

Fluorescent liquid pyrene derivative-in-water microemulsions

Supporting Information

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Experimental

Chemicals

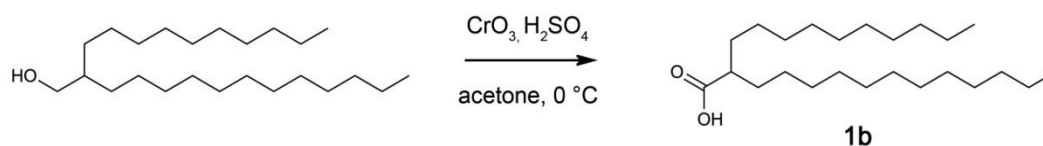
2-Decyl-1-tetradecanol, Zn powder, HgCl₂, CrO₃, pyrene, hexaethylene glycol mono dodecyl ether (C₁₂E₆) and D₂O (99.5% D) were purchased from Sigma-Aldrich. Oxalyl chloride and anhydrous AlCl₃ was purchased from Acros Organics, while CDCl₃ and CD₂Cl₂ were purchased from Goss Scientific. Organic solvents and reagents CH₂Cl₂, CHCl₃, n-hexane, petroleum ether 40-60, diethyl ether, H₂SO₄, HCl and anhydrous MgSO₄ were all sourced from Fisher Scientific. All chemicals were used without further purification.

Techniques

NMR measurements were carried out using a Bruker Avance 300 spectrometer. All UV-visible absorption spectroscopy measurements were carried out on a Jasco V660 spectrophotometer. Photoluminescence spectroscopy measurements of the solutions of pyrene and 1, and of the film state of 1 were carried out on a JASCO FP-8300 Spectrofluorometer, while those on the microemulsion droplets were carried out on a Varian Cary Eclipse Fluorescence Spectrophotometer. The photoluminescence quantum yields were measured using a Hamamatsu C9920-02 instrument. MALDI-TOF-MS was performed using a 4800 Tof/Tof instrument (ABSciex, Framingham, MA). Samples were prepared using 2-(4-Hydroxyphenylazo)benzoic acid matrix solution (mass spectrometry grade, Sigma Aldrich) prepared at 10 mg ml⁻¹ in CHCl₃, spotting at sample:matrix 1:1 (v/v) using a dried-droplet method.¹ The following parameters were used: acquisition in positive ion reflectron mode, 500-1500 m/z, automatic control with fixed laser power, 50 shots per sub-spectrum. 150-200 sub-spectra were summed to create a final summed spectrum. The laser power was optimised for each sample, with a laser fluence being selected above threshold irradiance without detector saturation. Close external calibration was performed using C₆₀ molecular ion. Data processing (peak labelling) was performed using Data Explorer.

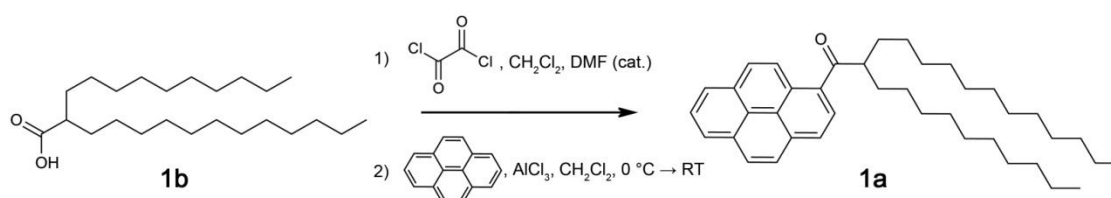
Synthesis

Step 1: Jones oxidation of 2-decyl-1-tetradecanol to form **1b**



To prepare the Jones reagent, CrO_3 (70 g, 0.7 mol) was dissolved in 100 mL water and cooled to $0\text{ }^\circ\text{C}$. 18 M H_2SO_4 (61 mL, 1.1 mol) was then added cautiously, alongside 200 mL water. Then, 2-decyl-1-tetradecanol (10 g, 0.0282 mol) was dissolved in acetone (280 mL) and the Jones reagent slowly added, until the reaction mixture changed colour from green to orange/brown. Water (400 mL) was then added and the product was extracted with *n*-hexane. The organic layer was washed with brine, dried over anhydrous MgSO_4 and the solvent was removed via evaporation. The crude product was purified by silica column chromatography (10 vol% acetone in petroleum ether 40-60) to yield **1b** as a white solid (9.60 g, 92.3%). ^1H NMR (300 MHz, CDCl_3) δ_{H} / ppm: 11.3 (1H, broad, COOH), 2.35 (1H, m, $-\text{CH}-$), 1.63 - 1.27 (40H, m, $-\text{CH}_2-$), 0.90 (6H, m, $-\text{CH}_3$).

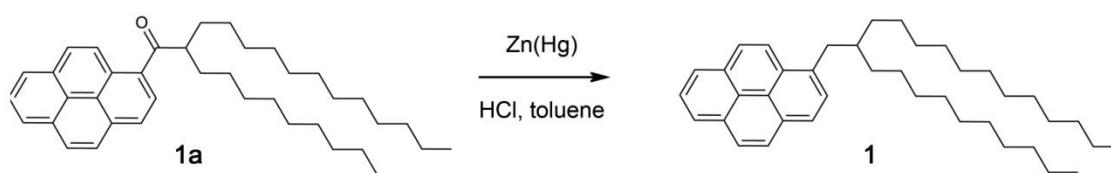
Step 2: Friedel-Crafts acylation to form **1a** from **1b** and pyrene



1b (5 g, 0.0136 mol) was dissolved in CH_2Cl_2 (20 mL). Oxalyl chloride (2.4 mL, 0.028 mol) was added, followed by a drop of dimethylformamide to initiate the reaction. After 1 hr, the intermediate acyl chloride was recovered by evaporation, and immediately re-dissolved in CH_2Cl_2 (20 mL). In a separate flask, pyrene (2.635 g, 0.0130 mol) and anhydrous AlCl_3 (2.855 g, 0.0214 mol) were suspended in CH_2Cl_2 (20 mL). The intermediate acyl chloride solution was added drop-wise to the suspension, and the reaction was left to stir overnight. After completion, the vessel contents were poured over a mixture of ice (50 g) and conc. HCl (25 mL) and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over anhydrous MgSO_4 and the solvent was removed via evaporation. The crude product was

purified by silica column chromatography (25 vol% CHCl₃ in *n*-hexane) to yield **1a** as a yellow solid (4.58 g, 61.0%). ¹H NMR (300 MHz, CDCl₃) δ_H / ppm: 8.74 (1H, d, *J* = 9.2 Hz, pyr-H [2-position]) 8.29–8.04 (7H, m, pyr-H), 3.57 (1H, m, -CH-), 1.91 (2H, m, CH-CH₂-CH₂), 1.61 (2H, m, CH-C₂H₄-CH₂) 1.45–1.19 (36H, m, -CH₂-), 0.88 (6H, m, -CH₃).

Step 3: Clemmensen reduction to form 1 from 1a



Zn powder (33 g) was activated by vigorous stirring in 5% HCl (50 mL × 3). The activated powder was then washed sequentially in H₂O, acetone and diethyl ether and any remaining solvent was removed under reduced pressure. Activated Zn powder (2 g) was mixed with an aqueous 5% HgCl₂ solution (4.2 mL) and left for 1 hr. The solution was decanted and the Zn(Hg) was covered with conc. HCl (10 mL) and water (7 mL). To this, ketone **1a** (0.4 g, 0.725 mmol) dissolved in toluene (2.5 mL) was added. The mixture was then heated under reflux for 1.5 hr, then allowed to cool. The mixture was extracted with diethyl ether, washed with water then brine, dried over anhydrous MgSO₄ and the solvent was removed via evaporation. The crude product was purified by silica column chromatography (5 vol% toluene in *n*-hexane) to yield **1** as a light yellow oil (0.106 g, 27.1%). MALDI-TOF-MS [M⁺] calc.: 538.45, found: 538.46. ¹H NMR (300 MHz, CD₂Cl₂) δ_H / ppm: 8.32–7.84 (9H, m, pyr-H), 3.26 (2H, d, *J* = 7.2 Hz, pyr-CH₂-CH), 1.93 (1H, m, CH), 1.45–1.23 (40H, m, -CH₂-), 0.96–0.86 (6H, m, -CH₃). ¹³C NMR (75 MHz, CDCl₃) δ_C / ppm: 136.48, 131.47, 130.95, 129.67, 129.06, 128.39, 127.55, 126.91, 126.44, 125.70, 125.14, 125.09, 124.72, 124.56, 124.46, 123.81, 40.10, 38.51, 33.61, 31.94, 31.92, 30.92, 29.68, 29.65, 29.64, 29.62, 29.36, 29.33, 26.61, 22.70, 22.68, 14.11. MALDI-TOF-MS, plus ¹H and ¹³C NMR spectra are provided for reference.

Microemulsion preparation

Microemulsions were prepared by mixing **1** with C₁₂E₆ and water, and gently agitating. The C₁₂E₆ concentrations 25 – 100 mM were chosen as they span a reasonable range and are high enough to obtain a good SANS signal in reasonable measurement times (< 1 hr), without being so high as to risk multiple scattering and/or large structure factors.

Small-angle neutron scattering, SANS

SANS measurements were carried out on the LOQ beamline at the ISIS Neutron and Muon source, Rutherford Appleton Laboratory, UK. The samples were contained in 2 mm path-length Hellma cells. A thermostated sample changer provided temperature control. A beam width of 8 mm was used, providing a detectable Q range of order 0.008 – 0.3 Å⁻¹. Absolute intensities for $I(Q)$ (in cm⁻¹) were determined by calibrating the received signal for a polymer standard and correcting for sample transmission and solvent background.

SANS Model fitting

The scattering from microemulsion droplets was modelled as originating from disperse interacting cylinders using the SASfit fitting software,² and the following equations have been taken from the SASfit documentation. The $P(Q)$ for a monodisperse cylinder can be expressed as follows:

$$I_{cyl} = 16(\pi R^2 L)^2 \Delta\rho^2 \int_0^1 \left(\frac{J_1(QR\sqrt{1-x^2}) \sin(QLx/2)}{Q^2 RLx\sqrt{1-x^2}} \right)^2 dx \quad (1)$$

Here, $J_1(x)$ is a first order Bessel function of the first kind, while R is the radius of the cylinder and L is the length. $\Delta\rho$ is the difference between the scattering length density of the cylinder (**1** + C₁₂E₆) and the solvent (D₂O), which was calculated for each value of X based on the densities of C₁₂E₆ and **1** being 0.99 and 0.97 g cm⁻³ respectively.

A Schultz-Zimm^{3,4} distribution of cylinder radii, R was assumed, which is described as:

$$SZ(R, R_a, k, N) = \frac{N_{SZ}}{R_a} \left(\frac{R}{R_a} \right)^{k-1} \frac{k^k \exp(-kR/R_a)}{g(k)} \quad (2)$$

Where $g(k)$ is the gamma function. The parameter k is related to the variance σ by $k = 1 / \sigma^2$. In this case, R is the distributed cylinder radius, while R_a is a scaling parameter that defines the maximum of the size distribution for large values of k .

As explained in the main text, one of two different $S(Q)$ functions were used to explain the SANS, depending on $X = [\mathbf{1}]/[C_{12}E_6]$. The first of these is a hard sphere $S(Q)$ of the type previously used by Vrij⁵ and Kotlarchyk et al.⁶ In that case, fitted parameters are effective hard sphere radius R_{HS} and volume fraction ϕ_{HS} . The other is an attractive Ornstein-Zernike $S(Q)$, given as follows:

$$S(Q) = 1 + \left[\frac{\kappa}{1+(Q\zeta)^2} \right] \quad (3)$$

This describes a decaying distribution, where ζ is a correlation length, and κ is related to the strength of interactions via the isothermal compressibility.⁶

Using the above equations, the overall scattering is then calculated by SASfit using the monodisperse approach as follows:

$$I(Q) = \left[\int_0^\infty SZ(R, R_a, Z, N) I_{cyl} \right] S(Q) \quad (4)$$

Supporting Figures and Tables

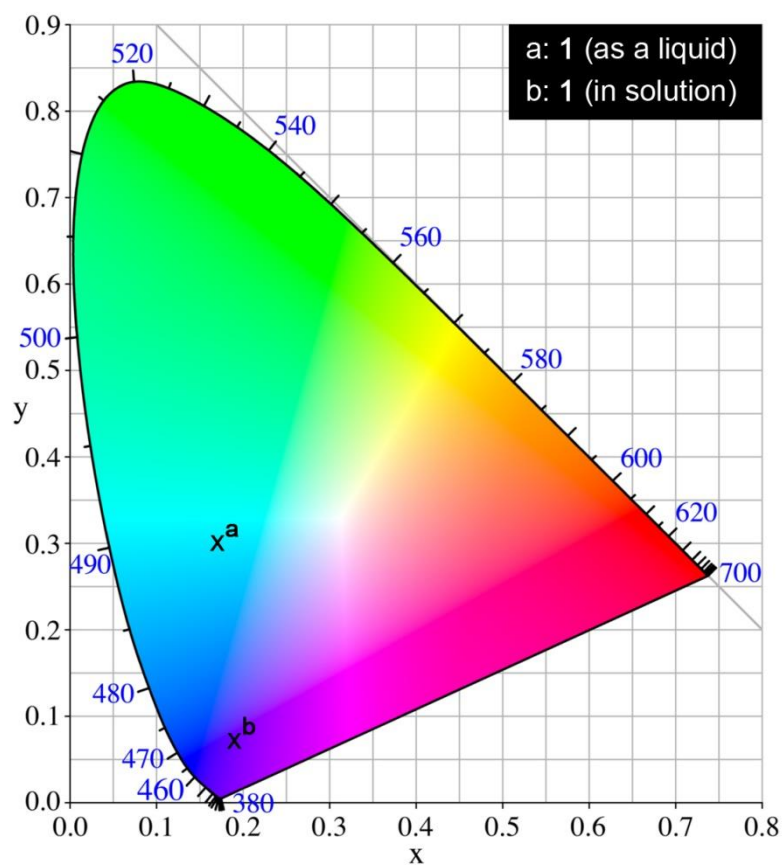


Figure S1. CIE xy chromaticity diagram showing the emission colour of **1** as a liquid film, marked by point x^a , and in solution ($[1] = 10^{-5}$ M in CH_2Cl_2), marked by point x^b .

Table S1. Parameters arising from SANS data analysis, using a cylindrical form factor and structure factors $S(Q)_{OZ}$ or $S(Q)_{HS}$ as described in the text, for 1/C₁₂E₆/water microemulsions at 25 °C (unless otherwise specified).

X	[C ₁₂ E ₆] / M	$R / \text{Å}$	σ	$L / \text{Å}$	L:2R	$S(Q)_{OZ}$		$S(Q)_{HS}$		χ^2
						κ	$\zeta / \text{Å}$	$R_{HS} / \text{Å}$	ϕ_{HS}	
0.02	25	22	0.24	54	1.2	0.2	54	-	-	0.9
0.035	25	25	0.11	62	1.3	-	-	48	0.010	1.1
0.05	25	26	0.08	63	1.2	-	-	48	0.012	0.9
0.1	25	28	0.09	69	1.2	-	-	48	0.016	1.0
0	50	21	0.11	64	1.5	1.6	52	-	-	1.5
0.02	50	23	0.14	61	1.3	0.5	54	-	-	1.0
0.035	50	25	0.11	66	1.3	-	-	31	0.023	0.8
0.05	50	25	0.11	64	1.3	-	-	41	0.026	1.1
0.1	50	28	0.08	70	1.3	-	-	44	0.035	1.3
0.2 ¹	50	33	0.16	86	1.3	0.9	86	-	-	2.1
0	100	22	0.11	65	1.5	1.0	63	-	-	1.5
0.02	100	23	0.14	60	1.3	1.0	150	-	-	3.1
0.035	100	24	0.13	67	1.4	-	-	33	0.049	3.0
0.05	100	25	0.10	65	1.3	-	-	40	0.057	1.3
0.1	100	27	0.11	69	1.3	-	-	43	0.069	1.5
0.2 ¹	100	32	0.17	84	1.3	1.7	210	-	-	7.9

¹These samples were measured at 45 °C

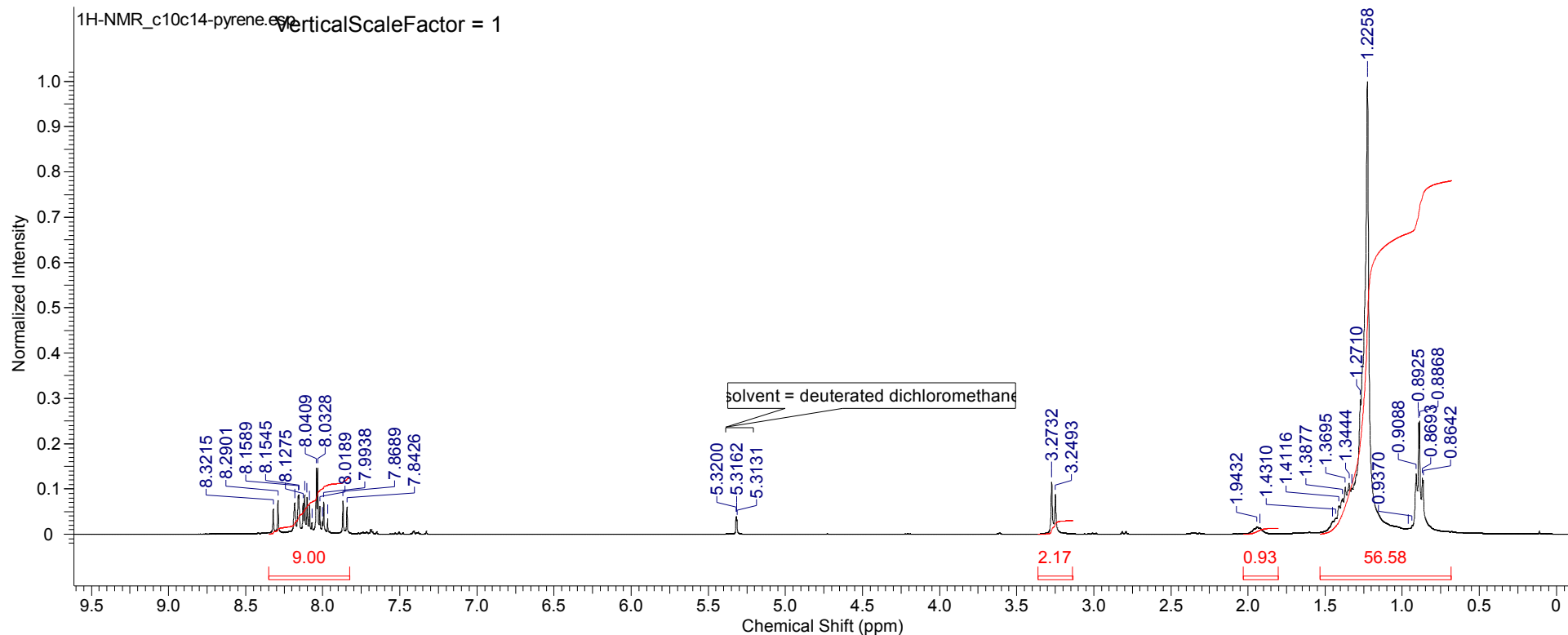
Table S2. Summary of values calculated from the fitted parameters using a cylindrical form factor (Table S4) : (i) The number of C₁₂E₆ (N_{surf}) and n -decane (N_1) molecules per micelle; (ii) the approximate area occupied by a C₁₂E₆ molecule at the interface (a_h); (iii) the difference between the number density of C₁₂E₆ + n -decane molecules found by SANS analysis and known to be in solution ($n_{\text{exp}}/n_{\text{calc}}$).

X	[C ₁₂ E ₆] / M	N_{surf}	N_1	$a_h / \text{\AA}^2$	$a_{h,\text{IF}} / \text{\AA}^2$	$n_{\text{fit}}/n_{\text{calc}}$
0.02	25	110	2	95	76	1.0
0.035	25	160	6	86	70	1.1
0.05	25	170	9	85	70	1.0
0.1	25	200	22	84	70	1.0
0	50	120	0	92	73	0.94
0.02	50	130	3	90	73	1.0
0.035	50	170	6	85	70	1.1
0.05	50	160	9	86	71	1.1
0.1	50	200	22	84	70	1.0
0.2	50	300	75	81	70	0.85
0	100	130	0	91	72	0.99
0.02	100	130	3	91	73	1.0
0.035	100	160	6	86	70	1.1
0.05	100	170	9	86	71	1.0
0.1	100	190	21	85	71	1.1
0.2	100	280	71	83	71	0.96

Supporting references

- 1 U. Bahr, M. Karas and F. Hillenkamp, *Z. Anal. Chem.*, 1994, **348**, 783–791.
- 2 I. Breßler, J. Kohlbrecher and A. F. Thünemann, *J. Appl. Cryst.*, 2015, **48**, 1587–1598.
- 3 G. V. Z. Schulz, *Phys. Chem.*, 1939, **B43**, 25.
- 4 B. H. Zimm, *J. Chem. Phys.*, 1948, **16**, 1099.
- 5 A. Vrij, *J. Chem. Phys.*, 1979, **71**, 3267–3270.
- 6 M. Kotlarchyk, S.-H. Chen, J. S. Huang and M. W. Kim, *Phys. Rev. A*, 1984, **29**, 2054–2069.

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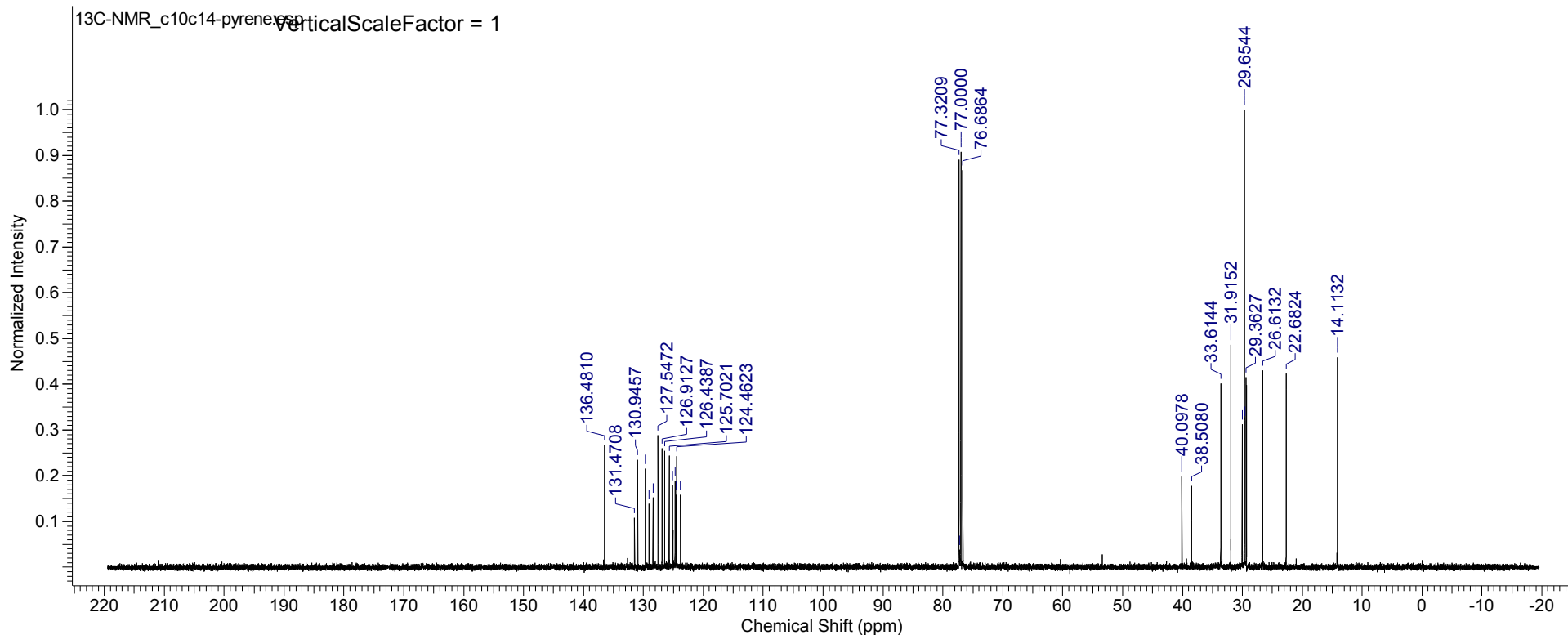
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3	1373 .. 3.362.17322803		8.93534320e+7	2.17322803
4	3243 .. 8.349.00000000		3.70039808e+8	9.00000000

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

No.	(ppm)	(Hz)	Height
1	0.86	259.4	0.1196
2	0.87	260.9	0.1249
3	0.89	266.2	0.2496
4	0.89	267.9	0.2472
5	0.91	272.8	0.1336
6	0.94	281.2	0.0191
7	0.96	288.8	0.0132
8	1.23	367.9	1.0000
9	1.27	381.5	0.2971
10	1.33	398.6	0.1011
11	1.34	403.5	0.1124
12	1.37	411.0	0.1038
13	1.39	416.5	0.0783
14	1.41	423.6	0.0623
15	1.43	429.5	0.0351
16	1.45	435.7	0.0284
17	1.92	577.6	0.0135
18	1.94	583.2	0.0168
19	3.25	975.2	0.0880
20	3.27	982.4	0.1150
21	5.31	1594.6	0.0323
22	5.32	1595.6	0.0395
23	5.32	1596.7	0.0387
24	7.84	2353.8	0.0604
25	7.87	2361.7	0.0734
26	7.97	2391.5	0.0342
27	7.99	2399.2	0.0711
28	8.00	2401.8	0.0285
29	8.02	2406.7	0.0621
30	8.03	2410.9	0.1462
31	8.04	2413.3	0.1467
32	8.07	2422.4	0.0259
33	8.09	2426.9	0.0643
34	8.10	2431.6	0.0817
35	8.12	2436.1	0.0863
36	8.13	2439.3	0.0693
37	8.15	2447.4	0.0877
38	8.16	2448.7	0.0860
39	8.18	2455.9	0.0693
40	8.29	2488.1	0.0745
41	8.32	2497.5	0.0556

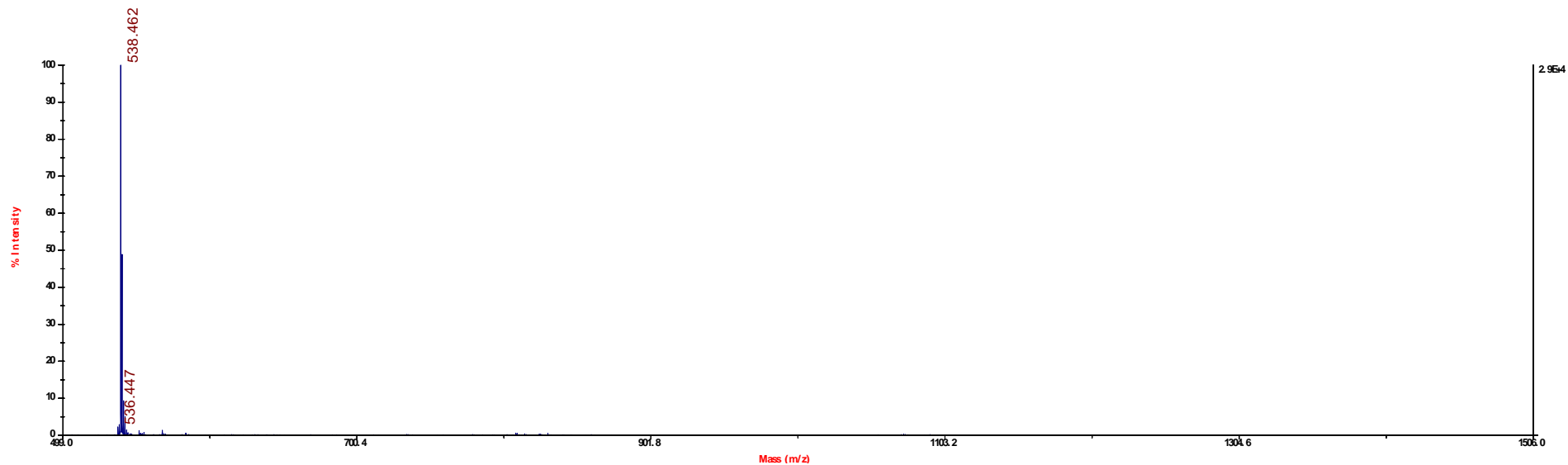
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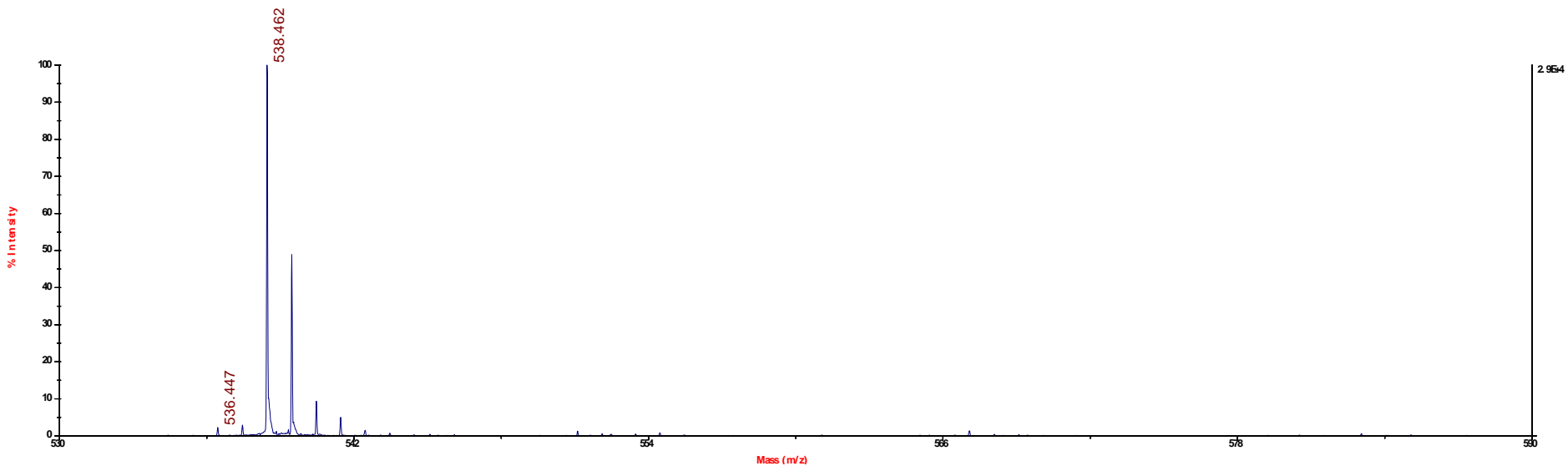
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2	22.68	2281.6	0.4234	11	30.04	3021.8	0.3128	20	77.32	7777.7	0.8908	29	126.91	12766.2	0.2601
3	22.70	2283.1	0.3887	12	31.92	3210.4	0.4865	21	123.81	12453.7	0.1577	30	127.55	12830.0	0.2890
4	26.61	2677.0	0.4296	13	31.94	3212.6	0.3655	22	124.46	12519.7	0.2425	31	128.39	12915.1	0.1524
5	29.33	2950.7	0.3979	14	33.61	3381.3	0.4013	23	124.56	12529.2	0.1582	32	129.06	12982.6	0.1388
6	29.36	2953.6	0.4158	15	38.51	3873.5	0.1771	24	124.72	12546.1	0.1892	33	129.68	13044.2	0.2153
7	29.62	2979.3	0.3205	16	40.10	4033.4	0.1982	25	125.09	12582.8	0.0806	34	130.95	13171.8	0.2352
8	29.64	2981.5	0.6557	17	76.69	7713.9	0.8679	26	125.14	12587.9	0.1796	35	131.47	13224.7	0.1080
9	29.65	2982.9	1.0000	18	77.00	7745.4	0.9075	27	125.70	12644.4	0.2433	36	136.48	13728.6	0.2670

4700 Reflector Spec #1 [BP = 538.5, 29310]



Laser power at 3720, c = 10 mg ml⁻¹, matrix = HABA 1:1 (v/v)

4700 Reflector Spec #1 [BP = 538.5, 29310]



Zoom of m/z 538 region