Synthesis and 2D self-assembly at the liquid-solid interface of novel H-bonding linear π-conjugated oligomers terminated by uracil and melamine units†

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Electronic Supplementary Information (ESI)

† Electronic Supplementary Information (ESI) available: synthetic details of the preparation of the precursors toward GR1, GR2 and GR3; ^{1}H NMR spectra; MALDI TOF mass spectra; UV-visible and photoluminescence spectra. See DOI: 10.1039/b000000x/

1-Hexyluracil (1)

To a suspension of uracil (5.6 g, 49.9 mmol) in DMSO (50 mL), K2CO3 (8 g, 57.9 mmol) was added, and the suspension was stirred for 20 min. 1-Bromohexane (7 mL, 55.0 mmol) was added and the reaction mixture stirred for 20 h at 40 °C. The suspension was diluted with CHCl3, washed with 0.1 M HCl solution (30 mL × 3), H2O (30 mL × 2), and brine (50 mL), and dried over MgSO4. The organic layer was concentrated and poured into cold hexane with vigorous stirring. The resulting precipitate was filtered and washed with cold hexane to afford compound **1** (4.4 g, 90%) as a white solid.

^{1}H NMR (400 MHz, CDCl3) δ 9.62 (br. s, 1H, NH), 7.15 (d, 1H, J = 8), 5.70 (d, 1H, J = 8), 3.71 (t, 2H, J = 8), 1.67 (m, 2H), 1.30 (m, 6H), 0.87 (m, 3H).

1-Hexyl-6-iodouracil (2)

To a THF solution (55 mL) of 1-hexyluracil 4 (1.7 g, 8.7 mmol), LDA (24 mL of a 1.8 M solution, 43.5 mmol) was added dropwise, and the resulting solution was stirred under argon at -78 °C for 1.5 h. Iodine (11 g, 43.5 mmol) was added and the reaction mixture stirred for 2 h. The solution was then treated with acetic acid (1.2 mL) and allowed to warm to room temperature. The organic phase was diluted with chloroform (30 mL), washed with saturated aqueous sodium bicarbonate solution (30 mL × 3), saturated aqueous sodium sulfite solution (30 mL × 3), and brine (30 mL), and dried over MgSO4. Evaporation of the solvents in vacuo and purification of the crude product by column chromatography (ethyl acetate/hexane 2:3) yielded **2** (2.02 g, 72%) as a white solid.

^{1}H NMR (400 MHz, CDCl3) δ 9.66 (br. s, 1H, NH), 6.41 (s, 1H), 4.04 (t, 2H), 1.66 (m, 2H), 1.33 (m, 6H), 0.89 (m, 3H).

1-Hexyl-6-[(trimethylsilyl)ethynyl]uracil (3)

Dry triethylamine(45 mL) and toluene (45 mL) were added to a round bottomed flask. The solution was degassed under N2 stream for 20 min. Idoduracil derivative **2** (1.22 g, 3.8 mmol), palladium catalyst (0.16 g, 0.23 mmol), and copper iodide (0.1 g, 0.53 mmol) were then added and the solution degassed a second time. Finally, Ethynyltrimethylsilane (2.5 mL, 17.6 mmol) was added, the reaction mixture degassed one last time and the whole mixture stirred overnight at room temperature under N2 atmosphere. The resulting dark mixture was filtered over celite and washed with toluene (50 mL). Removal of the solvents under vacuum and purification of the crude product by column chromatography (ethyl acetate/hexane 2:3) yielded an intermediate. The intermediate (1.108 g, 3.79mmol) and aqueous potassium hydroxide (1.0 M) were added to methanol (50 mL). The reaction mixture was stirred overnight at room temperature under N2 which yielded **3** (0.66 g, 60%) as a brown solid.

^{1}H NMR (400 MHz, CDCl3) δ 10.03 (br. s, 1H, NH), 5.98 (s, 1H), 3.95 (t, 2H, J = 8), 3.68 (s, 1H), 1.67(m, 2H), 1.30(m, 6H), 0.86 (t, 3H).

1,1′-hexyl-6,6′-[(1,4-bis(dodecyloxy)-2,5-phenylene)diethynyl]bisuracil (GR1)

To a degassed solution of dry Triethylamine (20 mL) and THF (20 mL), 1,4-bis(dodecyloxy)-2,5-diiodobenzene (0.77 g, 1.102 mmol), Palladium Catalyst (0.06 g, 0.052 mmol), and copper iodide (0.018 g, 0.095 mmol) were added and the mixture degassed a second time. Ethynyl uracil derivative **3** (0.6 g, 2.72mmol) was then added, and the reaction mixture was degassed one last time and stirred overnight at 85 °C under nitrogen. The mixture was filtered through celite then the solvent was concentrated under vacuum. The precipitate purified by several precipitations from chloroform upon addition methanol, yielding **GR1** (0.97 g, 40.3%) as a yellow solid.

1H NMR (400 MHz, CDCl3) δ 8.36 (br. s, 2H, NH), 6.97 (s, 2H), 5.99 (d, 2H, J = 4), 4.10 (t, 4H), 4.01 (t, 4H) 1.78 (m, 8H), 1.44 (m, 4H), 1.30 (m, 44H), 0.86 (m, 12H). MALDI-TOF MS: m/z = 883.1 [M+] (calcd for $C_{54}H_{82}N_4O_6$=882.62). UV-Vis (CHCl3) λmax=306,320,399 nm.

Biscyano adduct 5

Diiodocompound (1.0 g, 1.43 mmol) 4, 4-cyanophenylboronic ester (0.72 g, 3.15 mmol), 30 mL of THF/water (2:1), and Sodium Carbonate (10 mL, 20 mmol) were mixed in a 100 mL flask and degassed with Nitrogen gas. After 10 minutes Palladium catalyst (0.221 g, 0.315mmol) was added, and the mixture refluxed for 24 h. The mixture was cooled to room temperature, and the organic phase was separated and filtered through Celite. The precipitate was purified by several precipitations by addition of Ethanol, yielding **5** (0.28 g, 30%) as a white solid.

1H NMR (400 MHz, DMSO-d6) δ 8.30 (d, 4H, J = 8), 7.65 (d, 4H, J = 8), 7.05 (s, 2H), 6.70 (br. s, 8H, NH), 3.95 (t, 4H), 1.62-1.64 (br. m, 4H), 1.19-1.33 (br. m, 44H), 0.82 (t, 6H).

13C NMR (400 MHz, DMSO-d6) δ 166.9, 149.7, 140.5, 129.6, 128.8, 127.2, 115.4, 68.7, 39.5, 31.2, 29.0, 28.9, 28.9, 28.6, 28.5, 25.4, 22.0, 13.8.

Melamine derivative GR2

To a mixture of **5** (300 mg, 0.46 mmol), powdered Potassium Hydroxide (0.143 g, 2.54 mmol) and dicyanodiamide (0.1 g, 2.57 mmol) was added 20 mL of 2-methoxyethanol. The reaction mixture was stirred at 125 °C overnight, and then poured into dichloromethane. The organic layer was washed with water. Ethanol is added to the crude product and **GR2** was afforded as a white solid (0.22 g, 58%).

1H NMR (400 MHz, DMSO-d6) δ 8.30 (d, 8H, NH, J = 8), 7.65 (d, 8H, J = 8), 7.05 (br. s, 4H), 6.70 (br. s, 12H), 3.97-3.94 (br. m, 8H), 1.63 (br. d, 8H, j = 8), 1.33-1.19 (br. m, 84H), 0.82 (t, 12H).

13C NMR (400 MHz, DMSO-d6) δ 166.86, 149.74, 140.51, 129.58, 128.77, 127.22, 115.40, 68.71, 39.50, 31.21, 28.96, 28.93, 28.89, 28.64, 28.53, 25.40, 22.02, 13.79.

Biscyanoadduct 7

Diiodocompound 6 (1.0 g, 2.172 mmol), 4-cyanophenylboronic ester (1.045 g, 4.56 mmol), 30 mL of DME/water (2:1), and Sodium Carbonate (2.12 g, 20 mmol) were mixed in a 100 mL flask and degassed with Nitrogen gas. After 10 min Palladium catalyst (0.152 g, 0.217 mmol) was added and the mixture refluxed for 24 hours. The mixture was cooled to room temperature, and the organic phase was separated and filtered through Celite. The organic filtrate was concentrated Ethanol is added to crystallize **7** (0.39g, 36%) as a white solid.

1H NMR (400 MHz, CDCl3) δ 7.71 (d, 4H, J = 8), 7.44 (d, 4H, J = 8), 7.07 (s, 2H), 2.52-2.48 (br. m, 4H), 1.43-1.14 (br. m, 28H), 0.85-0.82 (br. m, 6H).

13C NMR (400 MHz, CDCl3) δ 146.47, 139.85, 137.63, 131.95, 130.70, 130.01, 118.88, 110.87, 77.32, 77.00, 77.00, 76.68, 32.48, 31.76, 31.33, 29.38, 29.16, 29.07, 22.60, 14.07.

Melamine derivative GR3

To a mixture of **7** (300 mg, 0.594 mmol), powdered Potassium Hydroxide (0.183 g, 3.27 mmol) and dicyanodiamide (0.1 g, 1.189 mmol) was added 20 mL of 2-methoxyethanol. The reaction mixture was stirred at 125 °C overnight, and then poured into Dichloromethane. The organic layer was washed with water. Ethanol is added to the crude product and **GR3** was afforded as a white solid (0.190 g, 50%).

1H NMR (400 MHz, DMSO-d6) δ 8.32 (d, 4H, J = 8), 7.41 (d, 4H, J = 8), 7.12 (s, 2H), 6.72 (br. s, 8H), 2.57 (br. t, 4H), 1.39 (br. d, 4H, J = 8), 1.25-1.10 (br. m, 26H), 0.78 (t, 6H).

13C NMR (101 MHz, DMSO-d6) δ 139.66, 138.37, 136.81, 130.15, 128.68, 127.53, 106.43, 39.50, 31.10, 30.74, 28.77, 28.52, 28.42, 26.68, 21.92, 13.56.

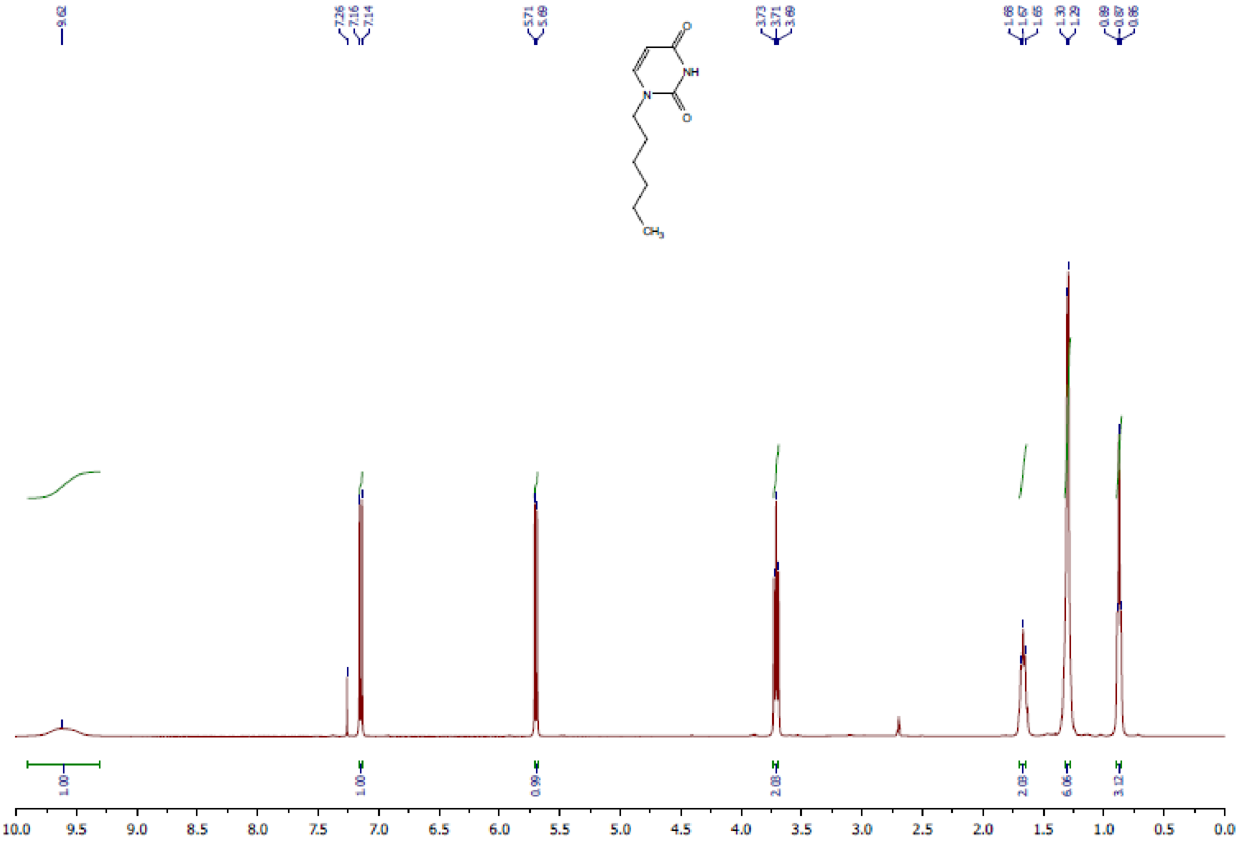


Figure S1 ^{1}H NMR spectrum of compound **1**

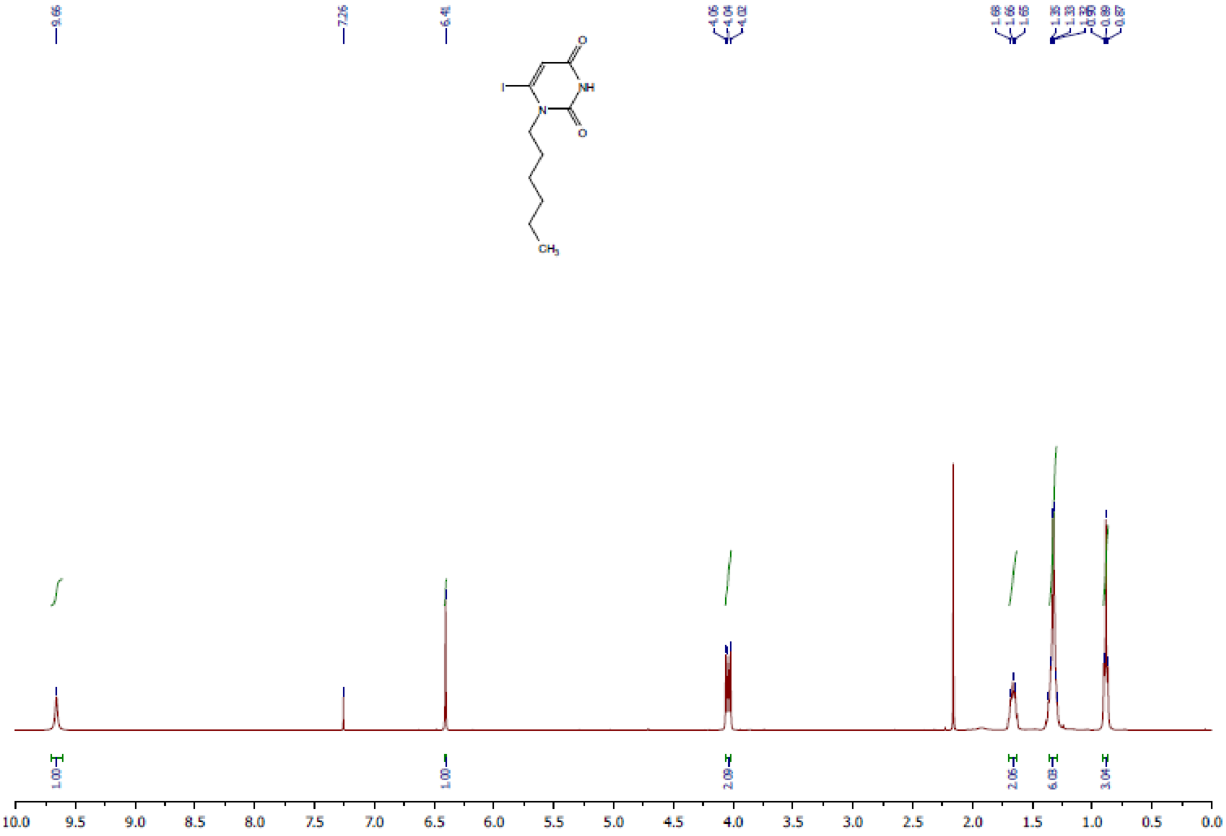


Figure S2 ^{1}H NMR spectrum of compound **2**

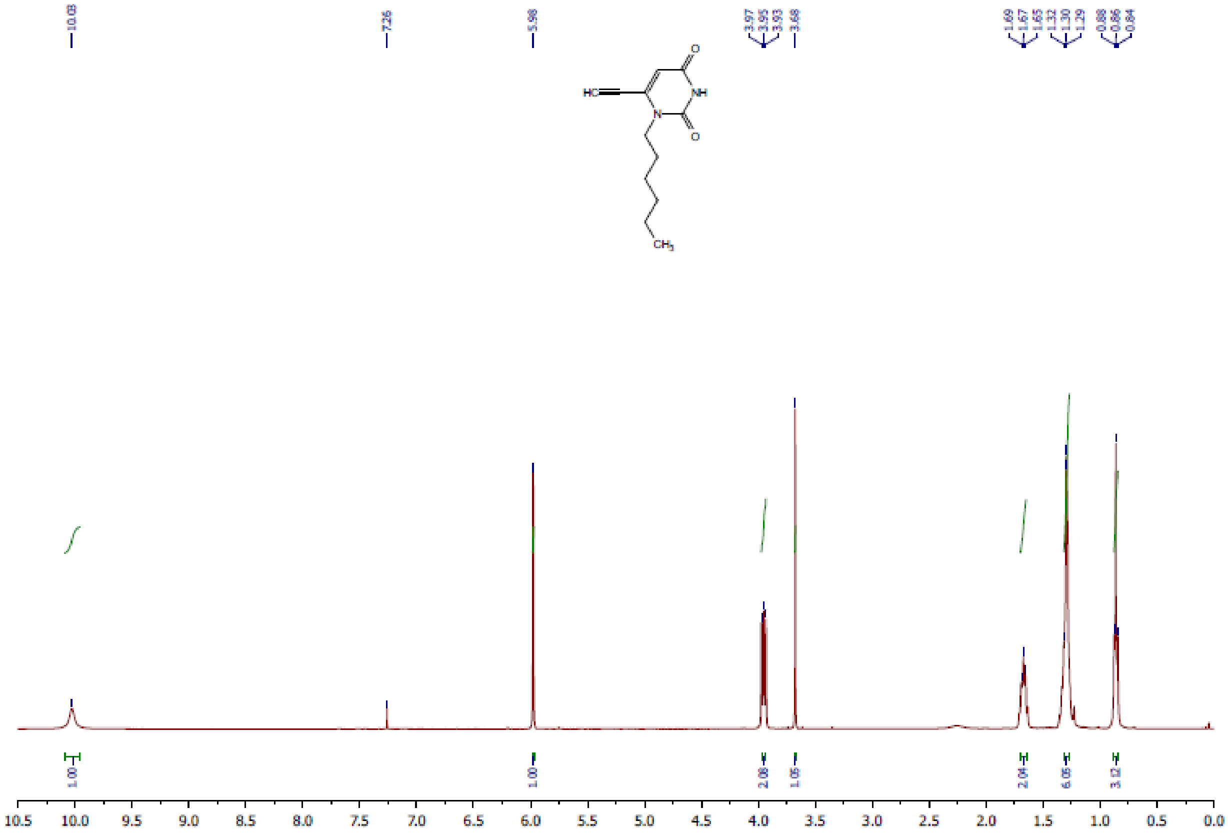


Figure S3 ^{1}H NMR spectrum of compound **3**

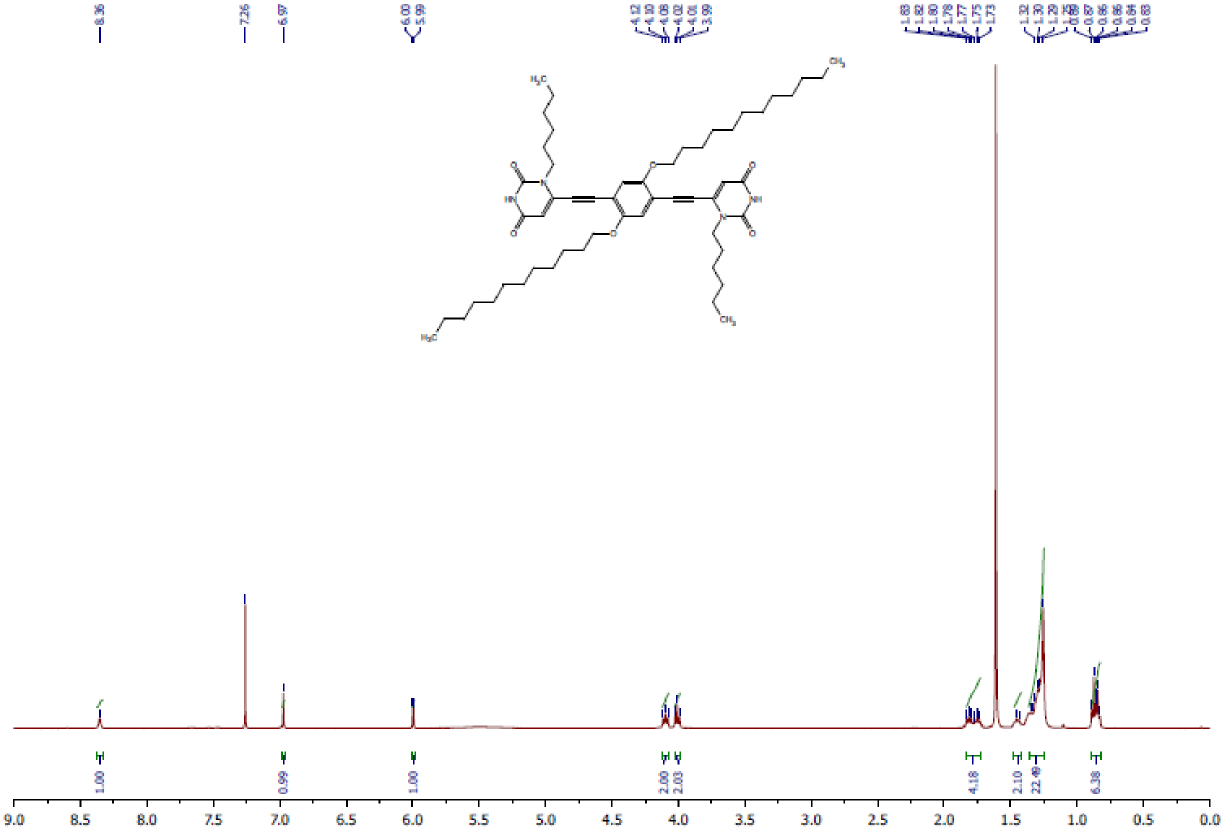
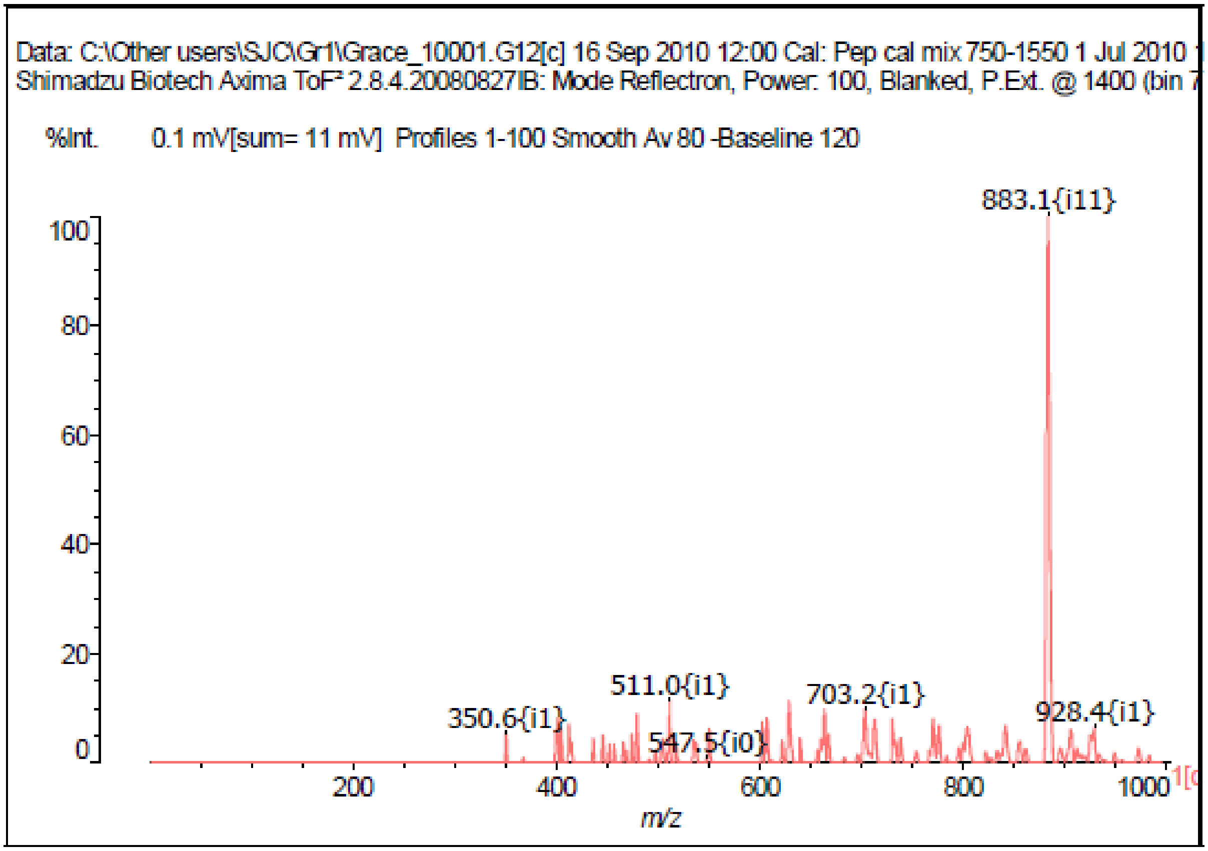


Figure S4 ^{1}H NMR spectrum of the bis(uracil) derivative **GR1**



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Shimadzu Biotech Axima ToF² 2.8.4.20080827IB: Mode Reflectron, Power: 100, Blanked, P.Ext. @ 1400 (bin

Figure S5 MALDI-TOF MS of the bis(uracil) compound **GR1**

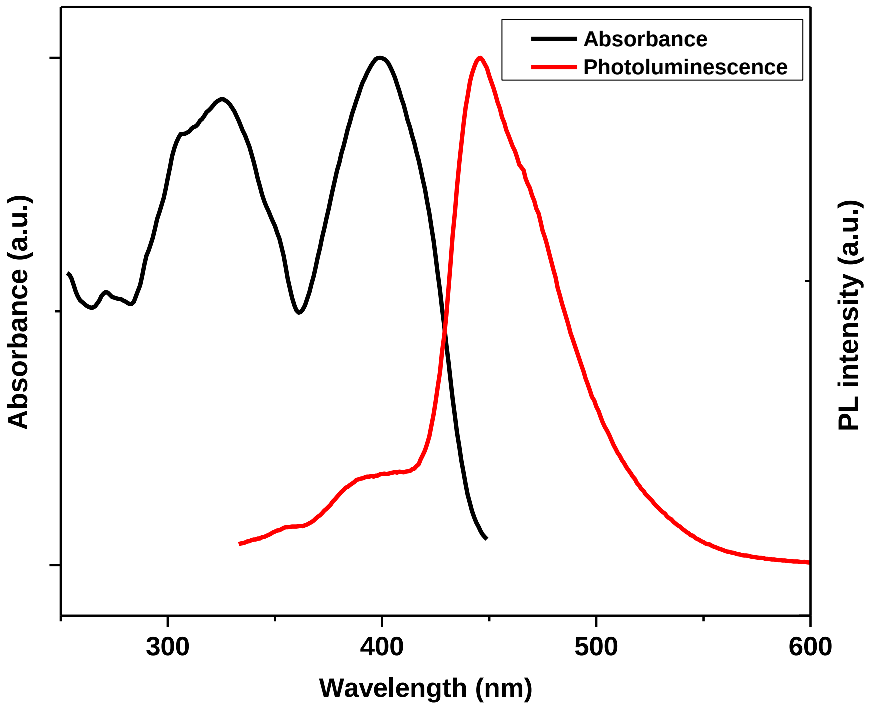

Figure S6 UV-visible absorption and photoluminescence emission spectra of **GR1** in chloroform.

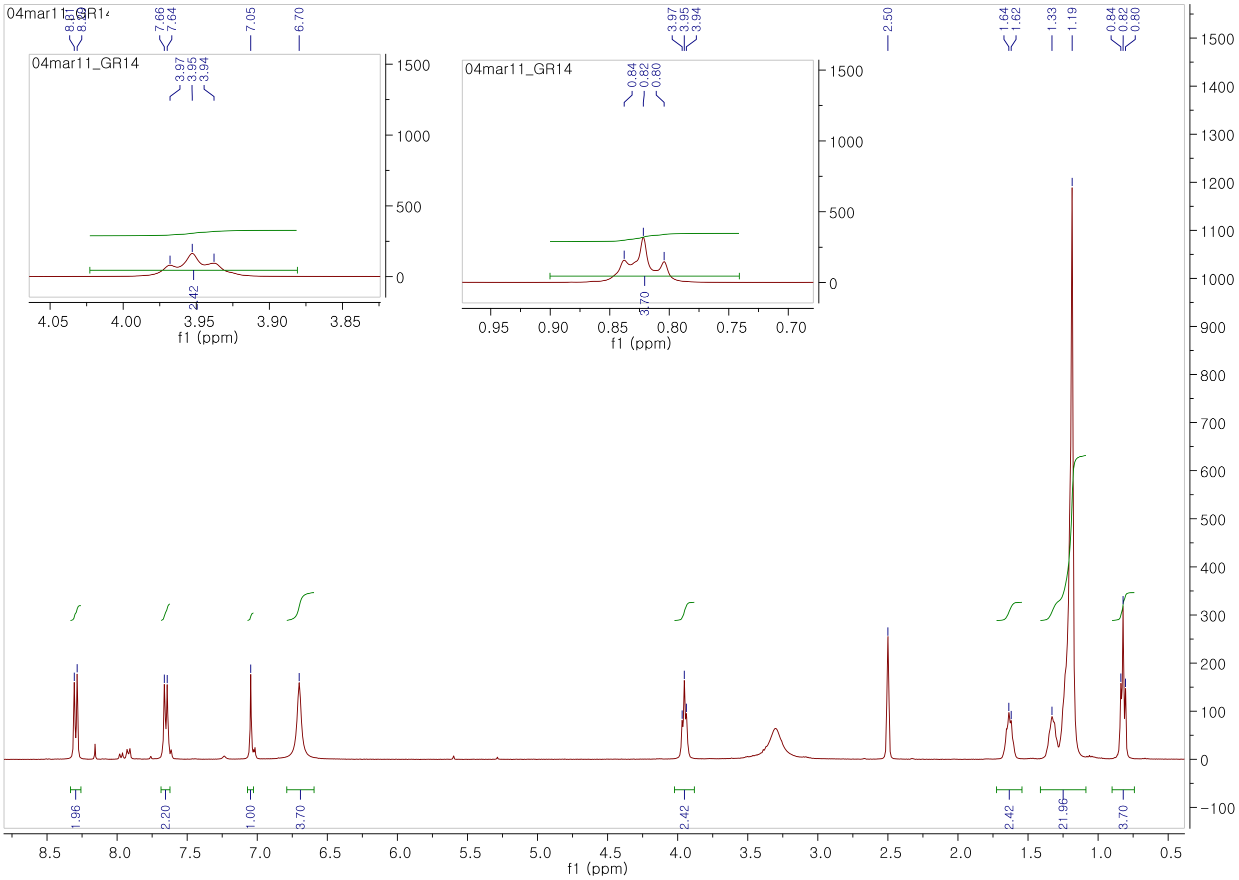

Figure S7 ^{1}H-NMR spectrum of the bis(melamine) compounds **GR2** (R=$OC_{12}H_{25}$)

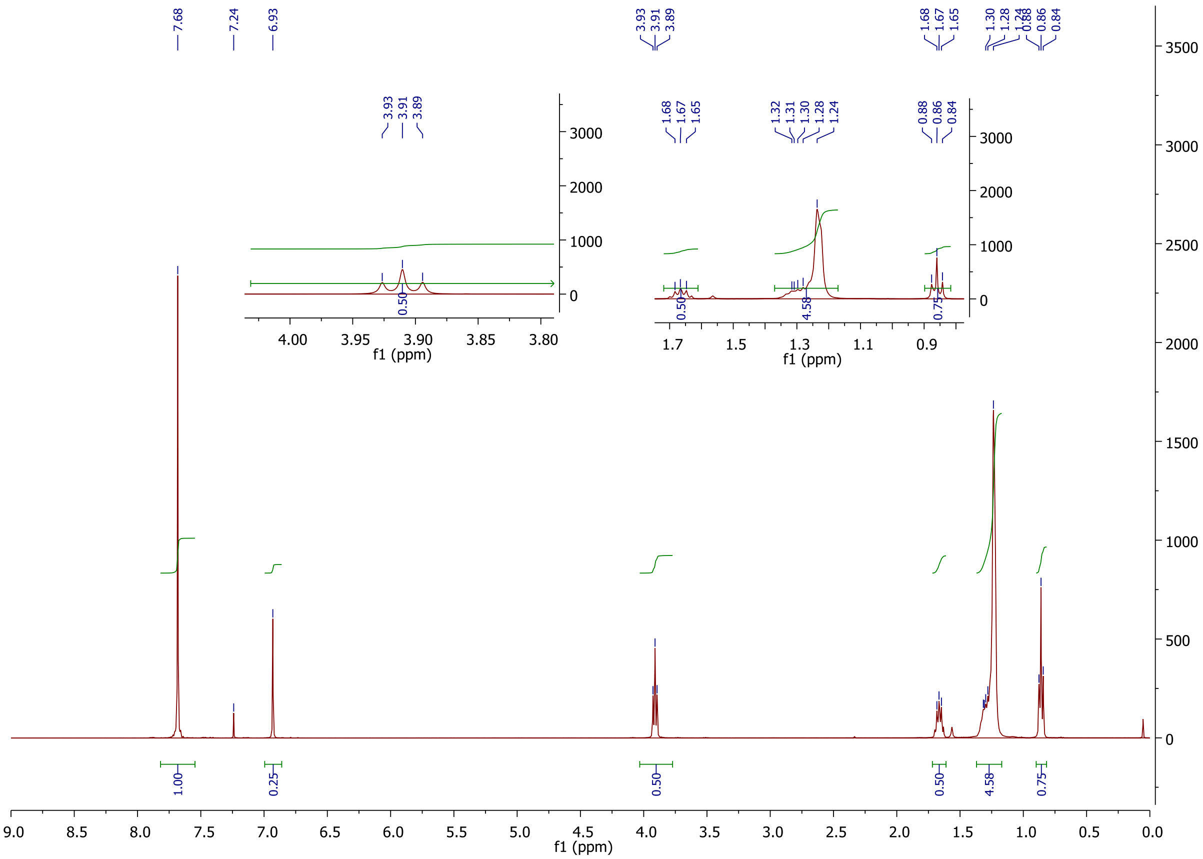

Figure S8 ^{1}H-NMR spectrum of compound **6**

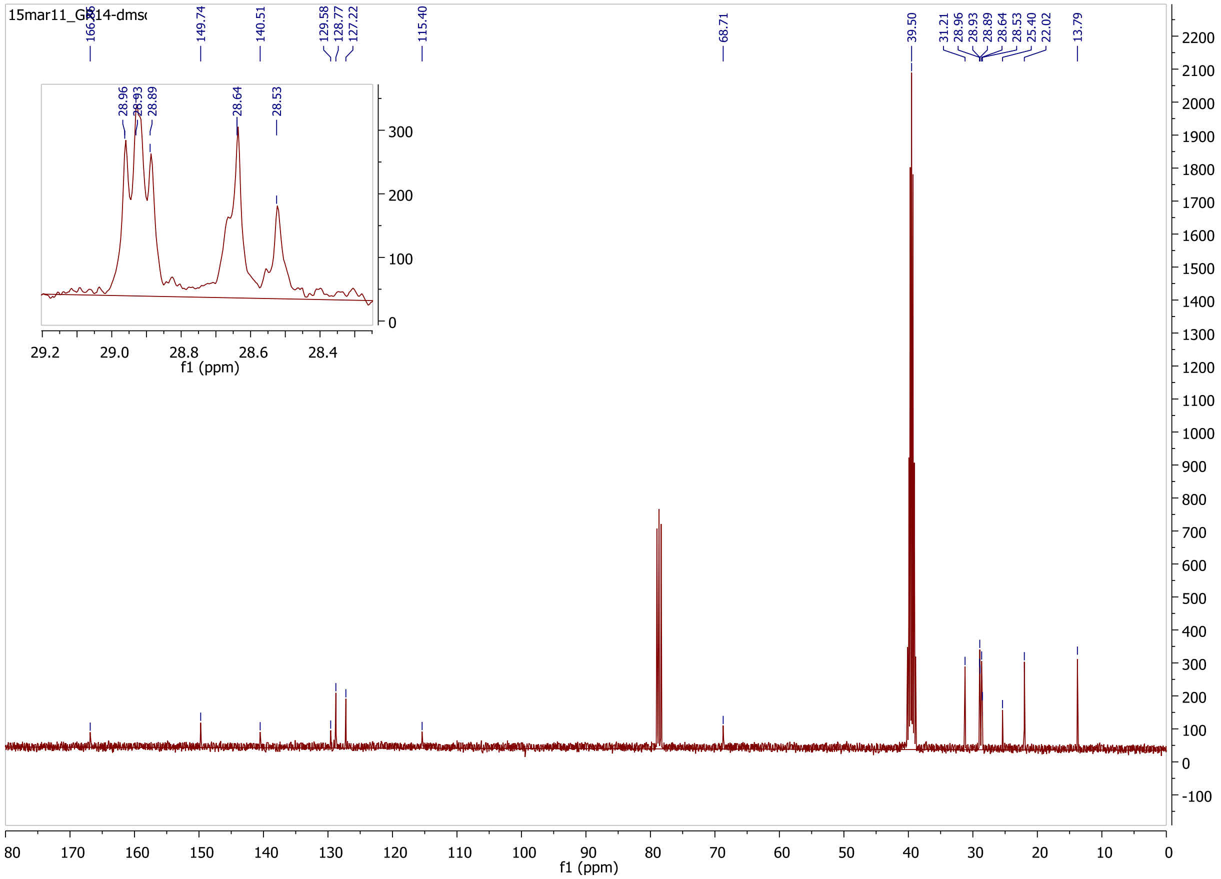

Figure S9 ^{13}C-NMR spectrum of the bis(melamine) derivative **GR2** (R=$OC_{12}H_{25}$)

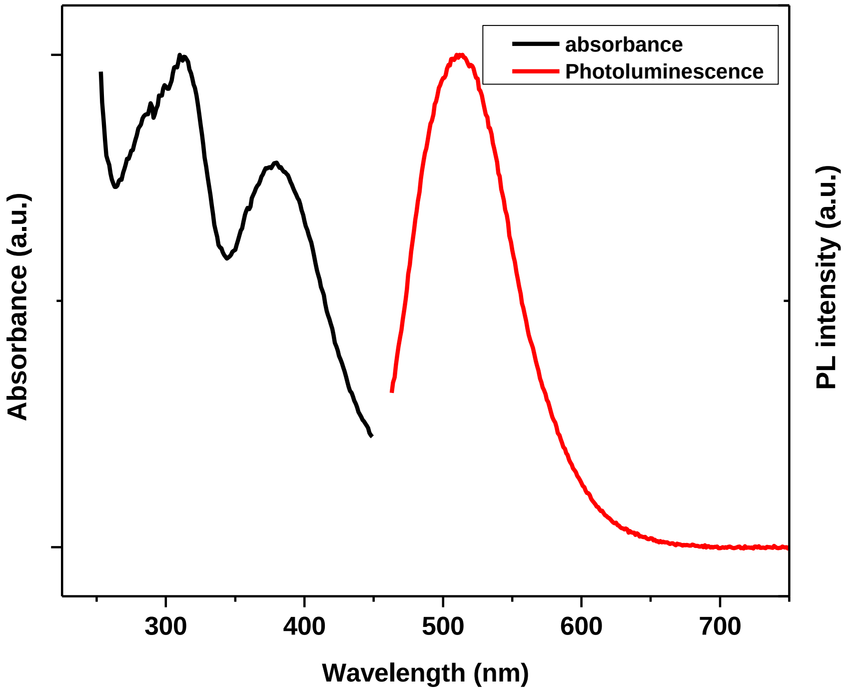

Figure S10 UV-visible absorption and photoluminescence emission spectra of **GR2** in chloroform

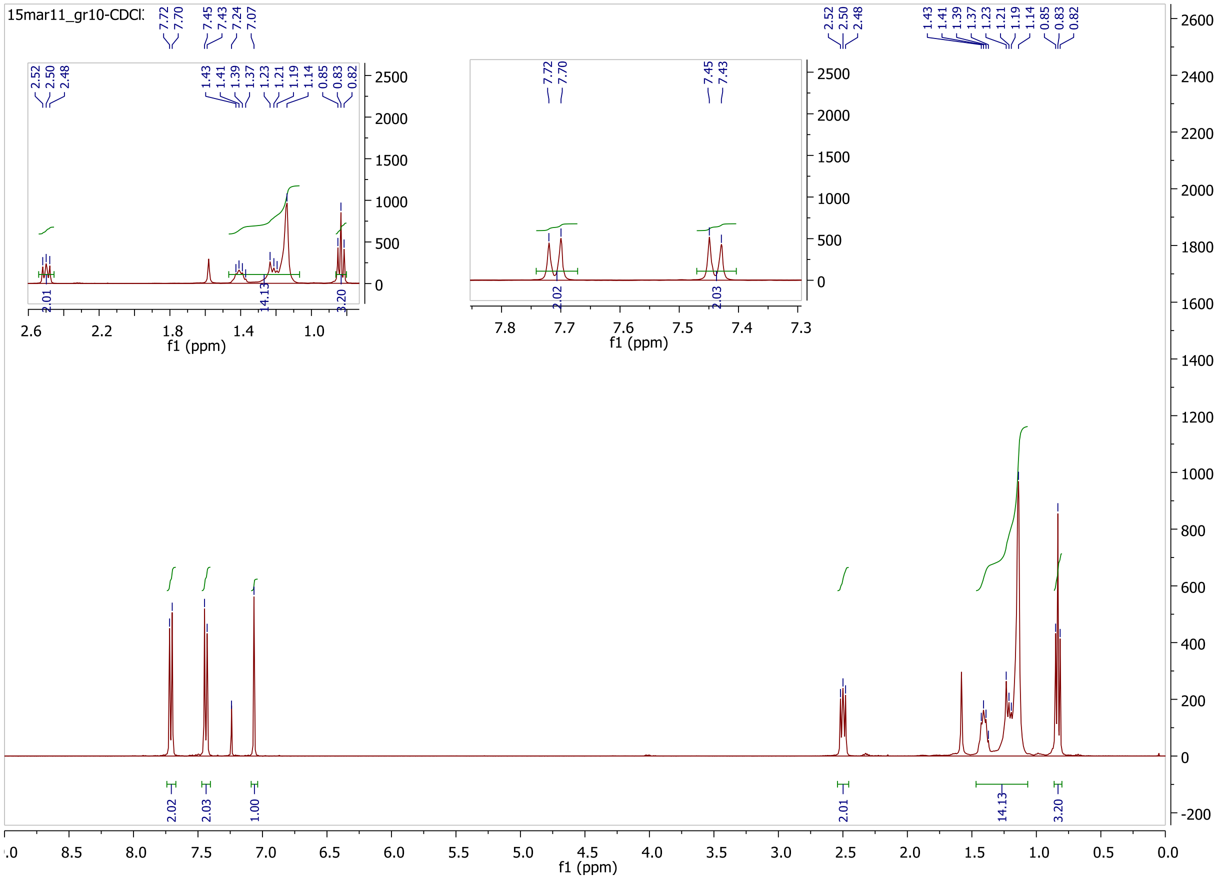

Figure S11 ^{1}H-NMR spectrum of compound **7**

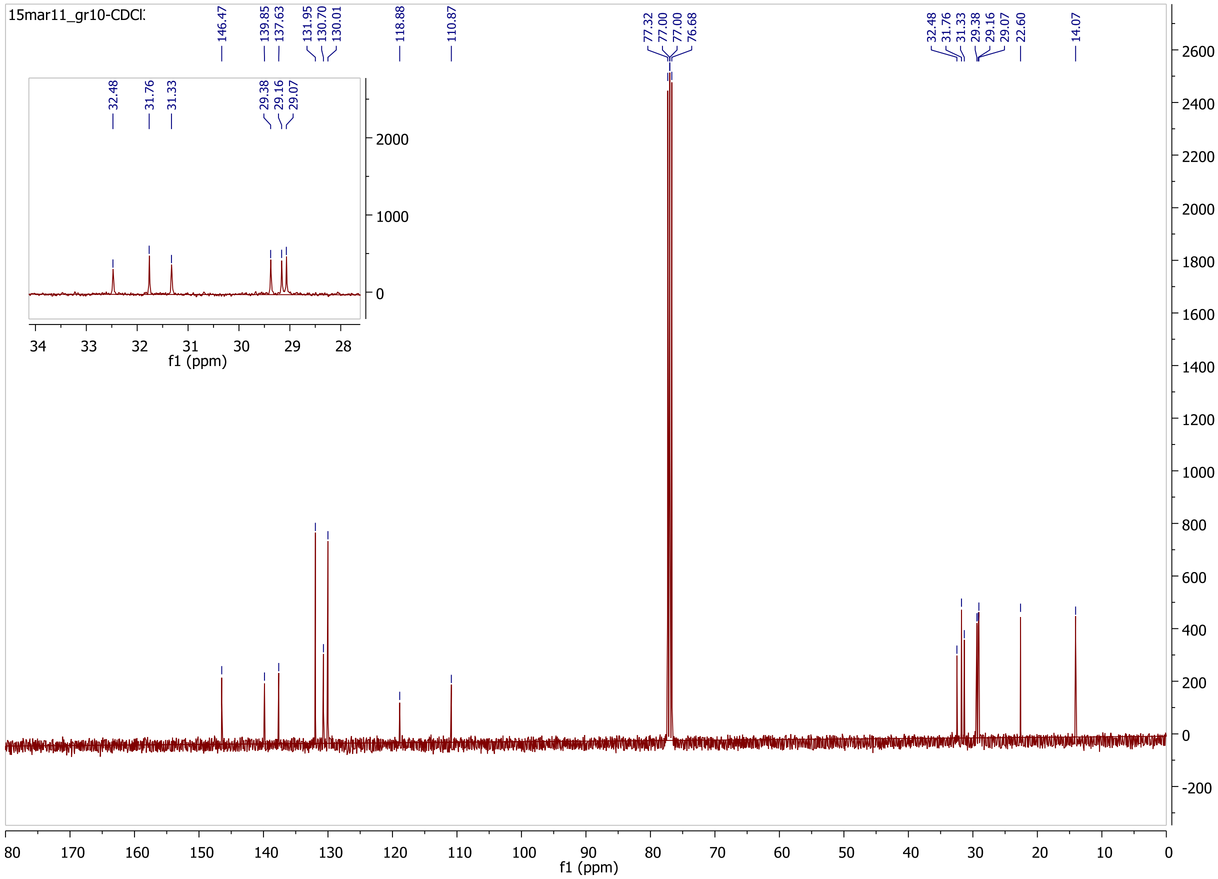

Figure S12 ^{13}C-NMR spectrum of compound **7**

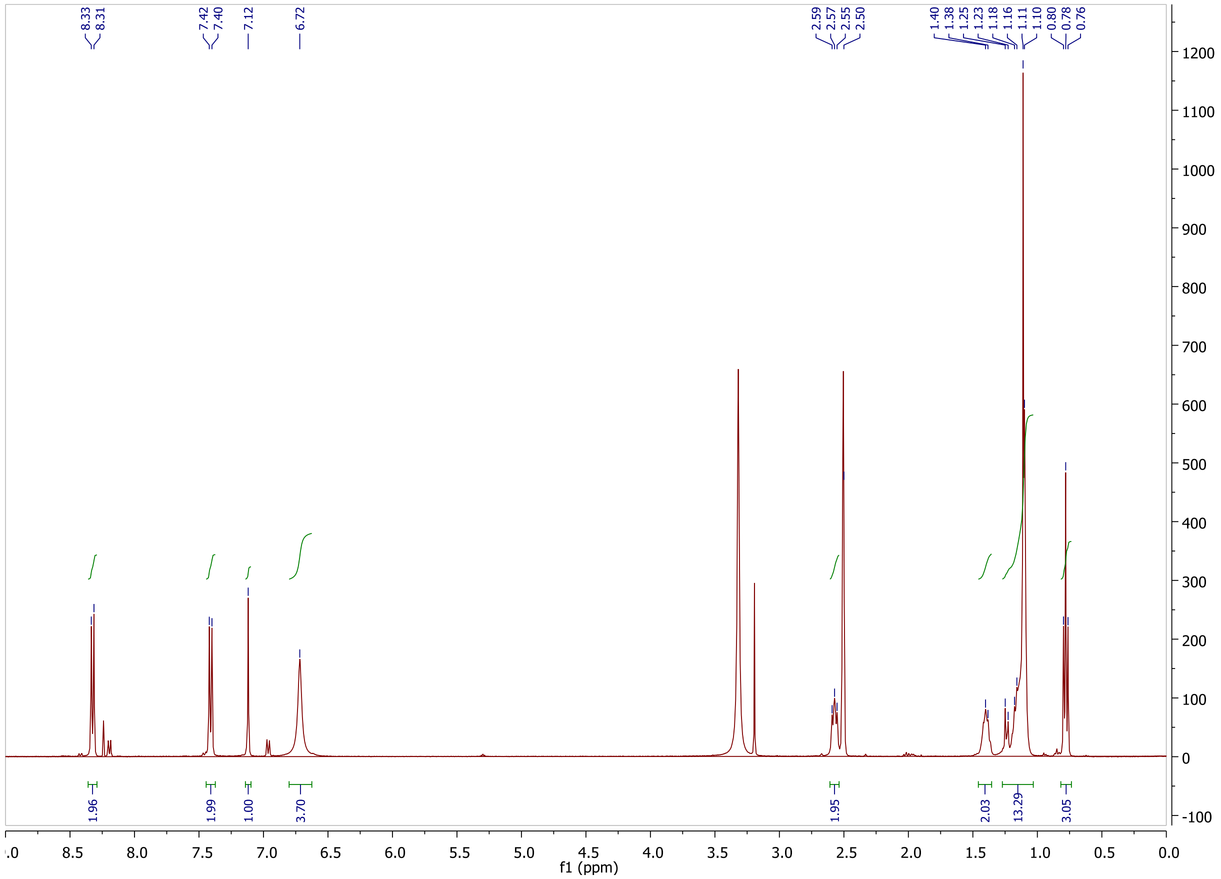

Figure S13 ^{1}H-NMR spectrum of the bis(melamine) derivative **GR3** (R=C_8H_{17})

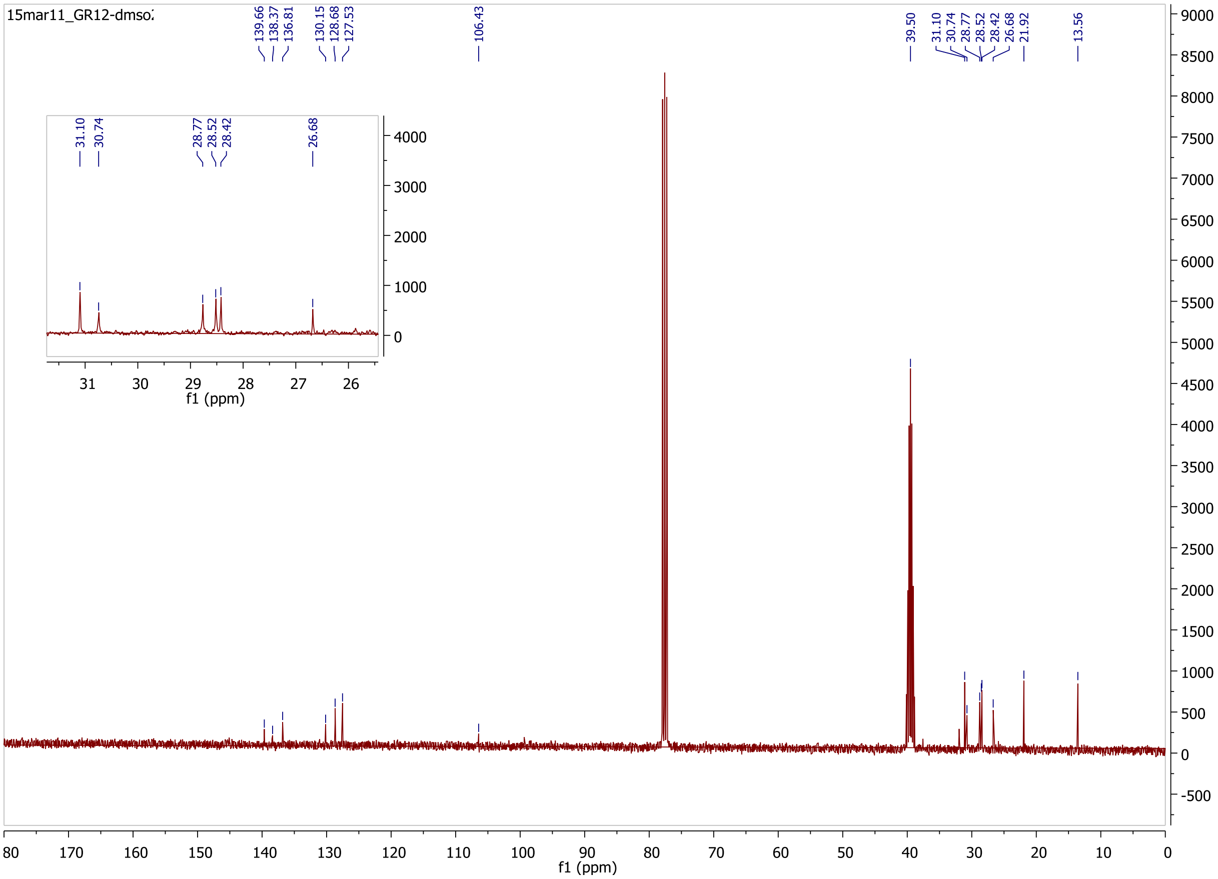

Figure S14 ^{13}C-NMR spectrum of the bis(melamine) derivative **GR3** (R=C_8H_{17})

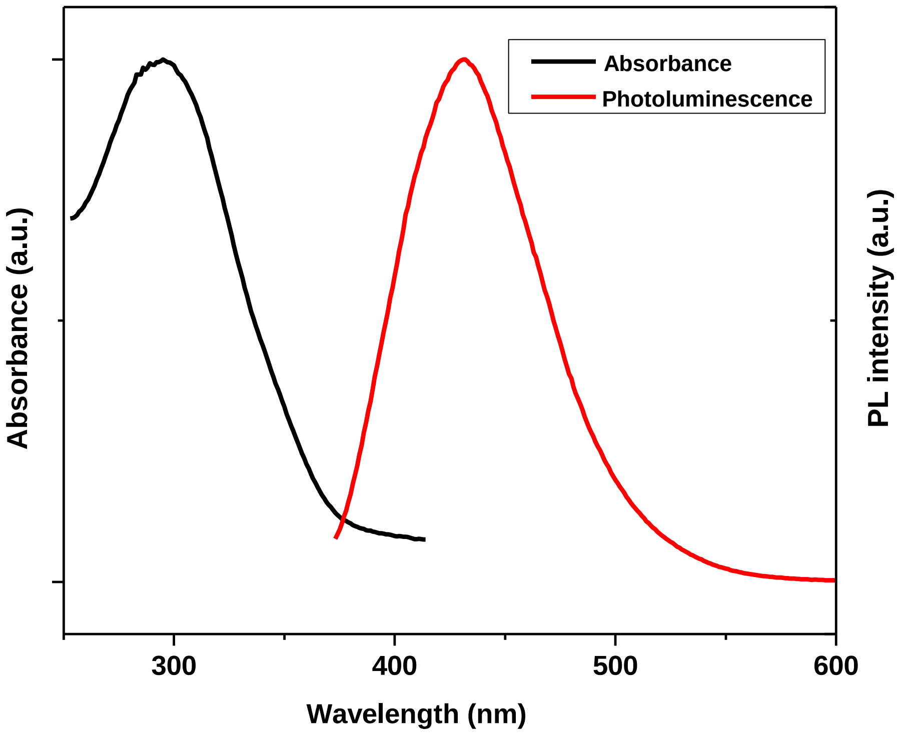

Figure S15 Absorption and emission spectra of the bis(melamine) derivative **GR3** (R=C_8H_{17}) in chloroform