Electronic Supplementary Material (ESI) for RSC Applied Interfaces.

Enhancement of Replacement Lithography by Combination of Photocleavable Groups with Ultrashort Thiolates

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KEYWORDS ONB-group, UV-Irradiation, SAM Exchange, Infrared-Reflection Absorption Spectroscopy.

Supporting Information

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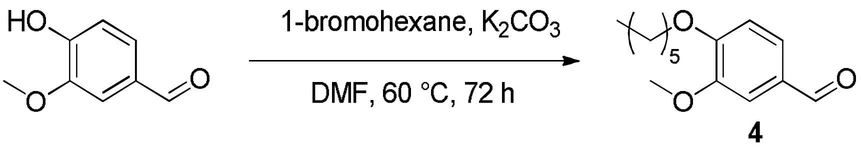
1. Experimental Procedures

1.1 Materials

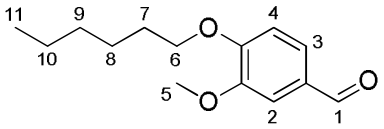
All solvents and chemicals were purchased from commercial suppliers and used as received unless otherwise state. Ethyl acetate (99.5%), DCM (99.9%), diethylether (99.8), acetic acid (99.8%), ethanol (p.a. 99.8%), $NaBH_4$ (99%) and vanillin (reagentplus grade) were purchased from Sigma-Aldrich, THF (ACS reagent grade), acetonitrile (HPLC grade) and $K_2S_2O_3$ (GPR reactapur grade) from VWR, $K_3Fe(CN)_6$ (99%), Na_2SO_4 (99%) and 3,4-dihydroxy-benzaldehyde (98%) from Roth, thioglycolic acid (96%) from TCI, KOH (99.5%) from Bernd Kraft, $K_4Fe(CN)_6$ (extra pure grade) from Merck, $NaHCO_3$ (extra pure grade) and K_2CO_3 (extra pure grade) from Grüssing, DMF (99.5%) and HNO_3 (70%, reagent grade) from Fisher Scientific, DIAD (98%) from Carbolution and 1-bromohexane (99+%) from Acros. Hexane was received in technical grade and distilled prior to use in chromatography. Absolute (abs.) THF was obtained by heating THF over sodium metal in a nitrogen atmosphere with benzophenone as indicator and freshly distilled before use and kept under nitrogen over 3A molar sieve.

1.2 Synthesis of *O*-hexylvanillin **4**[1]

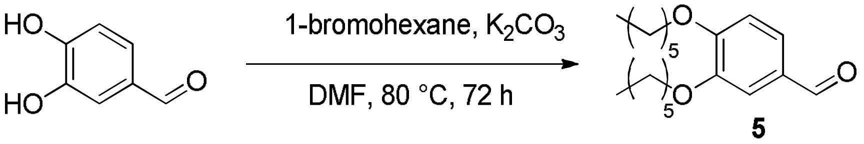


To solution of vanillin (10.00 g, 65.73 mmol) in DMF (50 mL) was added K_2CO_3 (14.53 g, 105.2 mmol) and 1-bromohexane (11.0 mL, 78.9 mmol) before heating at 60 °C for 72 h. The mixture was poured into ice water (100 mL), extracted with diethylether three times, before washing the combined organic layers with a saturated $NaHCO_3$ solution and brine. After drying over Na_2SO_4, the solvent was removed in vacuum and the obtained crystalline crude product washed with a small amount of *n*-hexane. The product was isolated as colorless crystals in 74% yield (11.74 g, 48.64 mmol).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 9.84 (s, 1H, H-1), 7.40 – 7.45 (m, 2H, H-2, H-3) 6.96 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H, H-4) 4.10 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, H-6), 3.93 (s, 3H, H-5), 1.88 (quin, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, H-7), 1.40 – 1.54 (m, 2H, H-8), 1.30 – 1.39 (m, 4H, H-9 and H-10), 0.85 – 0.95 (m, 3H, H-11).

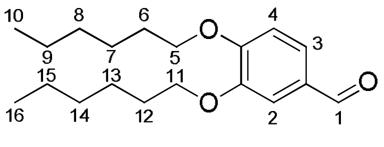


1.3 Synthesis of 3,4-Di(hexyloxy)benzaldehyde 5[2]

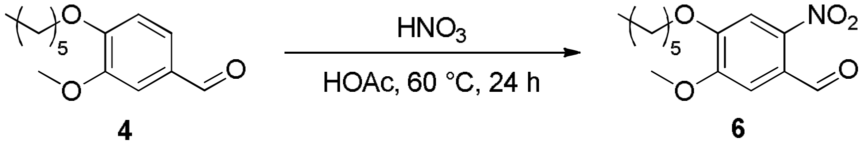


Compound **5** was synthesized as described in literature[2], using 3,4-dihydroxybenzaldehyde (5.00 g, 74.2 mmol), K_2CO_3 (15.01 g, 108.6 mmol) and 1-bromohexane (11.1 mL, 79.6 mmol) at slightly higher temperatures of 80 °C for 24 hours. The product was obtained after washing with *n*-hexane as an off-white solid in 97% yield (10.76 g, 7.020 mmol).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 9.83 (s, 1H, H-1), 7.41 (m, 2H, H-2 and H-4), 6.95 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H, H-3), 4.06 (q, $^3J_{H\text{-}H}$ = 7.5 Hz, 4H, H-5 and H-11), 1.76 – 1.92 (m, 4H, H-6 and H-12), 1.42 – 1.54 (m, 4H, H-7 und H-13), 1.28 – 1.40 (m, 8H, H-8, H-9, H-14 and H-15), 0.85 – 0.96 (m, 6H, H-10 and H-16).

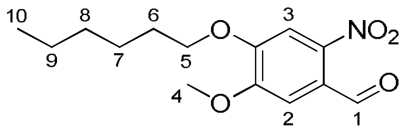


1.4 Synthesis of 4-Hexyloxy-5-methoxy-2-nitrobenzaldehyde **6**

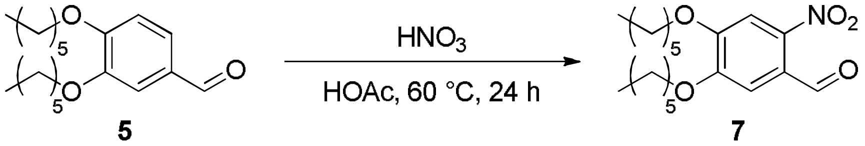


Compound **4** (11.47 g, 48.54 mmol) was dissolved in acetic acid (100 mL), 65% HNO_3 (17.0 mL, 244.0 mmol) was added, and the mixture heated for 24 h at 60 °C. After addition of water (50 mL) and extraction with DCM, the organic phase was washed with saturated $NaHCO_3$ solution and brine, before drying over Na_2SO_4. The solvent was removed in vacuum to yield a bright yellow solid (12.01 g, 75% purity, equivalent to 9.00 g of pure **6**, 32.0 mmol, 66%), which was used without further purification in the next reaction step. The impurity is the corresponding 4-hexyloxy-3-methoxybenzoic acid formed by oxidation under the reaction conditions.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 10.44 (s, 1H, H-1), 7.59 (s, 1H, H-3), 7.41 (s, 1H, H-2), 4.15 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, H-5), 4.01 (s, 3H, H-4), 1.81 – 1.97 (m, 2H, H-6), 1.41 – 1.59 (m, 2H, H-7), 1.26 – 1.41 (m, 4H, H-8 and H-9), 0.84 – 0.98 (m, 3H, H-10); (compare ref.[3]).

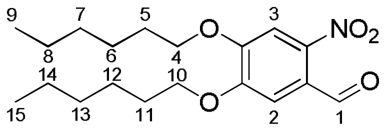


1.5 Synthesis of 4,5-Di(hexyloxy)-2-nitrobenzaldehyde **7**

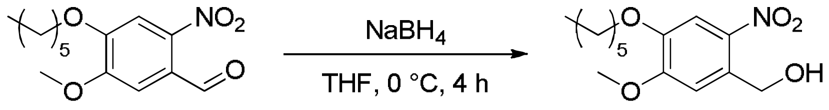


Compound **7** was prepared similar to compound **6** from **5** (12.85 g, 41.93 mmol) and 65% HNO_3 (14.6 mL, 210 mmol) in acetic acid (120 mL). The crude product was obtained as a yellow solid (12.51 g, 80% purity, equivalent to 10.00 g of pure **7**, 28.5 mmol, 68%) and used without further purification. Like in chapter 1.4 the impurity is the oxidized species 3,4-Dihexyloxybenzoic acid.

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 10.43 (s, 1H, H-1), 7.57 (s, 1H, H-3), 7.37 (s, 1H, H-2), 4.09 - 4.17 (m, 4H, H-4 and H-10), 1.79 – 1.94 (m, 4H, H-5 and H-11), 1.42 – 1.56 (m, 4H, H-6 and H-12), 1.27 – 1.42 (m, 8H, H-7, H-8, H-13 and H-14), 0.85 – 0.96 (m, 6H, H-9 and H-15).



1.6 Synthesis of 4-Hexyloxy-5-methoxy-2-nitrobenzylalcohol **8**[3]

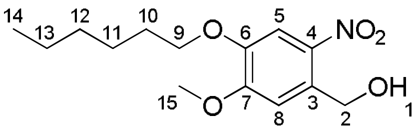


6 **8**

The crude compound **6** (8.00 g, equivalent to 6.00 g of pure **6**, 21.33 mmol) was dissolved in abs. THF (200 mL), cooled to 0 °C in an ice bath, and treated with NaBH$_4$ (2.15 g, 56.9 mmol). After four hours the suspension was poured into water (200 mL) and extracted three times with EE, before drying the combined organic phase over Na$_2$SO$_4$ and removing the solvent. The crude product was recrystallized from *n*-hexane to yield a yellow solid in 85% (5.13 g, 18.2 mmol, 56% over both steps).

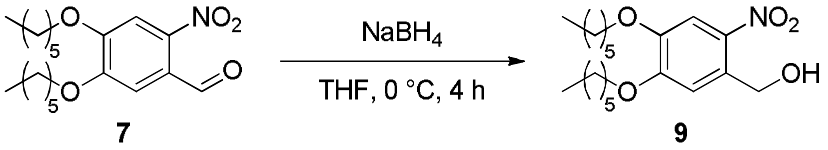
^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.70 (s, 1H, H-5), 7.14 (s, 1H, H-8), 4.96 (d, $^{3}J_{H\text{-}H}$ = 5.7 Hz, 2H, H-2), 4.07 (t, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 2H, H-9), 3.99 (s, 3H, H-15), 2.60 (t, $^{3}J_{H\text{-}H}$ = 6.5 Hz, 1H, H-1) 1.87 (quin, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 2H, H-10), 1.43 – 1.52 (m, 2H, H-11), 1.31 – 1.39 (m, 4H, H-12 und H-13), 0.88 – 0.95 (m, 3H, H-14); (compare ref.[3]).

^{13}C-NMR (126 MHz, CDCl$_3$): δ = 154.4 (C-7), 147.7 (C-6), 140.0 (C-4), 132.1 (C-3), 111.4 (C-8), 109.5 (C-5), 69.7 (C-9), 63.1 (C-2), 56.6 (C-15), 31.7 (C-12), 29.0 (C-10), 25.7 (C-11), 22.7 (C-13), 14.1 (C-14).



MS [m/z]: calc.: 306.13 [M + Na]$^+$, found: 306.00 [M + Na]$^+$.

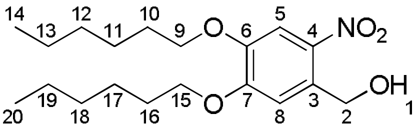
1.7 Synthesis of 4,5-Di(hexyloxy)-2-nitrobenzylalcohol **9**



Compound **9** was synthesized similarly to compound **8**, using **7** (8.00 g, equivalent to 6.40 g of pure **7**, 18.2 mmol) and $NaBH_4$ (1.75 g, 45.5 mmol) in abs. THF (180 mL), yielding an oily crude product, which was further purified by column chromatography (silica, *n*-hexane/EE gradient from 1:10 to 1:1). The resulting light-yellow solid was obtained in 82% yield (5.28 g, 15.0 mmol, mp. 62 °C, 56% over both steps).

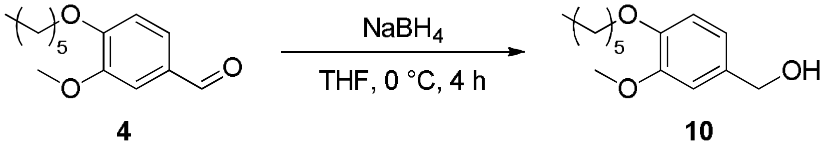
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.67 (s, 1H, H-5), 7.11 (s, 1H, H-8), 4.92 (s, 2H, H-2), 4.11 (t, $^3J_{H\text{-}H}$ = 6.3 Hz, 2H, H-15), 4.04 (t, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, H-9), 2.57 (s, 1H, OH), 1.84 (h, $^3J_{H\text{-}H}$ = 7.0 Hz, 4H, H-10, H-16), 1.53 – 1.43 (m, 4H, H-11, H-17), 1.39 – 1.29 (m, 8H, H-12, H-13, H-18, H-19), 0.90 (t, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, H-14, H-20).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 154.3 (C-7), 147.9 (C-6), 139.7 (C-4), 132.2 (C-3), 112.4 (C-8), 110.0 (C-5), 69.7 (C-9, C-15), 63.1 (C-2), 31.6 (C-12, C-18), 29.0 (C-10,C-16), 25.7 (C-11, C-17), 22.7 (C-13, C-19), 14.1 (C-14, C-20).



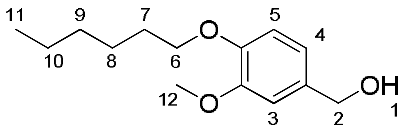
MS [m/z]: calc.: 376.20 [M + Na]$^+$, found: 376.08 [M + Na]$^+$.

1.8 Synthesis of 4-Hexyloxy-3-methoxy-benzylalcohol **10**

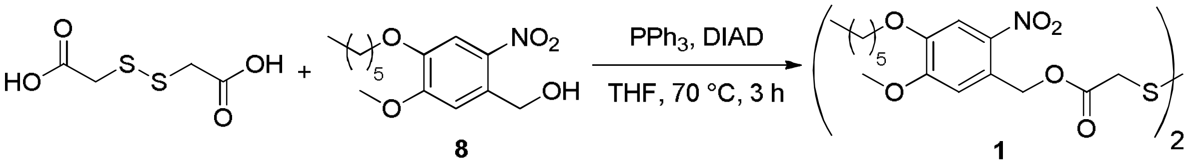


Compound 4 (3.00 g, 12.7 mmol) was reacted with $NaBH_4$ (0.96 g, 25.4 mmol) in abs. THF (100 mL). After work-up the crude product was further purified by column chromatography (silica, *n*-hexane/EE gradient from 1:10 to 3:2) to yield a colorless solid in 83% yield (2.50 g, 10.5 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.94 – 6.92 (m, 1H, H-3), 6.89 – 6.83 (m, 2H, H-5, H-4), 4.62 (s, 2H, H-2), 4.01 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H-6), 3.88 (s, 3H, H-12), 1.89 – 1.78 (m, 2H, H-7), 1.51 – 1.40 (m, 2H, H-8), 1.42 – 1.28 (m, 4H, H.9, H-10), 0.90 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, H-11).



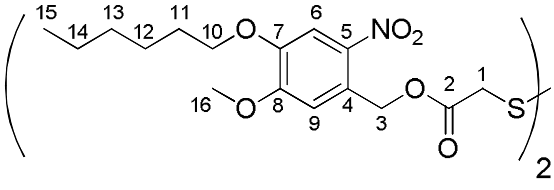
1.9 Synthesis of Bis-(4-hexyloxy-5-methoxy-2-nitrobenzyl)-dithioglycolate **1**



To PPh$_3$ (1.32 g, 5.01 mmol) dissolved in THF (12 mL) was slowly added DIAD (0.92 mL, 5.01 mmol) at 0 °C. After warming to room temperature, compound **8** (1.42 g, 5.01 mmol) and dithiodiglycolic acid (0.44 g, 2.39 mmol) were added, before heating to 70 °C for three hours. After addition of water, the mixture was extracted three times with EE (20 mL each), the combined organic phases dried over Na$_2$SO$_4$, and the solvent removed in vacuum. The crude product was purified by column chromatography (silica, DCM/EE gradient from 99:1 to 4:1) to yield a light yellow solid (0.95 g, 1.33 mmol, 56%, mp. 73 °C).

^{1}H-NMR (500 MHz, CDCl$_3$) δ = 7.69 (s, 2H, H-6), 7.05 (s, 2H, H-9), 5.55 (s, 4H, H-3), 4.06 (t, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 4H, H-10), 3.97 (s, 6H, H-16), 3.67 (s, 4H, H-1), 1.86 (p, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 4H, H-11), 1.51 – 1.42 (m, 4H, H-12), 1.40 – 1.29 (m, 8H, H-13 and H-14), 0.90 (t, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H, H-15).

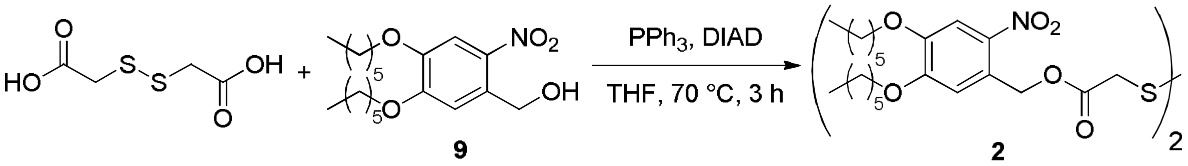
^{13}C-NMR (126 MHz, CDCl$_3$) δ = 168.6 (C-2), 154.0 (C-8), 148.0 (C-7), 139.8 (C-5), 126.0 (C-4), 110.6 (C-9), 109.3 (C-6), 69.6 (C-10), 64.3 (C-3), 56.6 (C-16), 41.2 (C-1), 31.5 (C-13), 28.8 (C-11), 25.6 (C-12), 22.6 (C-14), 14.0 (C-15).



MS [m/z]: calc.: 713.83 [M + H]$^{+}$, found: 714.48 [M + D]$^{+}$.

UV/Vis = 346 nm (6425 L/mol), 300 nm (4942 L/mol).

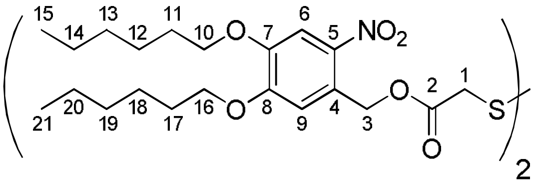
1.10 Synthesis of Bis-(4,5-di(hexyloxy)-2-nitrobenzyl)-dithioglycolate **2**



Compound **2** was obtained through the same protocol as compound **1**, by reacting dithiodiglycolic acid (0.25 g. 1.35 mmol) with PPh_3 (0.74 g, 2.83 mmol), DIAD (0.52 mL, 2.83 mmol) and compound **9** (1.00 g, 2.83 mmol) in THF (14 mL). The obtained crude product was further purified by column chromatography (silica, DCM/EE 99:1), to yield a light-yellow solid in 53% (0.61 g, 0.72 mmol, mp. 106 °C) as the final product.

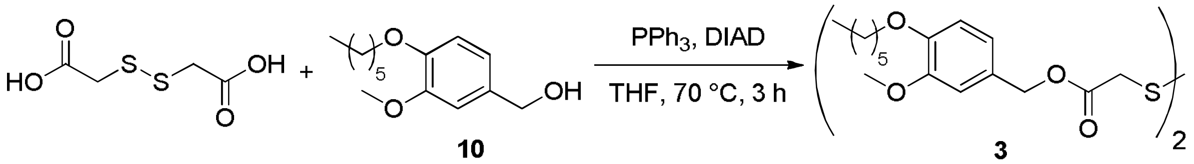
^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.69 (s, 2H, H-6), 7.02 (s, 2H, H-9), 5.55 (s, 4H, H-3), 4.10 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, H-16), 4.04 (t, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, H-10), 3.67 (s, 4H, H-1), 1.84 (p, $^3J_{H\text{-}H}$ = 6.8 Hz, 8H, H-11, H-17), 1.53 – 1.43 (m, 8H, H-12, H-18), 1.40 – 1.27 (m, 16H, H-13, H-14, H-19, H-20), 0.97 – 0.85 (m, 12H, H-15, H-21).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 168.6 (C-2), 153.9 (C-8), 148.3 (C-7), 139.6 (C-5), 126.0 (C-4), 111.7 (C-9), 109.8 (C-6), 69.6 (C-10, C-16), 64.4 (C-3), 41.3 (C-1), 31.5 (C-13, C-19), 28.9 (C-11, C-17), 25.7 (C-12, C-18), 22.6 (C-14, C-20), 14.0 (C-15, C-21).



MS [m/z]: calc.: 854.10 [M + H]$^+$, found: 854.92 [M + D]$^+$.

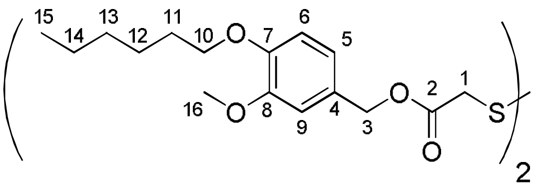
1.11 Synthesis of Bis-(4-hexyloxy-3-methoxy-benzyl)-dithioglycolate **3**



Similar to compound **1** (1.9), dithiodiglycolic acid (0.73 g. 4.0 mmol) was reacted with PPh_3 (2.22 g, 8.46 mmol), DIAD (1.7 mL, 8.5 mmol) and compound **10** (2.00 g, 8.46 mmol) in THF (35 mL). After aqueous work-up, the crude product was further purified by column chromatography (silica, *n*-hexane/EE gradient from 10:1 to 3:2) to give the final product as an off-white solid in 53% yield (1.27 g, 2.04 mmol).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.94 – 6.87 (m, 4H, H-9, H-5), 6.86 – 6.80 (m, 2H, H-6), 5.09 (s, 4H, H-3), 3.99 (t, ${}^3J_{H\text{-}H}$ = 6.9 Hz, 4H, H-19), 3.86 (s, 6H, H-16), 3.56 (s, 4H, H-1), 1.82 (p, ${}^3J_{H\text{-}H}$ = 7.0 Hz, 4H, H-11), 1.44 (p, ${}^3J_{H\text{-}H}$ = 7.2 Hz, 4H, H-12), 1.36 – 1.29 (m, 8H, H-13, H-14), 0.89 (t, ${}^3J_{H\text{-}H}$ = 6.6 Hz, 6H, H-15).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 169.3 (C-2), 149.5 (C-8), 149.0 (C-7), 127.7 (C-4), 121.6 (C-5), 112.7 (C-6), 112.4 (C-9), 69.2 (C-10), 67.6 (C-3), 56.1 (C-16), 41.5 (C-1), 31.7 (C-13), 29.2 (C-11), 25.7 (C-12), 22.7 (C-14), 14.1 (C-15).



MS [m/z]: calc.: 623.21 [M + H]$^+$, found: 645.10 [M + Na]$^+$.

UV/Vis = 280 nm (3933 L/mol).

2. NMR Data

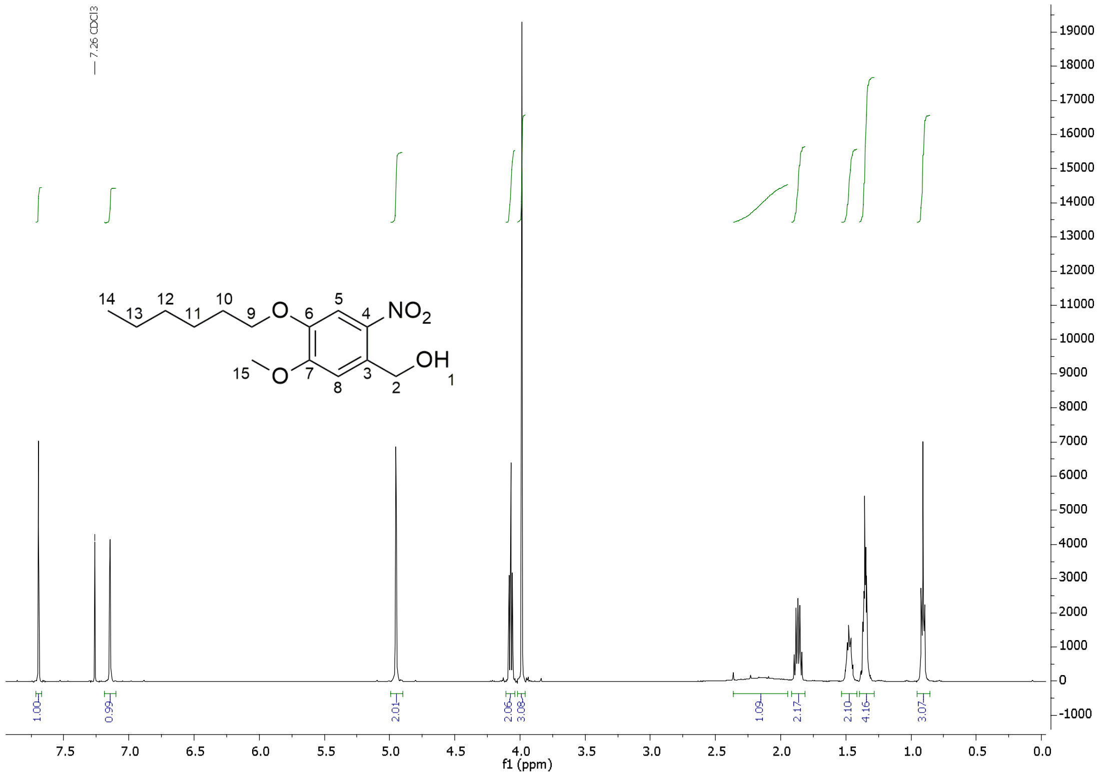


Figure S1: ^{1}H-NMR of 4-Hexyloxy-5-methoxy-2-nitrobenzylalcohol **8** in CDCl$_3$.

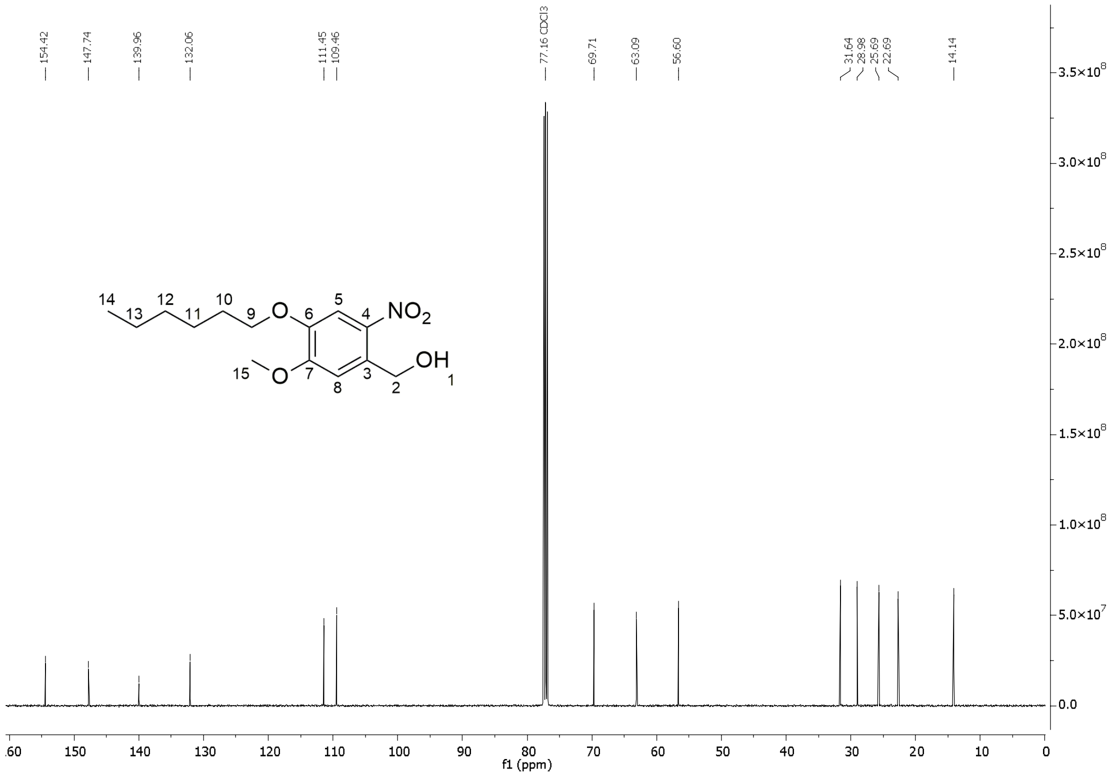


Figure S2: ^{13}C-NMR of 4-Hexyloxy-5-methoxy-2-nitrobenzylalcohol **8** in CDCl$_3$.

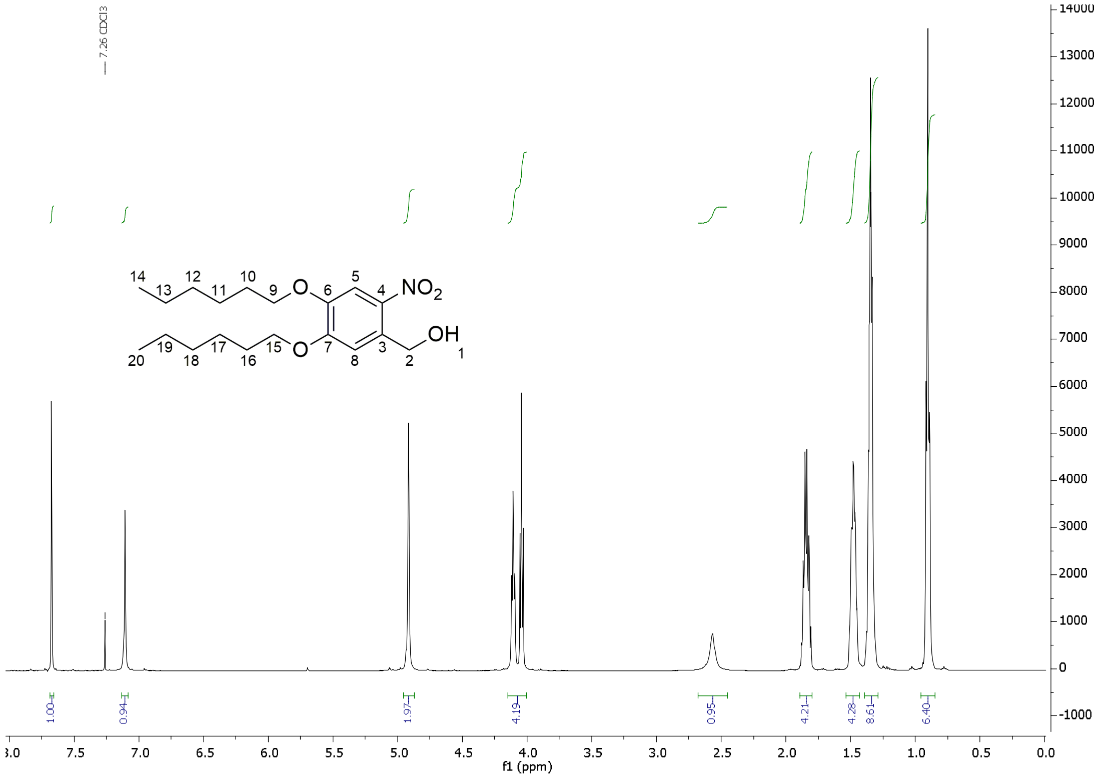


Figure S3: ^{1}H-NMR of 4,5-Di(hexyloxy)-2-nitrobenzylalcohol **9** in CDCl$_3$.

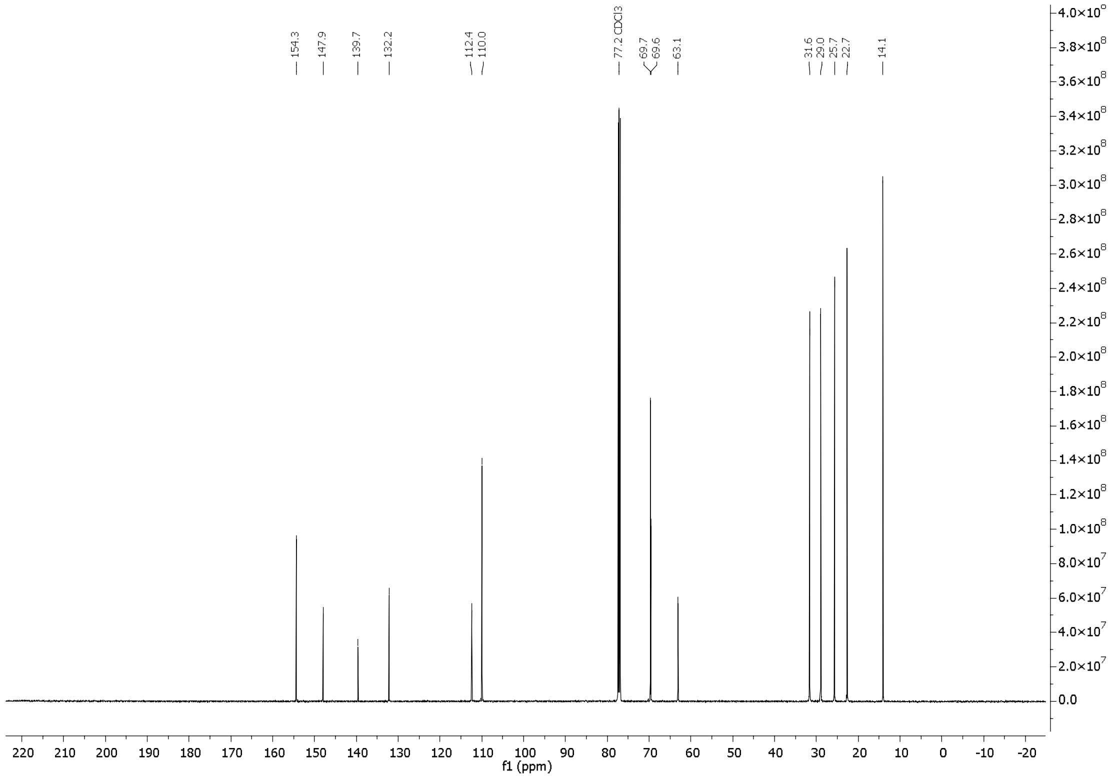


Figure S4: ^{13}C-NMR of 4,5-Di(hexyloxy)-2-nitrobenzylalcohol **9** in CDCl$_3$.

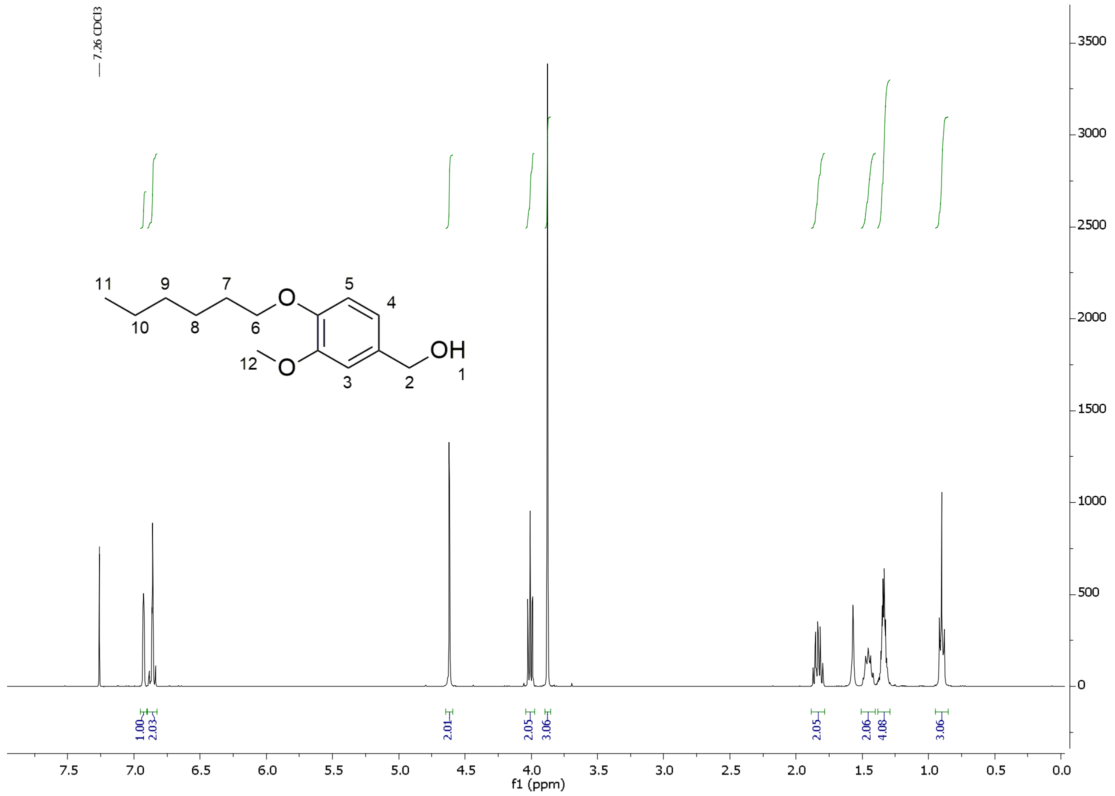


Figure S5: ^{1}H-NMR of 4-Hexyloxy-3-methoxybenzylalcohol **10** in $CDCl_3$.

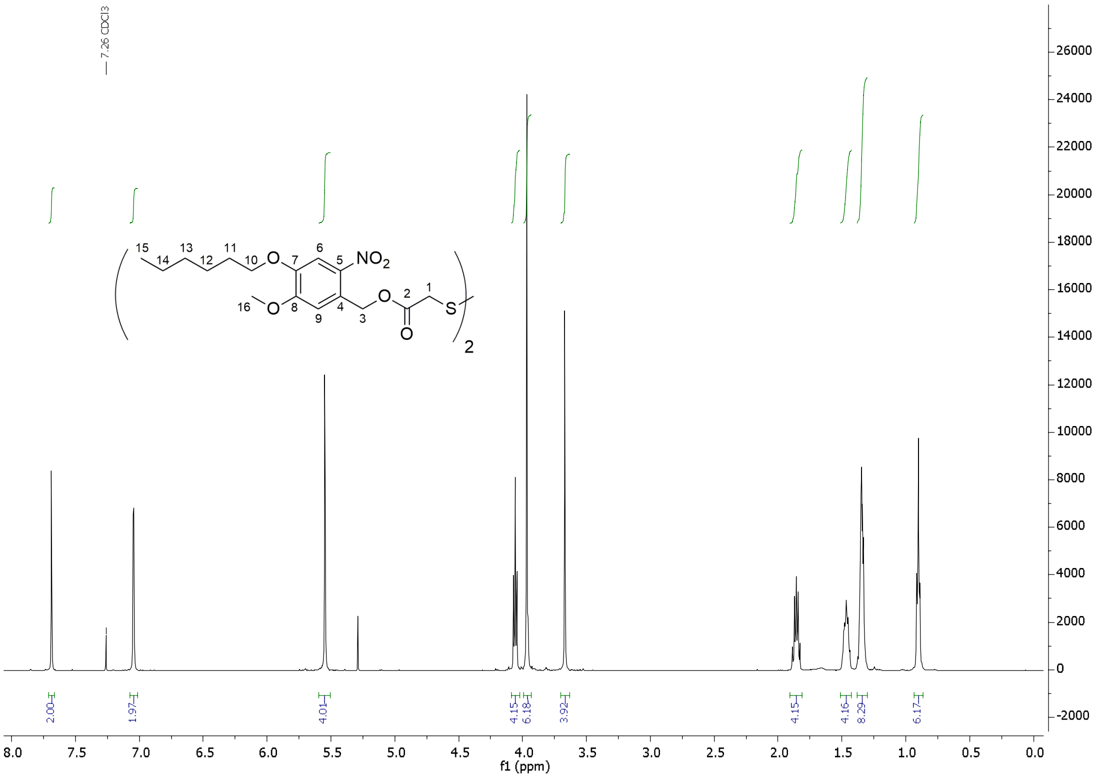


Figure S6: ^{1}H-NMR of Bis-(4-hexyloxy-3-methoxy-2-nitrobenzyl)-dithioglycolate **1** in CDCl$_3$.

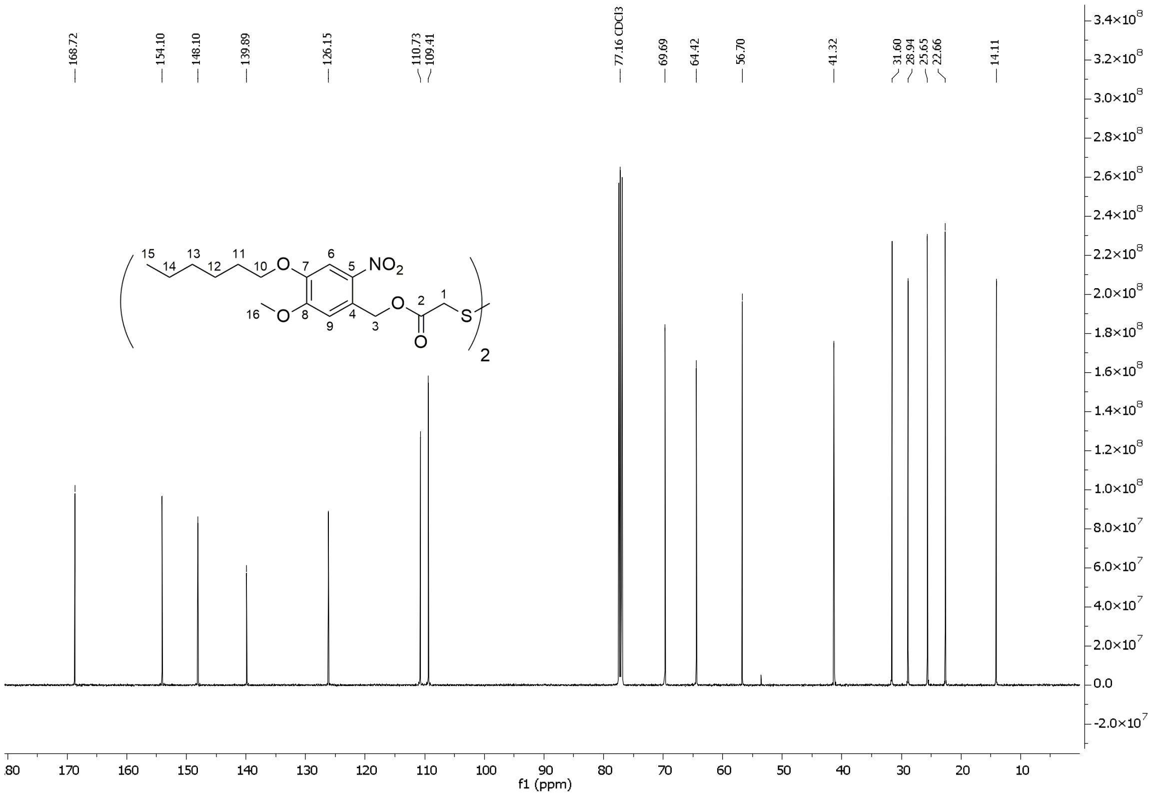


Figure S7: ^{13}C-NMR of Bis-(4-hexyloxy-3-methoxy-2-nitrobenzyl)-dithioglycolate **1** in CDCl$_3$.

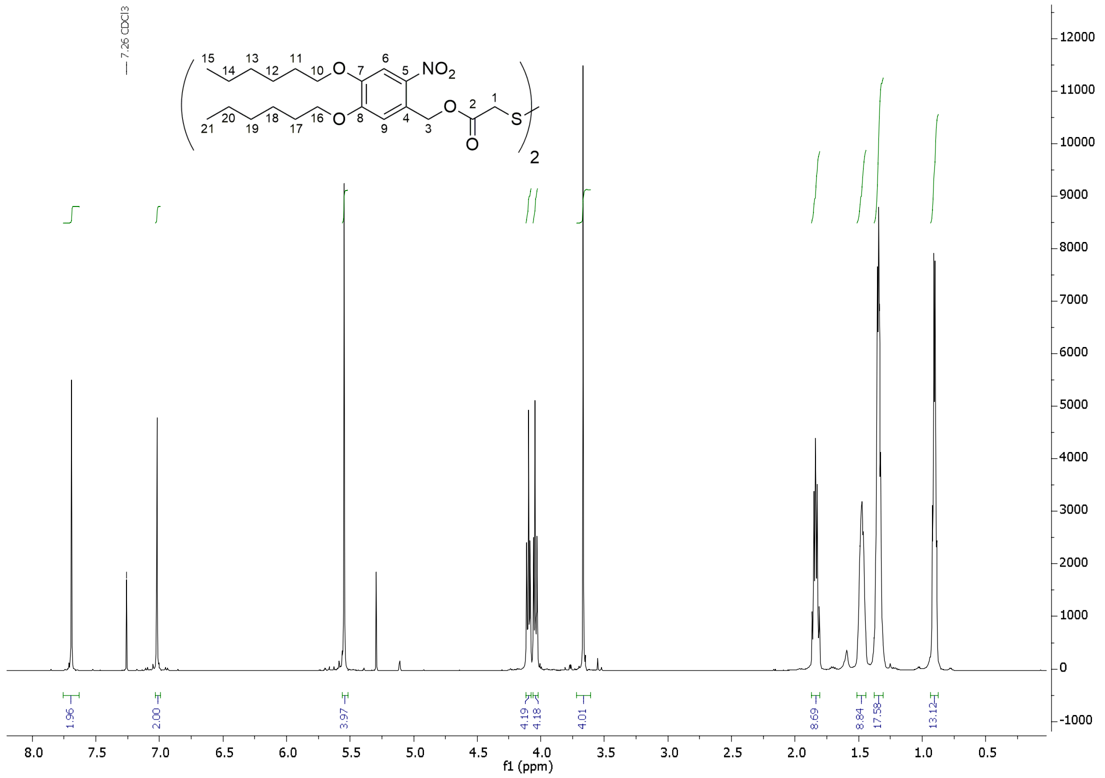


Figure S8: ^{1}H-NMR of Bis-(4,5-di(hexyloxy)-2-nitrobenzyl)-dithioglycolate **2** in CDCl$_3$.

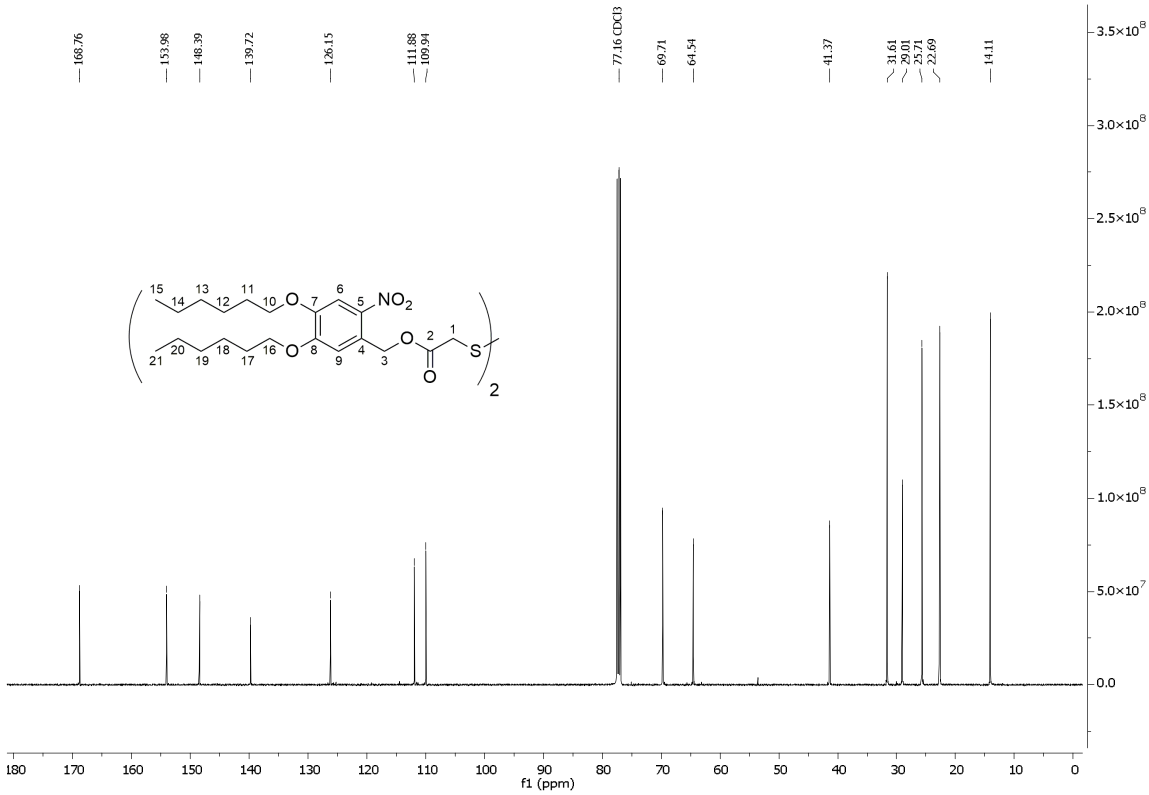


Figure S9: ^{13}C-NMR of Bis-(4,5-di(hexyloxy)-2-nitrobenzyl)-dithioglycolate **2** in CDCl$_3$.

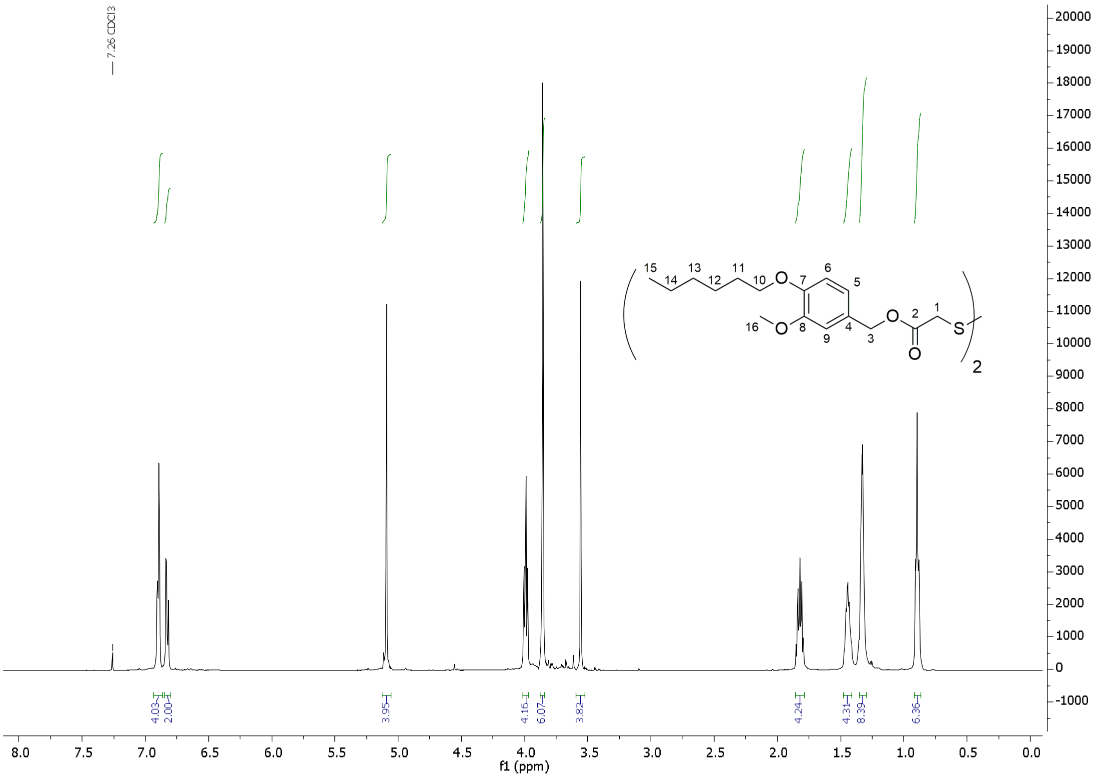


Figure S10: ^{1}H-NMR of Bis-(4-hexyloxy-3-methoxy-benzyl)-dithioglycolate **3** in CDCl$_3$.

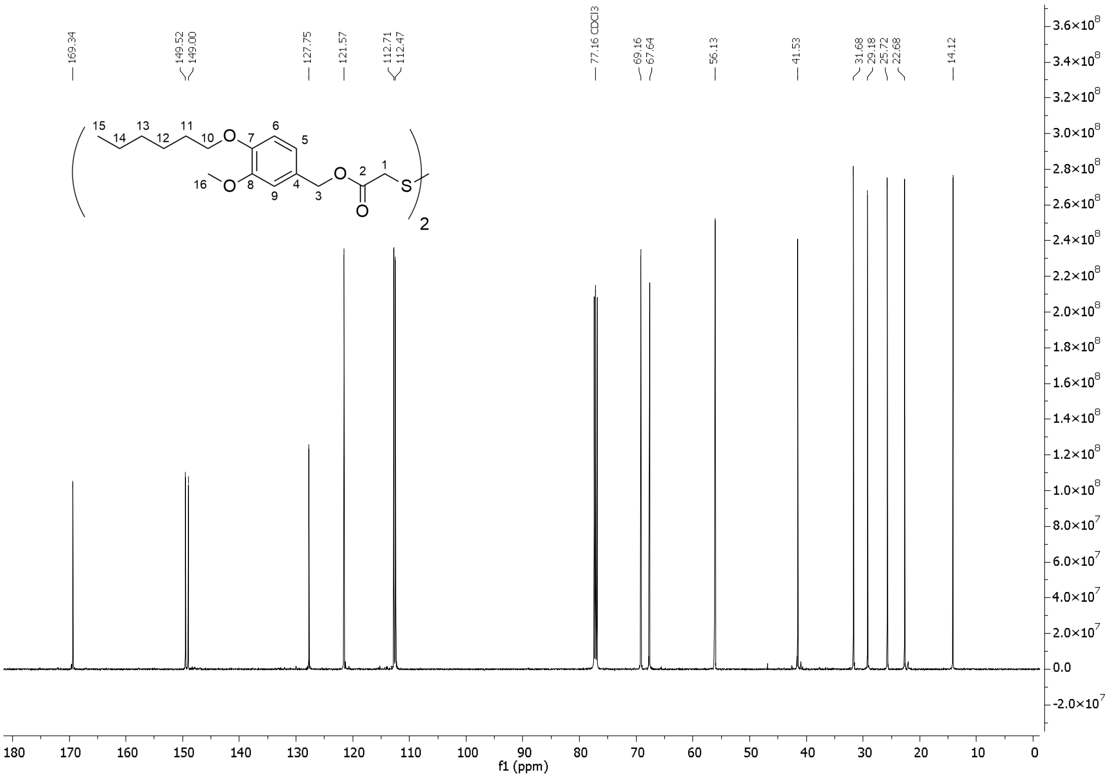


Figure S11: ^{13}C-NMR of Bis-(4-hexyloxy-3-methoxy-benzyl)-dithioglycolate **3** in CDCl$_3$.

3. IR Data

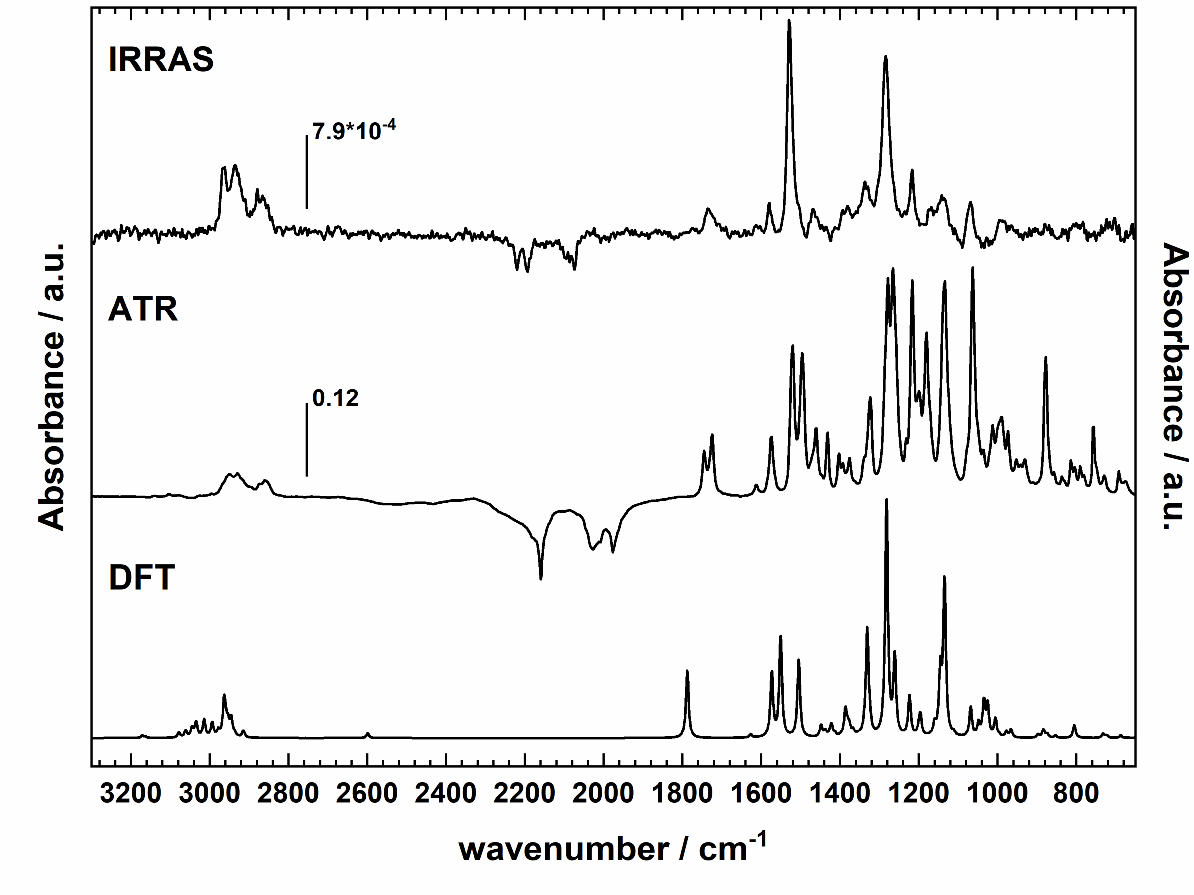


Figure S12: Full IR comparison for ONB-HM. ATR spectrum measured of disulfide **1**.

Table S1: IR band assignment of ONB-HM from DFT calculation of their vibrational modes and orientation of the transition dipole moments (TDM) according to the axis given in Figure X of the paper. **ν** stretching vibration, **Δ** in-plane deformation vibration, **γ** wagging vibration, **ω** aromatic out-of-plane vibration, **ρ** rocking vibration and **τ** twisting vibration.

No.	Mode	IRRAS [cm^{-1}]	ATR [cm^{-1}]	DFT [cm^{-1}]	TDM	weakening
1	$\nu_{CH_2,as.}$	2935	2929	3014	-	-
2	ν_{CO}	1736	1735	1788	⊥- axis A	Y
3	$\nu_{CC,\,arom.} + \Delta_{CH}$	1614	1612	1626	/	-
4	$\nu_{as,\,NO_2}$ anti-phase	1581	1575	1573	‖ - axis A	Y
5	$\nu_{CC,\,arom.} + \nu_{as,\,NO_2}$	1528	1519	1551	‖ - axis B	-
6	$\nu_{CC,\,arom.} + \Delta_{CH}$	-	1496	1505	‖ - axis B	Y
7	$\nu_{s,\,NO_2}$	1335	1324	1331	⊥- axis B	Y
8	$\nu_{CO,\,arom.} + \nu_{CO,\,carboxy}$	1285	1279	1282	⊥- axis B	Y
9	γ_{CH_2}(glycolate)	-	1226	1261	⊥- axis B	extinguished
10	$\nu_{CO,\,arom.}$ anti-phase	1220	1217	1224	between axis A and B	-
11	$\Delta_{CH,\,arom.}$	1185	1181	1196	‖ - axis B	Y
12	$\gamma_{CH_2} + \rho_{CH_3}$	1138	1134	1135	‖ - axis B	Y
13	$\gamma_{CN,\,arom.}$	1070	1064	1068	⊥- axis B	Y
14	$\omega_{CH,\,arom.}$	-	877	884	out-of-plane	extinguished

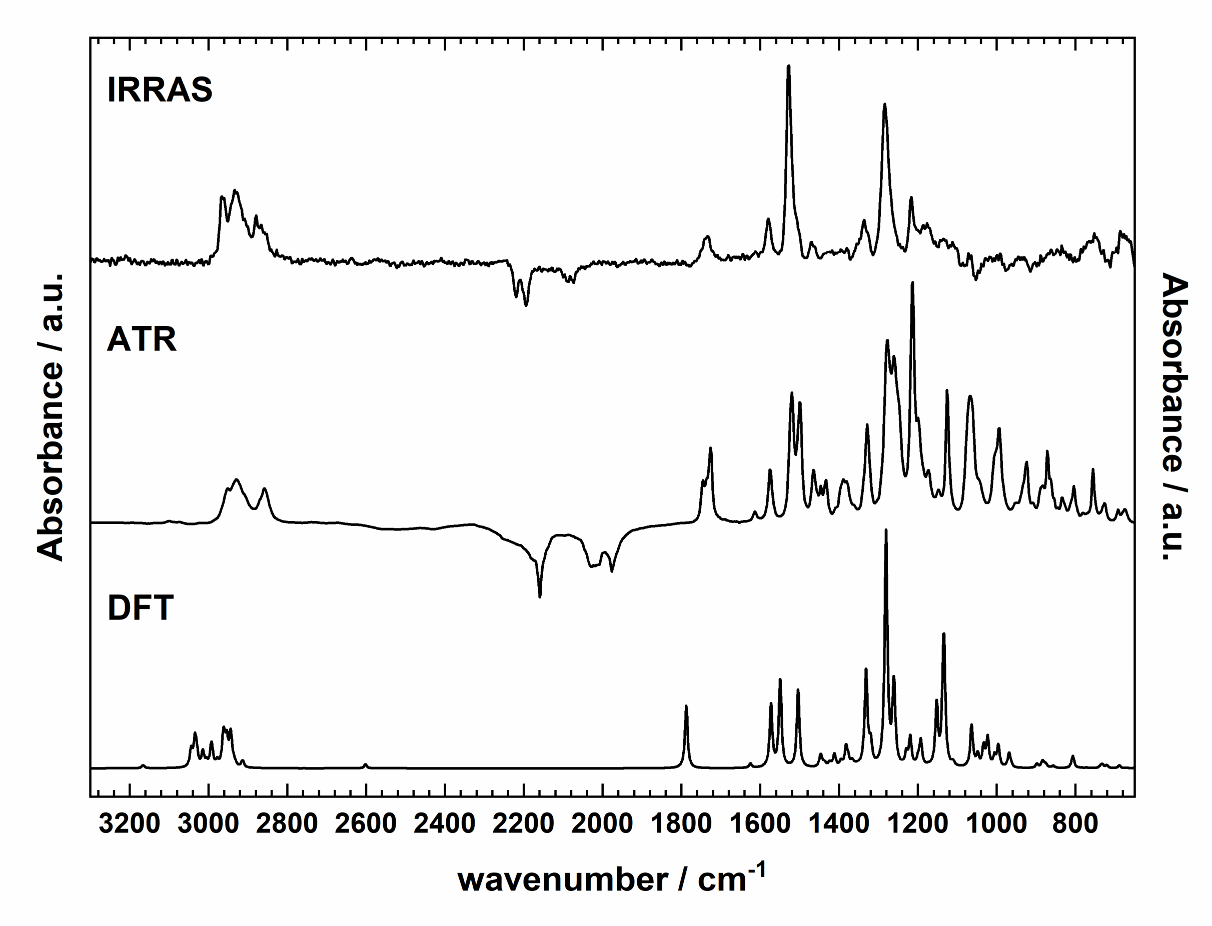


Figure S13: Full IR comparison for ONB-HH. ATR spectrum measured of disulfide **2**.

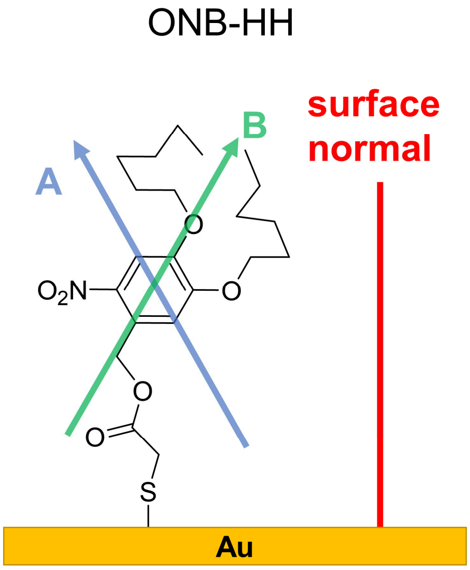


Figure S14: Surface configuration of the ONB-HH molecules in the SAM as depicted by the IR analysis. The shown axis A, along the center of the aromatic ring, and B through the benzyl-CH_2-group and hexoxy-oxygen, serve as an orientation for the TDMs shown in the IR analysis.

Table S2: IR band assignment of ONB-HH from DFT calculation of their vibrational modes and orientation of the transition dipole moments (TDM) according to the axis given in Figure S14. **ν** stretching vibration, **Δ** in-plane deformation vibration, **γ** wagging vibration, **ω** aromatic out-of-plane vibration, **ρ** rocking vibration and **τ** twisting vibration.

No.	Mode	IRRAS [cm^{-1}]	ATR [cm^{-1}]	DFT [cm^{-1}]	TDM	weakening
1	$\nu_{CH_2,as.}$	2933	2929	3014	-	-
2	ν_{CO}	1733	1734	1788	⊥- axis A	Y
3	$\nu_{CC,\,arom.} + \Delta_{CH}$	1612	1614	1625	⊥- axis B	Y
4	$\nu_{as,\,NO_2}$ anti-phase	1579	1575	1573	ǁ - axis A	Y
5	$\nu_{CC,\,arom.} + \nu_{as,\,NO_2}$	1527	1519	1549	ǁ - axis B	-
6	$\nu_{CC,\,arom.} + \Delta_{CH}$	1506	1500	1504	⊥- axis A	Y
7	$\nu_{s,\,NO_2}$	1336	1327	1332	⊥- axis B	Y
8	$\nu_{CO,\,arom.} + \nu_{CO,\,carboxy}$	1284	1275	1281	⊥- axis A	Y
9	$\nu_{CO,\,arom.}$ anti-phase	1216	1215	1220	ǁ - axis A	Y
10	$\nu_{CO,\,arom.}$	1176	1174	1193	⊥- axis B	Y
11	γ_{CH_2}	1147	1144	1152	ǁ - axis B	-
12	$\tau_{CH_2} + \rho_{CH_3}$	1135	1126	1134	ǁ - axis B	Y
13	$\gamma_{CN,\,arom.}$	-	1062	1064	⊥- axis B	extinguished
14	$\omega_{CH,\,arom.}$	-	870	884	out-of-plane	extinguished

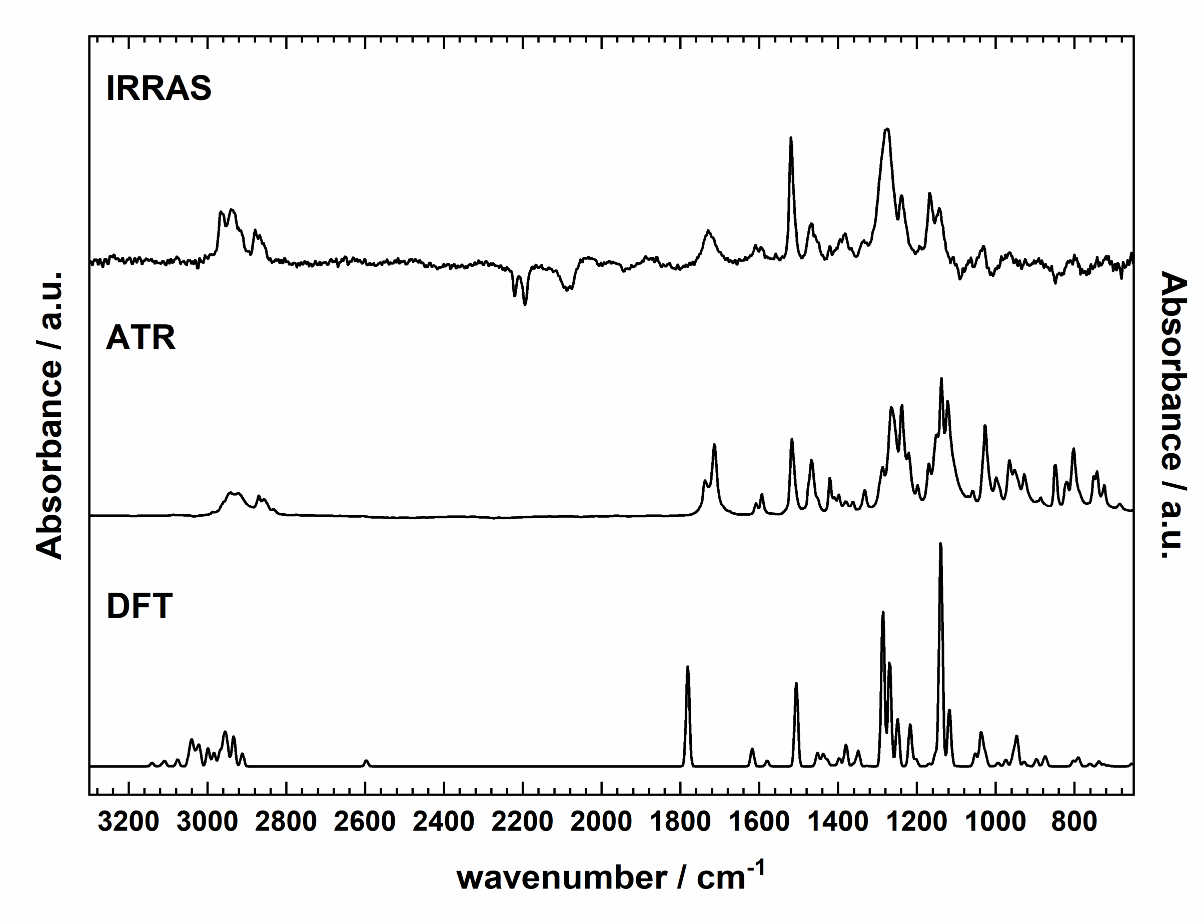


Figure S15: Full IR comparison for B-MH. ATR spectrum measured of disulfide **3**.

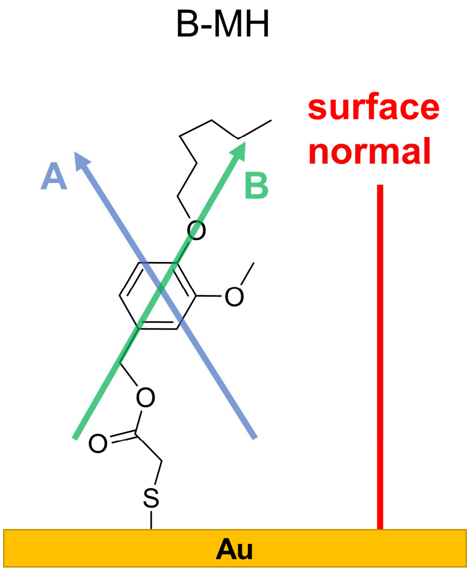


Figure S16: Surface configuration of the B-MH molecules in the SAM as depicted by the IR analysis. The shown axis A, along the center of the aromatic ring, and B through the benzyl-CH_2-group and hexoxy-oxygen, serve as an orientation for the TDMs shown in the IR analysis.

Table S3: IR band assignment of B-MH from DFT calculation of their vibrational modes and orientation of the transition dipole moments (TDM) according to the axis given in Figure S16. **ν** stretching vibration, **Δ** in-plane deformation vibration, **γ** wagging vibration, **ω** aromatic out-of-plane vibration, **ρ** rocking vibration and **τ** twisting vibration.

No.	Mode	IRRAS [cm^{-1}]	ATR [cm^{-1}]	DFT [cm^{-1}]	TDM	weakening
1	$\nu_{CH_2,as.}$	2933	2929	3014	-	-
2	ν_{CO}	1729	1737	1775	⊥- axis A	Y
3	$\nu_{CC,arom.} + \Delta_{CH}$	1594	1593	1581	ǁ- axis B	Y
4	$\nu_{CC,arom.} + \Delta_{CH}$	1519	1517	1507	ǁ- axis A	Y
5	$\nu_{CO,arom.}$ in-phase $+\Delta_{CH}$	1467	1467	1448	ǁ - axis B	Y
6	$\nu_{CC,arom.} + \Delta_{CH}$	1382	1380	1380	ǁ - axis A	-
7	γ_{CH_2}	1334	1332	1347	between axis A and B	-
8	$\nu_{CO,arom.} + \nu_{CO,carboxy}$	1274	1265	1268	⊥- axis A	Y
9	$\nu_{CO,arom.}$ anti-phase	1240	1238	1250	ǁ - axis A	Y
10	τ_{CH_2}	1193	1198	1218	⊥- axis B	extinguished
11	$\gamma_{CH_2} + \rho_{CH_3}$	1166	1137	1153	⊥- axis A	Y
12	ρ_{CH_2}	1143	1122	1138	ǁ - axis B	Y
13	Δ_{CH_2}	1031	1027	1034	ǁ - axis B	Y
14	τ_{CH_2}	-	849	872	⊥- surface normal	extinguished
15	$\omega_{CH,arom.}$	-	802	792	out-of-plane	extinguished

4. Wettability images

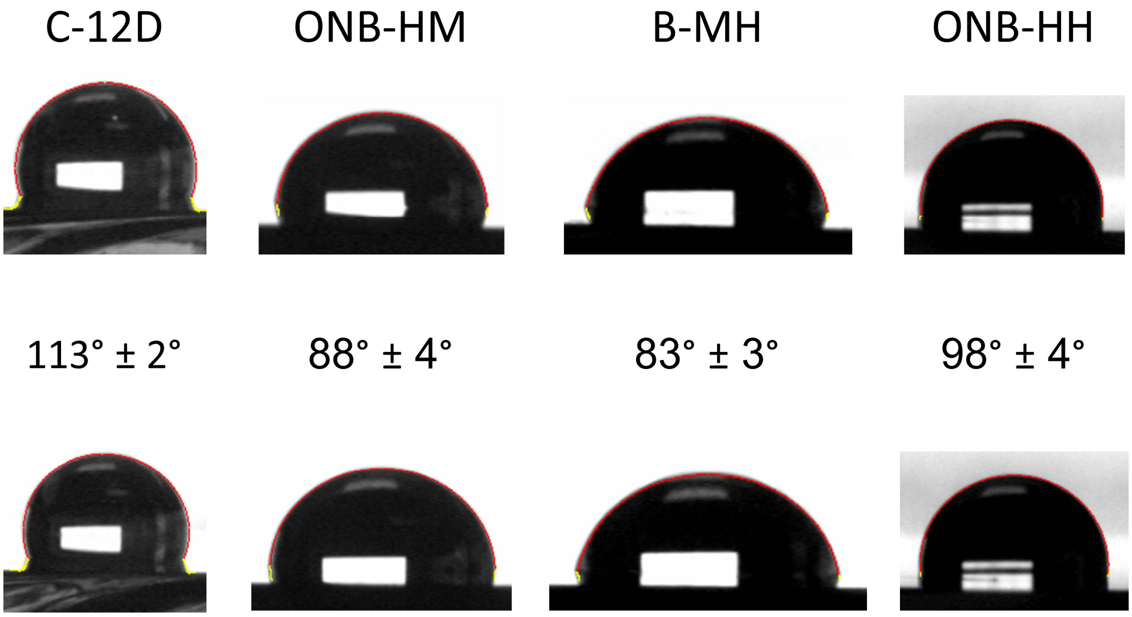


Figure S17: WCA images of the three tested SAMs ONB-HM, ONB-HH and B-MH and C12-D as reference, together with the measured WCAs.

5. LED-Datasheet

Table S4: Data sheet of the used 5W High Power 365nm LED.

Item Type	LED Bulb
LED Chip Brand	2 x Epiled 45mil Chip
LED Chip Model	2 x 3W High Power
Base Type	2 Pins
Diameter Bulb	5mm
Diameter Package	8mm
Viewing Angle	140°
Dominant Wavelength	365-370nm
Emitting Color	UV
Luminous Intensity(max)	17.589 lm
DC Forward Voltage	3.4V-3.8V
DC Forward Current	1400mA
Max. Power Dissipation	5320mW
Max. Reverse Voltage	5V

8. REFERENCE

(1) Rocha-Ortiz, J. S.; Insuasty, A.; Insuasty, B.; Ortiz, A. Evaluating the Intramolecular Charge Transfer in Novel Meso-Alkoxyphenyl and β-Ethynylphenolic BODIPY Derivatives. *J. Mol. Struct.* **2020**, *1206*, 127774. https://doi.org/10.1016/j.molstruc.2020.127774.

(2) Zhang, Q.; Peng, H.; Zhang, G.; Lu, Q.; Chang, J.; Dong, Y.; Shi, X.; Wei, J. Facile Bottom-Up Synthesis of Coronene-Based 3-Fold Symmetrical and Highly Substituted Nanographenes from Simple Aromatics. *J. Am. Chem. Soc.* **2014**, *136* (13), 5057–5064. https://doi.org/10.1021/ja413018f.

(3) Füser, Matthias. Dissertation: Darstellung Funktionalisierter SAM-Präkursoren Und MOF-Linker Für Den Aufbau von Strukturierten Organischen Dünnschichtsystemen, Goethe Universität Frankfurt am Main, Frankfurt am Main, 2018.