SUPPORTING INFORMATION

Photoswitchable triple hydrogen-bonding motif

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General methods. Solvents and commercial starting materials were used as received. 1-Bromo-4-*n*-hexyloxybenzene **4**,[1] 3,4-dibromo-1*H*-pyrrole-2,5-dione **9**,[2] and 4,6-diamino-2-chloro-1,3,5-triazine **13**[3] were prepared following literature procedures. All reactions requiring inert gas atmosphere were performed under argon atmosphere. Toluene and THF were distilled under argon atmosphere over sodium and triethylamine over KOH prior to use. Column chromatography was carried out with 130 – 400 mesh silica gel using eluents as specified. NMR spectra were recorded on a 300 MHz (75.6 MHz for ^{13}C) Bruker DPX 300 spectrometer at 25 °C using residual protonated solvent signals as internal standards (^{1}H: $\delta(CHCl_3) = 7.26$ ppm and ^{13}C: $\delta(CHCl_3) = 77.16$ ppm). UPLC/MS was performed with a Waters UPLC Acquity equipped with a Waters LCT Premier XE Mass detector for UPLC-HR-MS, with Waters Alliance systems (consisting of a Waters Separations Module 2695, a Waters Diode Array detector 996 and a Waters Mass Detector ZQ 2000). TLC was performed on Merck Silica Gel 60 F254 TLC plates with a fluorescent indicator with a 254 nm excitation wavelength. Compounds were visualized under UV light at 254 nm.

Photochemistry. UV vis spectroscopy was performed on a Cary 50 spectrophotometer equipped with a Peltier thermostated cell holder at 25 ± 0.05 °C using spectrophotometric grade solvents. Irradiation experiments were carried out in CH_2Cl_2 (see MS-Figure 2, MS-Table 1) and CH_3CN (see SI-Figure S1, SI-Table S1) in a quartz cuvette using a 1000 W high pressure xenon-lamp. Wavelength selection was achieved by using an interference filter ($\lambda_{T,max} = 313$ nm, 12 % T) or a cut-off filter (100 % T for $\lambda > 500$ nm). For determination of quantum yields an Oriel 68810 500 W mercury-lamp was used in combination with an Oriel 77200 monochromator. The reaction yields for the cyclisation and the cycloreversion of the diarylethenes were compared against azobenzene in methanol[4] and the commercial furyl fulgide Aberchrome 670 in toluene,[5] respectively. Irradiation of compounds **1a** and **2a** on a preparative scale was performed on a Rayonet RPR 100 photochemical reactor equipped with 300 nm lamps.

[1] G. W. Gray, M. Hird, D. Lacey, K. J. Toyne, *J. Chem. Soc. Perkin Trans II*, **1989**, 2041.
[2] M. Dubernet, V. Caubert, J. Guillard, M. C. Viaud-Massuard, *Tetrahedron*, **2005**, *61*, 4585.
[3] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer, D. Holm-Hansen, *J. Am. Chem. Soc.*, **1951**, *73*, 2981.
[4] G. Gauglitz, S. Hubig, *J. Photochem.*, **1985**, 30, 121.
[5] A. P. Glaze, H. G. Heller, J. Whittall, *J. Chem. Soc. Perkin Trans. II*, **1992**, 591.

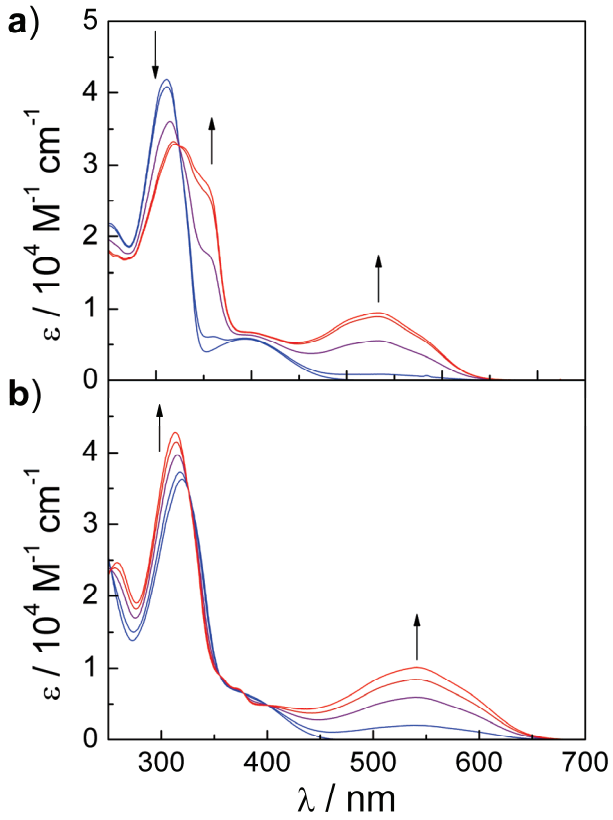


Figure S1. UV/vis absorption spectra during the course of irradiation (λ_{irr} = 313 nm) until reaching the PSS of a) **1a** (time intervals: t = 0, 1, 10, 35, and 55 min) and b) **2a** (time intervals: t = 0, 10, 30, 60, and 120 s) in CH_3CN (c = $2.5 \cdot 10^{-5}$ M in each case, 25 °C).

Table S1 Photochromic properties of both switch pairs in acetonitrile.

	photochromism[a]			
	λ_{max} [nm]	$\Phi_{\mathbf{a}\rightarrow\mathbf{b}}^{313\,nm}$	$\Phi_{\mathbf{b}\rightarrow\mathbf{a}}^{546\,nm}$	conv.[b]
1a	311, 396	0.01	0.02	44%
1b	353, 534			
2a	320, 371	0.15	0.01	78%
2b	313, 542			

[a] in CH_3CN at 25 °C; [b] composition of the PSS upon irradiation of the open form (**1a** or **2a**) with UV-light (λ_{irr} = 313 nm) determined by UPLC.

Table S2 Quantum yields for both switch pairs in methylene chloride in presence of melamine **3**.[a]

	$\Phi_{\mathbf{a}\rightarrow\mathbf{b}}^{313\,nm}$	$\Phi_{\mathbf{b}\rightarrow\mathbf{a}}^{546\,nm}$
1a/b	0.08	0.02
2a/b	0.23	0.01

[a] c(melamine) = $1 \cdot 10^{-2}$ M; under these conditions approximately 60 % of the open and 75 % of the closed switch are complexed by melamine **3**. Note that **3** shows negligible absorption at the irradiation wavelengths.

NMR-titration studies. All binding studies were carried out in $CDCl_3$ at 25 °C. The solvent was treated with anhydrous K_2CO_3 and dried over molecular sieves (4 Å) prior to use.

For determination of association constants ^{1}H-NMR-titrations were performed varying the concentration of the guest molecule $[G]_0$ while the concentration of the host $[H]_0$ was held constant during the course of the experiment.[6] $[H]_0$ was chosen in such a way that at a 1:1 stoichiometry approximately 50 % of the host are bound.[7] A host-solution ($c = 7\cdot10^{-3}$ M), containing compounds **1** or **2** in their open or closed form, respectively, and a guest-solution, containing both the melamine receptor **3** ($c = 7\cdot10^{-2}$ M) and the host ($c = 7\cdot10^{-3}$ M) were prepared in $CDCl_3$. An NMR-tube was charged with an initial volume of 600 µL of the host-solution and after each addition of small portions of the guest-solution an ^{1}H-NMR-spectrum was recorded. For obtaining binding isotherms (see MS-Figure 3) the observed difference in the chemical shift of the imide proton ($\Delta\delta_{obs}$) was plotted against the total guest concentration $[G]_0$ of the sample obtained by comparing the integrated proton-signals of host and guest in each spectrum. Nonlinear least-squares regression analysis of these data was performed using equation *(1)* allowing to extract K_a (association constant) and $\Delta\delta_{max}$ (maximum difference in chemical shift) as free parameters.

$$\Delta\delta_{obs} = \frac{\Delta\delta_{\max}}{2[H]_0}\left([H]_0 + [G]_0 + \frac{1}{K_a} - \sqrt{\left([H]_0 + [G]_0 + \frac{1}{K_a}\right)^2 - 4[H]_0[G]_0}\right) \qquad (1)$$

For determination of the binding stoichiometry the method of continuous variation (Job plot)[6] was used (see SI-Figure S2). A host-solution containing **1a** or **2a** and a guest-solution containing melamine receptor **3** in the same concentration ($3.5\cdot10^{-2}$ M for **1a·3**, $1.2\cdot10^{-2}$ M for **2a·3**) were prepared in $CDCl_3$. By adding equivalents of the guest-solution to the host-solution and vice versa the molar fraction of the guest $x_G = [G]_0/([H]_0 + [G]_0)$ was varied while the overall concentration was held constant. Thus the concentration of the formed complex, expressed by its molar fraction $\Delta\delta_{max}\cdot x_{complex} = (1-x_G)\cdot\Delta\delta_{obs}$, is highest when the exact stoichiometry is reached, i.e. for the formation of a 1:1 complex this occurs at $x_G = 0.5$.

[6] K. A. Connors, *Binding Constants*, Wiley & Sons, New York, 1987.
[7] C. S. Wilcox, in *Frontiers of Supramolecular Chemistry and Photochemistry,* ed. H. J. Schneider and H. Dürr, VCH, Weinheim, 1991, pp. 123-143.

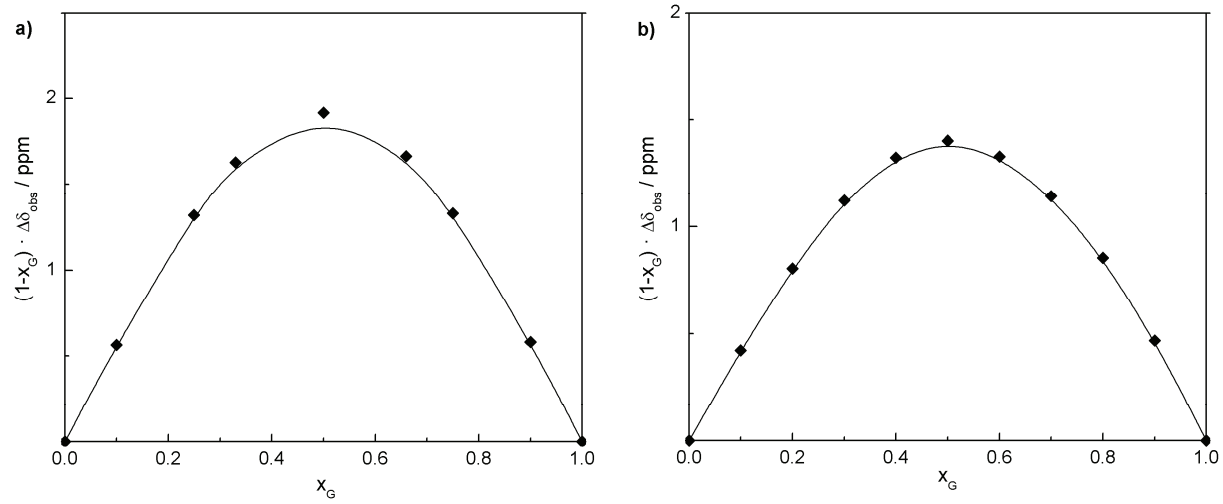


Figure S2. ^{1}H-NMR Job plots for complexes *a)* **1a·3** ($c_{total} = 3.5 \cdot 10^{-2}$ M) and *b)* **2a·3** ($c_{total} = 1.2 \cdot 10^{-2}$ M) in $CDCl_3$ at 25 °C.

Cyclic voltammetry. Cyclic voltammetry was performed using a PG310 USB (HEKA Elektronik) potentiostat, a platinum-disc (1 mm diameter) working electrode and a standard calomel electrode (SCE) as reference. Ferrocene was used as external standard. Measurements were carried out in acetonitrile or DMF containing 0.1 M Bu_4NPF_6 using a scan rate dE/dt = 1 V s^{-1}. For data evaluation PotMaster v2x43 software (HEKA Elektronik) was used. Irradiation was performed directly on the CV-cell using a standard laboratory UV-lamp (365 nm).

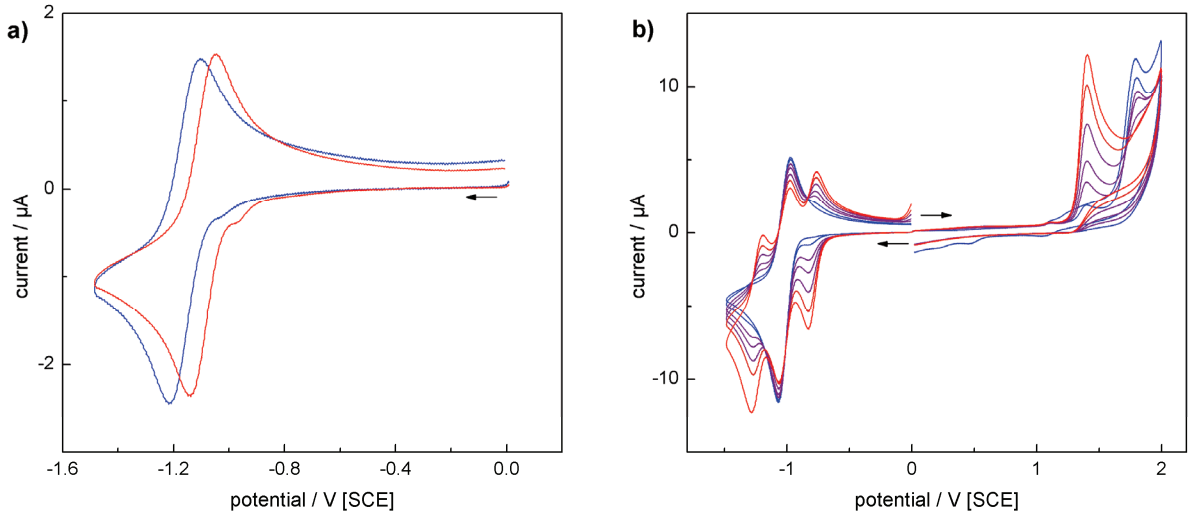


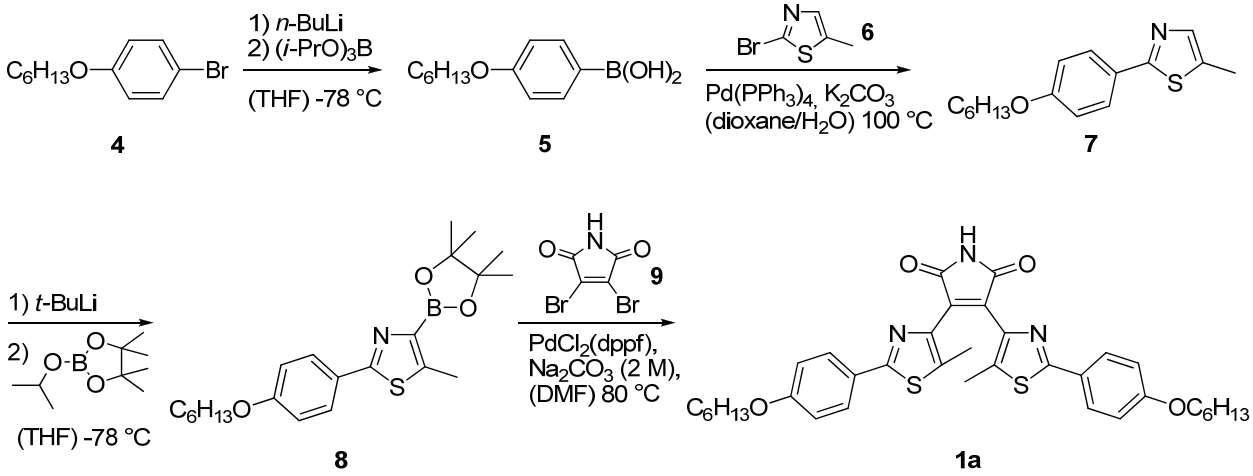
Figure S3. Cyclic voltammetry of a) isolated compounds **1a** (blue) and **1b** (red) in DMF ($1 \cdot 10^{-3}$ M) and b) during the course of irradiation of a solution of **2a** in acetonitrile ($2.5 \cdot 10^{-3}$ M) with UV-light (365 nm).

Table S3 Oxidation and reduction potentials of **1a/b** and **2a/b**.

	E_p^{ox} [V][a]	E_p^{red} [V][a]
1a	1.003[b]	-1.738[c]
1b	0.703[b]	-1.664[c]
2a	1.365[b]	-1.497[b]
2b	0.981[b]	-1.253[b]
maleimide		-1.719[b]

[a] vs. Fc/Fc^+, $E_{SCE\ vs.\ Fc/Fc+}$ = 0.425 V (acetonitrile), 0.522 V (DMF); [b] in acetonitrile; [c] in DMF.

Synthesis.



Scheme S1. Synthesis of photochromic switch **1a**.

4-*n*-Hexyloxyphenylboronic acid (5). 1-Bromo-4-*n*-hexyloxybenzene **4** (14.60 g, 56.80 mmol) was dissolved in 250 mL of dry THF and cooled down to -78 °C. *n*-Butyllithium (1.6 M in hexane, 42.0 mL, 68.2 mmol) was added dropwise via a syringe and the mixture was stirred for further 45 min. Then, triisopropyl borate (15.7 mL, 68.2 mmol) was added and the mixture was allowed to warm up to room temperature over a period of 1 h. After the addition of water a white solid precipitated, which was then collected, washed with hexane, and dried *in vacuo* to afford **5** (9.79 g, 44.1 mmol, 78 %). Boronic acid **5** was used without further purification.

2-Bromo-5-methylthiazole (6). In analogy to a literature procedure[8] 2-amino-5-methylthiazole (10.00 g, 87.58 mmol) was dissolved in 40 mL of aqueous HBr (48 %) and cooled to 0 °C. After adding slowly $NaNO_2$ (7.252 g, 105.10 mmol), dissolved in 15 mL of water, the mixture was stirred for further 3 h at that temperature. Then, the mixture was extracted with 3 x 30 mL of Et_2O and the combined organic layers were dried over $MgSO_4$ and evaporated. For purification the crude product was dissolved in dichloromethane and filtered through a pad of silica. Evaporation of the solvent afforded **6** (9.448 g, 53.06 mmol, 61 %) as a colourless liquid.

^{1}H-NMR: δ(ppm) = 7.22 (q, ^{4}J(H,H) = 1.2 Hz, 1 H, CH_{ar}), 2.40 (d, ^{4}J(H,H) = 1.2 Hz, 3 H, CH_3). **^{13}C-NMR:** δ(ppm) = 140.4, 137.9, 133.5, 12.1.

[8] H.-J. Kim, S. Liu, Y.-S. Keum, Q. X. Li, *J. Agric. Food. Chem.*, **2003**, *51*, 1823.

2-(4-*n*-Hexyloxyphenyl)-5-methylthiazole (7). 2-Bromo-5-methylthiazole **6** (4.27 g, 24.00 mmol) and boronic acid **5** were dissolved in 144 mL of dioxane and the solution was degassed by bubbling Ar through the mixture for 10 min. After the addition of a solution of K_2CO_3 (9.95 g, 72.00 mmol) in 36 mL of water and $Pd(PPh_3)_4$ (1.30 g, 1.20 mmol) the mixture was refluxed at 100 °C overnight. Then, it was diluted with ethyl acetate and filtered through a pad of Celite. The organic layer was washed with brine and dried over $MgSO_4$. Purification by column chromatography (petroleum ether/ethyl acetate 5:1) afforded **7** (3.70 g, 13.50 mmol, 56 %) as a white solid.

^{1}H-NMR: δ(ppm) = 7.81 (d, ^{3}J(H,H) = 9.0 Hz, 2 H, CH_{ar}), 7.43 (q, ^{4}J(H,H) = 1.2 Hz, 1 H, CH_{ar}), 6.92 (d, ^{3}J(H,H) = 9.0 Hz, 2 H, CH_{ar}), 3.99 (t, ^{3}J(H,H) = 6.6 Hz, 2 H, OCH_2), 2.48 (d, ^{4}J(H,H) = 1.2 Hz, 3 H, CH_3), 1.85 – 1.72 (m, 2 H, CH_2), 1.55 – 1.28 (m, 6 H, CH_2), 0.91 (t, ^{3}J(H,H) = 6.9 Hz, 3 H, CH_3). **^{13}C-NMR:** δ(ppm) = 167.0, 160.7, 140.9, 132.9, 127.8, 126.5, 114.9, 68.3, 31.7, 29.3, 25.8, 22.7, 14.1, 12.2**. HRMS (ESI$^+$):** *m/z* = 276.131 (calcd. 276.142 for $C_{16}H_{22}NOS^+$).

2-(4-*n*-Hexyloxyphenyl)-5-methylthiazol-4-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8).

Thiazole **7** (2.96 g, 10.8 mmol) was dissolved in 100 mL of dry THF and the mixture was cooled to -78 °C. *tert*-Butyllithium (1.6 M in pentane, 8.06 mL, 12.9 mmol) was added dropwise via a syringe and the mixture was stirred for 30 min. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.86 mL, 14.04 mmol) was added and the mixture was allowed to warm up to room temperature over a period of 1 h. After the addition of 10 mL of methanol the mixture was extracted with 4 x 50 mL of ethyl acetate, the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvents gave crude **8** (4.30 g, 8.0 mmol, 63 %), which was used without further purification.

^{1}H-NMR: δ(ppm) = 7.86 (m, 2 H, CH_{ar}), 6.88 (m, 2 H, CH_{ar}), 3.97 (t, ^{3}J(H,H) = 6.6 Hz, 2 H, OCH_2), 2.71 (s, 3 H, CH_3), 1.84 – 1.74 (m, 2 H, CH_2), 1.51 – 1.20 (m, 6 H, CH_2), 1.37 (s, 12 H, CH_3), 0.94 (br, 3 H, CH_3).

3,4-Bis(2-(4-*n*-hexyloxyphenyl)-5-methylthiazol-4-yl)-1*H*-pyrrole-2,5-dione (1a).

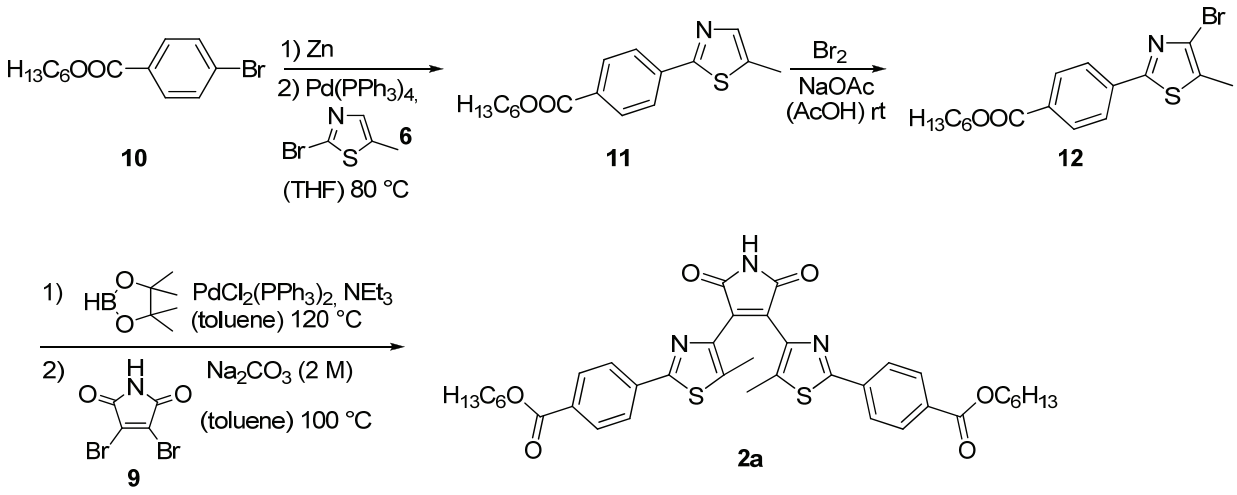
Borolane **8** (4.30 g, 8.00 mmol) and 3,4-dibromo-1*H*-pyrrole-2,5-dione **9** (678 mg, 2.66 mmol) were dissolved in 75 mL of DMF and the mixture was degassed by bubbling argon through the solution for 10 min. After the addition of an aqueous solution of Na_2CO_3 (2 M, 6.65 mL, 13.30 mmol) and $PdCl_2$(dppf) (217 mg, 0.27 mmol) the mixture was stirred

for 5 h at 80°C. After cooling to room temperature it was poured into 200 mL of water and extracted with 4 x 50 mL of dichloromethane. The combined organic layers were washed with brine and dried over $MgSO_4$. Purification by column chromatography (petroleum ether/ethyl acetate 4:1 → 1:1) afforded **1a** (916 mg, 1.42 mmol, 53 %) as a yellow solid.

^{1}H-NMR: δ(ppm) = 7.72 (d, ^{3}J(H,H) = 8.7 Hz, 4 H, CH_{ar}), 7.70 (s, 1 H, N*H*), 6.87 (d, ^{3}J(H,H) = 8.7 Hz, 4 H, CH_{ar}), 3.97 (t, ^{3}J(H,H) = 6.6 Hz, 4 H, OCH_2), 2.21 (s, 6 H, CH_3), 1.83 – 1.73 (m, 4 H, CH_2), 1.50 – 1.25 (m, 12 H, CH_2), 0.91 (t, ^{3}J(H,H) = 6.6 Hz, 6 H, CH_3). **^{13}C-NMR:** δ(ppm) = 169.3, 165.6, 161.0, 141.0, 136.4, 135.5, 128.1, 126.0, 114.9, 68.3, 31.7, 29.3, 25.8, 22.7, 14.2, 12.7. **HRMS (ESI$^+$):** *m/z* = 644.223 (calcd. 644.262 for $C_{36}H_{42}N_3O_4S_2^+$). **UPLC:** See appendix.

Isolation of closed form 1b. A solution of **1a** (120 mg, 0.19 mmol) in 300 mL of dichloromethane was irradiated over a period of 35 min. After evaporating the solvent the mixture of open and closed form was separated by column chromatography (petroleum ether/ethyl acetate 1:2) affording **1b** (82 mg, 0.13 mmol, 68 %) as a dark solid. In addition, 23 % of the starting material could be recovered.

^{1}H-NMR: δ(ppm) = 8.03 (d, ^{3}J(H,H) = 9.0 Hz, 4 H, CH_{ar}), 8.01 (s, 1 H, N*H*), 6.96 (d, ^{3}J(H,H) = 9.0 Hz, 4 H, CH_{ar}), 4.05 (t, ^{3}J(H,H) = 6.3 Hz, 4 H, OCH_2), 1.95 (s, 6 H, CH_3), 1.86 – 1.77 (m, 4 H, CH_2), 1.50 – 1.25 (m, 12 H, CH_2), 0.91 (t, ^{3}J(H,H) = 6.9 Hz, 6 H, CH_3). **^{13}C-NMR:** δ(ppm) = 181.6, 164.3, 161.9, 132.0, 125.1, 114.9, 112.3, 70.4, 68.7, 31.7, 29.1, 26.6, 25.8, 22.7, 14.2. **HRMS (ESI$^+$):** *m/z* = 644.218 (calcd. 644.262 for $C_{36}H_{42}N_3O_4S_2^+$). **UPLC:** See appendix.



Scheme S2. Synthesis of photochromic switch **2a**.

1-Bromo-4-*n*-hexyloxycarbonylbenzene (10).

In analogy to a literature procedure[9] a mixture of 4-bromobenzoic acid (7.50 g, 37.31 mmol), *n*-hexanol (4.69 mL, 37.31 mmol), and 4-(dimethylamino)pyridine (456 mg, 3.73 mmol) in 150 mL of dichloromethane was treated with 1,3-dicyclohexylcarbodiimide (9.24 g, 44.77 mmol) in two portions over 15 min. The mixture was stirred for 3 d at room temperature. After the addition of water (3.79 g, 210.22 mmol) and further stirring for 1 h the mixture was filtered, the precipitate was washed with petroleum ether and the combined filtrate was evaporated. Column chromatography (petroleum ether/ethyl acetate 13:1) of the crude product afforded **10** (9.51 g, 33.3 mmol, 89 %) as a colourless oil that solidifies in the refridgerator.

^{1}H-NMR: δ(ppm) = 7.90 (m, 2 H, CH_{ar}), 7.57 (m, 2 H, CH_{ar}), 4.31 (t, ^{3}J(H,H) = 6.6 Hz, 2 H, OCH_2), 1.80 – 1.71 (m, 2 H, CH_2), 1.46 – 1.32 (m, 6 H, CH_2), 0.90 (t, ^{3}J(H,H) = 6.9 Hz, 3 H, CH_3). **^{13}C-NMR:** 166.1, 131.8, 131.2, 129.6, 128.0, 65.6, 31.6, 28.8, 25.8, 22.7, 14.1. **HRMS (ESI$^+$):** *m/z* = 285.043 (calcd. 285.049 for $C_{13}H_{28}BrO_2^+$).

2-(4-*n*-Hexyloxycarbonylphenyl)-5-methylthiazole (11). Following a literature procedure[10] zinc (4.943 g, 75.6 mmol) was suspended in 15 mL of dry THF. 1,2-Dibromoethane (0.58 mL, 6.80 mmol) was added and the mixture was heated twice to reflux until gas evolution ceased. After the addition of TMSCl (0.39 mL, 3.00 mmol) and stirring for 5 min a solution of 2-bromo-5-methylthiazole **6** (4.49 g, 25.20 mmol) in 10 mL of THF was added to

[9] C. G. Caldwell, K. M. Rupprecht, S. S. Bondy, A. A. Davis, *J. Org. Chem.*, **1990**, *55*, 2355.
[10] J. Jensen, N. Skærbæk, P. Vedsø, *Synthesis*, **2001**, 128.

the reaction mixture via a syringe and it was heated for ca. 1 h to 70 °C until TLC indicated consumption of the starting material. Then, **10** (9.35 g, 32.80 mmol), dissolved in 10 mL THF, and $Pd(PPh_3)_4$ (866 mg, 0.75 mmol) were added and the mixture was refluxed at 80 °C overnight. After cooling to room temperature it was diluted with ethyl acetate and filtered through a pad of Celite. After washing with water and brine the organic layer was dried over $MgSO_4$. Purification by column chromatography (petroleum ether/ethyl acetate 9:1 → 4:1) afforded **11** (4.31 g, 14.2 mmol, 56 %) as a white solid.

^{1}H-NMR: δ(ppm) = 8.08 (d, ^{3}J(H,H) = 8.7 Hz, 2 H, CH_{ar}), 7.95 (d, ^{3}J(H,H) = 8.7 Hz, 2 H, CH_{ar}), 7.55 (q, ^{4}J(H,H) = 1.2 Hz, 1 H, CH_{ar}), 4.32 (t, ^{3}J(H,H) = 6.6 Hz, 2 H, OCH_2), 2.52 (d, ^{4}J(H,H) = 1.2 Hz, 3 H, CH_3), 1.81 – 1.72 (m, 2 H, CH_2), 1.49 – 1.30 (m, 6 H, CH_2), 0.90 (t, ^{3}J(H,H) = 6.9 Hz, 3 H, CH_3). **^{13}C-NMR:** δ(ppm) = 166.3, 165.4, 142.1, 137.7, 135.3, 131.3, 130.3, 126.1, 65.5, 31.6, 28.8, 25.8, 22.7, 14.1, 12.3. **HRMS (ESI$^+$):** *m/z* = 304.128 (calcd. 304.137 for $C_{17}H_{22}NO_2S^+$).

4-Bromo-2-(4-*n*-hexyloxycarbonylphenyl)-5-methylthiazole (7). Thiazole **6** (4.31 g, 14.2 mmol) was added to a solution of sodium acetate (28 g) in 200 mL of acetic acid. After bromine (2.19 mL, 42.6 mmol) was added slowly to this mixture it was stirred at room temperature for 2 h. Then a saturated aqueous solution of $NaHSO_3$ was added until excess bromine was reduced and the mixture was extracted with 3 x 100 mL of ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 9:1) to afford **7** (2.95 g, 7.70 mmol, 54 %) as a white solid.

^{1}H-NMR: δ(ppm) = 8.08 (d, ^{3}J(H,H) = 8.7 Hz, 2 H, CH_{ar}), 7.93 (d, ^{3}J(H,H) = 8.7 Hz, 2 H, CH_{ar}), 4.33 (t, ^{3}J(H,H) = 6.6 Hz, 2 H, OCH_2), 2.46 (s, 3 H, CH_3), 1.82 – 1.73 (m, 2 H, CH_2), 1.49 – 1.29 (m, 6 H, CH_2), 0.90 (t, ^{3}J(H,H) = 6.9 Hz, 3 H, CH_3). **^{13}C-NMR:** δ(ppm) = 166.1, 164.1, 136.6, 131.9, 130.3, 130.2, 126.2, 125.9, 65.6, 31.6, 28.8, 25.8, 22.7, 14.1, 13.2. **HRMS (ESI$^+$):** *m/z* = 382.036 (calcd. 382.048 for $C_{17}H_{21}BrNO_2S^+$).

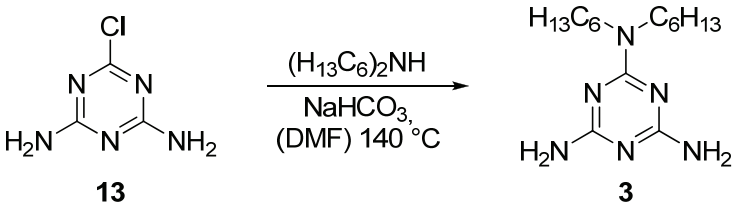
3,4-Bis(2-(4-*n*-hexyloxycarbonylphenyl)-5-methylthiazol-4-yl)-1*H*-pyrrole-2,5-dione (2a). Triethylamine (3.00 mL, 21.72 mmol) and **7** (2.77 g, 7.24 mmol) were dissolved in 40 mL of dry toluene and the mixture was degassed by bubbling argon through the solution for 10 min. After the addition of $PdCl_2(PPh_3)_2$ (253 mg, 0.36 mmol) and pinacolborane (3.16 mL, 21.72 mmol) the mixture was refluxed for 3 h at 120 °C until TLC indicated consumption of the starting material. After cooling down to 100 °C an aqueous solution of Na_2CO_3 (2 M,

4.8 mL, 9.62 mmol) was added very slowly due to sincere gas evolution. Then, 3,4-dibromo-1*H*-pyrrole-2,5-dione **9** (615 mg, 2.41 mmol) was added and the mixture was stirred at 100 °C for 2 h. After cooling down to room temperature the mixture was extracted with ethyl acetate and the combined organic layers where washed with brine and dried over $MgSO_4$. Purification by column chromatography (petroleum ether/ethyl acetate 9:1 → 2:1) yielded **2a** (149 mg, 0.21 mmol, 9 %) as a yellow solid.

^{1}H-NMR: δ(ppm) = 8.40 (s, 1 H, N*H*), 8.02 (d, ^{3}J(H,H) = 8.4 Hz, 4 H, CH_{ar}), 7.82 (d, ^{3}J(H,H) = 8.4 Hz, 4 H, CH_{ar}), 4.31 (t, ^{3}J(H,H) = 6.6 Hz, 4 H, OCH_2), 2.33 (s, 6 H, CH_3), 1.80 – 1.70 (m, 4 H, CH_2), 1.47 – 1.29 (m, 12 H, CH_2), 0.89 (t, ^{3}J(H,H) = 6.9 Hz, 6 H, CH_3). **^{13}C-NMR:** δ(ppm) = 169.3, 166.1, 164.2, 141.8, 138.5, 136.8, 135.7, 131.7, 130.3, 126.3, 65.5, 31.5, 28.7, 25.8, 22.6, 14.1, 12.9. **HRMS (ESI$^+$):** *m/z* = 700.238 (calcd. 700.252 for $C_{38}H_{42}N_3O_6S_2^+$). **UPLC:** See appendix.

Isolation of closed form 2b. A solution of **2a** (149 mg, 0.21 mmol) in 300 mL of dichloromethane was irradiated over a period of 25 min. After evaporating the solvent the mixture of open and closed form was separated by column chromatography (dichloromethane/ ethyl acetate 6:1) yielding **2b** (55 mg, 0.08 mmol, 37 %) as a dark solid. In addition, 61 % of mixed fractions of **2a** and **2b** were obtained.

^{1}H-NMR: δ(ppm) = 8.15 (m, 8 H, CH_{ar}), 8.07 (s, 1 H, N*H*), 4.36 (t, ^{3}J(H,H) = 6.6 Hz, 4 H, OCH_2), 2.03 (s, 6 H, CH_3), 1.84 – 1.75 (m, 4 H, CH_2), 1.48 – 1.35 (m, 12 H, CH_2), 0.91 (t, ^{3}J(H,H) = 6.9 Hz, 6 H, CH_3). **^{13}C-NMR:** δ(ppm) = 181.8, 165.7, 163.3, 161.5, 135.8, 135.1, 130.1, 129.6, 114.7, 70.6, 66.0, 31.6, 28.7, 26.6, 25.8, 22.7, 14.2. **HRMS (ESI$^+$):** *m/z* = 700.235 (calcd. 700.252 for $C_{38}H_{42}N_3O_6S_2^+$). **UPLC:** See appendix.



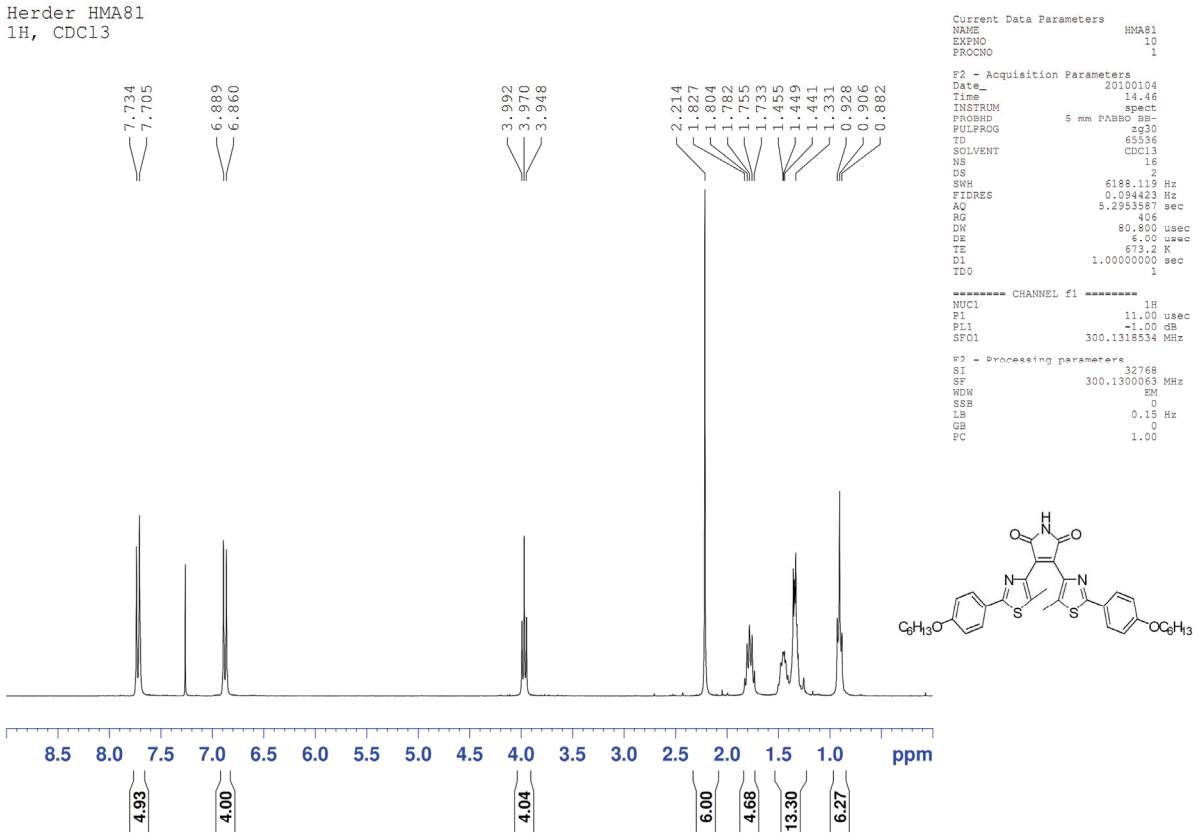
Scheme S3. Synthesis of *N,N*-dihexylmelamine receptor **3**.

2,4-Diamino-6-*N,N*-di-*n*-hexylamino-1,3,5-triazine (3). Following a procedure by Würthner *et al.*[11] 4,5-diamino-2-chloro-1,3,5-triazine **13** (8.09 g, 50.0 mmol) was suspended together with $NaHCO_3$ (4.65 g, 55.0 mmol) and di-*n*-hexylamine (12.74 mL, 55 mmol) in 200 mL of DMF. The mixture was refluxed at 140 °C for 7 h. After cooling it was poured into 500 mL of water and the resulting suspension was extracted with 6 x 100 mL dichloromethane. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by recrystallization from acetonitrile and subsequent washing with cold diethylether to afford **3** (10.57 g, 36 mmol, 72 %) as colourless crystals.

^{1}H-NMR: δ(ppm) = 4.64 (br, 4 H, NH_2), 3.43 (t, ^{3}J(H,H) = 7.5 Hz, 4 H, NCH_2), 1.59 – 1.48 (m, 4 H, CH_2), 1.36 – 1.24 (m, 12 H, CH_2), 0.89 (t, ^{3}J(H,H) = 6.5 Hz, 6 H, CH_3). **^{13}C-NMR:** δ(ppm) = 167.2, 165.7, 46.7, 31.8, 27.9, 26.8, 22.8, 14.2. **HRMS (ESI$^+$):** *m/z* = 295.252 (calcd. 295.261 for $C_{15}H_{31}N_6^+$). **UPLC:** See appendix.

[9] F. Würthner, C. Thalacker, A. Sautter, W. Schärtl, W. Ibach, O. Hollricher, *Chem. Eur. J.*, **2000**, *6*, 3871.

Appendix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7.734
7.705
6.889
6.860
3.992
3.970
3.948
2.214
1.827
1.804
1.782
1.755
1.733
1.455
1.449
1.441
1.331
0.928
0.906
0.882
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.93
4.00
4.04
6.00
4.68
13.30
6.27
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PROCNO 1
F2 - Acquisition Parameters
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Time 14.46
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 406
DW 80.800 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -1.00 dB
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F2 - Processing parameters
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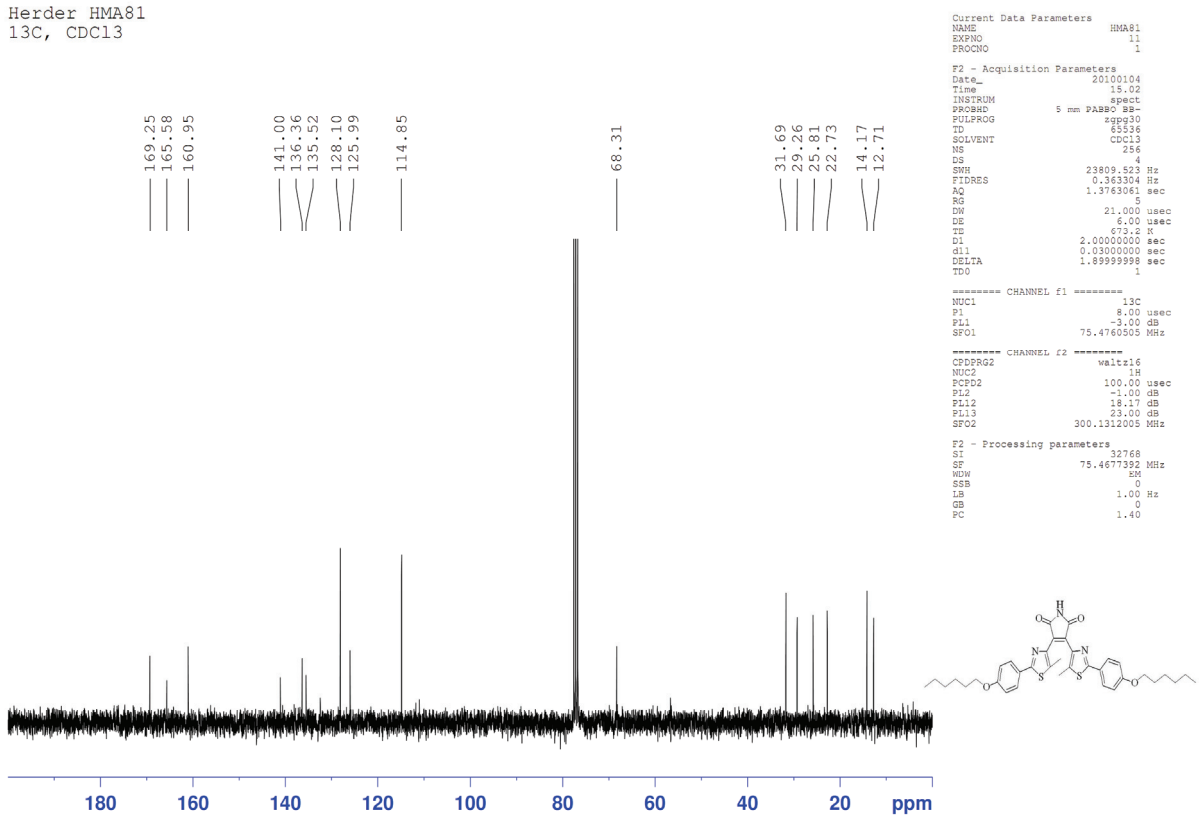
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.15 Hz
GB 0
PC 1.00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13C, CDCl3
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165.58
160.95
141.00
136.36
135.52
128.10
125.99
114.85
68.31
31.69
29.26
25.81
22.73
14.17
12.71
180 160 140 120 100 80 60 40 20 ppm
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EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100104
Time 15.02
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23809.523 Hz
FIDRES 0.363304 Hz
AQ 1.3763061 sec
RG 5
DW 21.000 usec
DE 6.00 usec
TE 673.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.00 dB
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.17 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677392 MHz
WDW EM
SSB 0
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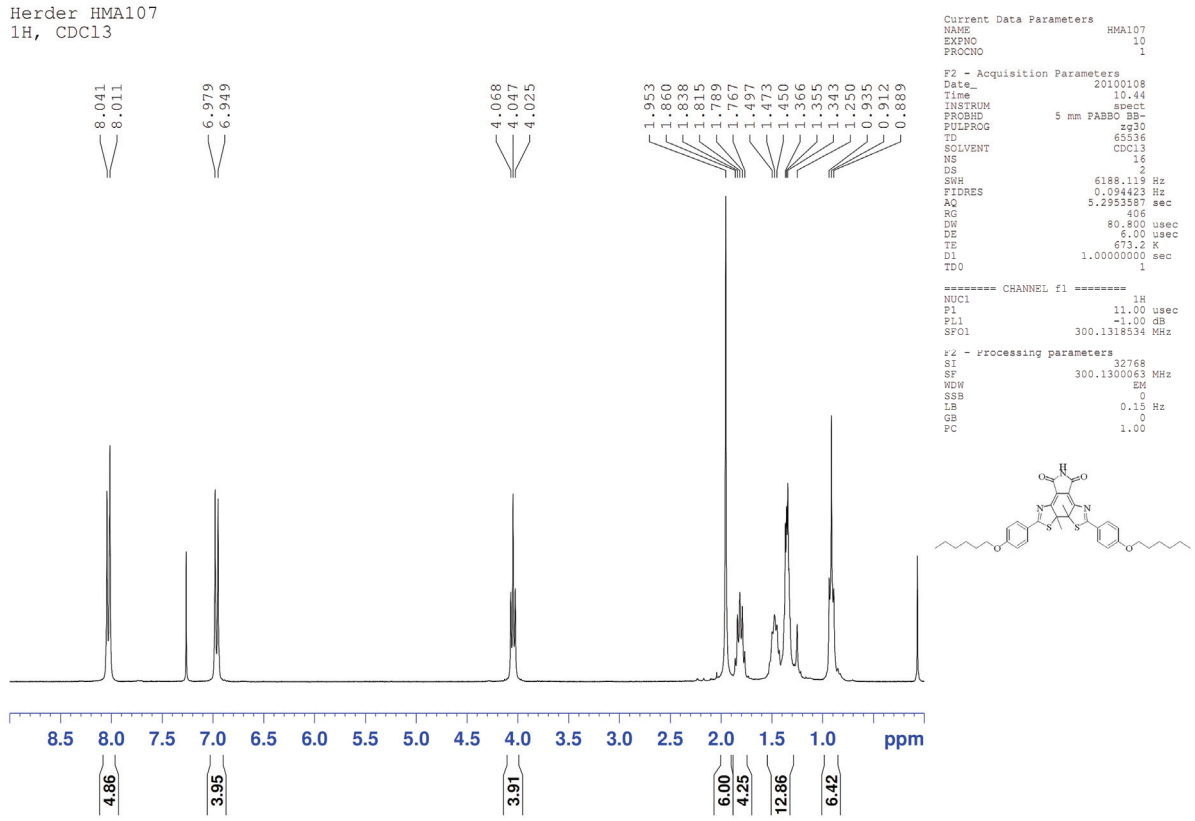
GB 0
PC 1.40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8.011
6.979
6.949
4.068
4.047
4.025
1.953
1.860
1.838
1.815
1.789
1.767
1.497
1.473
1.450
1.366
1.355
1.343
1.250
0.935
0.912
0.889
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.86
3.95
3.91
6.00
4.25
12.86
6.42
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NAME HMA107
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
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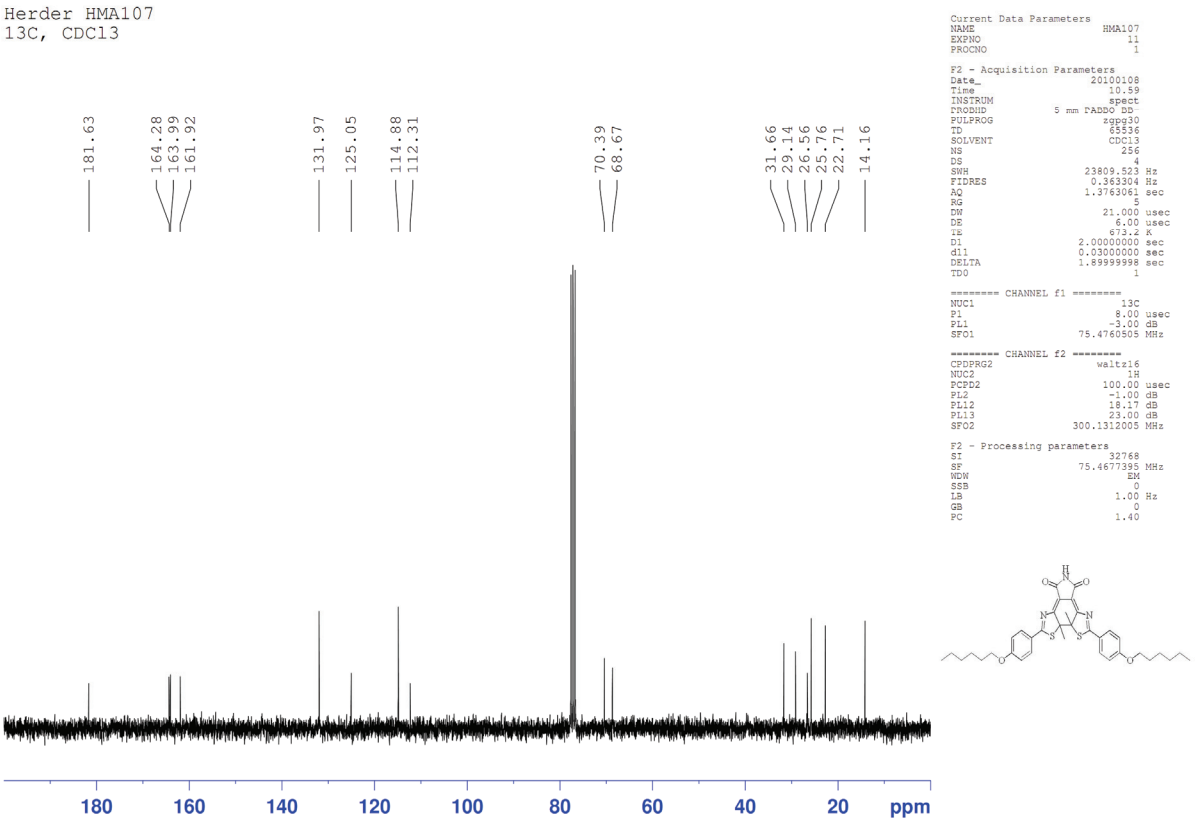
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 406
DW 80.800 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -1.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.15 Hz
GB 0
PC 1.00


Herder HMA107
13C, CDCl3
181.63
164.28
163.99
161.92
131.97
125.05
114.88
112.31
70.39
68.67
31.66
29.14
26.56
25.76
22.71
14.16
180 160 140 120 100 80 60 40 20 ppm
Current Data Parameters
NAME HMA107
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100108
Time 10.59
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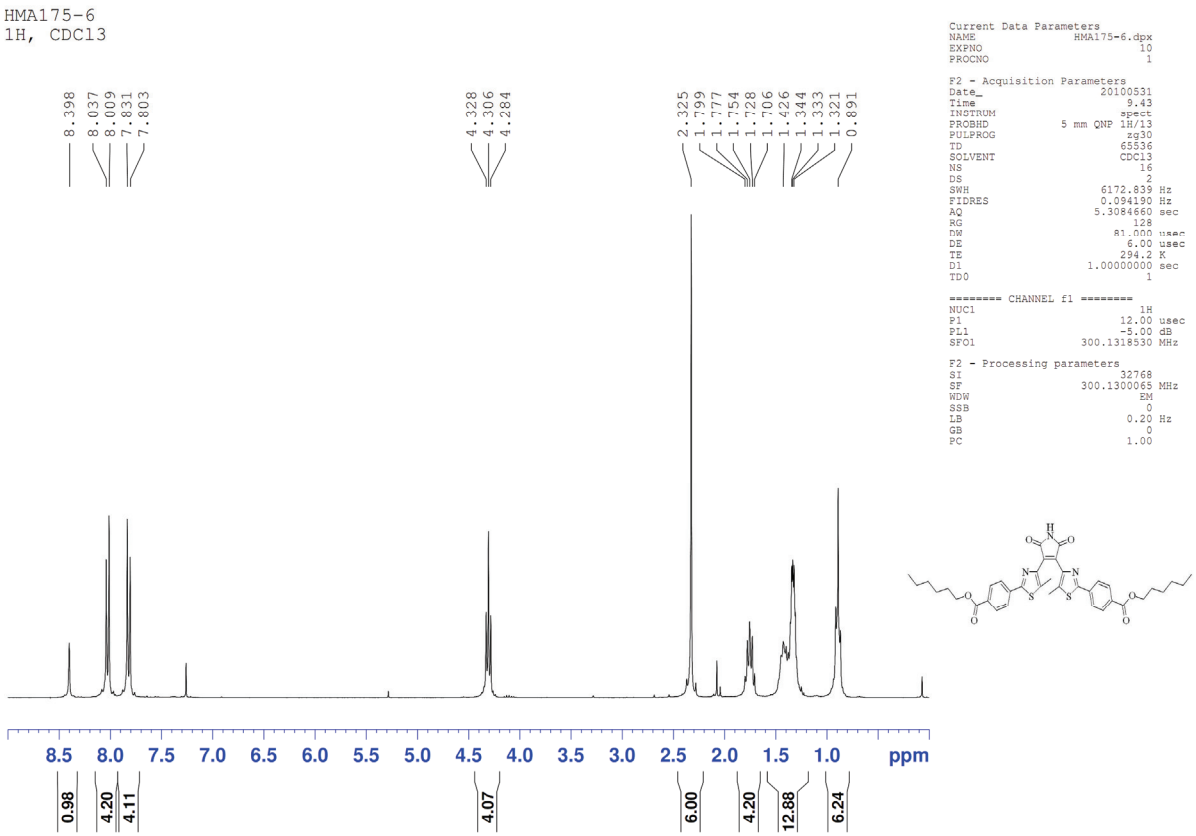
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23809.523 Hz
FIDRES 0.363304 Hz
AQ 1.3763061 sec
RG 8
DW 21.000 usec
DE 6.00 usec
TE 673.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.00 dB
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.17 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677395 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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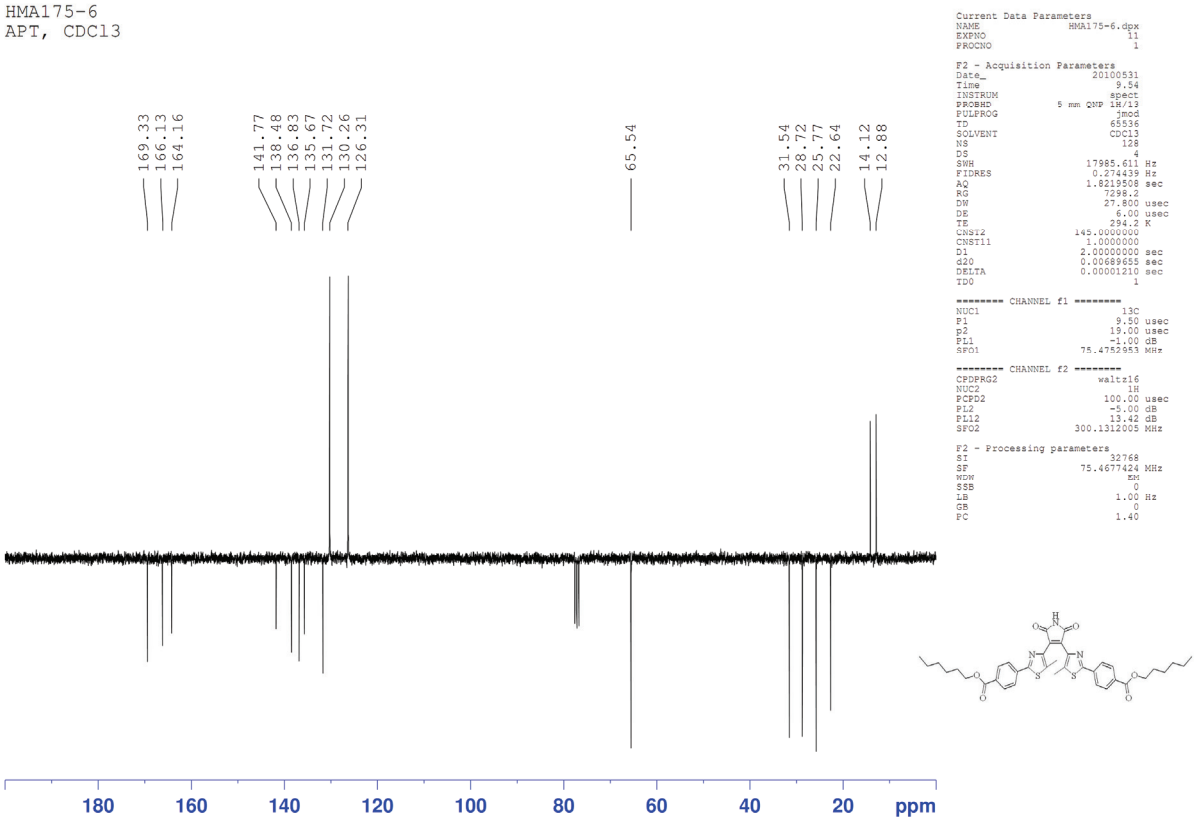
8.398
8.037
8.009
7.831
7.803
4.328
4.306
4.284
2.325
1.799
1.777
1.754
1.728
1.706
1.426
1.344
1.333
1.321
0.891
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.98
4.20
4.11
4.07
6.00
4.20
12.88
6.24
Current Data Parameters
NAME HMA175-6.dpx
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100531
Time 9.43
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 32768
SF 300.1300065 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00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166.13
164.16
141.77
138.48
136.83
135.67
131.72
130.26
126.31
65.54
31.54
28.72
25.77
22.64
14.12
12.88
180 160 140 120 100 80 60 40 20 ppm
Current Data Parameters
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EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
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Time 9.54
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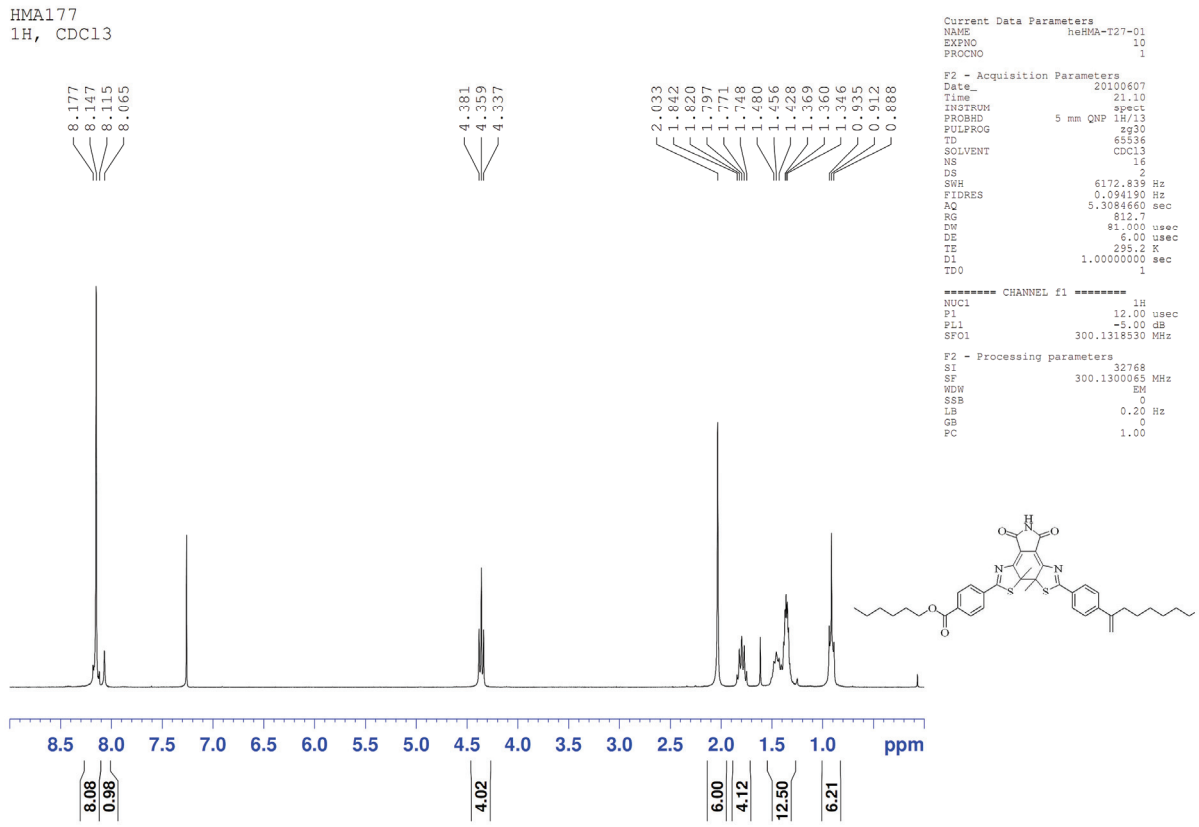
PULPROG jmod
TD 65536
SOLVENT CDC13
NS 128
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 7298.2
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
CNST12 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001210 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
p2 19.00 usec
PL1 -1.09 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -5.00 dB
PL12 13.42 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677424 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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1H, CDC13
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8.147
8.115
8.065
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4.359
4.337
2.033
1.842
1.820
1.797
1.771
1.748
1.480
1.456
1.428
1.369
1.360
1.346
0.935
0.912
0.888
Current Data Parameters
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EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100607
Time 21.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 812.7
DW 81.000 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 32768
SF 300.1300065 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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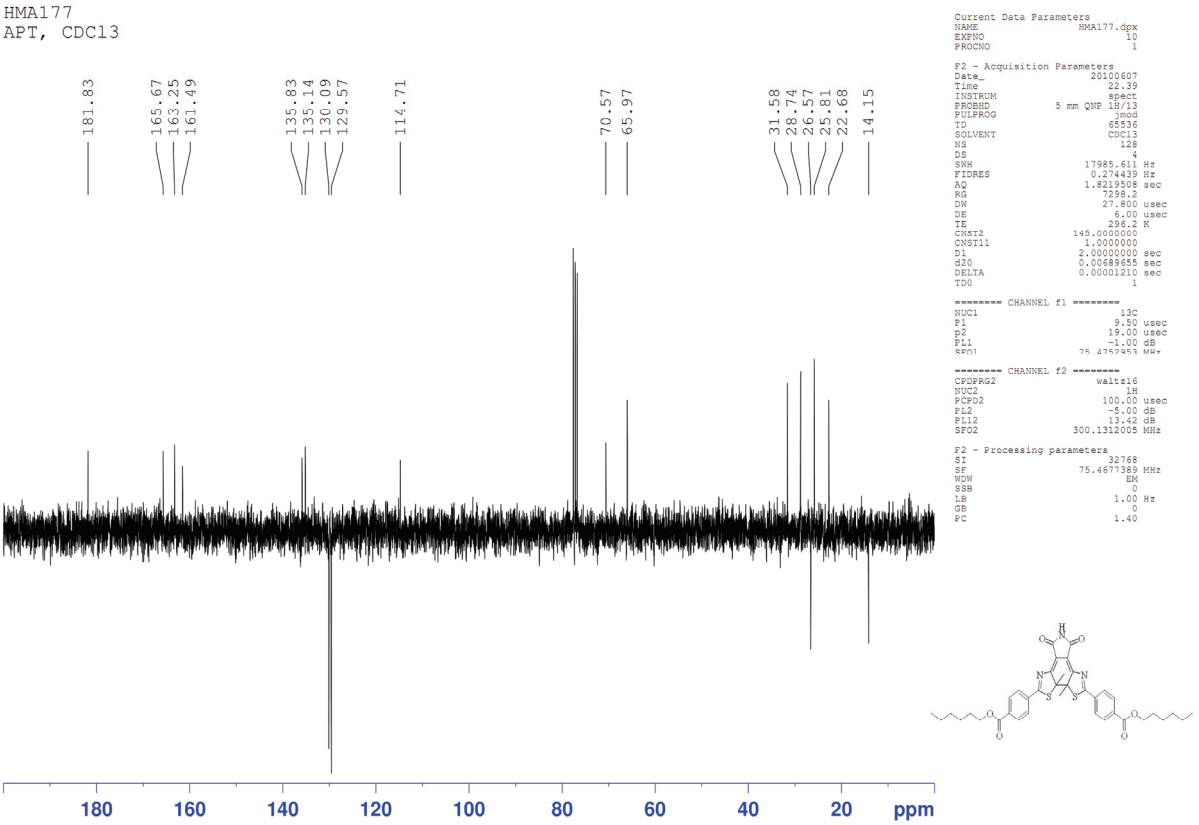
0.98
4.02
6.00
4.12
12.50
6.21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APT, CDC13
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165.67
163.25
161.49
135.83
135.14
130.09
129.57
114.71
70.57
65.97
31.58
28.74
26.57
25.81
22.68
14.15
Current Data Parameters
NAME HMA177.dpx
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100607
Time 22.39
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG jmod
TD 65536
SOLVENT CDC13
NS 128
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 7298.2
DW 27.800 usec
DE 6.00 usec
TE 296.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001210 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
p2 19.00 usec
PL1 -1.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -5.00 dB
PL12 13.42 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
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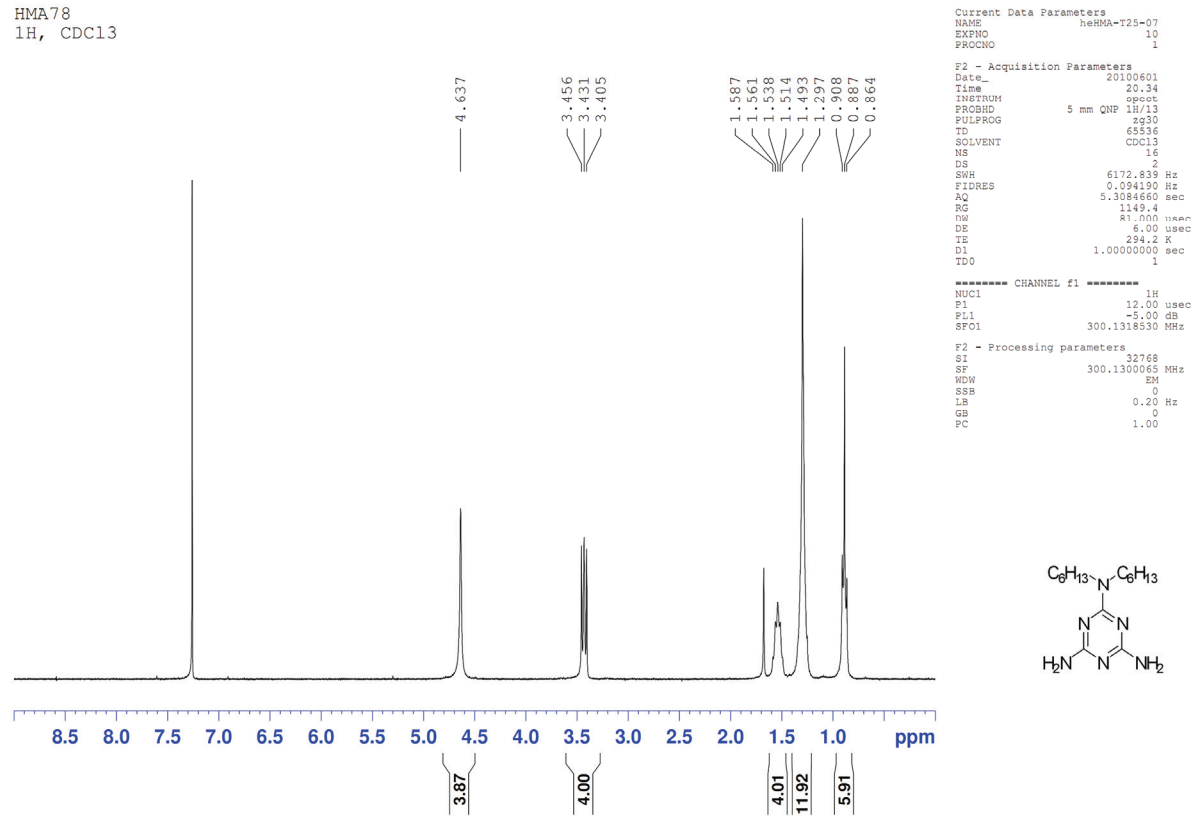
SF 75.4677389 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 160 140 120 100 80 60 40 20 ppm

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PROCNO                           1

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Time                         20.34
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PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                    6172.839 Hz
FIDRES                    0.094190 Hz
AQ                     5.3084660 sec
RG                        1149.4
DW                        81.000 usec
DE                         6.00 usec
TE                        294.2 K
D1                  1.00000000 sec
TD0                             1

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NUC1                           1H
P1                         12.00 usec
PL1                        -5.00 dB
SFO1                 300.1318530 MHz

F2 - Processing parameters
SI                          32768
SF                   300.1300065 MHz
WDW                            EM
SSB                             0
LB                         0.20 Hz
GB                              0
PC                           1.00
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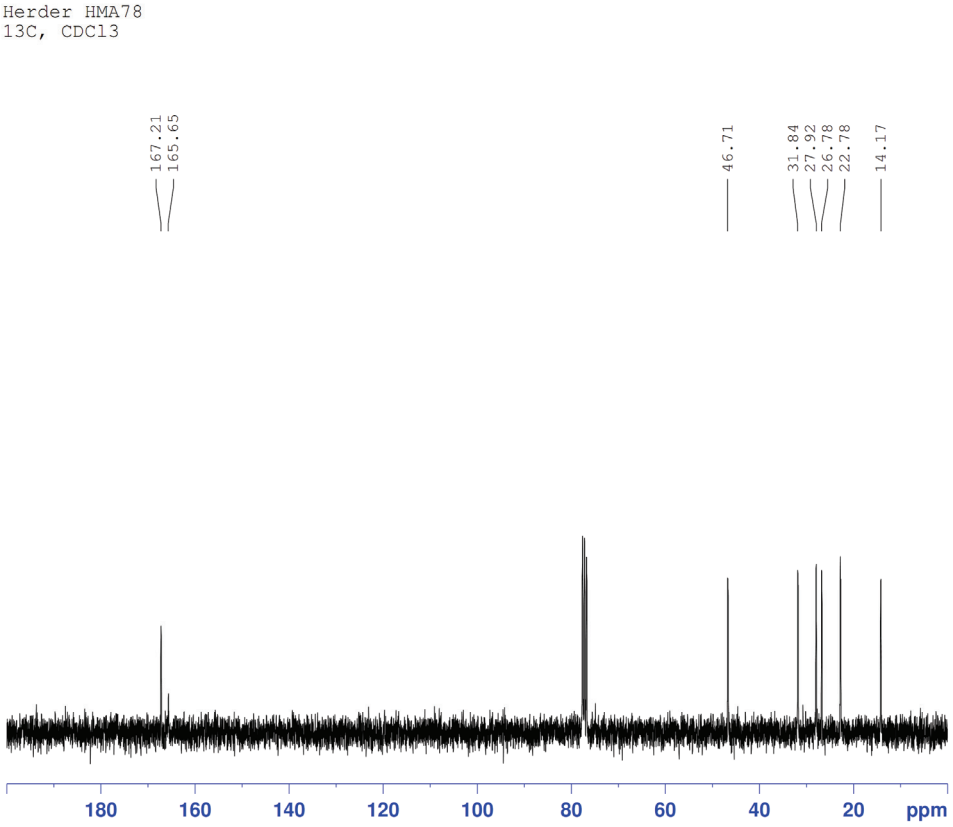


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PROCNO                         1

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PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          256
DS                            4
SWH                  23809.523 Hz
FIDRES                0.363304 Hz
AQ                    1.3763061 sec
RG                            5
DW                       21.000 usec
DE                         6.00 usec
TE                       295.9 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         13C
P1                         8.00 usec
PL1                        -3.00 dB
SFO1                75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                           1H
PCPD2                    100.00 usec
PL2                       -1.00 dB
PL12                      18.17 dB
PL13                      23.00 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
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SF                   75.4677412 MHz
WDW                            EM
SSB                             0
LB                         1.00 Hz
GB                              0
PC                           1.40
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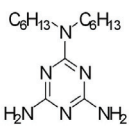

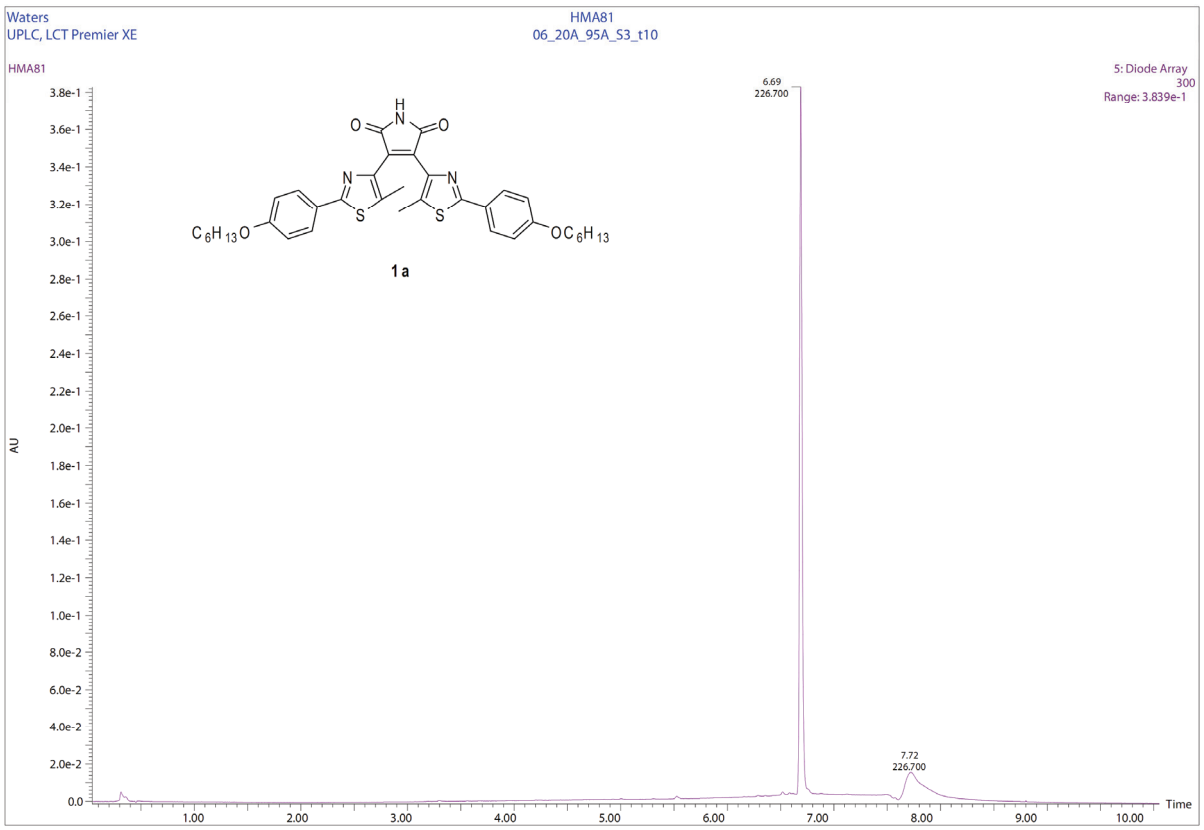
Waters
UPLC, LCT Premier XE
HMA81
06_20A_95A_S3_t10
HMA81
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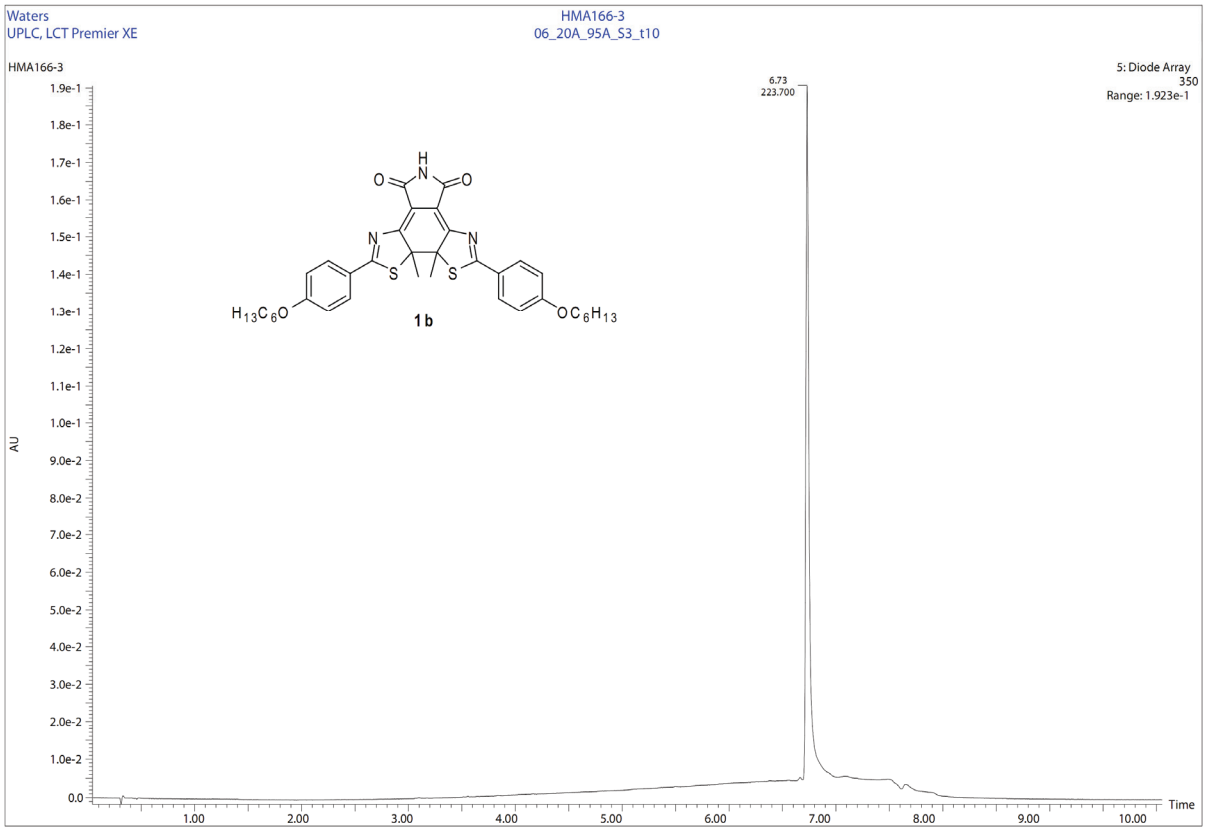
300
Range: 3.839e-1
6.69
226.700
7.72
226.700
AU
Time
1 a


Waters
UPLC, LCT Premier XE
HMA166-3
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HMA166-3
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Range: 1.923e-1
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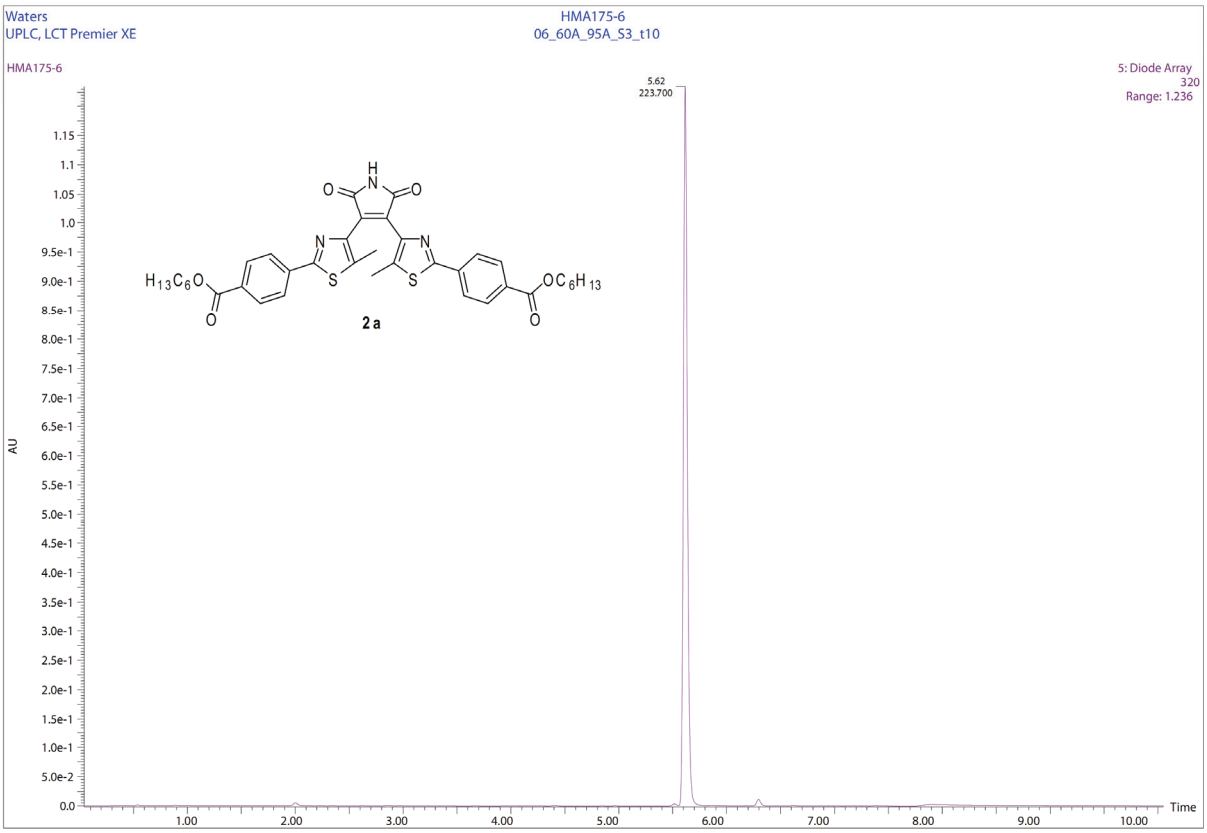
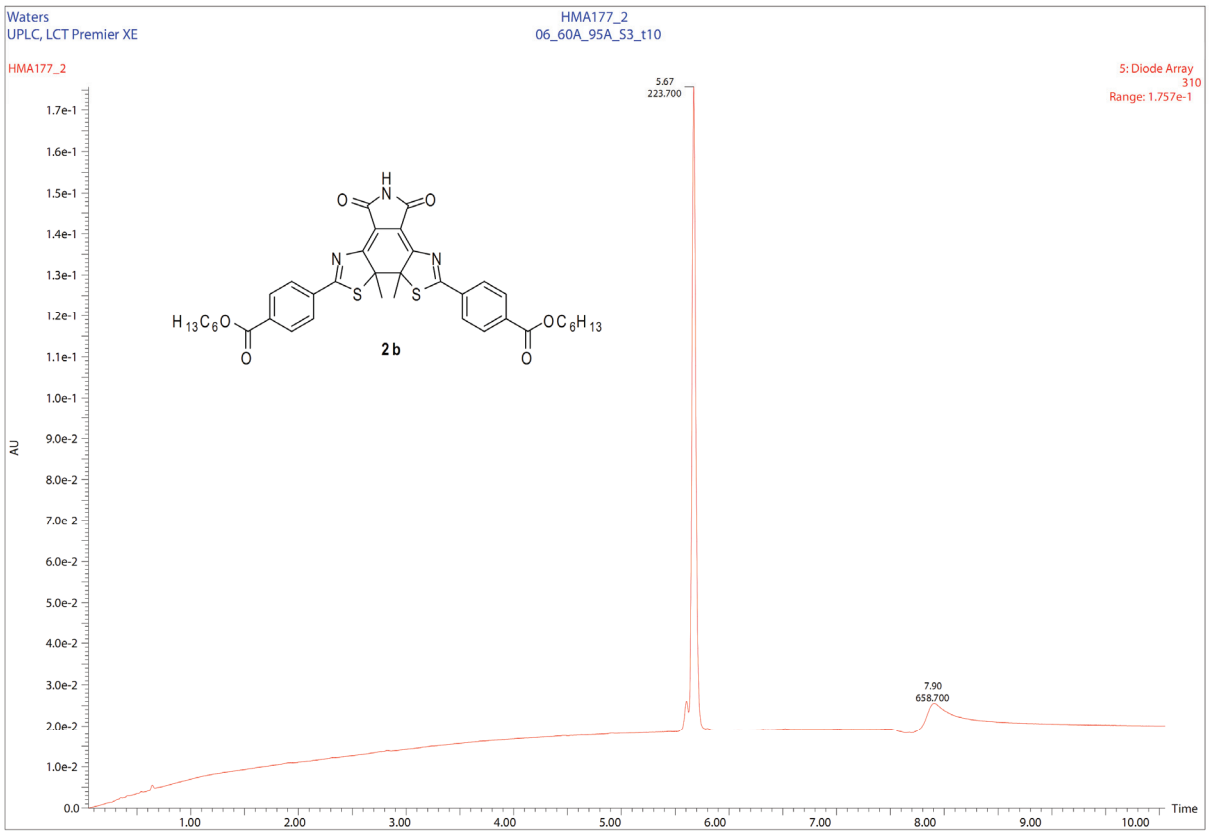
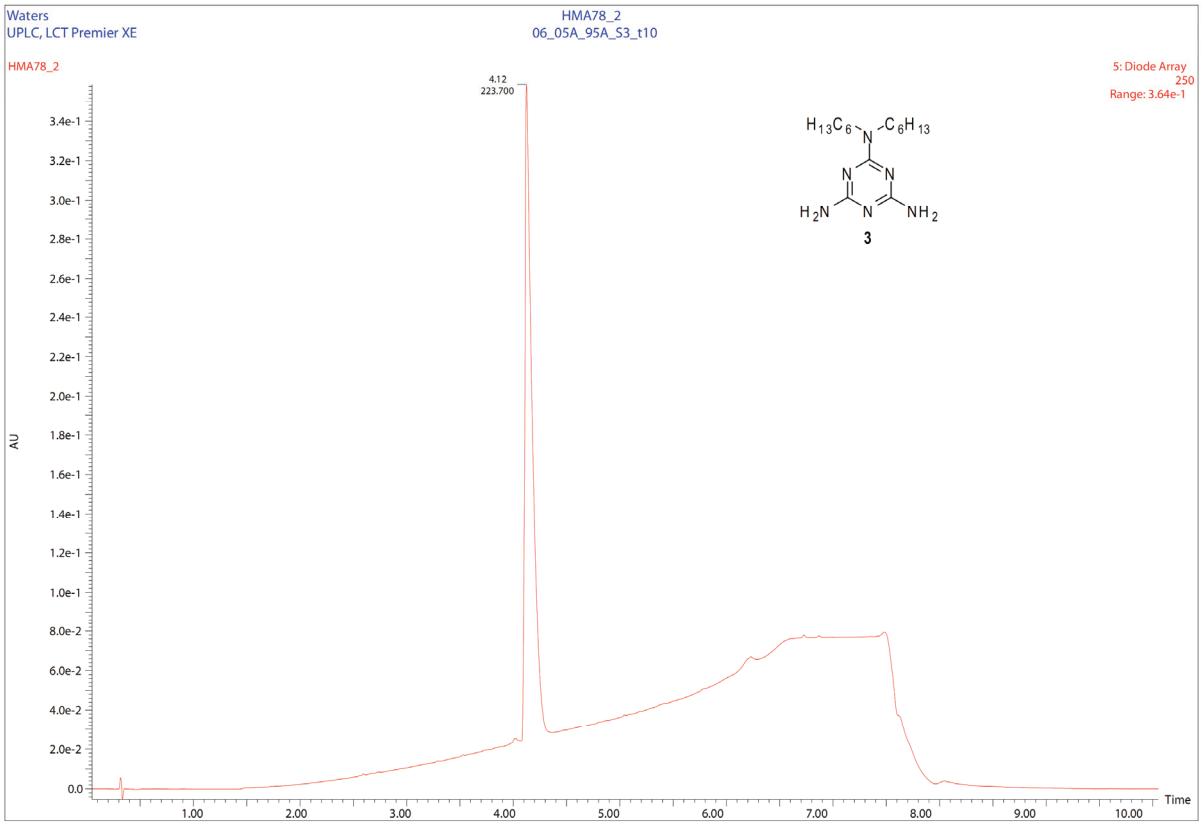
AU
Time
1 b


Waters
UPLC, LCT Premier XE
HMA175-6
06_60A_95A_S3_t10
HMA175-6
5: Diode Array
320
Range: 1.236
5.62
223.700
AU
Time
2a


Waters
UPLC, LCT Premier XE
HMA177_2
06_60A_95A_S3_t10
HMA177_2
5: Diode Array
310
Range: 1.757e-1
5.67
223.700
7.90
658.700
AU
Time
2b


Waters
UPLC, LCT Premier XE
HMA78_2
06_05A_95A_S3_t10
HMA78_2
5: Diode Array
250
Range: 3.64e-1
4.12
223.700
AU
Time
3
H13C6
C6H13
H2N
NH2