

## Studies of Synthesis and Characterization of Second Generation Organic Dyes Attached to Silica Surface Through Meijer-type H-Bonding

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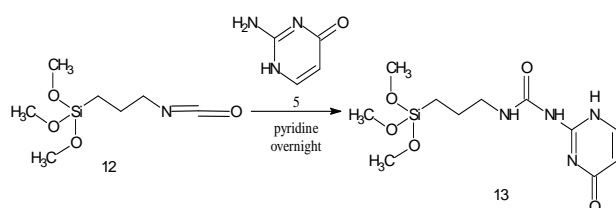
### Abstract

The organic dyes of second generation those are attached of silica surface through Meijer-type hydrogen bonding were synthesized. The synthesis was completed by using simple and common organic reactions. Thereafter structure of the dyes were confirmed by spectral analysis of nuclear magnetic resonance.

**Keywords:** Silica, Dyes, H-bonding, NMR.

### Introduction

**1-(3-Triethoxysilylpropyl)ureido-3-[2-(4-pyrimidone)], (13), (TEOS-UPy).** (3-Isocyanatopropyl)triethoxysilane (**12**) (1.5 g, 6.2 mmol) was added to isocytosine (**5**) (0.7 g, 6 mmol) in dry pyridine and brought to reflux for 18 hours. The solvent was removed under reduced pressure and the resulting solid recrystallized from methanol. The product was collected as a fine colorless solid (1.2 g, 3.3 mmol, 54% yield). Mp: 170-174 °C. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 0.52-0.58 (m, 2H), 1.15 (t, 9H, *J* = 6 Hz), 1.45-1.55 (m, 2H), 3.11 (q, 2H, *J* = 6 Hz), 3.75 (quartet, 6H, *J* = 6 Hz), 5.88 (br, 1H), 7.38 (br, 1H), 7.71 (br, 1H), 9.73 (br, 1H), 11.77 (br, 1H). <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>): δ 7.08, 18.12, 22.72, 41.61, 57.65, 107.14, 139.76, 152.44, 154.81, 160.56. FT-IR (KBr): cm<sup>-1</sup> 3037, 2972, 1699, 1657, 1596, 1267, 1188, 1078, 956. EI-MS: *M/z* 358 (15%), 312 (17%), 246 (4%), 220 (5%), 202 (20%), 175 (38%), 163 (100%), 138 (69%). Anal. Calcd for C<sub>14</sub>H<sub>26</sub>N<sub>4</sub>O<sub>5</sub>Si: C, 46.91; H, 7.31; N, 15.63. Found: C, 46.32; H, 7.21; N, 15.64.

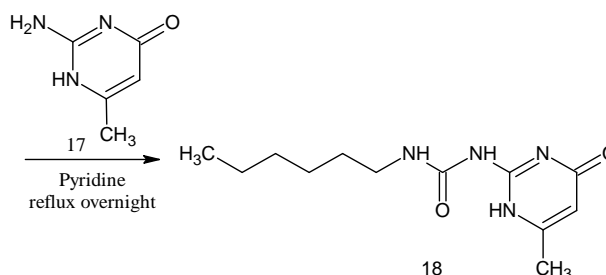
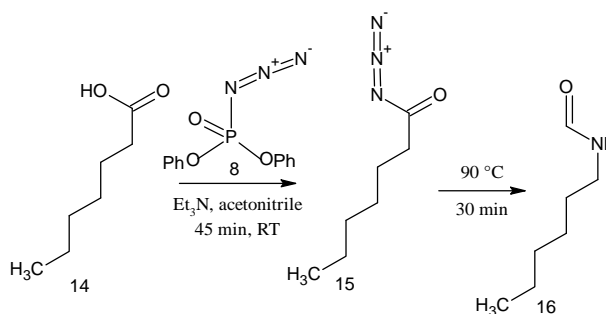


**1-Hexylureido-3-[2-(6-methyl-4-pyrimidone)], (18), (Hex-UPy).**

An acetonitrile solution of heptanoic acid (**14**) (1.25 mL, 8.8 mmol), diphenylphosphoryl azide (**8**) (1.90 mL, 8.8 mmol), and triethylamine (1.22 mL, 8.8 mmol) was stirred for 45 minutes at room temperature, then brought to reflux for 30 minutes until gas evolution ceased. 2-Amino-4-hydroxy-6-methylpyrimidine (**17**) (1.323 g, 10.6 mmol) in dry pyridine was added and the reaction mixture was held at reflux overnight<sup>1</sup>. The precipitate was collected, washed with water, and dried. The product was collected as a fluffy colorless solid (1.72 g, 6.82 mmol, 77% yield). Mp: 192-193 °C. <sup>1</sup>H NMR (300 MHz

DMSO-d<sub>6</sub>): δ 0.84-0.88 (m, 3H), 1.27 (s, 6H), 1.39-1.48 (br, 2H), 2.098 (s, 3H), 3.09-3.15 (m, 2H), 3.31 (s, 1H), 5.77 (s, 1H), 7.38 (br, 1H), 9.70 (br, 1H), 11.61 (br, 1H). <sup>13</sup>C NMR

(300 MHz, DMSO-d<sub>6</sub>): δ 13.17, 21.42, 22.39, 25.41, 28.58, 30.35, 38.75, 103.97, 151.09, 154.44, 161.35, 163.07. FT-IR (KBr): cm<sup>-1</sup> 2961, 2932, 1703, 1666, 1580, 1528, 1254. CI-MS (isobutane): *M/z* 253 (97%), 152 (100%), 126 (43%), 102.2 (52%). Anal. Calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 57.12; H, 7.99; N, 22.20. Found: C, 57.03; H, 8.09; N, 22.28.



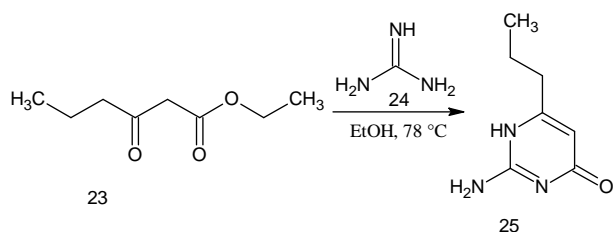
**1-Ethylureido-3-[2-(6-methyl-4-pyrimidone)], (22), (Et-UPy).**

An acetonitrile (30.0 mL) solution of propionic acid (**19**) (0.66 mL, 8.9 mmol), diphenylphosphoryl azide (**8**) (1.90 mL, 8.8 mmol), and triethylamine (1.25 mL, 9.0 mmol) was stirred for 45 minutes at room temperature, then brought to reflux for 30 minutes until gas evolution ceased. 2-Amino-4-hydroxy-6-methylpyrimidine (**17**) (1.31 g, 10.5 mmol) in 15.0 mL dry pyridine was added and the reaction mixture was held at reflux overnight. The precipitate was collected, washed with water, and dried. The product was collected as tiny colorless needle-like crystals (1.37 g, 6.98 mmol, 79% yield). Mp: 224-229 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.23 (t, 3H, *J* = 7Hz), 2.23 (s, 3H), 3.26-3.35 (m,

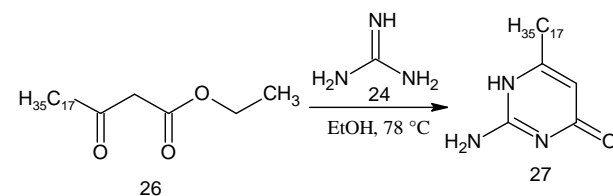
2H,  $J = 7$  Hz,  $J = 5$  Hz,  $J = 2$  Hz), 5.81 (s, 1H), 10.16 (br, 1H), 11.84 (br, 1H), 13.13 (br, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.75, 19.03, 34.84, 106.57, 148.06, 154.53, 156.26, 172.86. ATR-FT-IR (neat):  $\text{cm}^{-1}$  3209, 3143, 3049, 2929, 2866, 1707, 1647, 1564, 1523, 1441, 1242. EI-MS:  $M/z$  196 (24%), 181 (10%), 151 (100%), 125 (86%), 109 (13%), 97 (18%), . Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{N}_4\text{O}_2$ : C, 48.97; H, 6.16; N, 28.56. Found: C, 49.07; H, 6.40; N, 28.68.

**6-Propylisocytosine, (25).**<sup>4</sup> Guanidine carbonate (**24**) (23.5 g, 130 mmol) was added to ethyl butyrylacetate (**23**) (20.0 mL, 126 mmol) in absolute ethanol and brought to reflux for 18 hours. The solvent was removed under reduced pressure and the resulting sticky yellow paste was suspended in chloroform and held at reflux for 1 hour to extract impurities, before cooling and aqueous workup<sup>2</sup>. The product was recrystallized from ethanol and collected as a shiny pale yellow solid (17.8 g, 116 mmol, 92.1% yield). Mp: 209-212 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.86 (t, 3H,  $J = 6$  Hz), 1.5 (sextet, 2H,  $J = 6$  Hz), 2.19 (t, 2H,  $J = 6$  Hz), 5.33 (s, 1H), 6.66 (br, 2H), 11.15 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  168.31, 165.22, 157.10, 100.29, 39.53, 21.59, 14.56. FT-IR

(KBr):  $\text{cm}^{-1}$  3376, 3135, 3044, 2964, 2690, 1641, 1566, 1463, 1403. EI-MS:  $M/z$  153 (17%), 138 (26%), 125 (100%), 110 (6%), 97 (14%). NNO.

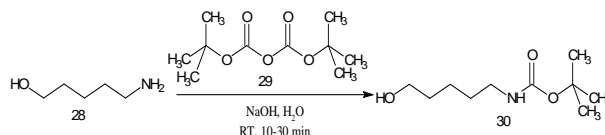


**6-Heptadecylisocytosine, (27).** Guanidine carbonate (**24**) (1.18 g, 6.46 mmol) was added to ethyl stearoylacetate (**26**) (2.05 g, 5.78 mmol) in 50.0 mL absolute ethanol and brought to reflux for 18 hours. The solvent was removed under reduced pressure and the resulting waxy yellow solid was suspended in 75.0 mL chloroform and subjected to aqueous workup. The product was then recrystallized from ethanol with a Norite treatment and collected as an off-white solid (0.998 g, 2.85 mmol, 49.3% yield). Mp: 161-165 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.85 (t, 3H,  $J = 7$  Hz), 1.23 (s, 28H), 1.51 (m, 2H), 2.21 (t, 2H,  $J = 7$  Hz), 5.36 (s, 1H), 6.44 (br, 2H), 10.59 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  13.88, 22.02, 27.98, 28.63, 28.80, 28.97, 31.22, 36.89, 98.94, 158.51, 165.7, 168.53. ATR-FT-IR (neat):  $\text{cm}^{-1}$  3340, 3139, 3066, 2916, 2848, 2671, 1660, 1635, 1614, 1552, 1468, 1400, 1198, 1117, 991, 930. EI-MS:  $M/z$  349 (5%), 321 (6%), 208 (2%), 180 (6%), 166 (4%), 138 (24%), 125 (100%), 97 (4%).



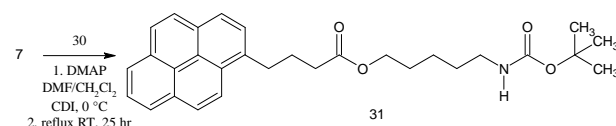
**Tert-Butyl (5-hydroxypentyl)carbamate, (30)**-Aminopentanol (**28**) (2.0 mL, 18 mmol), sodium hydroxide

(0.3 g, 8 mmol), and *t*-butyl dicarbonate (**29**) (4.1 g, 19 mmol) were combined in water and stirred at room temperature for 1 hour. The product was extracted into  $\text{CH}_2\text{Cl}_2$  and after aqueous workup, afforded (1.6 g, 8 mmol, 100%) of a yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.35-1.62 (m, 15H), 1.71 (br, 1H), 3.10 (m, 2H), 3.62 (t, 2H,  $J = 6$  Hz), 4.57 (br, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.95, 27.43, 28.45, 29.87, 32.26, 40.42, 62.54, 155.92. ATR-FT-IR (neat):  $\text{cm}^{-1}$  3340, 2972, 2931, 2866, 1685, 1525, 1365, 1275, 1250, 1163, 1011. EI-MS:  $M/z$  204 (83%), 130 (20%), 102 (27%), 85 (20%), 57 (91%). Anal. Calcd for  $\text{C}_{10}\text{H}_{21}\text{NO}_3$ : C, 59.09; H, 10.41; N, 6.89. Found: C, 58.70; H, 10.24; N, 5.90.



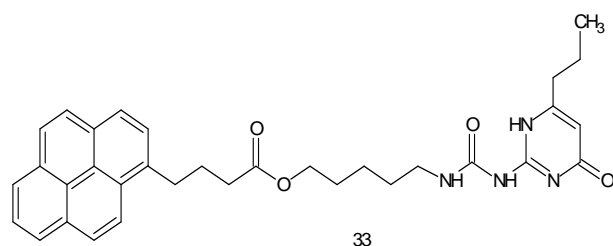
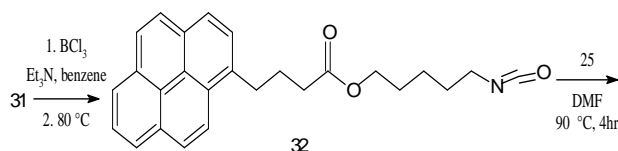
**4-Pyren-2-yl-butyric acid, 5-tert-butoxycarbonylamino-pentyl ester, (31).** A DMF (10.0 mL) solution of 1,1'-carbonyldiimidazole (CDI) (1.13 g, 6.03 mmol) was added dropwise at 0 °C to a solution of 4-(1-pyrenyl)butyric acid (**7**) (1.55 g, 5.39 mmol), *t*-butyl (5-hydroxypentyl)carbamate (**30**) (1.19 g, 5.86 mmol), and 4-dimethylaminopyridine (DMAP) (0.11 g, 0.90 mmol) in 40.0 mL dry DMF and the resulting solution heated at 90 °C overnight under argon<sup>3,4</sup>. The solvent was removed under reduced pressure and the product purified on a silica gel column (95:5  $\text{CH}_2\text{Cl}_2$ /acetone). The product was collected as a clear, brownish oil (0.82 g, 1.7 mmol, 32% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.41-1.49 (m, 13H), 1.58-1.65 (m, 2H), 2.20 (pentet, 2H,  $J = 7$  Hz), 2.46 (t, 2H,  $J = 7$  Hz), 3.10 (m, 2H), 3.40 (m, 2H), 4.07 (t, 2H,  $J = 6$  Hz), 4.49 (br, 1H), 7.85-8.32 (m, 9H). EI-MS:  $M/z$  399 (87%), 288 (2%), 271 (9%), 215 (100%), 153 (6%), 125 (37%), 107 (13%). FAB-MS (thioglycerol):  $M/z$  1105 (2%), 553 (75%), 512 (100%), 271 (58%). Anal.

Calcd for  $\text{C}_{30}\text{H}_{35}\text{NO}_4$ : C, 76.08; H, 7.45; N, 2.96. Found: C, 75.92; H, 7.30; N, 2.99.

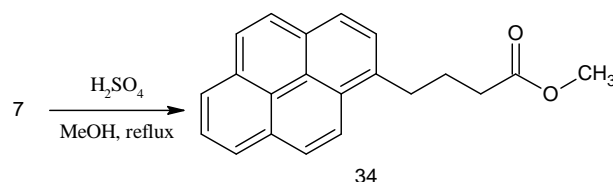


**4-Pyren-2-yl-butyric acid, 5-[3-(4-oxo-6-propyl-1,4-dihydropyrimidin-2-yl)ureido]pentyl ester, (33), (Py-UPy).** A 1 M hexane solution of  $\text{BCl}_3$  (1.0 mL, 1.0 mmol) was added dropwise at 0 °C to 4-pyren-2-yl-butyric acid 5-*tert*-butoxycarbonylamino-pentyl ester (**31**) (1.30 g, 2.74 mmol) and triethylamine (0.42 mL, 3.01 mmol) in 10.0 mL dry benzene and the solution brought to reflux for 30 minutes. The  $\text{Et}_3\text{NHCl}$  salt was filtered off under argon and the solvent removed under vacuum. To the resulting isocyanate oil, 6-propylisocytosine (**25**) (0.51 g, 3.3 mmol) in 20.0 mL DMF was added and the mixture held at reflux overnight. The solvent was removed under reduced pressure and the product purified on a silica gel column (90:10  $\text{CH}_2\text{Cl}_2$ /EtOAc). The product was collected as a brownish oil, which crystallized upon sitting (0.65 g, 1.2 mmol, 44% yield). Mp: 72-77 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.92-1.03 (m, 3 H), 1.41-1.46 (m, 4H), 1.56-1.73 (m, 5H), 2.15-

2.24 (m, 2H), 2.41-2.47 (m, 2H), 3.04-3.12 (m, 2H), 3.19-3.31 (m, 2H), 3.33-3.41 (m, 2H), 4.02-4.09 (m, 2H), 5.67-5.85 (m, 1H), 7.81-8.35 (m, 9H), 10.04-10.35 (br, 1H), 11.50-11.91 (m, 1H), 12.90-13.22 (m, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.60, 152.08, 128.69, 127.45, 127.32, 126.64, 125.76, 124.91, 124.84, 124.77, 123.29, 105.67, 64.43, 39.79, 34.43, 33.94, 32.77, 29.14, 28.35, 26.85, 23.56, 20.24, 13.34. ATR-FT-IR (neat):  $\text{cm}^{-1}$  3213, 3033, 2952, 2868, 1728, 1695, 1649, 1573, 1522, 1456, 1250, 1167, 839. FAB-MS (thioglycerol):  $M/z$  271 (57%), 512 (100%), 553 (75%). Anal. Calcd for  $\text{C}_{33}\text{H}_{36}\text{N}_4\text{O}_4$ : C, 71.72; H, 6.57; N, 10.14. Found: C, 70.41; H, 6.67; N, 9.57.



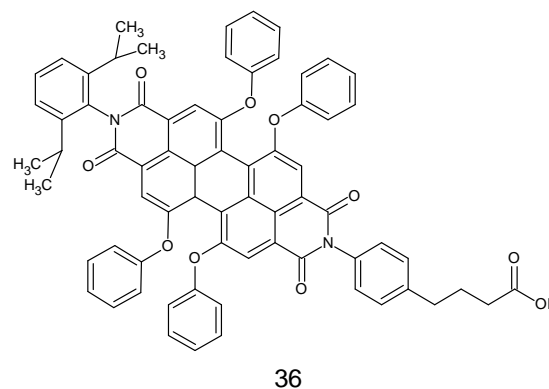
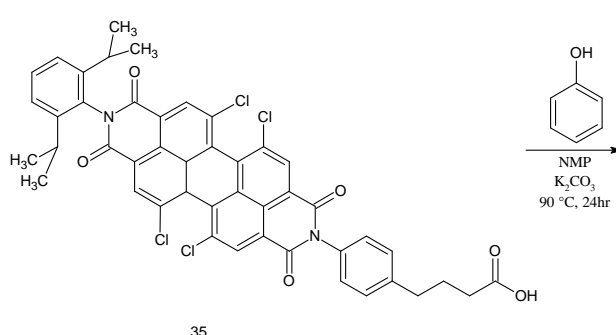
**Methyl 4-(1-pyrenyl)butyrate, (34), (Py-Me).** A catalytic amount (2 drops) of concentrated  $\text{H}_2\text{SO}_4$  was added to a solution of 4-(1-pyrenyl)butyric acid (**7**) (0.251 g, 0.870 mmol) in 125 mL methanol and held at reflux overnight. The solution was sonicated over  $\text{NaHCO}_3$  for 2 hours to neutralize the acid catalyst, then filtered and the solvent removed under reduced pressure. The product ester was collected as a pale yellow solid in quantitative yield. Mp: 49-51 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.20 (pentet, 2H,  $J = 7$  Hz), 2.47 (t, 2H,  $J = 7$  Hz), 3.40 (s, 3H), 3.69 (t, 2H,  $J = 7$  Hz), 7.85-8.32 (m, 9H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.13, 135.92, 130.21, 127.71, 127.62, 127.57, 126.94, 126.07, 125.14, 125.03, 123.54, 51.81, 33.86, 32.99, 26.99. ATR-FT-IR (neat):  $\text{cm}^{-1}$  3033, 2997, 2949, 2906, 2871, 1730, 1585, 1427, 1365, 1300, 1248, 1207, 1157, 1099, 1032, 993, 839. FAB-MS (MNBA):  $M/z$  302 (100%), 271 (23%), 243 (5%), 215 (48%), 202 (16%).



**4-{4-[9-(2,6-Diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetra phenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'ef']diisoquinolin-2-yl]phenyl}butyric acid:**

4-{4-[5,6,12,13-Tetrachloro-9-(2,6-diisopropylphenyl)-1,3,8,10-tetraoxo-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'ef']diisoquinolin-2-yl]phenyl}butyric acid (**35**) (0.94 g, 1.1 mmol), phenol (1.1 g, 12 mmol), and potassium carbonate (1.5g, 10.8 mmol) were combined in dry *N*-

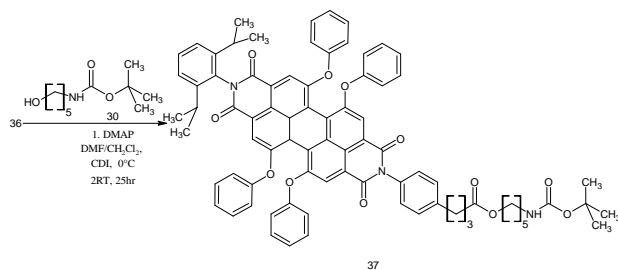
methyl-2-pyrrolidinone (NMP) and heated at 90 °C for 48 hours. The solvent was removed under reduced pressure and the crude product suspended in water and collected by filtration. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through a thin layer of silica gel to remove impurities. The purified phenoxyated perylene was then precipitated from a  $\text{CH}_2\text{Cl}_2$ /water mixture and collected via filtration as a crystalline dark purple solid (1.0 g, 0.94 mmol, 85% yield). Mp: 219-227 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.12 (d, 11H,  $J = 6$  Hz), 1.26-1.29 (m, 1H), 2.00 (pentet, 2H,  $J = 9$  Hz), 2.40 (t, 2H,  $J = 9$  Hz), 2.64-2.76 (m, 4H), 6.94-7.43 (m, 27H), 8.23 (s, 2H), 8.26 (s, 2H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.97, 25.93, 29.05, 33.09, 34.66, 119.78, 119.87, 120.34, 120.73, 120.80, 122.74, 122.84, 123.87, 124.61, 128.35, 129.38, 129.95, 130.52, 132.92, 133.05, 141.84, 145.57, 155.23, 155.84, 163.17, 163.45, 178.48. FT-IR (KBr):  $\text{cm}^{-1}$  3446, 3063, 3034, 2960 2929, 2872, 1700, 1672, 1652, 1585, 1489, 1412, 1340, 1278, 1199, 875, 750, 667. FAB-MS (MNBA):  $M/z$  1081 (15%), 1063 (2%).



**4-{4-[9-(2,6-Diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetraphenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'ef']diisoquinolin-2-yl]phenyl}butyric acid 6-tert-butoxycarbonylamino-hexyl ester:**

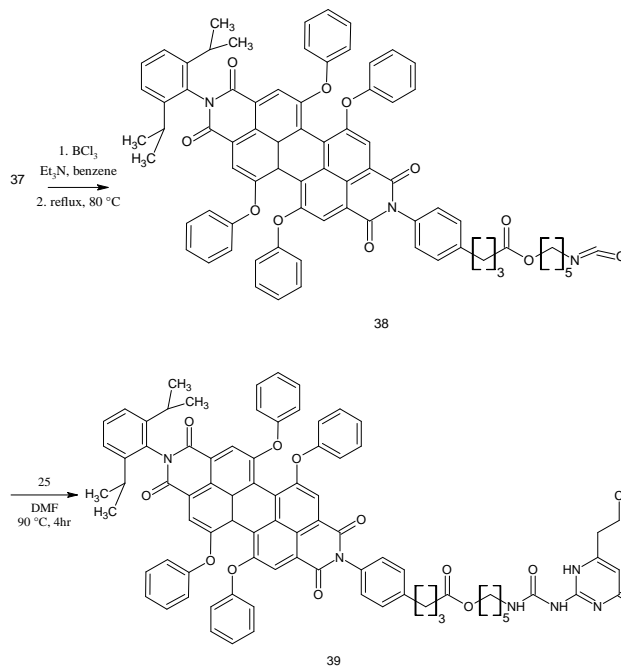
A DMF solution of 1,1'-carbonyldiimidazole (CDI) (114 mg, 0.703 mmol) was added dropwise at room temperature to a solution of 4-{4-[9-(2,6-diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetraphenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'ef']diisoquinolin-2-yl]phenyl}butyric acid (**36**) (501 mg, 0.463 mmol), *t*-butyl (5-hydroxypentyl)carbamate (**30**) (219 mg, 0.9 mmol), and 4-dimethylaminopyridine (DMAP) (23 mg, 0.19 mmol) in dry DMF and the resulting solution heated at 90 °C for 24 hours. The solvent was removed<sup>6</sup> under reduced pressure and the product purified on a silica gel column (95:5):  $\delta$  1.12 (d, 11H,  $J = 6$  Hz), 1.26-1.29 (m, 1H), 1.43 (s, 9H), 1.44-1.53 (m, 4H), 1.64 (pentet, 2H,  $J = 6$  Hz), 1.99 (pentet,

2H,  $J = 9$  Hz), 2.35 (t, 2H,  $J = 9$  Hz), 2.65-2.74 (m, 4H), 3.10-3.12 (m, 2H), 4.06 (t, 2H,  $J = 6$  Hz), 4.53 (br, 1H), 6.93-7.46 (m, 27H), 8.23 (s, 2H), 8.27 (s, 2H).  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ ). The product was collected as a dark purple crystalline solid (233 mg, 0.176 mmol, 38.0% yield). Mp: 134-142 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.17, 23.97, 26.22, 27.75, 28.29, 28.38, 29.04, 29.70, 33.50, 34.78, 40.40, 64.16, 119.77, 119.86, 120.12, 120.32, 120.72, 120.78, 122.76, 122.86, 123.85, 124.58, 128.32, 129.34, 129.94, 130.53, 132.88, 133.06, 141.98, 145.54, 155.24, 155.82, 155.90, 163.13, 163.42, 173.41. FT-IR (KBr):  $\text{cm}^{-1}$  3427, 3064, 2962, 2919, 2871, 1706, 1672, 1587, 1486, 1403, 1335, 1284, 1199, 876, 750, 606, 517. FAB-MS (thioglycerol):  $M/z$  1266 (6%), 1167 (12%), 1074 (2%), 248 (39%). Anal. Calcd for  $\text{C}_{80}\text{H}_{71}\text{N}_3\text{O}_{12}\cdot\text{H}_2\text{O}$ : C, 74.81; H, 5.73; N, 3.27. Found: C, 75.09; H, 5.75; N, 3.32.

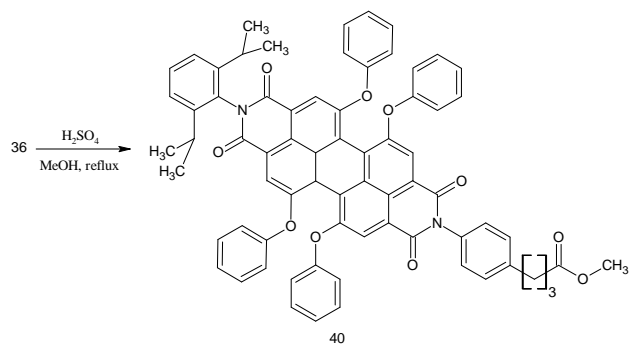


**4-{4-[9-(2,6-Diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetraphenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinolin-2-yl]phenyl}butyric acid, 6-{ureido-3-[2-(6-propyl-4-pyrimidinyl)hexyl ester], (39), (PDI-UPy).** A 1 M hexane solution of  $\text{BCl}_3$  (75  $\mu\text{L}$ , 0.075 mmol) was added dropwise at room temperature to 4-{4-[9-(2,6-diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetraphenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinolin-2-yl]phenyl}butyric acid (36) (275 mg, 0.217 mmol) and triethylamine (35  $\mu\text{L}$ , 0.25 mmol) in dry benzene and the solution brought to reflux for 2 hours. To the hot solution, 6-propylisocytosine (25) (55 mg, 0.36 mmol) in 5 mL DMF was added and the mixture returned to reflux for 20 hours. The solvent was removed under reduced pressure and the product purified on a silica gel column (90:10  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ ). The product was collected as a dark purple crystalline solid (62 mg, 0.046 mmol, 22% yield). Mp: 164-171 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.96-1.01 (m, 2H),

1.12 (d, 10H,  $J = 9$  Hz), 1.26-1.29 (m, 2H), 1.41-1.44 (m, 2H), 1.62-1.69 (m, 4H), 1.98 (pentet, 2H,  $J = 6$  Hz), 2.34 (t, 2H,  $J = 6$  Hz), 2.42-2.45 (m, 2H), 2.66-2.73 (m, 4H), 3.24-3.26 (m, 2H), 4.06 (t, 2H,  $J = 6$  Hz), 5.82 (s, 1H), 6.94-7.43 (m, 27H), 8.22 (s, 2H), 8.26(s, 2H), 10.23 (br, 1H), 11.89 (br, 1H), 13.15 (br, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):



**4-{4-[9-(2,6-Diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetraphenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinolin-2-yl]phenyl}methylbutyrate, (40), (PDI-Me).** A catalytic amount (1 drop) of concentrated  $\text{H}_2\text{SO}_4$  was added to a solution of 4-{4-[9-(2,6-diisopropylphenyl)-1,3,8,10-tetraoxo-5,6,12,13-tetraphenoxy-3,8,9,10-tetrahydro-1H-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinolin-2-yl]phenyl}butyric acid (36) (115 mg, 0.106 mmol) in methanol and brought to reflux for 18 hours. The solution was sonicated over  $\text{NaHCO}_3$  for 2 hours to neutralize the acid catalyst, then filtered and the solvent removed under reduced pressure. The product ester was then crashed out of a  $\text{CH}_2\text{Cl}_2/\text{water}$  mixture and collected via filtration as a crystalline dark purple solid in quantitative yield. Mp: 200-209 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.12 (d, 10H,  $J = 9$  Hz), 1.25-1.29 (m, 2H), 1.99 (pentet, 2H,  $J = 9$  Hz), 2.36 (t, 2H,  $J = 9$  Hz), 2.65-2.74 (m, 4H), 3.66 (s, 3H), 6.94-7.46 (m, 27H), 8.23 (s, 2H), 8.26 (s, 2H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.71, 23.98, 26.18, 29.06, 33.30, 34.77, 51.51, 119.78, 119.88, 120.34, 120.79, 122.78, 122.86, 123.87, 124.60, 128.32, 129.35, 129.42, 129.95, 130.34, 130.53, 132.89, 133.07, 141.97, 145.56, 155.24, 155.84, 163.15, 163.44, 173.83. FT-IR (KBr):  $\text{cm}^{-1}$  3429, 3064, 2962, 2929, 2862, 1707, 1672, 1587, 1486, 1405, 1335, 1282, 1199, 877, 750, 607. ESI-MS:  $M/z$  1095 (13%), 1066 (4%), 1052 (6%), 990 (2%), 981 (3%), 952 (5%), 928 (2%), 554 (42%), 538 (96%).: C, 77.86; H, 4.97; N, 2.56. Found: C, 77.18; H, 4.92; N, 2.58. Anal. Calcd for  $\text{C}_{71}\text{H}_{54}\text{N}_2\text{O}_{10}$ .



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