Supporting Information for

Supramolecular chemistry with ureido-benzoic acids

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1. General Methods

Materials - All reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. Chloroform, was dried over 4Å molsieves for at least 1 day prior to use. Triethylamine was dried over KOH pellets. 2-(1-Imidazolylcarbonylamino)-6-(2(S),6-dimethylheptyl)-4[1H]-pyrimidinone (**2b**),[1] 2-(1-imidazolyl carbonylamino)-6-methyl-4[1H]-pyrimidinone (**2a**),[1] *N*-[(butylamino)carbonyl] -6-(1-ethylpentyl)isocytosine[2] and 2,7-bis-(dodecanoylamino)-1,8-naphthyridine[3] were synthesized according to previously published procedures. Silica gel column chromatography was carried out with silica gel 60 (mesh 70-230).

Instrumentation - ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz NMR (Varian Mercury, 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). For deuterated 1,1',2,2',-tetrachloroethane a small amount of TMS was added to the solvent. The splitting patterns are designated as: b, broad; s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; sep, septet; m, multiplet. Carbon chemical shifts are reported downfield from TMS using the resonance of the deuterated solvent as the internal standard. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were obtained using a PerSeptive Biosystems Voyager-DE PRO spectrometer using an acid α-cyanohydroxycinnamic acid (CHCA) or a neutral 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) matrix. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O Analyzer. GPC was measured on a Shimadzu LC-10DVP system with a Shimadzu RID-10A detector and a PLgel 5-µm mixed-D column with THF as the eluent (flow rate: 1 mL/min) and poly(styrene) standards for the calibration. Differential Scanning Calorimetry (DSC) measurements were performed on a Thermal Advantage Q2000 apparatus between -80 and 150 °C at a rate of 10 K/min with a sample weight of 5-10 mg. Integration of the melting endotherm was performed with the TA Instruments Universal Analysis software. Atomic Force Microscopy (AFM) measurements were performed on a Digital Instrument Multimode Nanoscope IV using PPP-NCHR-50 silicon tips (Nanosensors) in the tapping mode. Polymer films were made by casting a 1 mg/mL solution in chloroform on pre-cleaned glass slides and subsequent evaporation to air for at least 1 hour, followed by annealing *in vacuo* overnight at 40 °C. Fourier Transform Infrared (FTIR) spectra for analysis at room temperature were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with a Universal ATR Sampling Accessory. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. Fluorescent measurements were performed on an Edinburgh Analytical Instruments spectrometer equipped with a Xe900 light source.

Tensile testing – Tensile tests were performed on a Zwick Z100 Materialprüfung device equipped with a 100 N loadcell. Samples were prepared by casting a solution of 2 gram precipitated polymer in 20 mL $CHCl_3$ in Teflon cups of 10.5x4.5 cm. The solvent was allowed to evaporate in 3 days at room temperature and subsequent drying at 40 °C *in vacuo* overnight, yielding a 0.3 mm thick film. Testing was done according to ASTM 1708-

96 with n = 6. Therefore the calculated modulus is only an indicative modulus. This modulus was determined between 1 and 3% strain. Strain rate was 2.0 mm/min.

Single crystal X-ray structure determination – Crystals suitable for single crystal X-ray diffraction analysis were obtained by slow diffusion of water vapor into a few mg/ml solution of molecule 1a in DMF. $C_{14}H_{14}N_4O_4$, F_w = 302.29, colourless block, 0.33 x 0.27 x 0.21 mm^3, triclinic, P**Error!**(no. 2), a = 7.1654(2), b = 8.2062(2), c = 11.6136(3) Å, α = 85.818(1), β = 88.406(1), γ = 82.354(1)°, V = 674.90(3) $Å^3$, Z = 2, D_x = 1.488 g/cm^3, μ = 0.11 mm^{-1}. 8680 reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) up to a resolution of (sin Θ/λ)max = 0.65 $Å^{-1}$ at a temperature of 150(2) K. The Eval14 software[4] was used for intensity integration. Absorption correction and scaling based on multiple measured reflections was performed with SADABS[5] (0.66-0.75 correction range). 3102 Reflections were unique (R_{int} = 0.021), of which 2591 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97 and refined with SHELXL-97 against F^2 of all reflections.[6] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference-Fourier maps. N-H and O-H hydrogen atoms were refined freely with isotropic displacement parameters. C-H hydrogen atoms were refined with a riding model. 217 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0382 / 0.1005. R1/wR2 [all refl.]: 0.0485 / 0.1070. S = 1.058. Residual electron density between 0.25 and 0.30 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[7] CCDC 992565 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1: Hydrogen bond geometries in the crystal structure of **1a**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [°]
O12-H12O...N22^{i}	0.94(2)	1.71(3)	2.6341(14)	169(2)
N1-H1N...O11	0.877(19)	1.981(19)	2.6829(14)	136.2(16)
N1-H1N...O21^{ii}	0.877(19)	2.536(18)	3.1307(15)	125.8(14)
N2-H2N...O21^{ii}	0.87(2)	2.19(2)	2.9033(14)	138.2(18)
N2-H2N...O11^{i}	0.87(2)	2.44(2)	3.1507(14)	139.3(17)
N21-H21N...O1	0.881(18)	1.909(17)	2.6058(14)	134.7(15)
N21-H21N...O11^{iii}	0.881(18)	2.412(17)	2.9556(14)	120.2(13)

Symmetry operations i: 1-x, 1-y, 1-z; ii: x+1, y, z; iii: x-1, y, z.

UV-Vis experiments – The measurements were performed at 20 °C in chloroform. The concentration of NaPy was held constant during the titration experiments. For optimal resolution, a concentration of NaPy around 20 μM was used. After the addition of the appropriate UBA **6** or **8**, the 1 cm cuvet was shaken thoroughly and the solution was allowed to equilibrate for 1 minute prior to measurement. The absorbance data of **6** was fitted to a 1:1 binding model, i.e. dimerization of compound **6** was neglected.[8]

^{1}H NMR titration experiment - ^{1}H NMR titration experiments of UBA molecule **8** were performed at 2mM concentration in deuterated tetrachloroethane dried over 4 Å molsieves. The concentration of **8** was kept constant during the experiment by the addition of a stock solution of NaPy (10 mM) containing molecule **8** (2 mM). Integration of the peaks and subsequent fitting of the results was performed using a 1:1 binding model.[8]

On/off switching experiments – ^{1}H NMR switching experiments were performed at 25 °C in deuterated tetrachloroethane dried over 4 Å molsieves. Due to the acidic workup of UBA molecules **8-10**, the starting spectra are in the 'on' state. Stock solutions of base (1 M triethylamine) and acid (1 M trifluoroacetic acid) were made in $CDCl_3$ dried over molsieves. NaOH (1 M) and HCl (1 M) solutions were made in deionized water. Fluorescence switching experiments were performed at room temperature on 10 μM solutions of molecules **6** and **8-10** in chloroform (fresh bottle). The excitation wavelength was set at 330 nm. Stock solutions containing 0.1 M triethylamine and 0.1 M trifluoroacetic acid were made in chloroform (fresh bottle). 3 mL of solution was put in a cuvet and measured, after which 3 μL (10 eq) of base stock solution was added. The cuvet was shaken vigorously and left to equilibrate for 1 minute prior to measurement. Subsequent addition of acid was done according to the same procedure.

2. Experimental Procedures

5-Methyl-2-[3-(4-methyl-6-oxo-1,6-dihydro-pyrimidin-2-yl)-ureido]-benzoic acid (1a)

2-(1-Imidazolylcarbonylamino)-6-methyl-4[1H]-pyrimidinone (**2a**) (552 mg, 2.52 mmol) and 2-amino-5-methyl-benzoic acid (344 mg, 2.28 mmol) were stirred in dry chloroform (25 mL) under an argon atmosphere. Dry triethylamine (5 drops) was added and the mixture was stirred at reflux overnight. The solvent was removed *in vacuo*, chloroform (250 mL) and 1M HCl (200 mL) were added and stirred vigorously. A precipitate was formed, which was collected by filtration and subsequently washed with water and methanol to yield the product (510 mg, 1.69 mmol, 74%) as a white solid.

^{1}H NMR (DMSO): δ = 11.64 (bs, 1H), 11.04 (bs, 2H), 8.21 (bs, 1H), 7.75 (s, 1H), 5.74 (s, 1H), 2.27 (s, 3H), 2.15 (s, 1H). ^{13}C NMR (DMSO): δ = 169.3; 161.7; 152.5; 138.4; 134.7; 131.5; 121.0; 117.5; 104.0;.21.8; 20.6 FT-IR ν (cm^{-1}) = 3169, 3091, 2921, 2479, 1717, 1676, 1625, 1585, 1505, 1444, 1400, 1371, 1296, 1277, 1233, 1210, 1196, 987. MALDI-TOF-MS: Calculated mass: 302.10 g/mol. Measured mass: m/z = 303.00 [M+H^+], 324.98 [M+Na^+]. Elemental analysis: Calculated for $C_{14}H_{14}N_4O_4$: C: 55.63%, N: 18.53%, H: 4.67%. Measured: C: 55.19%, N: 18.33%, H: 4.11%.

2-{3-[4-(2(*S*),6-Dimethyl-heptyl)-6-oxo-1,6-dihydro-pyrimidin-2-yl]-ureido}-5-methyl-benzoic acid (1b)

2-(1-Imidazolylcarbonylamino)-6-(2(*S*),6-dimethylheptyl)-4[1H]-pyrimidinone (**2b**) (143 mg, 0.43 mmol) and 2-amino-5-methyl-benzoic acid (65 mg, 0.43 mmol) were dissolved in dry chloroform (3 mL) under an argon atmosphere. Dry triethylamine (1 drop) was added and the mixture was stirred at reflux conditions overnight. The solution was cooled to room temperature and chloroform (7 mL) was added. The organic layer was extracted with 1M HCl (10 mL), water (10 mL) and brine (2x10 mL), dried over Na_2SO_4 and evaporated *in vacuo*. Recrystallization from toluene yielded the product (73 mg, 0.18 mmol, 41%) as a white solid.

^{1}H NMR ($CDCl_3$): δ = 17.84 (s, 1H), 12.59 (s, 1H), 12.23 (s, 1H), 11.03 (s, 1H), 8.18 (d, 1H), 7.91 (d, 1H), 7.32 (dd, 1H), 5.88 (s, 1H), 2.55 (dd, 1H), 2.34 (s, 3H), 2.23 (dd, 1H), 1.85 (bs, 1H), 1.55-1.13 (m, 8H), 0.94 (d, 3H), 0.83 (dd, 6H). ^{13}C NMR ($CDCl_3$): δ = 174.5; 162.5; 159.5; 152.3; 152.0; 136.9; 134.6; 133.2; 132.0; 121.1; 118.4; 107.5; 42.5; 39.1; 37.1; 32.6; 27.8; 24.6; 22.6; 22.5; 20.7; 19.1 FT-IR ν (cm^{-1}) = 3160, 3065, 2957, 2928, 2869, 2472, 1726, 1693, 1662, 1620, 1587, 1506, 1449, 1398, 1377, 1293, 1228, 1209, 1188, 989. MALDI-TOF-MS: Calculated mass: 414.23 g/mol. Measured mass: m/z = 415.20 [M+H^+], 437.19 [M+Na^+], 453.16 [M+K^+]. Elemental analysis: Calculated for $C_{22}H_{30}N_4O_4$: C: 63.75%, N: 13.52%, H: 7.30%. Measured: C: 63.89%, N: 13.59%, H: 7.06%.

Methyl 2-amino-5-hydroxy-benzoate (4)

2-Amino-5-hydroxy-benzoic acid (**3**) (12.00 g, 78.4 mmol) was dissolved in a mixture of MeOH (125 mL) and concentrated sulphuric acid (14 mL) and stirred at reflux conditions overnight. The MeOH was removed *in vacuo*, H_2O (10 mL) was added and the solution was cooled on an ice bath. NaOH pellets (9.91 g) were added

portionwise and was further neutralized to pH 7 with 1 M NaOH. The precipitate was filtered and washed with H_2O to yield the product (10.87 g, 65.0 mmol, 83%) as a brown solid.

^{1}H NMR (DMSO): δ = 8.65 (s, 1H), 7.09 (d, 1H), 6.79 (dd, 1H), 6.63 (d, 1H), 6.05 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (DMSO): δ = 168.1; 147.1; 145.2; 124.0; 118.3; 114.8; 109.3; 51.8; FT-IR ν (cm^{-1}) = 3379, 3297, 2996, 2947, 2790, 2664, 2588, 1707, 1590, 1510, 1453, 1432, 1375, 1296, 1269, 1246, 1209, 1186, 1154, 1106, 1063.

Methyl 2-amino-5-hexyloxy-benzoate (5)

Methyl benzoate **4** (2.51g, 14.98 mmol) was dissolved in dry DMF (40 mL) under an argon atmosphere and cooled on an ice bath. NaH (60 wt% in mineral oil, 600 mg, 15.00 mmol) was added portionwise over 15 minutes, and the mixture was subsequently stirred at 70 °C for 4 hours. A few drops of H_2O were added and the solvent was removed *in vacuo*. Column chromatography (DCM, R_f = 0.30) yielded the product (1.71 g, 6.79 mmol, 45%) as a brown solid.

^{1}H NMR ($CDCl_3$): δ = 7.35 (d, 1H), 6.95 (dd, 1H), 6.62 (s, 1H), 5.42 (s, 2H), 3.89 (t, 2H), 3.87 (s, 3H), 1.74 (q, 2H), 1.45 (q, 2H), 1.33 (m, 4H), 0.90 (t, 3H). ^{13}C NMR ($CDCl_3$): δ = 168.3; 150.1; 145.0; 123.8; 118.1; 114.3; 110.8; 68.8; 51.6; 31.6; 29.3; 25.7; 22.6; 14.0 FT-IR ν (cm^{-1}) = 3481, 3373, 2952, 2931, 2860, 1694, 1588, 1563, 1496, 1472, 1437, 1286, 1245, 1206, 1095 MALDI-TOF-MS: Calculated mass: 251.15 g/mol. Measured mass: m/z = 251.20 [M^+].

Methyl 5-hexyloxy-2-[3-(4-methyl-6-oxo-1,6-dihydro-pyrimidin-2-yl)-ureido]-benzoate (6)

Methyl benzoate **5** (168 mg, 0.67 mmol) was dissolved in dry chloroform (10 mL) under an argon atmosphere, 2-(1-imidazolylcarbonylamino)-6-methyl-4[1H]-pyrimidinone (**2a**) (172 mg, 0.78 mmol) was added and the mixture was stirred at reflux conditions overnight. The solvent was removed *in vacuo* and the product was recrystallized from methanol twice to yield the product (163 mg, 0.41 mmol, 60%) as a white solid.

^{1}H NMR (DMSO): δ = 12.04-10.06 (m, 3H), 8.08 (bs, 1H), 7.38 (d, 1H), 7.22 (dd, 1H), 5.80 (bs, 1H) 3.98 (t, 2H), 3.86 (s, 3H), 2.19 (s, 3H), 1.70 (sep, 2H), 1.41 (m, 2H), 1.30 (m, 4H), 0.88 (t, 3H). ^{13}C NMR (DMSO): δ = 167.0; 161.9; 154.2; 152.1; 132.9; 123.9; 120.9; 119.3; 115.2; 104.4; 68.3; 52.9; 31.4, 29.0; 25.6; 22.5; 14.3 FT-IR ν (cm^{-1}) = 3096, 3040, 2952, 2935, 2856, 2597, 1721, 1672, 1614, 1586, 1547, 1527, 1503, 1465, 1430, 1392, 1328, 1287, 1212, 1075 MALDI-TOF-MS: Calculated mass: 402.19 g/mol. Measured mass: m/z = 403.09 [$M+H^+$], 425.08 [$M+Na^+$]. Elemental analysis: Calculated for $C_{20}H_{26}N_4O_5$: C: 59.69%, N: 13.92%, H: 6.51%. Measured: C: 59.73%, N: 13.90%, H: 6.07%.

2-Amino-5-hexyloxy-benzoic acid (7)

Methyl benzoate **5** (1.42 g, 5.66 mmol) was dissolved in MeOH (50 mL) with H_2O (5 mL), $LiOH.H_2O$ (1.19 g, 28.3 mmol) was added and stirred at reflux conditions overnight. The solvent was removed *in vacuo* and EtOAc (100 mL) was added and extracted with 1 M HCl (100 mL), H_2O (2x100 mL), brine (100 mL), dried over Na_2SO_4 and evaporated *in vacuo* to yield the product (1.05 g, 4.43 mmol, 78%) as a pale brown solid.

^{1}H NMR ($CDCl_3$): δ = 7.40 (d, 1H), 7.00 (dd, 1H), 6.64 (s, 1H), 3.91 (t, 2H), 1.75 (q, 2H), 1.45 (sep, 2H), 1.33 (m, 4H), 0.91 (t, 3H). ^{13}C NMR ($CDCl_3$): δ = 172.8; 150.1; 145.7; 125.2; 118.4; 114.4; 109.5; 68.8; 31.6; 29.3; 25.7; 22.6; 14.0 FT-IR ν (cm^{-1}) = 2955, 2928, 2859, 2640, 1635, 1562, 1503, 1477, 1417, 1364, 1315, 1255, 1201, 1168, 1028 MALDI-TOF-MS: Calculated mass: 237.17 g/mol. Measured mass: m/z = 237.19 [M^+].

5-Hexyloxy-2-[3-(4-methyl-6-oxo-1,6-dihydro-pyrimidin-2-yl)-ureido]-benzoic acid (8)

Benzoic acid **7** (226 mg, 0.95 mmol) was dissolved in dry chloroform (10 mL) and dry Et_3N (5 drops) under an argon atmosphere and 2-(1-imidazolylcarbonylamino)-6-methyl-4[1H]-pyrimidinone (231 mg, 1.05 mmol) was added. The mixture was stirred at reflux conditions for 3 hours. The solvent was evaporated *in vacuo* and the residual solids were dissolved in methanol (10 mL). The solution was acidified using 1 M HCl to pH 1, filtered and washed with methanol. The product was stirred in hot methanol and filtered to yield the product (331 mg, 0.852 mmol, 89%) as a white solid.

^{1}H NMR (TCE-d_2): δ = 17.98 (s, 1H), 12.71 (s, 1H), 12.10 (s, 1H), 10.91 (s, 1H), 8.14 (d, 1H), 7.60 (d, 1H), 7.04 (dd, 1H), 5.81 (s, 1H), 3.94 (t, 2H), 2.26 (s, 3H) 1.77 (sep, 2H), 1.46 (m, 2H), 1.35 (m, 4H), 0.92 (t, 3H). ^{13}C NMR (DMSO): δ = 168.8; 161.7; 153.9; 152.3; 133.6; 123.1; 120.7; 119.7; 115.7; 103.9; 68.3; 31.4; 29.0; 25.6; 22.5; 14.4 FT-IR ν (cm^{-1}) = 3127, 3068, 2946, 2926, 2868, 1706, 1678, 1649, 1593, 1500, 1474, 1459, 1401, 1365, 1300, 1271, 1199, 1104, 1034, 985 MALDI-TOF-MS: Calculated mass: 388.17 g/mol. Measured mass: m/z = 389.08 [M+H^+], 411.08 [M+Na^+]. Elemental analysis: Calculated for $C_{19}H_{24}N_4O_5$: C: 58.75%, N: 14.42%, H: 6.23%. Measured: C: 58.38%, N: 14.30%, H: 5.78%.

5-Hexyloxy-2-[3-(pyridin-2-yl)-ureido]-benzoic acid (9)

2-Amino-pyridine (141 mg, 1.50 mmol) was dissolved in dry chloroform (15 mL) under an argon atmosphere, 1,1'-carbodiimidazole (244 mg, 1.50 mmol) and dry triethylamine (1 drop) were added and stirred at room temperature overnight. Benzoic acid **7** (355 mg, 1.50 mmol) and dry triethylamine (4 drops) were added and the mixture was stirred for 5 hours under an argon atmosphere at 60 °C. The solvent was removed *in vacuo*, methanol (10 mL) and H_2O (10 mL) were added and the mixture was acidified to pH 1 with 1 M HCl. The solids were collected by filtration, washed with H_2O and methanol and recrystallized from methanol to yield the product (132 mg, 0.35 mmol, 25%) as a white solid.

^{1}H NMR ($CDCl_3$): δ = 18.40 (s, 1H), 11.37 (s, 1H), 10.94 (s, 1H), 8.41 (m, 2H), 8.13 (d, 1H), 7.85 (t, 1H), 7.68 (s, 1H), 7.12 (d, 1H, 7.07 (t, 1H), 4.00 (t, 2H), 1.80 (sep, 2H), 1.49 (m, 2H), 1.35 (m, 4H), 0.92 (t, 3H). ^{13}C NMR ($CDCl_3$): δ = 174.4; 153.7; 152.5; 151.9; 142.8; 141.1; 135.1; 121.8; 121.2; 118.5; 117.7; 115.8; 115.1; 68.4; 31.6; 29.3; 25.7; 22.6; 14.1 FT-IR ν (cm^{-1}) = 3246, 3038, 2931, 2859, 2417, 1718, 1589, 1525, 1474, 1437, 1417, 1334, 1291, 1207 MALDI-TOF-MS: Calculated mass: 357.17 g/mol. Measured mass: m/z = 358.05 [M+H^+]. Elemental analysis: Calculated for $C_{19}H_{29}N_3O_4$: C: 63.85%, N: 11.76%, H: 6.49%. Measured: C: 63.82%, N: 11.66%, H: 6.34%.

5-Hexyloxy-2-[3-(1H-benzimidazol-2-yl)-ureido]-benzoic acid (10)

2-Amino-benzimidazole (103 mg, 0.77 mmol) was dissolved in dry dimethylformamide (4 mL) under an argon atmosphere, 1,1'-carbodiimidazole (125 mg, 0.77 mmol) was added and stirred at room temperature for 6 hours. Benzoic acid **7** (170 mg, 0.72 mmol) and dry triethylamine (2 drops) were added and the mixture was stirred under an argon atmosphere at 60 °C overnight. The solvent was removed *in vacuo* and methanol (3 mL) and H_2O (2 mL) were added. The solution was acidified to pH 1 with 1 M HCl and filtered. The solids were washed with 1 M HCl, H_2O and methanol. Recrystallization from toluene yielded the product (231 mg, 0.58 mmol, 81%) as a white solid.

^{1}H NMR ($CDCl_3$): δ = 19.11 (s, 1H), 14.32 (s, 1H), 12.08 (s, 1H), 11.51 (s, 1H), 8.30 (d, 1H), 7.76 (d, 1H), 7.60 (d, 1H) 7.39-7.29 (m, 3H), 6.91 (dd, 1H), 3.92 (t, 2H), 1.77 (sep, 2H), 1.49 (m, 2H), 1.37 (m, 4H), 0.94 (t, 3H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ = 174.5; 154.1; 151.2; 147.2; 133.0; 129.6; 123.7; 123.4; 121.1; 118.9; 116.1; 112.8; 68.2; 31.6; 29.3; 25.7; 22.6; 14.0 FT-IR ν (cm^{-1}) = 3312, 3056, 2944, 2875, 2852, 2623, 1694, 1653, 1594, 1510, 1473, 1462, 1418, 1376, 1293, 1260, 1237, 1200, 1081, 1028, 1012, 937. MALDI-TOF-MS: Calculated mass: 396.18 g/mol. Measured mass: m/z = 397.01 [$M+H^+$], 419.00 [$M+Na^+$]. Elemental analysis: Calculated for $C_{21}H_{24}N_4O_4$: C: 63.62%, N: 14.13%, H: 6.10%. Measured: C: 63.65%, N: 14.17%, H: 5.90%.

Methyl 2-amino-5-(6-*tert*-butoxycarbonylamino-hexyloxy)-benzoate (11)

2-Amino-5-hydroxy-benzoic acid methyl ester **4** (2.32 g, 13.9 mmol) was dissolved in dry dimethylformamide (30 mL) under an argon atmosphere and cooled on an ice bath. NaH (60 wt% in mineral oil, 615 mg, 15.4 mmol) was added portionwise over 15 minutes, after which 6-(Boc-amino)hexyl bromide (3.86 g, 13.8 mmol) was added. The solution was stirred under an argon atmosphere at 75 °C overnight. The solvent was removed *in vacuo* and the product was purified using column chromatography ($CHCl_3$ with 0 to 1% MeOH, R_f = 0.28) to yield the product (3.44 g, 9.38 mmol, 68%) as a pale brown solid.

^{1}H NMR ($CDCl_3$): δ = 7.34 (d, 1H), 6.94 (dd, 1H), 6.62 (d, 1H), 5.45 (s, 2H), 4.51 (s, 1H), 3.89 (t, 2H), 3.87 (s, 3H), 3.12 (m, 2H), 1.75 (sept, 2H), 1.54-1.35 (m, 15H). ^{13}C NMR ($CDCl_3$): δ = 168.3; 155.9; 149.9; 145.0; 123.8; 118.1; 114.3; 110.7; 79.0; 68.6; 51.5; 30.0; 29.2; 28.4; 26.5; 25.8 FT-IR ν (cm^{-1}) = 3471, 3365, 2976, 2934, 2861, 1690, 1591, 1564, 1497, 1438, 1391, 1365, 1287, 1244, 1207, 1167, 1098 MALDI-TOF-MS: Calculated mass: 366.22 g/mol. Measured mass: m/z = 366.12 [M^+].

2-Amino-5-(6-*tert*-butoxycarbonylamino-hexyloxy)-benzoic acid (12)

Methyl benzoate **11** (2.83 g, 7.71 mmol) was dissolved in methanol (60 mL) with H_2O (6 mL), $LiOH.H_2O$ (1.09 g, 25.86 mmol) was added and the solution was stirred at reflux conditions overnight. The solvent was removed *in vacuo* and H_2O (100 mL) was added and acidified with saturated oxalic acid until a precipitate was formed. The solids were extracted with ethyl acetate (150 mL) and the organic layer was extracted with H_2O (100 mL), brine (100 mL), dried over Na_2SO_4, and evaporated *in vacuo* to yield the product (2.63 g, 7.44 mmol, 96%) as a pale brown solid.

^{1}H NMR ($CDCl_3$): δ = 7.40 (d, 1H), 6.98 (dd, 1H), 6.63 (d, 1H), 4.56 (s, 1H), 3.90 (t, 2H), 3.12 (m, 2H), 1.75 (q, 2H), 1.53-1.38 (m, 15H). ^{13}C NMR ($CDCl_3$): δ = 172.6; 156.0; 150.0; 145.6; 124.9; 118.4; 114.5; 109.8; 79.1;

68.6; 31.6; 30.0; 29.2; 28.4; 26.5; 25.7; 22.6; 14.1; FT-IR ν (cm^{-1}) = 3495, 3361, 2980, 2928, 2855, 2598, 1687, 1650, 1604, 1537, 1504, 1475, 1455, 1365, 1308, 1276, 1247, 1166, 1136, 1045, 1020, 984 MALDI-TOF-MS: Calculated mass: 352.20 g/mol. Measured mass: m/z = 352.12 [M^+].

5-(6-*tert*-Butoxycarbonylamino-hexyloxy)-2-[3-(4-methyl-6-oxo-1,6-dihydro-pyrimidin-2-yl)-ureido]-benzoic acid (13)

Benzoic acid **12** (437 mg, 1.24 mmol) and 2-(1-imidazolylcarbonylamino)-6-methyl-4[1H]-pyrimidinone (335 mg, 1.53 mmol) were dissolved in dry chloroform (10 mL) under an argon atmosphere and dry triethylamine (5 drops) was added. The solution was stirred at reflux conditions overnight. The solvent was removed *in vacuo* and to the residual solids methanol (10 mL) was added and acidified with saturated oxalic acid. The solids were collected by filtration and washed with H_2O and methanol. The solids were recrystallized from methanol to yield the product (443 mg, 0.88 mmol, 71%) as a white solid.

^{1}H NMR ($CDCl_3$): δ = 18.00 (s, 1H), 12.70 (s, 1H) 11.83 (s, 1H), 10.81 (s, 1H), 8.00 (d, 1H), 7.37 (d, 1H), 6.73 (dd, 1H), 5.51 (s, 1H), 4.73 (s, 1H), 3.79 (t, 2H), 3.15 (q, 2H), 2.11 (s, 3H), 1.76 (sept, 2H), 1.59-1.39 (m, 15H). ^{13}C NMR ($CDCl_3$): δ = 173.9; 158.5; 157.4; 156.1; 154.5; 151.5; 151.3; 131.8; 121.8; 120.0; 119.0; 116.2; 106.6; 79.0; 68.1; 40.5; 30.0; 29.1; 28.5; 26.6; 25.7; 20.3; FT-IR ν (cm^{-1}) = 3346, 3150, 2933, 2865, 2553, 1682, 1620, 1591, 1505, 1450, 1401, 1364, 1299, 1274, 1237, 1206, 1173, 1104, 1020, 988. MALDI-TOF-MS: Calculated mass: 503.24 g/mol. Measured mass: m/z = 504.27 [$M+H^+$], 526.28 [$M+Na^+$]. Elemental analysis: Calculated for $C_{24}H_{33}N_5O_7$: C: 57.25%, N: 13.91%, H: 6.61%. Measured: C: 57.25%, N: 13.65%, H: 6.32%.

5-(6-Amino-hexyloxy)-2-[3-(4-methyl-6-oxo-1,6-dihydro-pyrimidin-2-yl)-ureido]-benzoic acid TFA salt (14)

BOC protected ureidobenzoic acid **13** (261 mg, 0.52 mmol) was dissolved in dichloromethane (8 mL) with trifluoroacetic acid (8 mL) and stirred at room temperature for 2 hours. The solvents were removed *in vacuo*, and the solids were coevaporated with toluene (2x8 mL) to remove residual trifluoroacetic acid and H_2O. The product (353 mg) was obtained as a white solid and was used without further purification.

^{1}H NMR (MeOD): δ = 8.24 (d, 1H), 7.54 (d, 1H), 7.12 (d, 1H), 5.91 (s, 1H), 4.00 (t, 2H), 2.94 (t, 2H), 2.26 (s, 3H), 1.82 (sept, 2H), 1.70 (sept, 2H), 1.57 (sept, 2H), 1.49 (sept, 2H). FT-IR ν (cm^{-1}) = 3074, 2942, 2870, 2558, 1779, 1668, 1615, 1586, 1501, 1428, 1395, 1287, 1241, 1195, 1134, 1077, 1032. MALDI-TOF-MS: Calculated mass: 403.19 g/mol. Measured mass: m/z = 404.14 [$M+H^+$], 426.12 [$M+Na^+$], 442.10 [$M+K^+$].

Poly(ethylene-butylene)-α,ω-bis(6-{ureido-hexyloxy}-2-[3-(4-methyl-6-oxo-1,6-dihydro-pyrimidin-2-yl)-ureido]-benzoic acid (15)

Amino-ureidobenzoic acid **14** (353 mg, 0.52 mmol) was dried at 40 °C over P_2O_5 overnight prior to use. The amino-ureidobenzoic acid and *N*,*N*'-bis-imidazolylcarbonylamino-poly(ethylene-butylene) (740 mg, 0.20 mmol) were added to dry chloroform (20 mL) and dry triethylamine (0.2 mL) under an agron atmosphere and stirred at reflux conditions overnight. The mixture was cooled to room temperate, chloroform (30 mL) was added and the

organic layer was extracted with 1 M HCl (50 mL). The aqueous layer was extracted with chloroform (25 mL) and the combined organic layer was extracted with 1 M HCl (25 mL), brine (2x25mL), dried over Na_2SO_4, concentrated and the residue was precipitated in methanol twice to yield the product (381 mg, 0.088 mmol, 44%) as a white fibrous solid. T_g: -54.7 °C, T_m: 168 °C (DSC)

^{1}H NMR ($CDCl_3$): δ = 17.92 (s, 2H), 12.54 (s, 2H), 11.93 (bs, 2H), 10.83 (s, 2H), 8.10 (bs, 2H), 7.47 (bs, 2H), 6.77 (bs, 2H), 5.58 (bs, 2H), 5.25-4.61 (m, 4H), 3.85 (m, 6H), 3.27-2.96 (m, 8H), 2.20-0.76 (m). FT-IR ν (cm^{-1}) = 3349, 2960, 2921, 2853, 1720, 1689, 1636, 1592, 1531, 1460, 1379, 1277, 1210. Elemental analysis: Measured: C: 83.41%, N: 1.50%, H: 13.34%. GPC (THF): M_n: 11413, PDI: 1.60.

3. Additional Figures and Spectra

3.1 NOESY spectrum of molecule **8**

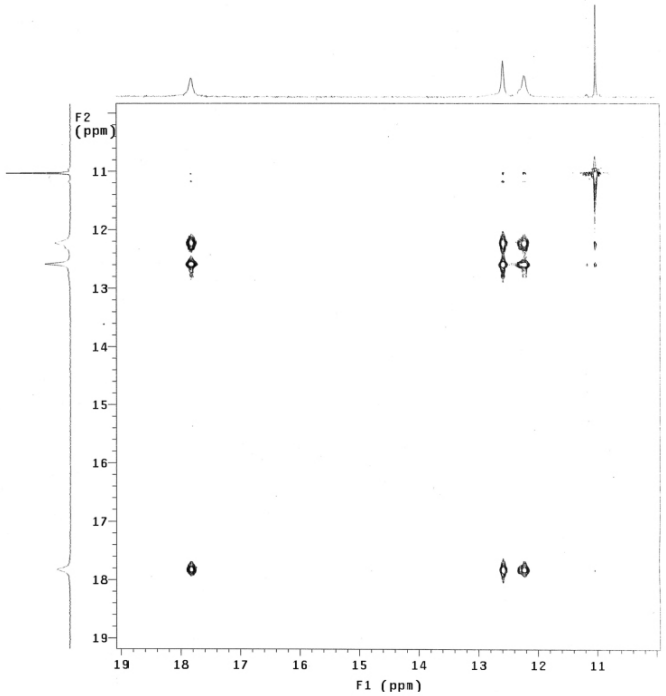

Figure S1 NOESY spectrum of molecule **8** in the 19-10 ppm region recorded in $CDCl_3$.

3.2 ^{1}H NMR spectrum of molecule **6**

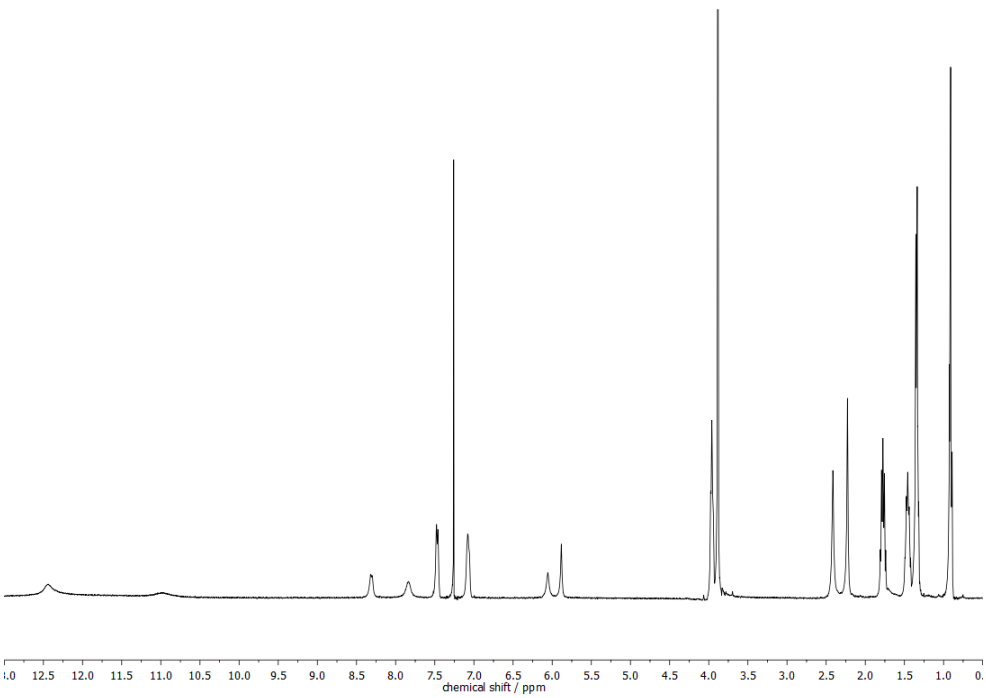

Figure S2 ^{1}H NMR spectrum of molecule **6** in $CDCl_3$.

3.3 UV-vis titration of molecule **6** with NaPy

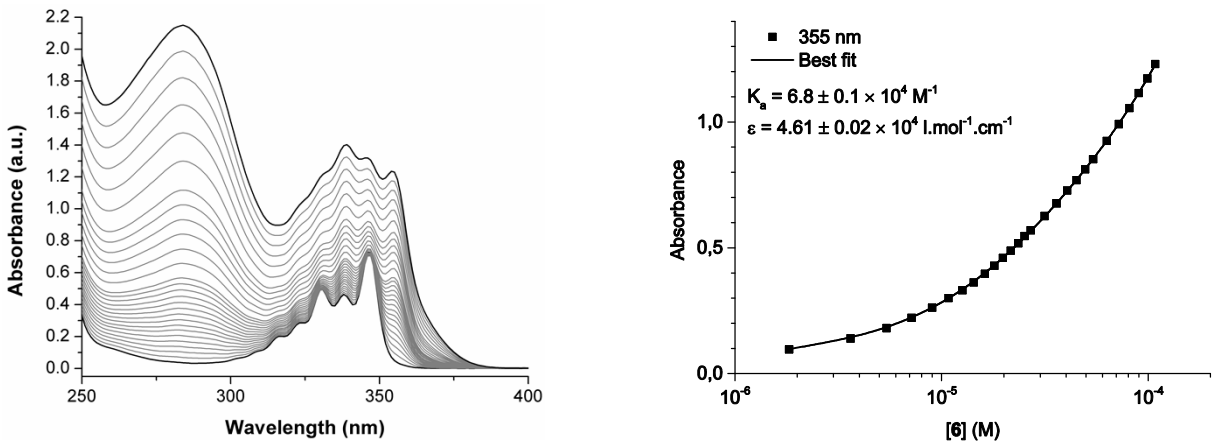

Figure S3 Results of the UV-vis titration upon addition of up to 6 equivalents of molecule **6** to a 18 μM solution of NaPy in chloroform.

3.4 ^{1}H-NMR titration of molecule **8** with NaPy

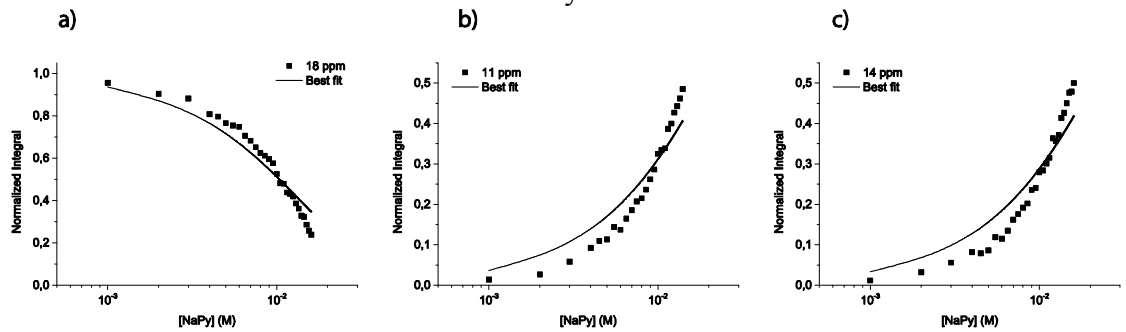

Figure S4 Results of the ^{1}H-NMR titration upon addition of up to 8 equivalents of NaPy to a 2 mM solution of **8** in deuterated tetrachloroethane. a) normalized integral corresponding to UBA dimer. b) and c) normalized integrals corresponding to UBA in the UBA:NaPy complex. The poor quality of the fit indicates the presence of additional interactions at these concentrations, for instance lateral aggregation of the UBA dimers and/or the UBA:NaPy complex. The nature of these interactions is currently under investigation.

Table 2 Association constants for the formation of the UBA:NaPy complex obtained from fitting the ^{1}H-NMR titration to a model describing 1:1 complexation in the presence of homodimerization of one of the components. Data was fitted using a conservative value of 10^8 M^{-1} for the dimerization of UBA.

δ (ppm)	K_a (10^4 M^{-1})
11.2	2.5 ± 0.1
14	2.3 ± 0.1
18	4.8 ± 0.2

3.5 Fluorescence spectra of molecules **6** and **8**

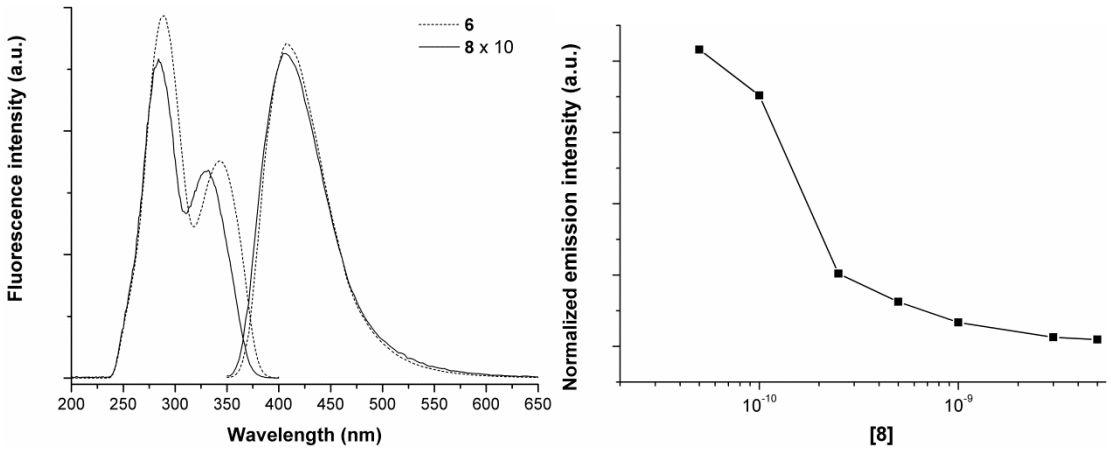

Figure S5 Left: Fluorescent properties of 10 μM solutions of molecules **6** (dashed lines) and **8** (solid lines, multiplied by 10) in chloroform. Right: change in emission intensity at 410 nm normalized to the concentration of molecule **8** upon dilution (right, line was added to guide the eye). Excitation wavelength = 330 nm, emission wavelength = 410 nm.

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