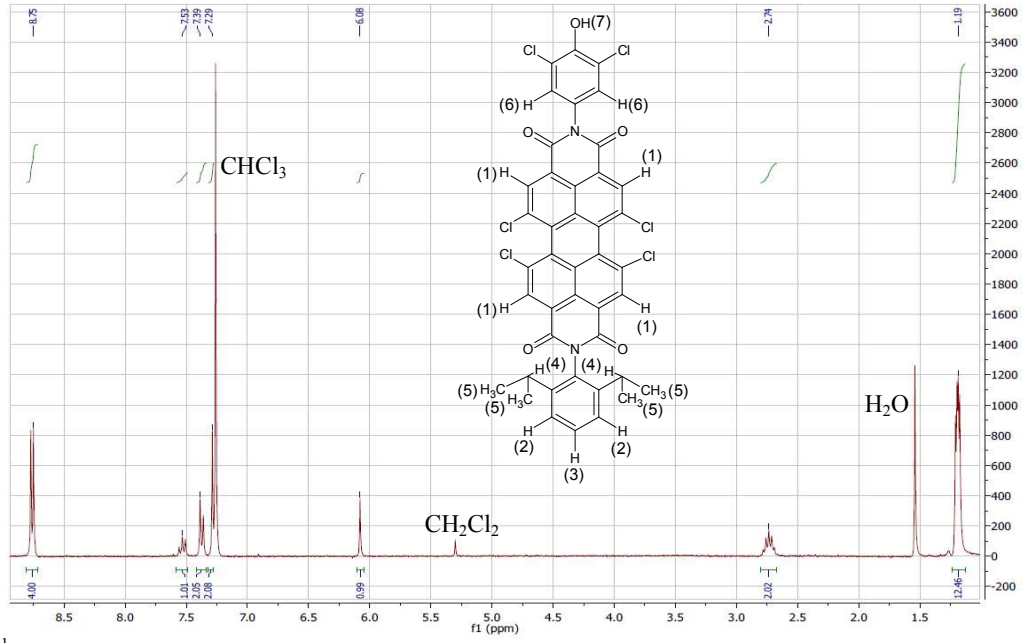


^{1}H NMR of **3C** (300 MHz, $(CD_3)_2SO$, TMS): δ = 11.50 (1H, broad s, H(9)); 8.45 – 8.7 (2H, broad, H(13)); 8.41 (2H, d, J = 8.4 Hz, H(2,3)); 8.25 – 8.35 (2H, 2d, J = 7.7 Hz, H(5,8)); 7.68 – 7.83 (4H, m, H(1,4,6,7)); 2.93 (4H, broad t, H(10)); 2.35 (4H, broad t, H(11)); 2.12 (3H, s, H(12)).

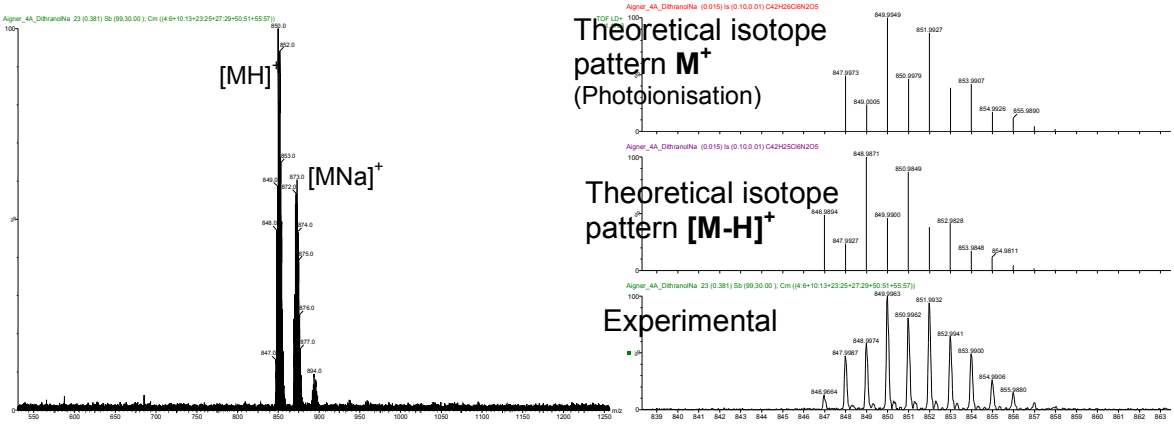


MALDI-TOF spectrum of **3C**

*N-(3,5-Dichloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tertracarboxylic bisimide (**4A**)*

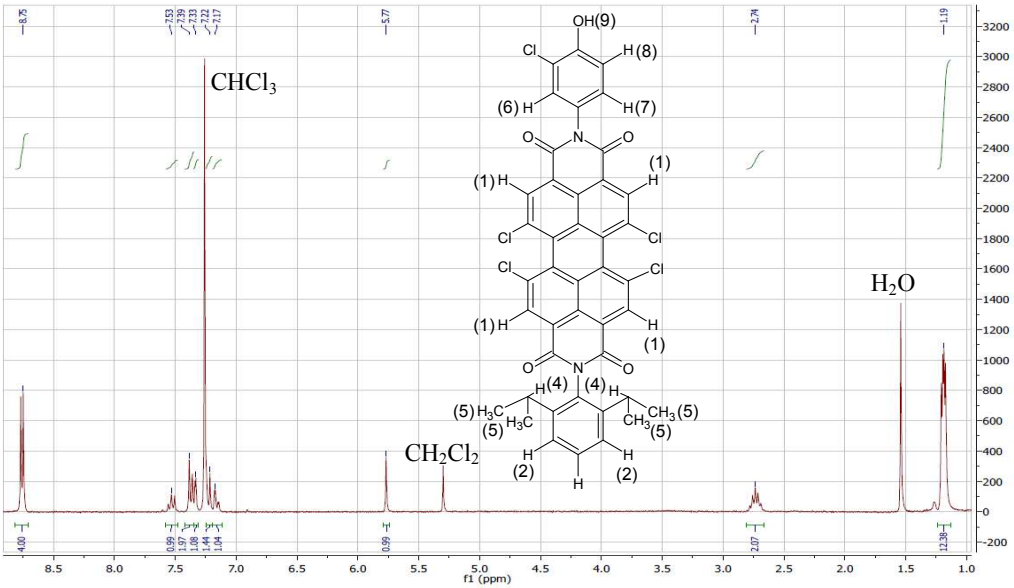


^{1}H NMR of **4A** (300 MHz, $CDCl_3$, TMS): δ = 8.75 (4H, 2s, H(1)); 7.53 (1H, t, J = 7.7 Hz, H(3)); 7.39 (2H, d, J = 7.9 Hz, H(2)); 7.29 (2H, s, H(6)); 6.08 (1H, s, H(7)); 2.74 (2H, quint, J = 6.7 Hz, H(4)); 1.19 (12H, dd, J_1 = 6.9 Hz, J_2 = 3.6 Hz, H(5)).

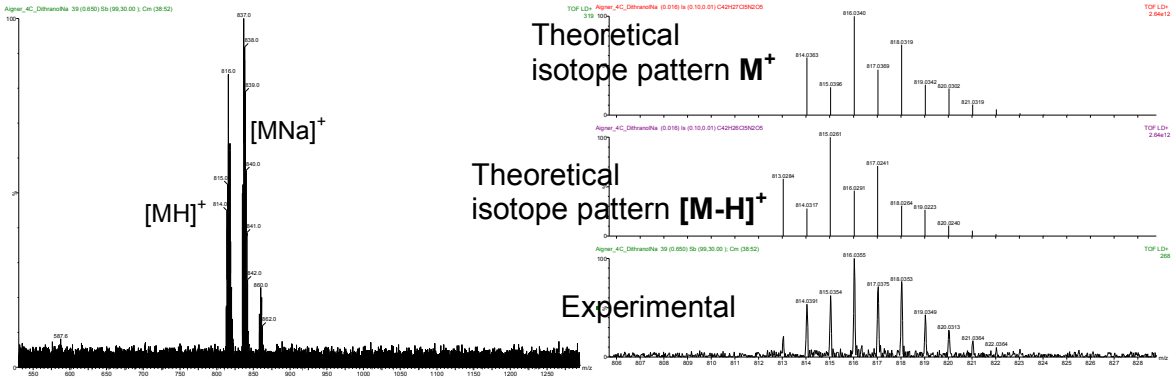


MALDI-TOF spectrum of **4A**

*N-(3-Chloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tertracarboxylic bisimide (**4B**)*

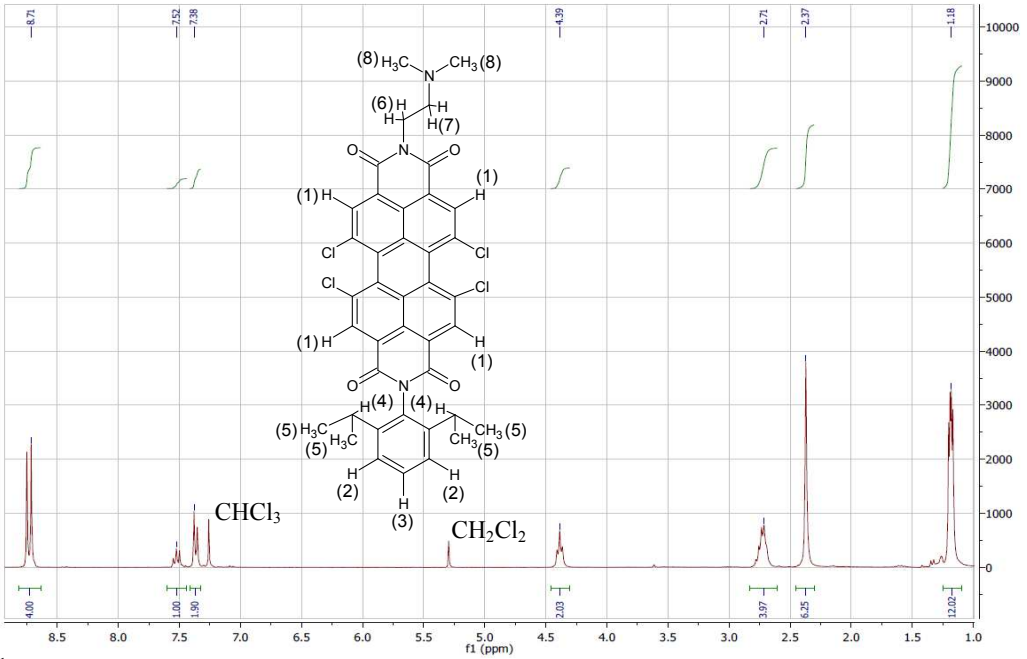


^{1}H NMR of **4B** (300 MHz, $CDCl_3$, TMS): δ = 8.75 (4H, 2s, H(1)); 7.53 (1H, t, J = 7.8 Hz, H(3)); 7.39 (2H, d, J = 7.8 Hz, H(2)); 7.33 (1H, d, J = 2.3 Hz, H(6)); 7.22 (1H, d, J = n.m. due to $CHCl_3$, H(8)); 7.17 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.3 Hz, H(7)); 5.77 (1H, s, H(9)); 2.74 (2H, quint, J = 6.8 Hz, H(4)); 1.19 (12H, dd, J_1 = 6.6 Hz, J_2 = 3.6 Hz, H(5)).

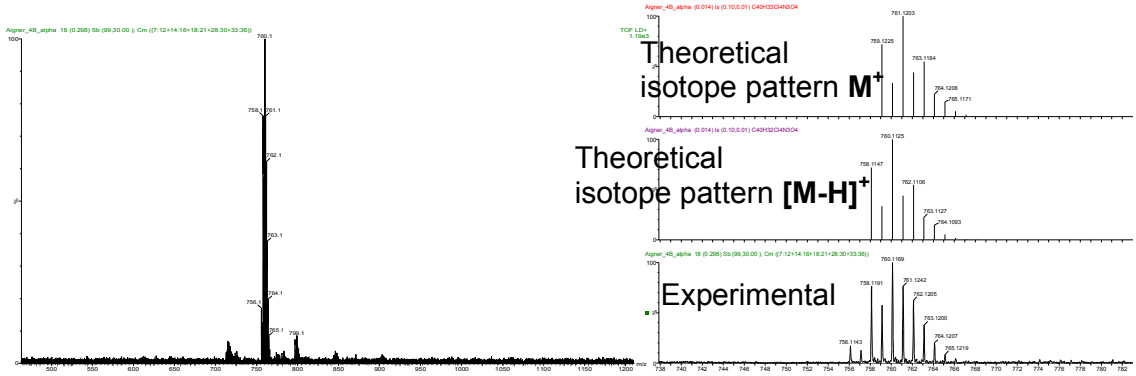


MALDI-TOF spectrum of **4B**

*N-(2,6-Diisopropylphenyl)-N'-(2-(dimethylamino)ethyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tertracarboxylic bisimide (**4D**)*

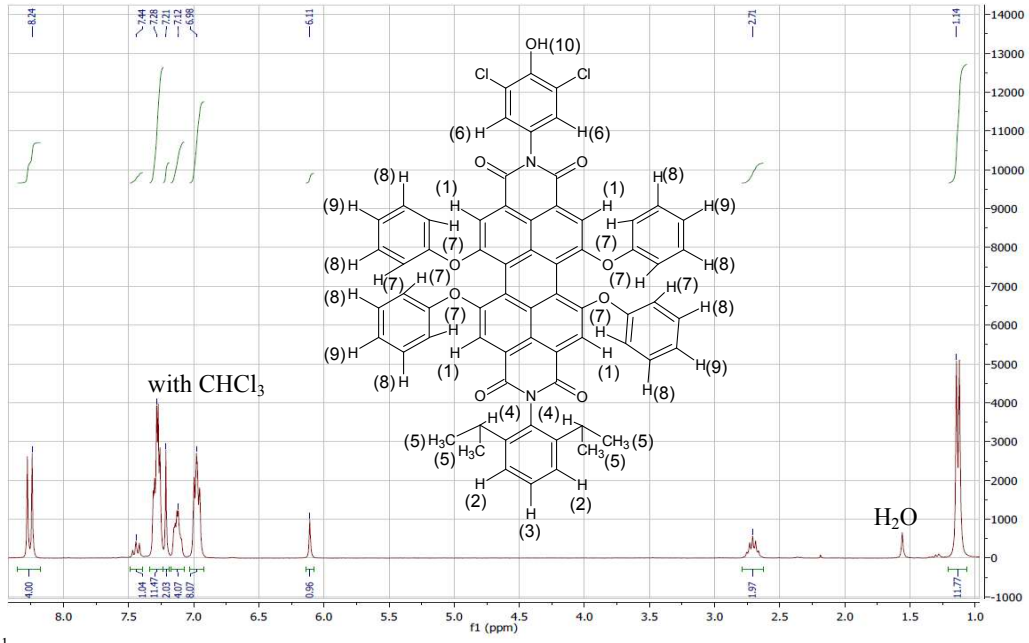


^{1}H NMR of **4D** (300 MHz, $CDCl_3$, TMS): δ = 8.71 (4H, 2s, H(1)); 7.52 (1H, t, J = 7.6 Hz, H(3)); 7.38 (2H, d, J = 7.7 Hz, H(2)); 4.41 (2H, t, J = 5.7 Hz, H(6)); 2.76 (4H, m, H(4,7)); 2.42 (6H, s, H(8)); 1.18 (12H, dd, J_1 = 3.7 Hz, J_2 = 3.2 Hz, H(5)).

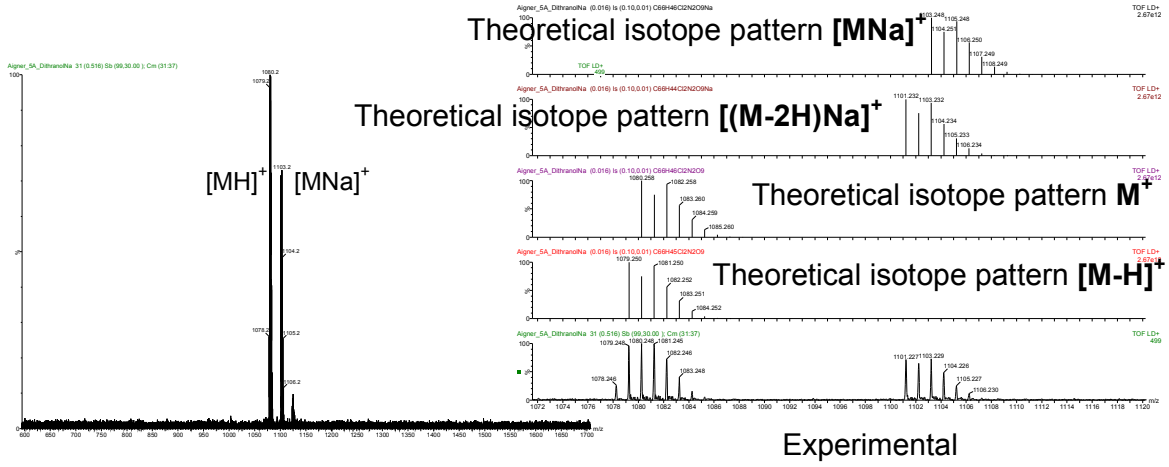


MALDI-TOF spectrum of **4D**

*N-(3,5-Dichloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tertracarboxylic bisimide (**5A**)*

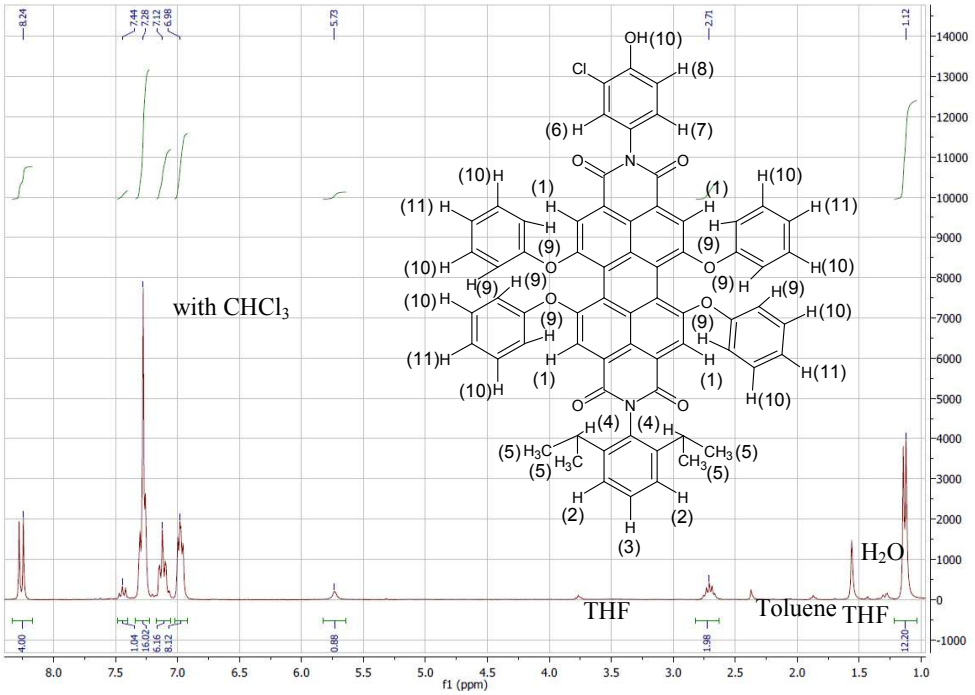


^{1}H NMR of **5A** (300 MHz, $CDCl_3$, TMS): δ = 8.24 (4H, 2s, H(1)); 7.44 (1H, t, J = 8.4 Hz, H(3)); 7.23 – 7.34 (10H, m, H(2,8)); 7.21 (2H, s, H(6)); 7.12 (4H, m, H(9)); 6.98 (8H, t, J = 6.5 Hz, H(7)); 6.11 (1H, s, H(10)); 2.71 (2H, quint, J = 6.4 Hz , H(4)); 1.14 (12H, d, J = 6.6 Hz, H(5)).



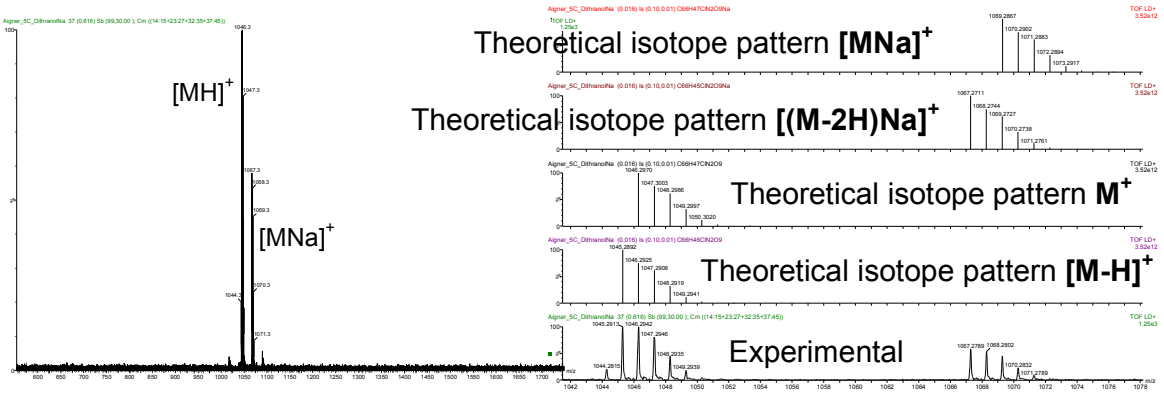
MALDI-TOF spectrum of **5A**

*N-(3-Chloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tertracarboxylic bisimide (**5B**)*



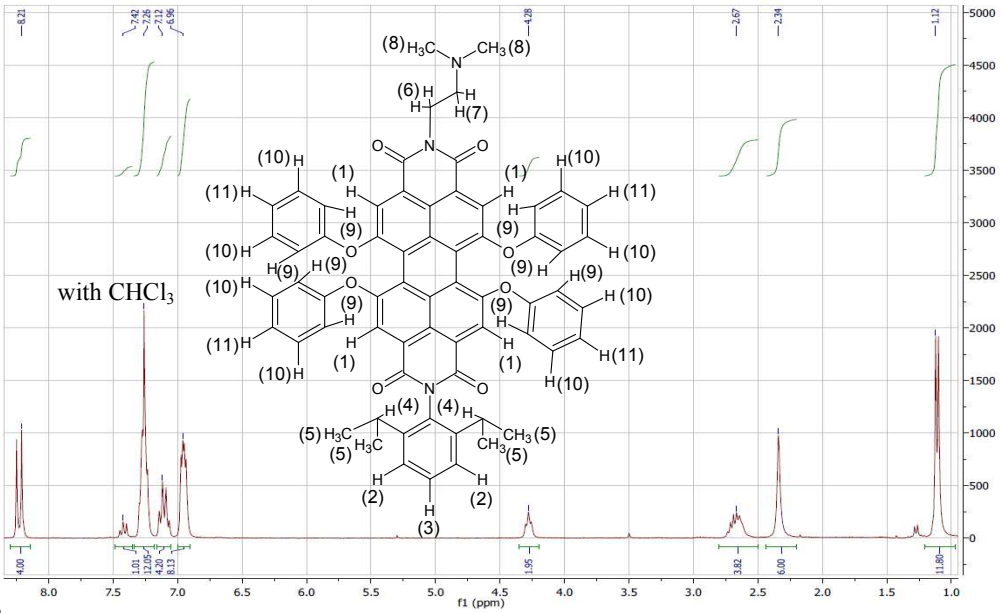
^{1}H NMR of **5B** (300 MHz, $CDCl_3$, TMS): δ = 8.24 (4H, 2s, H(1)); 7.44 (1H, t, J = 8.2 Hz, H(3)); 7.23 – 7.33 (11H, m, H(2,6,10)); 7.06 – 7.16 (6H, m, H(7,8,11)); 6.98 (4H, dd, J_1 = 5.1 Hz, J_2 = 7.5 Hz, H(9)); 5.73 (1H, s, H(12)); 2.71 (2H, quint, J = 6.3 Hz , H(4)); 1.12 (12H, d, J = 6.8 Hz, H(5)).

Sample **5B**



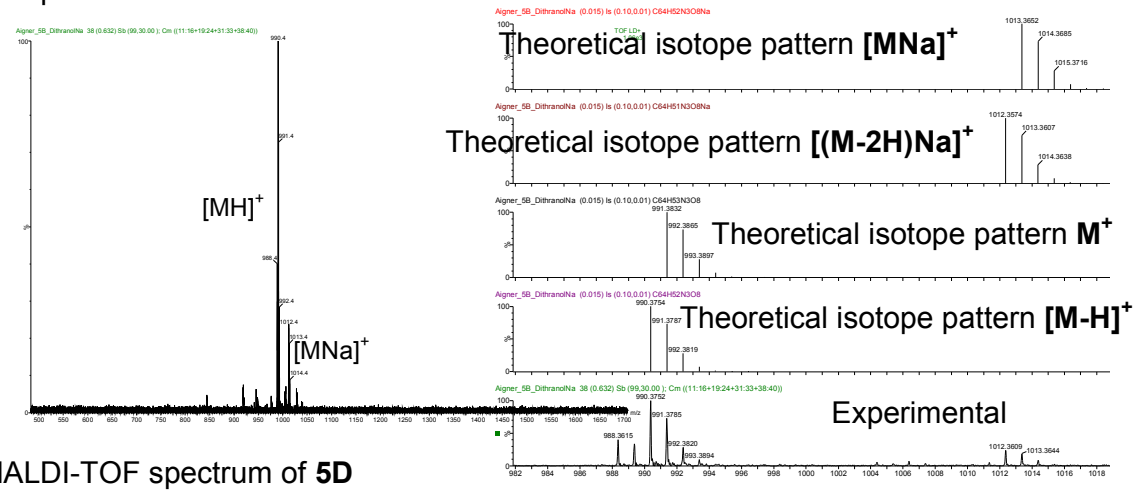
MALDI-TOF spectrum of **5B**

*N-(2,6-Diisopropylphenyl)-N'-(2-(dimethylamino)ethyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tertracarboxylic bisimide (**5D**)*



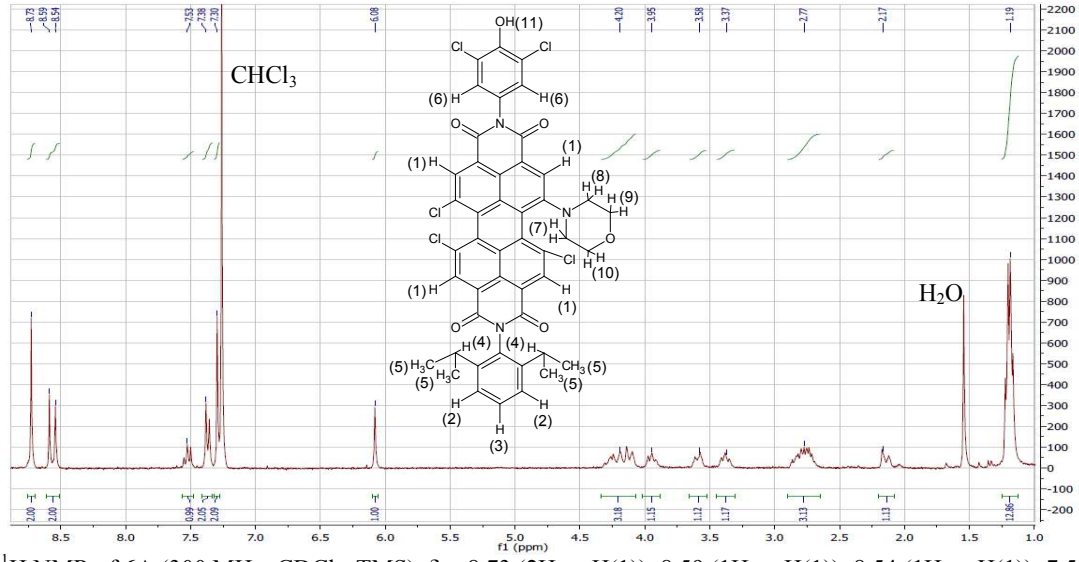
^{1}H NMR of **5D** (300 MHz, $CDCl_3$, TMS): δ = 8.21 (4H, 2s, H(1)); 7.42 (1H, t, J = 7.8 Hz, H(3)); 7.20 – 7.33 (10H, m, H(2,10)); 7.12 (4H, q, J = 7.8 Hz, H(11)); 6.96 (8H, q, J = 3.9 Hz, H(9)); 4.28 (2H, t, J = 6.8 Hz, H(6)); 2.58 – 2.75 (4H, m, (4,7)); 2.34 (6H, s, H(8)); 1.12 (12H, d, J = 6.8 Hz, H(5)).

Sample **5D**

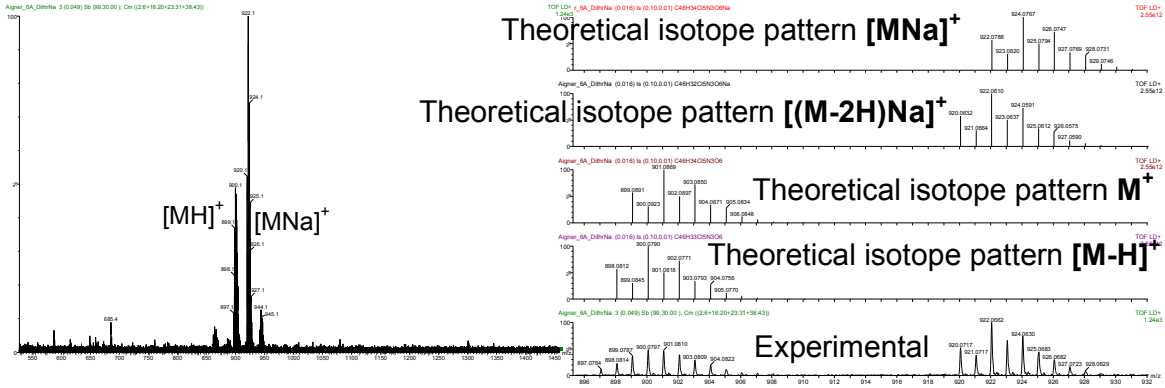


MALDI-TOF spectrum of **5D**

*N-(3,5-Dichloro-4-hydroxyphenyl)-N'-(2,6-diisopropylphenyl)-1-(1-morpholinyl)-6,7,12-trichloroperylene-3,4:9,10-tertracarboxylic bisimide (**6A**)*

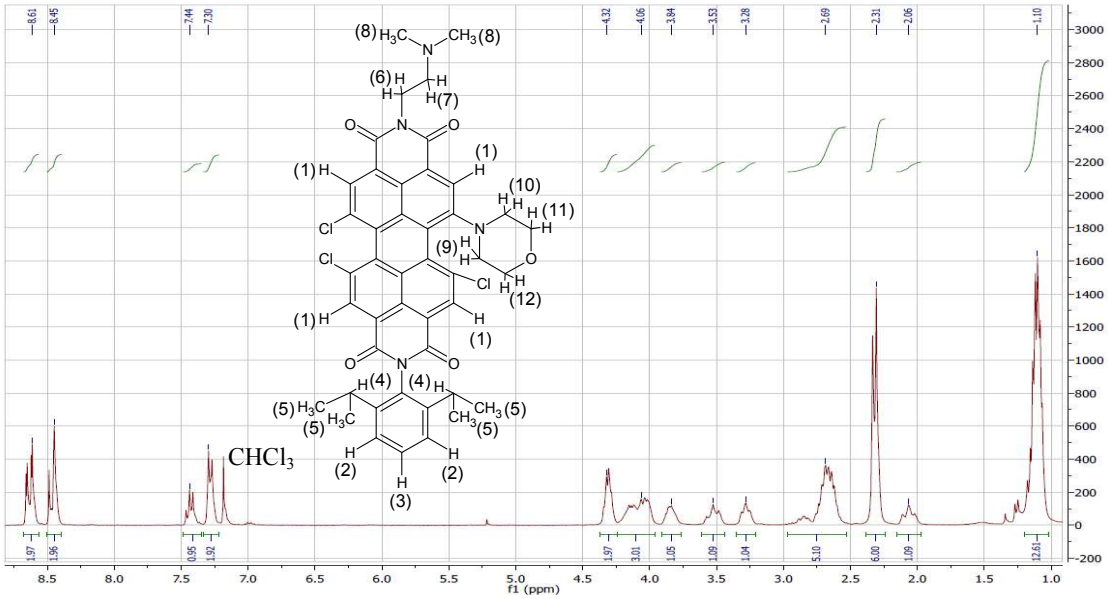


^{1}H NMR of **6A** (300 MHz, $CDCl_3$, TMS): δ = 8.73 (2H, s, H(1)); 8.59 (1H, s, H(1)); 8.54 (1H, s, H(1)); 7.53 (1H, t, J = 7.8 Hz, H(3)); 7.38 (2H, d, J = 7.7 Hz, H(2)); 7.30 (2H, s, H(6)); 6.08 (1H, s, H(11)); 4.07 – 4.32 (3H, m, H(7,10)); 3.95 (1H, t, J = 8.9 Hz, H(10)); 3.58 (1H, d, J = 11.4 Hz, H(9)); 3.37 (1H, t, J = 8.8 Hz, H(9)); 2.65 – 2.90 (3H, m, H(4,8)); 2.17 (1H, d, J = 13.7 Hz, H(8)); 1.19 (12H, dd, J_1 = 6.5 Hz, J_2 = 11.8 Hz, H(5)).

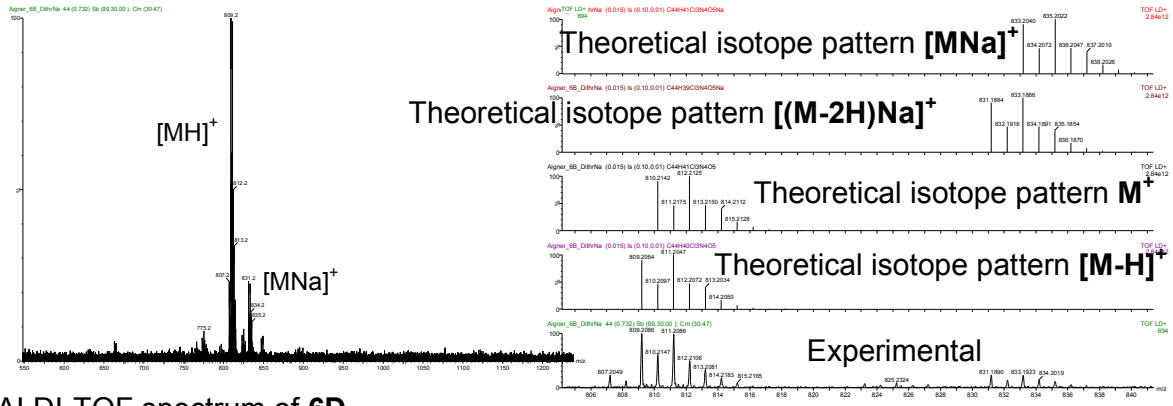


MALDI-TOF spectrum of **6A**

*N-(2,6-Diisopropylphenyl)-N'-(2-(dimethylamino)ethyl)-1-(1-morpholinyl)-6,7,12-trichloroperylene-3,4:9,10-tertracarboxylic bisimide (**6D**)*



^{1}H NMR of **6D** (300 MHz, $CDCl_3$, TMS): δ = 8.61 (2H, m, H(1)); 8.45 (2H, m, H(1)); 7.44 (1H, t, J = 7.8 Hz, H(3)); 7.30 (2H, d, J = 7.6 Hz, H(2)); 7.30 (2H, d, J = 7.6 Hz, H(2)); 4.32 (2H, m, H(6)); 3.95 – 4.25 (3H, m, H(9,12)); 3.84 (1H, m, H(12)); 3.53 (1H, t, J = 12.3 Hz, H(11)); 3.28 (1H, t, J = 8.4 Hz, H(11)); 2.55 – 2.95 (5H, m, H(4,7,10)); 2.31 (6H, 2d, H(8)); 2.06 (1H, t, J = 13.5 Hz, H(10)); 1.10 (12H, m, H(5)).



MALDI-TOF spectrum of **6D**

References

(1) Aigner, D.; Ungerböck, B.; Mayr, T.; Saf, R.; Klimant, I.; Borisov, S. M. *J. Mater. Chem. C* **2013**, *1*, 5685.