Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Alternation and Tunable Composition in Hydrogen Bonding Supramolecular Copolymers

Thorsten Felder, Tom F.A. de Greef, Marko M.L. Nieuwenhuizen and Rint P. Sijbesma*

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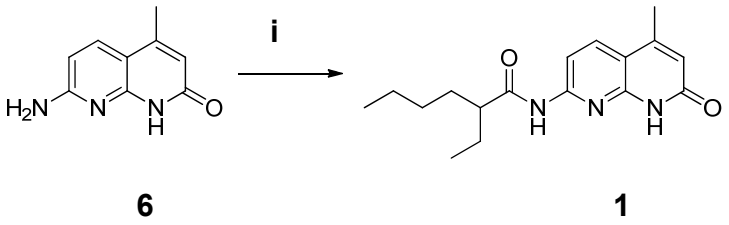
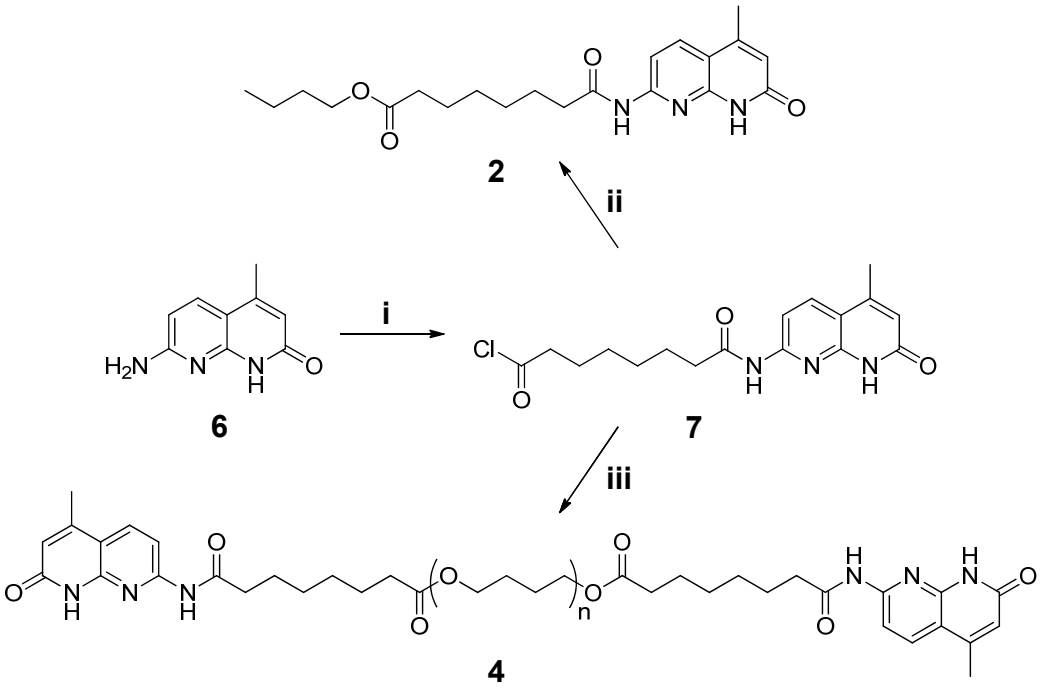
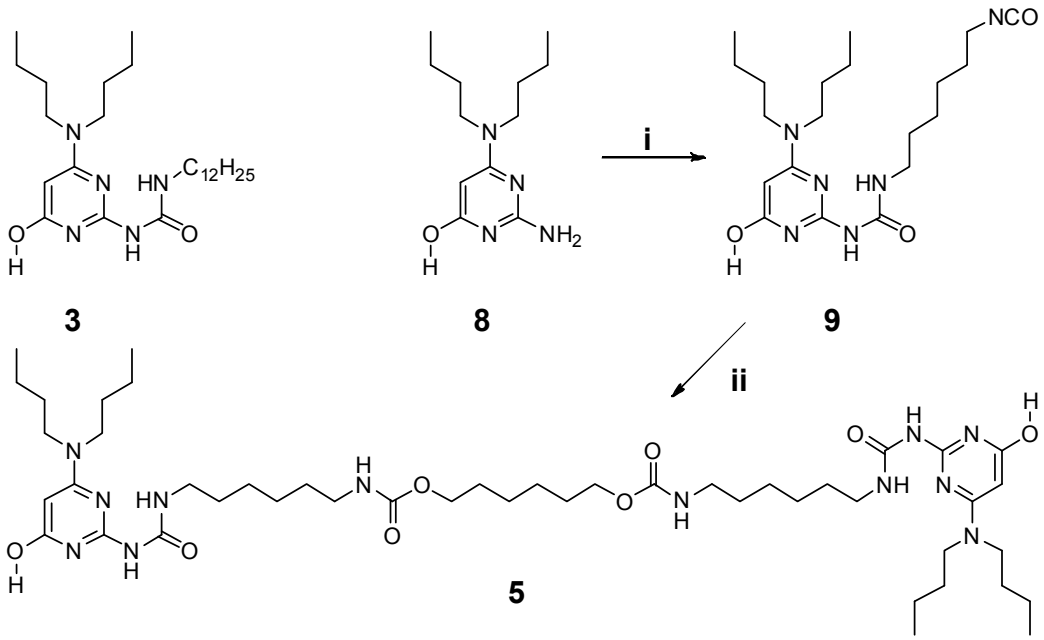


Scheme 1: Synthesis of **1**. (i) 2-ethylhexanoyl chloride, pyridine, RT; 81%.



Scheme 2: Synthesis of **2** and **4**. (i) suberoyl chloride, 100°C; 71%; (ii) n-butanol, pyridine, 50°C; 58%; (iii) Poly-THF_{2000}, $CHCl_3$, pyridine, 81°C; 56%.



Scheme 3: Synthesis of **5**. (i) hexamethylene diisocyanate, 60°C; 16%; (ii) 1,6-hexane diol, DBTL, $CHCl_3$, 50°C; 23%.

Experimental details:

General methods: All reagents were purchased from Adrich, Alfa Aesar or ACROS and used without any treatment or further purification. Solvents were used as purchased or dried prior to their use over molecular sieves with a pore size of 3Å (e.g. chloroform, pyridine). Thin-layer chromatography (TLC) was performed on silica gel plates (SiO_2, $60/F_{251}$) manufactured by the Merck KGaA. Column chromatography was performed on silica gel (SD Screening Devices b.v., 60-200μm, 60 Å). ^{1}H- (400 MHz) and ^{13}C- (100 MHz) NMR spectra were recorded on a VARIAN 400-MR spectrometer using deuterated chloroform or dimethylsulfoxide as the solvent. ^{1}H-NMR (500 MHz) dilution experiments in order to determine the dimerization constants (K_{dim}) of the self-associating molecules under study as well as the variable temperature (VT) experiments were performed on a VARIAN AS500 spectrometer. All chemical shifts are reported in ppm and corrected to the residual solvent signal as internal standard. Coupling constants (*J*) are given in Hertz (Hz). The following abbreviations are used to specify the multiplicities of the signals: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Mass spectrometric characterization was performed on a PerSeptive Biosystems MALDI-TOF spectrometer (Voyager-DE PRO) equipped with a N_2 laser (337 nm). Sample preparation was performed using DCTB (2-[(2E)-3-(4-*tert*-Butylphenyl)-2-methylprop-2-enylidene]-malononitrile) or CHCA (α-Cyanohydroxycinnamic acid) as the matrix. A Perkin Elmer Lambda 40 UV/Vis-spectrometer equipped with a water thermostatted cell holder was used for the titration experiments in order to determine the association constants. The UV/Vis- measurements were performed with a standard 1 cm glass cuvette. Infrared (IR) spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometer equipped with an ATR sampling accessory. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O analyzer. Melting points were measured on a Büchi Melting Point B-540 apparatus. Viscosity measurements of solutions were performed on a Schott-Geräte capillary Ubbelohde microviscosimeter with a suspended level bulb, thermostated at 25.00 (±0.01) °C. Solutions were freshly filtered prior to the measurements using 5-μm polytetrafluoroethylene filters. Specific viscosities were corrected using the appropriate Hagenbach correction factors.

Synthesis. 7-amino-4-methyl-1,8-naphthyridin-2(1*H*)-one (**6**) was synthesized according to a literature procedure published by Brown *et al.*[1] Preparation of 2-amino-6-(dibutylamino) 4-pyrimidinol (**8**) and 1-(4-(dibutylamino)-6-hydroxypyrimidin-2-yl)-3-dodecylurea (**3**) was described earlier by Meijer and Sijbesma *et al.*[2]

2-ethyl-*N*-(5-methyl-1,5-naphtyridine)hexanamide (**1**). 2-Ethylhexanoyl chloride (1.2 ml, 7.14 mmol) was slowly added to a solution of 7-amino-4-methyl-1,8-naphthyridin-2(1*H*)-one (**6**) (1.0 g, 5.71 mmol) in dry pyridine (10.0 ml). The mixture was stirred at room temperature for 24 h and the solvent removed *in vacuo*. The residue was diluted with dichloromethane (100.0 ml). The organic phase was washed with 0.1 M aqueous HCl solution (10.0 ml), water (10.0 ml), saturated $NaHCO_3$ solution (10.0 ml) and dried over anhydrous $MgSO_4$. After evaporation of the solvent the crude product was purified by re-crystallization from acetone yielding in 1.4 g (81%) of a colorless powder. ^{1}H NMR ($CDCl_3$) δ = 12.76 (s, 1H; NH), 11.88 (s, 1H; NH), 8.45 (d, ^3J(H,H) = 8.6 Hz, 1H; ArH), 8.03 (d, ^3J(H,H) = 8.6 Hz, 1H; ArH), 6.50 (s, 1H; ArH), 2.83 (br, 1H; CH), 2.59 (s, 3H; CH_3), 1.75 (m, 2H; CH_2), 1.59 (m, 2H; CH_2), 1.34 (br, 4H; CH_2), 0.97 (m, 3H; CH_3), 0.85 (m, 3H; CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ = 177.8, 164.8, 154.0, 148.5, 148.4, 136.0, 119.0, 112.0, 110.6, 48.4, 32.5, 29.7, 26.2, 22.9, 18.6, 14.0, 11.9 ppm; MALDI-TOF-MS: (m/z) calcd.: 301.39; observed: 302.1 ($M+H^+$), 324.1 ($M+Na^+$); FTR-IR (ATR): ν = 3175, 3135, 3069, 2960, 2933, 1705, 1657, 1616, 1579, 1525, 1461, 1388, 1340, 1308, 1296, 1175, 1140, 862, 821 cm^{-1}; Anal. calcd. for $C_{17}H_{23}N_3O_2$: C 67.75, H 7.69, N 13.94; found: C 67.78, H 7.69, N 13.92.

butyl 8-((5-methyl-7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)amino)-8-oxooctanoate (**2**). 8-((5-methyl-7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)amino)-8-oxooctanoyl chloride **7** (0.50 g, 1.43 mmol) was heated under reflux in a mixture of 1-butanol (20.0 ml) and pyridine (0.50 ml) for 0.5 h. The solvent was removed in vacuo and the residue dissolved in dichloromethane (20.0 ml). The organic phase was washed with 0.1 M aqueous HCl solution (10.0 ml), saturated $NaHCO_3$ solution (10.0 ml) and dried over

(1) E. V. Brown, *J. Org. Chem.* **1965**, *30*, 1607.
(2) T. F. A. de Greef, G. B. W. L. Ligthart, M. Lutz, A. L. Spek, E. W. Meijer and R. P. Sijbesma, *J. Am. Chem Soc.* **2008**, *130*, 5479.

anhydrous $MgSO_4$. The evaporation of the solvent yielded in 0.30 g (58%) of a white material. ^{1}H NMR ($CDCl_3$) δ = 12.59 (s, 1H; NH), 11.93 (s, 1H; NH), 8.33 (d, ^3J(H,H) = 9.4 Hz, 1H; ArH), 7.95 (d, ^3J(H,H) = 8.6 Hz, 1H; ArH), 6.42 (s, 1H; ArH), 4.05 (t, ^3J(H,H) = 6.7 Hz, 2H; CH_2), 2.63 (t, ^3J(H,H) = 7.4 Hz, 2H; CH_2), 2.46 (s, 3H; CH_3), 2.30 (t, ^3J(H,H) = 7.8 Hz, 2H; CH_2), 1.66 (m, 6H; CH_2), 1.38 (m, 6H; CH_2), 0.92 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ = 174.3, 173.9, 164.8, 154.0, 148.5, 148.3, 135.9, 118.9, 111.8, 110.2, 64.1, 36.8, 34.4, 30.7, 29.0, 28.9, 25.1, 24.9, 19.1, 18.6, 13.7 ppm; MALDI-TOF-MS: (m/z) calcd.: 387.47; observed: 388.2 ($M+H^+$), 410.1 ($M+Na^+$); Anal. calcd. for $C_{21}H_{29}N_3O_4$: C 65.09, H 7.54, N 10.84; found: C 65.00, H 7.60, N 10.94.

α,ω-Napy functionalized poly(tetrahydrofuran) (4). Polytetrahydrofuran 2000 (0.70 g) was dissolved in a mixture of dry $CHCl_3$ (20.0 ml) and dry pyrdine (1.00 ml) under an argon atmosphere. The acid chloride **7** (0.55 g, 1.57 mmol) was added portionwise to the solution and the resulting dispersion was heated at 60 °C for 12 hrs. Thereafter, the precipitate was removed by filtration and the solvent was evaporated *in vacuo*. The received residue was dissolved in $CHCl_3$ (20.0 ml) and organic phase was washed twice with 0.1 M aqueous HCl solution (2 x 10.0 ml) and water (2 x 10.0 ml).The organic phase was dried over $MgSO_4$ and finally the solvent was evaporated *in vacuo* to a quarter of the initial volume. The concentrated solution was dropped under vigorous stirring into a volume of ice cold methanol (150 ml) whereby the product precipitated in the form of a white material. The precipitate was filtered off, rinsed thoroughly with methanol (50.0 ml) and dried. 1.01 g of pure product (81 %) was obtained as a colorless rubber-like material. ^{1}H-NMR ($CDCl_3$): δ 12.68 (s, 2H; NH), 11.92 (s, 2H; NH), 8.39 (d, ^3J(H,H) = 8.6 Hz, 2H; ArH), 8.01 (d, ^3J(H,H) = 9.4 Hz, 2H; ArH), 6.49 (s, 2H; ArH), 4.07 (t, ^3J(H,H) = 6.3 Hz, 4H; CH_2), 3.41 (br, 172H; CH_2 polyTHF), 2.65 (t, ^3J(H,H) = 7.0 Hz, 4H; CH_2), 2.49 (s, 6H; CH_3), 2.30 (t, ^3J(H,H) = 7.4 Hz, 4H; CH_2), 1.66 (m, 154H; CH_2 & CH_2 polyTHF), 1.41 (m, 12H; CH_2) ppm; ^{13}C-NMR ($CDCl_3$): δ = 174.3, 173.8, 164.8, 154.0, 148.6, 148.2, 135.9, 118.8, 111.8, 110.2, 107.1*, 70.5, 70.1, 64.0, 36.8, 34.3, 28.9, 28.8, 26.4, 26.2, 25.5, 25.1, 24.8, 18.6 ppm. *impurity

Hexane-1,6-diyl bis(6-(3-(4-(dibutylamino)-6-hydroxypyrimidin-2-yl) ureido) hexyl-carbamate) (5). 2-(6-isocyanatohexylaminocarbonylamino)-6-(dibutylamino) 4-pyrimidinol **9** (1.33 g, 3.27 mmol) was dissolved under an atmosphere of argon in dry $CHCl_3$ (15.0 mL) and 1,6-hexanediol (0.17 g, 1.47 mmol) was added. Thereafter, a drop of DBTL (dibutyltin laurate) was added to the solution. The mixture was stirred for 5 hours at 50 ^oC. After cooling to room temperature, the solvent was evaporated *in vacuo*. Column chromatography (SiO_2, 6-9 % EtOH/$CHCl_3$) followed by re-crystallisation from hot acetone and subsequent drying of the material *in vacuo* afforded 0.70 g (23.0 %) of the product as a white solid. MP: 95 ^oC; %. ^{1}H-NMR ($CDCl_3$): δ 12.52 (s, 2H; OH), 11.16 (s, 2H; NH), 9.56 (s, 2H; NH), 5.26 (s, 2H; ArH), 4.81 (br, 2H; NH), 3.98 (t, 4H; CH_2), 3.28 (m, 12H; CH_2), 3.11 (t, 4H; CH_2), 1.55-1.21 (m, 32H; CH_2), 0.91 (t, 12H; CH_3); ^{13}C-NMR ($CDCl_3$): δ = 170.7, 162.3, 157.4, 156.8, 78.7, 64.6, 48.9, 40.8, 39.7, 29.8, 28.8, 26.4, 25.5, 20.3, 14.0, 13.8 ppm; IR (ATR): ν = 3331, 3218, 3124, 3021, 2955, 2931, 2860, 2551, 1675, 1612, 1557, 1522, 1506, 1442, 1369, 1320, 1279, 1241, 1205, 1146, 1111, 1058, 987, 909 cm^{-1}; MALDI-TOF-MS (m/z): calcd.: 930.64; observed: 931.61 ($M+H^+$). Anal. calcd for $C_{46}H_{82}N_{12}O_8$: C 59.33, H 8.88, N 18.05 found C 59.07, H 8.97, N 18.01.

8-((5-methyl-7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)amino)-8-oxooctanoyl chloride (**7**). 7-amino-4-methyl-1,8-naphthyridin-2(1*H*)-one **6** (0.50 g, 2.85 mmol) was heated at 100°C for 3 h in an excess of suberoyl chloride (10.0 ml, 11.7 g, 55.4 mmol). The formed precipitate was filtered off, thoroughly washed with cyclohexane (30.0 ml) and dried under vacuum yielding in 0.70 g (71%) of a yellow solid. The product was immediately used for the following steps without further purification or characterization.

2-(6-isocyanatohexylaminocarbonylamino)-6-(dibutylamino)-4-pyrimidinol (9). A solution of 2-amino-6-(dibutylamino) 4-pyrimidinol (3.04 g, 12.8 mmol) and 1,6-diisocyanatohexane (HDI, 30.0 mL, 31.2 g, 186 mmol) was heated to 60 ^oC and stirred for 1 h under Argon. The solution was cooled to room temperature and 7.00 mL of acetonitrile was added. To this solution, pentane (300 mL) was added and the solution was stirred for half a minute. Upon standing, the solution separated into two layers. The

upper layer (containing HDI and pentane) was decanted and the process was repeated an additional two times. After the third decantation step, acetonitrile (40.0 mL) was added and the solution was cooled to –40 °C. Upon cooling a white solid precipitated which was collected by vacuum filtration. The residue was washed several times with pentane (100 mL) and dried extensively *in vacuo* resulting in 0.85 g (16.0 %) of a white solid. MP: 96-100 °C; ^{1}H-NMR ($CDCl_3$): δ 12.60 (s, 1H; OH), 11.25 (s, 1H; NH), 9.63 (s, 1H, NH), 5.33 (s, 1H; ArH), 3.40 (m, 8H; CH_2), 1.61-1.31 (m, 18H, CH_2), 0.96 (t, 6H, CH_3) ppm; ^{13}C-NMR ($CDCl_3$): δ = 170.8, 162.4, 157.5, 157.0, 121.9, 78.7, 49.0, 42.9, 39.7, 31.2, 30.2, 29.8, 26.4, 26.3, 14.0 ppm; IR (ATR): ν = 3221, 3126, 2958, 2933, 2862, 2270, 1675, 1617, 1561, 1508, 1455, 1371, 1322, 1283, 1252, 1206, 1148, 1099, 1062, 987 cm^{-1}; MALDI-TOF-MS (m/z): calcd.: 406.26; observed: 407.17 ($M+H^+$) Anal. Calcd. for $C_{20}H_{34}N_6O_3$: C 59.09, H 8.43, N 20.67 found: C 59.09, H 8.43, N 20.72.

Determination of the dimerization constants using ^{1}H-NMR: The ^{1}H-NMR chemical shift of the amide NH protons of compounds **1** and **2** in dry $CDCl_3$ (dried over molecular sieves) show a strong concentration dependence. Dilution of these naphthyridines followed by ^{1}H-NMR shows an upfield shift of the amide NH protons, indicative of formation of a hydrogen bonded complex. The concentration dependent chemical shifts obtained from these titrations were fitted to a monomer-dimer isotherm:

$$\delta_{obs} = \delta_m + \left(\frac{\delta_d - \delta_m}{C_t}\right)\left(\left(C_t + \frac{1}{4K_{dim}}\right) - \left(\left(C_t + \frac{1}{4K_{dim}}\right)^2 - C_t^{\,2}\right)^{1/2}\right)$$

in which C_t represents the total concentration of analyte and δ_{obs} the observed shift. Parameters obtained through fitting are δ_m, the shift of the monomer, δ_d, the shift of the dimer, and K_{dim}, the dimerization constant. Microcal Origin Professional 8.0 software was used for curve fitting. Because at low concentrations, the resonance of the NH proton becomes extremely broad, deconvolution was used to calculate the chemical shift at maximum intensity.

Determination of the association constants using UV-Vis titration experiments: Determination of K_{ass} of the complementary pairs **1·3** and **2·3** was performed at 25°C using a 1cm path length cell. Dry chloroform was used as the solvent for the titration experiment. The concentration of Napy molecules **1** and **2** was kept constant throughout the whole titration experiment. Consequently, μL amounts of a combined solution containing the compounds **1** and **3 (**or **2** and **3,** respectively) at individual concentrations of 2.5 M·10^{-6} M and 3.0·10^{-4} M was continuously added to 2 ml of a 2.5·10^{-4} M solution of **1** (or **2**, respectively). At the end of the titration a total of 9 equivalents UPy **3** were added to the solution. The recorded UV spectra for each titration step were base-line corrected. The values of absorbance obtained for **1** and **2** at a wavelength of 355 nm were plotted against the concentration of added **3**. Fitting of the respective saturation curves was performed using Matlab in a procedure that is described in detail in the following section.

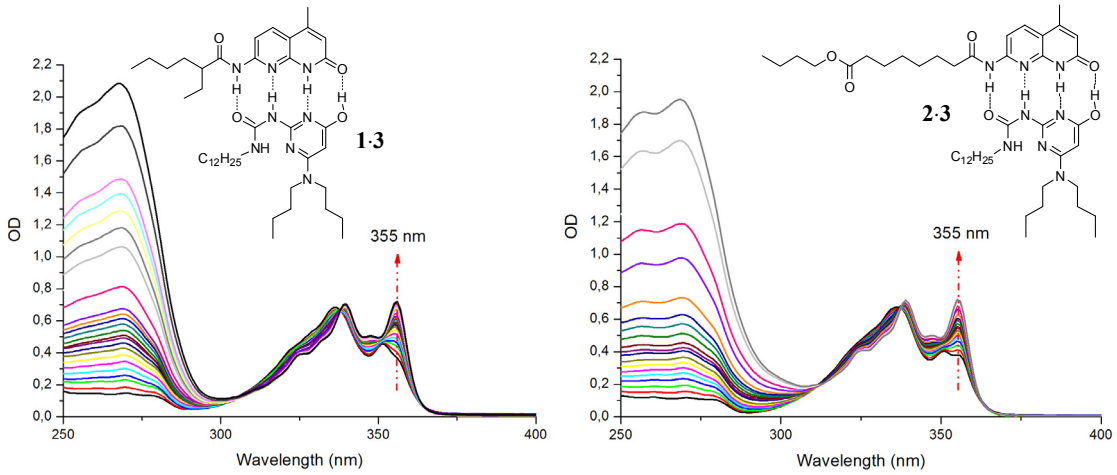


Figure S1. Absorbance development during the UV titration experiment using the compounds **1, 2** and **3.** The increasing absorption at the wavelength at 355 nm indicates he formation of the complex **1·3** and **2·3** in chloroform.

Curve fitting procedure of the UV-Vis titration data obtained from a single wavelength: A script was written in Matlab to determine the association constants K_{ass} for the complexes **1·3** and **2·3**. Using this script, the UV absorbance observed during the

titration described in the text, was fitted to the relevant binding model, which is described below:

In general, association between components A and B in a mixture can be described by equilibriums between 5 components: the free monomers A and B, and the dimers A_2, B_2 and AB, respectively.

The formation of the dimers is governed by the following equilibria:

$$2A \underset{}{\overset{K_{AA}}{\rightleftharpoons}} A_2$$
$$2B \underset{}{\overset{K_{BB}}{\rightleftharpoons}} B_2$$
$$A + B \underset{}{\overset{K_{AB}}{\rightleftharpoons}} AB$$

For these equilibria, the following equilibrium constants can be defined:

$$[A_2] = K_{AA}[A]^2$$
$$[B_2] = K_{BB}[B]^2$$
$$[AB] = K_{AB}[A][B]$$

The mass balances for compounds A and B are:

$$A_0 = 2[A_2] + [AB] + [A]$$
$$B_0 = 2[B_2] + [AB] + [B]$$

Here, A_0 and B_0 denote the analytical concentrations of compounds A and B.By substitution of the equilibrium constants as defined in equation 2, we obtain expressions that relate the analytical concentrations of compounds A and B to the actual concentration of free A and B monomer.

$$A_0 = 2K_{AA}[A]^2 + K_{AB}[A][B] + [A]$$
$$B_0 = 2K_{BB}[B]^2 + K_{AB}[A][B] + [B]$$

These equations can be solved numerically to obtain the concentration of free A and B in solution, from which the concentrations of the dimeric species can be calculated. If the

binding constants and extinction coefficients of the species are known, the UV absorbance at any concentration can be calculated.

Figure S2 shows simulations of a system as described above for three different values of K_{AB}: One where the heterodimerization constant K_{AB} is low compared to the homodimerization constants K_{AA} (9×10^5 M^{-1}) and K_{BB} (8×10^3 M^{-1}) in which case the system displays so-called narcissistic self-sorting. The second simulation is a case where K_{AB} is of the same order of magnitude as K_{AA} and K_{BB}, a regime that features a roughly statistical distribution over homodimers and heterodimers shows. The last simulation displays so-called social self-sorting. The value of K_{AB} is much higher than K_{AA} and K_{BB} and the selectivity for the formation of heterodimers is high. In the simulations, the concentration of B is kept constant, while the concentration of A is varied, as is the case during the titrations that were performed using compounds **1** and **3**. The UV absorbance is calculated for the case that the values of the extinction coefficients of A and B and of the AB complex are 20, 2000 and 35000 $l.mol^{-1}.cm^{-1}$ respectively, comparable to values that were determined previously for 2-ureido-pyrimidinone and 2,7-diamido-1,8-naphthyridine.

As can be seen from the simulations, this titration method allows to discriminate between K_{AB} values in a range from approximately 2×10^4 to 5×10^7 M^{-1}.

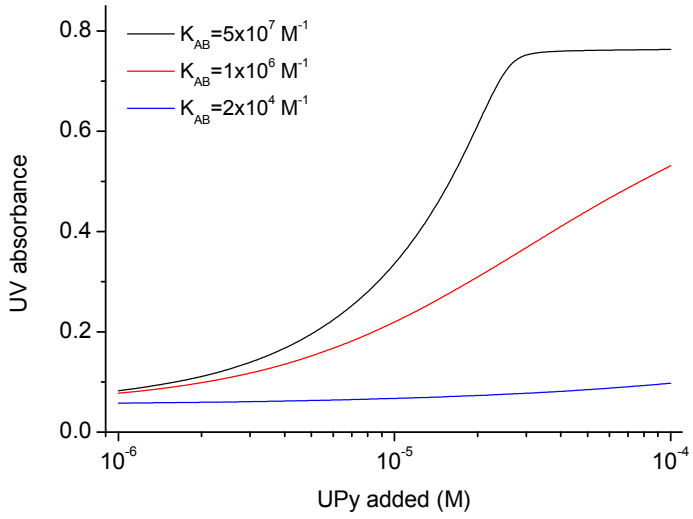


Figure S2. Simulated UV-absorbance during titrations, showing the feasibility of these titrations to determine K_{AB} values between 2×10^4 and 5×10^7 M^{-1}. The concentration NapyO is kept constant at 2.5×10^{-5} M while UPy is added. UV absorbance is calculated for values of the extinction coefficients of A and B, and of the AB complex of 20, 2000 and 35000 $l.mol^{-1}.cm^{-1}$ respectively. Homodimerization constants were set at $K_{AA} = 9 \times 10^5$ M^{-1} and $K_{BB} = 8 \times 10^3$ M^{-1}

For compounds **1** and **3**, K_{AA}, K_{BB} and K_{AB} equate to $K_{dim(3)}$, $K_{dim(1)}$ and $K_{ass(1\cdot3)}$ respectively. The actual value of the equilibrium constants K_{AB} and K_{BB} and the extinction coefficient ε_{AB} applied to the mixture of **1** and **3** were calculated by non-linear curve fitting of UV absorbance data obtained from a titration study. To this end, we used in-house written Matlab routines, based on routines we employed earlier for the determination of the association constant between 2-ureido-pyrimidinone and 2,7-diamido-1,8-naphthyridine.[2] The Matlab `leasqr` routine was used to estimate the binding constant K_{AB} and the extinction coefficient of the **1**·**3** heterocomplex ε_{AB} that serve as input values for the model. The equilibrium constant K_{AA} and the other extinction coefficients were determined in separate experiments and were used as fixed parameters in the curve fitting procedure. The same simulation routine as described above was used to generate model output based on these parameters.

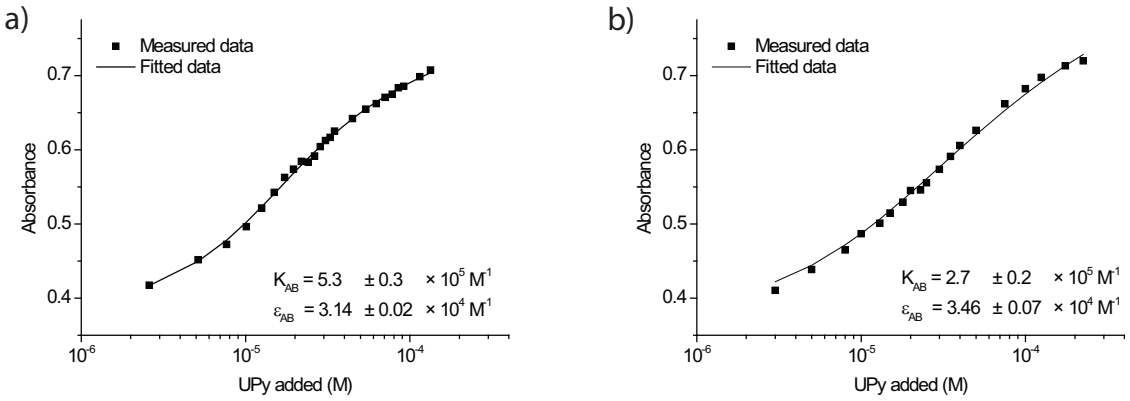


Figure S3. Nonlinear curve-fits of the UV absorbance at 355 nm in the titrations shown in Figure S2. Left: Binding between **1** and **3**. Right: Binding between **2** and **3**.

Variable temperature (VT) ^{1}H-NMR experiments: In order to gain insight into the hydrogen-bonding interactions of the complementary units, temperature dependent NMR experiments were performed. Consequently, **1** and **3** were mixed at an individual concentration of 10 mM of each compound in $CDCl_3$. ^{1}H-NMR spectra were recorded in a temperature range of -25 °C to 60 °C. Figure S3 shows the obtained spectra plotted in a stacked array. The NMR spectra taken at room- as well as at elevated temperatures exhibit broad signals in the aromatic region which can be attributed to a fast exchange process between the different components in the mixture, hence between the dimeric species **1**·**1** and **3**·**3** and the resulting hetero complex **1**·**3** (see scheme in Figure S4). Lowering the temperatures leads to sharpening and splitting of the NMR signals. Finally, at a temperature of –25 °C an assignment of the separated signals to the different species in the mixture was feasible (bottom spectrum) which reflects a superposition of the individual spectra of **1**, **3** and the hydrogen-bonded complex **1**·**3**. Lowering the temperature of the mixture leads also to an increased selectivity towards the formation of the heterocomplex (e.g. at -25°C a selectivity of 79% is observed) due to the temperature dependence of the association constants.

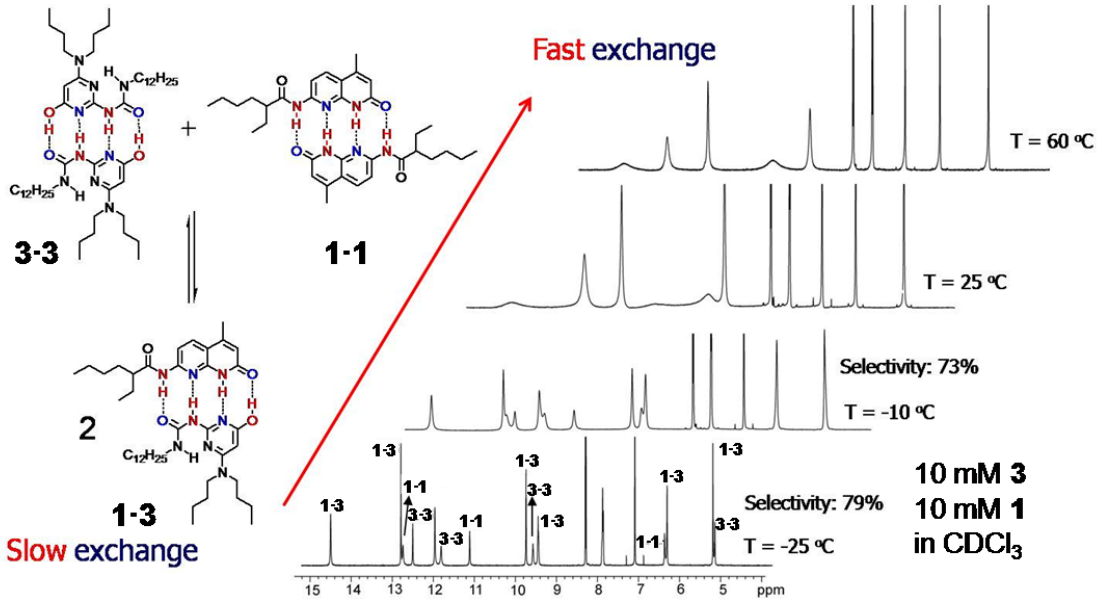


Figure S4. Temperature dependent NMR spectra (aromatic region) of a mixture of **1** and **3** at individual concentrations of 10 mM in chloroform. Left: Schematic presentation of

the exchange processes between the different components **3**·**3**, **1**·**1** and **1**·**3** in the analyzed mixture.

Determination of the concentration dependence of the specific viscosity using dilution experiments: In order to determine the concentration dependence of the specific viscosity η_{SP} of the prepared monomers **4** and **5**, viscosity dilution experiments were performed using a capillary Ubbelohde microviscometer setup. Adequate amounts of the respective monomers were weighed in and dissolved in dry chloroform (0.25 g **4** in 2.60 ml $CHCl_3$; conc. 98 g/L, 0.28 g **5** in 3.68 ml $CHCl_3$; conc. 77 g/L). In addition, a chloroform solution of $pTHF_{2000}$ (0.37 g $pTHF_{2000}$ dissolved in 3.80 ml $CHCl_3$; conc. 98 g/L) was prepared for comparison purposes. During the experiment, chloroform was added to the prepared solutions in the viscometer. After each addition step, at least 10 individual (5 runs for the higher viscous solution of **4**) flow runs were recorded and the measured run times were averaged. The effective volume of solvent in the viscosimeter used to calculate the concentration was determined through accurate weighing of the viscometer tube. The calculated specific viscosities for each addition step were corrected using the corresponding Hagenbach correction factors.

Viscosity titration experiments: The supramolecular co-polymer formation was investigated by viscosity titration experiments using the monomers **4**, **5** and the compound **3**. The titration was performed in a capillary Ubbelohde microviscometer setup using dry chloroform as the solvent. The concentration of monomer **4** was kept constant throughout the whole titration experiment. Consequently, a solution of **4** prepared at an intended concentration of 39 g/L (0.18 g **4** dissolved in 3.00 ml chloroform) was once titrated with a mixture of **5** + **4** at individual concentrations of 32 g/L and 39 g/L (0.06 g **5** and 0.08 g 7 dissolved in 2.00 mL chloroform) and in another titration experiment with a mixture of **3** + **4** at individual concentrations of 28 g/L and 39 g/L (0.06 g **3** and 0.08 g 7 dissolved in 2.00 mL chloroform). The flow time of six or more separate runs were recorded and evaluated. Possible evaporation of the solvent during the flow runs was determined through accurate weighing of the viscosimeter setup prior and directly after the measurements for each titration step.

Determined loss of solvent was adjusted through the addition chloroform. The calculated specific viscosities for each addition step were corrected using the corresponding Hagenbach correction factors. Subsequently, the solvent volumes of the final titration mixtures were determined and the solvent removed *in vacuo*. Thereafter, the dry residues were immediately re-dissolved in $CDCl_3$ to the priorly determined volumes to yield in equal concentrations as calculated for the last titration step.

^{1}H-NMR variable temperature spectra of a mixture of compounds 3 and 4 and of a mixture of compounds 4 and 5

The prepared solutions were further used for variable temperature (VT) NMR experiments in order to prove the binding between the components in the mixtures at same concentrations as present in last step of the viscosity titration experiments. As an example, the following stack plot (Figure S5) represents the ^{1}H-NMR spectra of the mixture **3·4** at temperatures of 20 °C and -20°C.

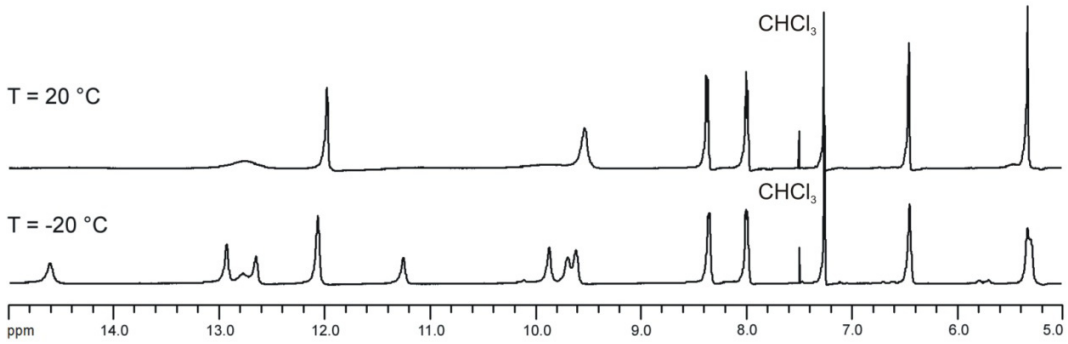


Figure S5. Aromatic region of the ^{1}H-NMR (500 MHz, $CDCl_3$) spectra of the mixture **3·4** recorded at temperatures of -20 °C (bottom spectrum) and 20°C (top spectrum).

The comparison of both spectra of the mixture of **3·4** spectrum recorded at 20°C and -20°C gives clear evidence for the binding interaction between the respective hydrogen-binding sites of bifunctional napthyridine **4** and AminoUPy stopper **3**. Fast exchange between the hydrogen-binding groups is observed at room temperature while slow exchange is visible at low temperatures. Consequently, similar ^{1}H-NMR spectra as obtained with the mixture **3·4** are observed with the mixture **1·3** (compare **Figure S4**).

Similar ^{1}H-NMR spectra were also obtained for the mixture of bifunctional monomers **4** and **5** indicating that true copolymerization occurs (Figure S6).

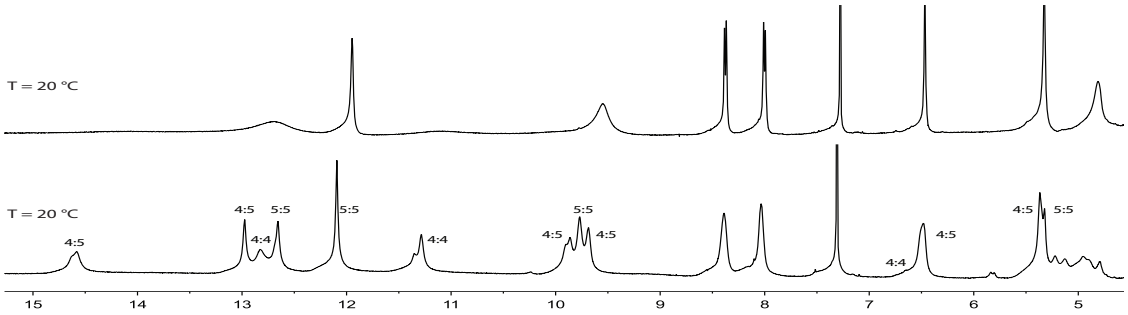


Figure S6. Aromatic region of the ^{1}H-NMR (500 MHz, $CDCl_3$) spectra of the mixture **4**·**5** recorded at temperatures of -20 °C (bottom spectrum) and 20°C (top spectrum).

^{1}H-NMR spectrum of compound 4