Selective Rearrangements of Quadruply Hydrogen-Bonded Dimer Driven by Donor–Acceptor Interaction

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Abstract: A general method has been developed to control the selective rearrangement of Meijer's AADD quadruply hydrogen-bonded homodimers by introducing an additional donor–acceptor interaction. Therefore, one donor-assembling monomer, **1**, in which the electron-rich bis(*p*-phenylene)-34-crown-10 moiety is connected to the hydrogen-bonding moiety, and two acceptor-assembling monomers, **2** and **3**, in which the electron-deficient pyromellitic diimide or naphthalene diimide group is incorporated, respectively, are synthesized and characterized. ^{1}H NMR and 2D-NOESY studies show that all these compounds exist as stable homodimers in chloroform. Mixing 1 equiv of **1** with 1 equiv of **2** in chloroform leads to the formation of heterodimers **1·2** in ≈60% yield, as a result of the electrostatic interaction between the bis(*p*-phenylene)-34-crown-10 moiety of **1** and the pyromellitic diimide group of **2**. Selective formation of heterodimer **1·3** (>97%) was achieved by mixing 1 equiv of **1** with 1 equiv of **3** in chloroform which resulted in a strengthened electrostatic interaction between the bis(*p*-phenylene)-[34]crown-10 moiety of **1** and the naphthalene diimide group of **3**. The structures of heterodimers **1·2** and **1·3**, which have been characterized by ^{1}H NMR and UV/Vis experiments, reveal a remarkable promoting effect between the donor–acceptor interaction and intermolecular hydrogen-bonding. ^{1}H NMR studies also reveal that heterodimers **1·2** and **1·3** can be fully and partially dissociated by addition of heterocycle **29**, leading to the formation of new more robust heterodimers **1·29** and **2·29**, or **3·29**,respectively, and partially regenerated by subsequent addition of heterocyclic compound **30** through the formation of a new heterodimer **29·30**. Heterodimers **1·2** and **1·3** represent a novel class of pseudo[2]rotaxanes constructed by two different noncovalent interactions.

Keywords: donor–acceptor systems · heterocycles · hydrogen bonds · self-assembly · supramolecular chemistry

Introduction

Nature utilizes the cooperative interaction of different noncovalent forces, such as hydrogen bonds, hydrophobic interaction, and electrostatic interaction, to realize highly specific molecular recognition and self-assembly events. As a result, nanoscale supramolecular systems of defined structures and functions are ubiquitous in nature. In the past decade, chemists have constructed a large number of discrete artificial assembling species.[1] Most of these supramolecular species are generated mainly based on one kind of noncovalent interaction, including transition metal–ligand interaction,[2] hydrophobic interaction,[3] hydrogen bonding,[4] and electrostatic interaction.[5] Although, in principle, incorporation of two or more different noncovalent interactions into one assembling system might also be useful or even more powerful in producing new generations of supramolecular structures and functions, examples of this kind of supramolecular assembly are obviously limited.[6]

Since 1998, self-complimentary quadruply hydrogen-bonded homodimers have received increasing attention because of their great binding strength and directionality.[4a, b, 7] Particularly the 2-ureido-4[1*H*]-pyrimidinone AADD (A = hydrogen-bonding acceptor, D = hydrogen-bonding donor) binding module developed by Meijer et al. had found extensive applications in assembling supramolecular oligomers and polymers.[8] However, the feature of self-complementarity also makes it difficult to selectively assemble specific heterodimers from two distinct monomers, since a statistical mixture of possible dimers would always be generated on account of

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the comparable binding stability of different heterodimers.[8b] Considering the great significance and potential of this class of binding motifs in the self-assembly of hydrogen-bonded supramolecular systems, it seems necessary to explore new general methods to control their assembling selectivity, which may be consequently utilized to further develop new assembling principles and systems. Herein, we present a highly efficient and general approach to address this issue, which is based on the cooperative interaction of intermolecular hydrogen bonds and donor–acceptor interactions. The new heterodimers, assembled by the cooperative interaction of intermolecular hydrogen bonds and donor–acceptor interaction, not only represent a new class of extremely stable pseudo[2]rotaxanes, in which two discrete noncovalent interactions can substantially promote each other, but can also undergo new unique supramolecular "rearrangement or substitution reactions", as a result of their different stabilities.

Results and Discussion

Donor–acceptor interaction between neutral electron-rich and electron-deficient moieties has been successfully applied to the self-assembly of a number of interlocked supramolecular species.[9] This principle was chosen to induce the rearrangement of Meijer's AADD hydrogen-bonding module since the corresponding building monomers designed in the present work were expected to be soluble in less polar solvents, such as chloroform, which is necessary for efficient hydrogen-bonding self-assembly. In order to reach optimal donor–acceptor interactions, a donor or acceptor group should be introduced in a suitable position within the corresponding hydrogen-bonding monomer. Thus, three compounds 1–3 were designed and synthesized that were based on the results of molecular modeling. For compound 1, the electron-rich bis(p-phenylene)-34-crown-10 moiety[10, 11] and the hydrogen-bonding moiety are connected by a rigid acetylene group to reduce its conformational flexibility, while for compounds 2 and 3, a typical neutral electron-deficient moiety,[12] pyromellitic diimide (PDI) or naphthalene diimide (NDI) is incorporated, respectively, to connect the hydrogen

moiety by a flexible ester chain to facilitate donor–acceptor interaction with the donor moiety in the expected heterodimers.
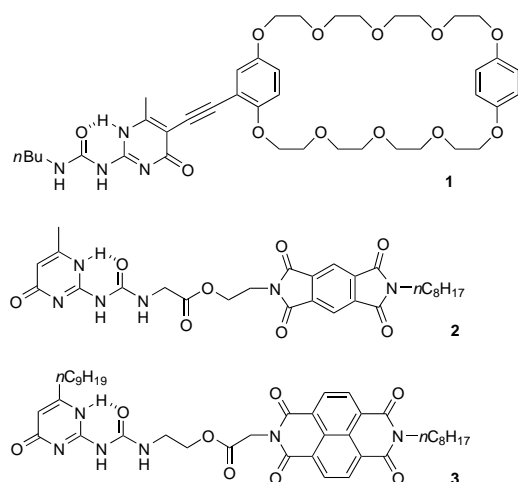
The synthesis of compound 1 is shown in Scheme 1. Treatment of tosylate 4 with bromide 5 in the presence of sodium hydroxide in refluxing acetonitrile afforded the key intermediate 6 in good yield. Heck reaction of 6 with alcohol 7, followed by deprotection of the acetylene group gave macrocycle 9, which was transformed to the first target molecule 1 by another Heck reaction with iodide 11.
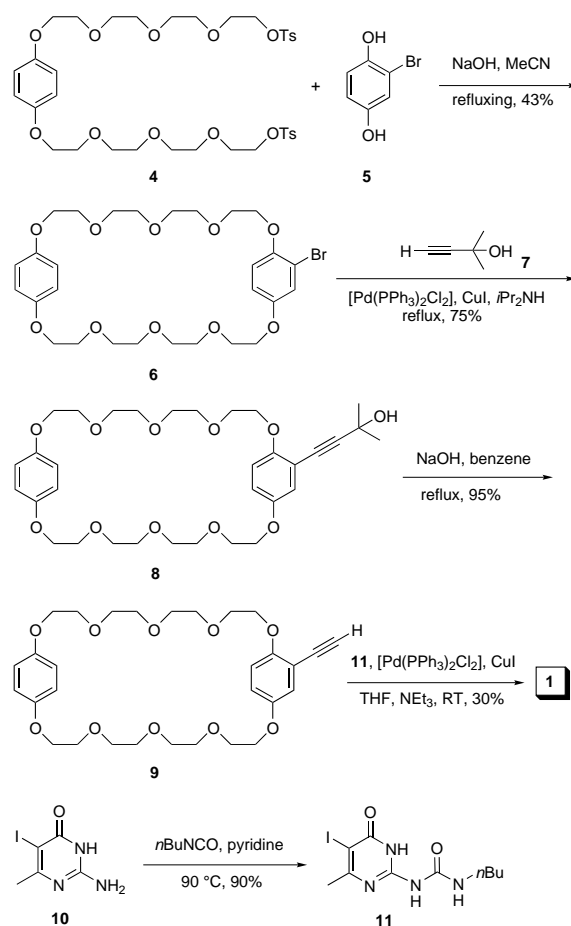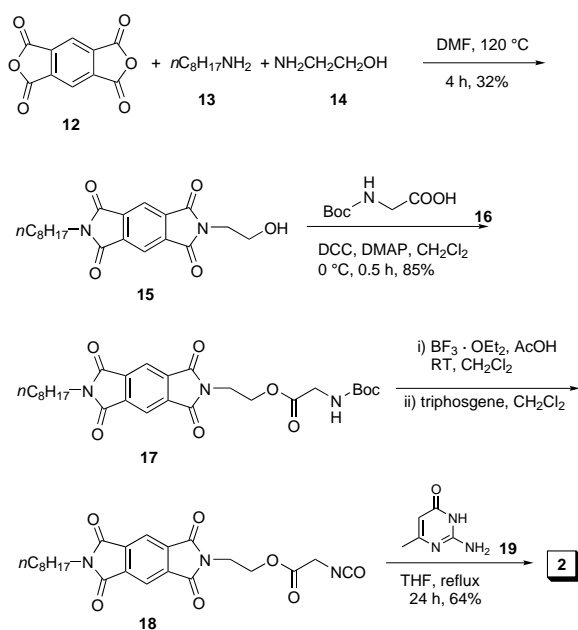

Scheme 1. Synthesis of compound 1.

The preparation of compound 2 started from anhydride 12 (Scheme 2). Treatment of 12 with the same molar amount of 13 and 14 in DMF afforded alcohol 15 in 32% yield. Compound 15 then coupled with 16 to give 17 in 85% yield. Ester 17 was quantitatively deprotected with boron trifluoride and then transformed to isocyanate 18 with triphosgene. Without further purification, compound 18 was treated with amine 19 in refluxing THF to afford compound 2 in good yield.

Starting from anhydride 24, a similar route to that shown in Scheme 2 had been attempted to prepare a target compound such as 2. However, no expected product could be obtained from the last reaction of the corresponding isocyanate with 19, probably because of the poor solubility of the naphthalene diimide intermediate. Therefore, compound 3 was prepared as

Scheme 2. Synthesis of compound **2**.

shown in Scheme 3. The key intermediate **23** was first prepared in good yield from compound **20**, and then acid **25** was obtained from the condensation reaction of **24** with **13** and glycine in DMF. Compound **3** was then prepared from the reaction of acyl chloride **26** with alcohol **23**. A long aliphatic chain was introduced in **23** in order to improve the solubility of compound **3**.

Compounds **11** and **23** are new precursors which can be readily modified to generate new hydrogen-bonding assembling blocks. Considering their convenient preparations, it is reasonable to expect that these compounds may find further applications in the synthesis of new assembling blocks in the future.
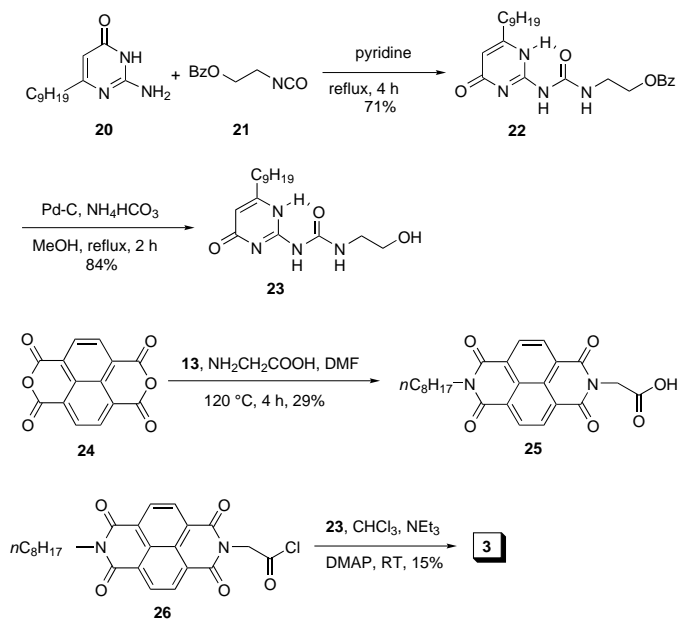
Scheme 3. Synthesis of compound **3**.

¹H NMR spectra (Figures 1 and 2) reveal that compounds **1**–**3** exist as homodimers **1·1**, **2·2**, and **3·3** in CDCl₃, respectively. The large downfield shift for NH protons provides direct evidence for their involvement in strong hydrogen bonding. Their AADD hydrogen binding motif was determined by NOESY spectra. No other binding modes were observed.[7f] Dilution of the solutions of all three compounds in CDCl₃ to 1.0×10^{-5} M did not lead to observable dissociation, thus giving a lowest estimate of the binding constant of $1 \times 10^7 \, M^{-1}$, which is in good agreement with the value obtained for a similar compound.[13]

Mixing 1 equiv of **1** with 1 equiv of **2** in CDCl₃ caused partial dissociation of homodimers **1·1** and **2·2** and led to the formation of the new heterodimer **1·2** (Scheme 4), as proved by the ¹H NMR spectra (Figure 1 a–c). The existence of homodimers **1·1** and **2·2** in the 1:1 mixture solution were
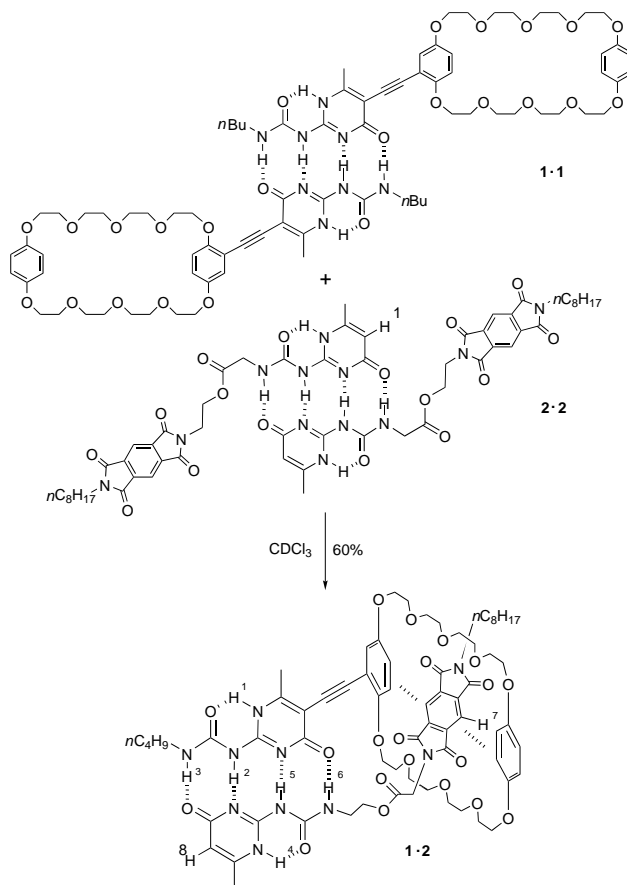
Scheme 4. Self-assembly of heterodimer **1·2** from homodimers **1·1** and **2·2** driven by donor–acceptor interaction.

proved by changing the ratio of **1** and **2** in the solution. This induced changes in the relative strength of the signals assigned to dimers **1·1** and **2·2** in the ¹H NMR spectra. The chemical shifts of the H1 (δ 13.49) of **1** and the H4 (δ 12.47) of **2** have no obvious change, implying that the intramolecular hydrogen bonds in both compounds are not broken after mixing.[7f] However, the new set of signals at δ 12.01 (H5 in **2**), 11.89 (H2 in **1**), 10.62 (H6 in **2**), 10.17 (H3 in **1**), 8.21 (H7 in **2**), and 5.84 (H8 in **2**), with the same integrated intensities, clearly show the formation of the new heterodimer **1·2**. The solution of the

1:1 mixture of **1** and **2** (10 mм) in chloroform turned pale orange. Its UV/Vis spectrum provided further evidence for the formation of heterodimer **1·2**. A typical charge-transfer absorption band ($\lambda_{max} = 432$ nm, $\varepsilon = 106\,\text{м}^{-1}\text{cm}^{-1}$) was observed. Controlling experiments revealed that no detectable absorption within $\lambda = 400–700$ nm were observed for the 1:1 mixture of **9** and **15** (10 mм) in chloroform. Therefore, this charge-transfer absorption band was obviously generated as a result of the donor–acceptor interaction between the bis(*p*-phenylene)-[34]crown-10 moiety of **1** and the PDI unit of **2** in the new heterodimer **1·2**. The solutions of the 1:1 mixture of **1** and **2** in [D$_6$]DMSO of high polarity is colorless, and its ^{1}H NMR spectrum reveals only the signals of the simple monomers **1** and **2**, as a result of the competitive interaction of the solvent. A NOESY experiment was also performed; however, it did not provide support for the formation of **1·2** because of the overlaps of the N–H signals. The yield of heterodimer **1·2** in the 1:1 mixture (10 mм) solution of CDCl$_3$ has been estimated to be $\approx 60\%$ from the integrated intensity of the H1 signal of homodimer **2·2** and the H8 signal of heterodimer **1·2**. Reducing the temperature to $-50\,^\circ$C did not have an obvious effect on the intensity ratio (Figure 1e), while raising the solution temperature to $55\,^\circ$C led to complete combination of the ^{1}H NMR signals of the homodimers and the heterodimer (Figure 1d), indicating that the exchanging processes between the three dimers are fast on the ^{1}H NMR timescale. The molar absorption coefficient of the 1:1 mixture (10 mм) in chloroform at $55\,^\circ$C was $\approx 65\,\text{м}^{-1}\text{cm}^{-1}$ ($\lambda_{max} = 430$ nm), showing that the yield of heterodimer **1·2** in chloroform is lower at a higher temperature. FT-IR spectra of pure **1** and **2** in CDCl$_3$ are very similar in the NH region (3215 and 3150 cm^{-1}), implying a similar DDAA binding mode in solution, whereas a mixture of **1** and **2** (molar ratio = 1:1) in CDCl$_3$ gives only one band at

$\tilde{\nu} = 3219$ cm^{-1}; this also suggests the formation of the new hetero-binding module.

The formation of heterodimer **1·2** from homodimers **1·1** and **2·2** was obviously driven by the additional donor–acceptor interaction between the electron-rich dioxybenzene groups of **1** and the threaded electron-deficient PDI of **2**. In order to check if more selective rearrangement of Meijer's AADD quadruply hydrogen-bonded homodimers could be achieved by the additional, increased donor–acceptor interaction, the possibility of selective self-assembly of heterodimer **1·3** from homodimers **1·1** and **3·3** was also explored. Indeed, this was the case. Mixing 1 equiv of **1** with 1 equiv of **3** in CDCl$_3$ caused full dissociation of dimers **1·1** and **3·3**, affording exclusively the new heterodimer **1·3** as an orange solution (Scheme 5), as indicated by the ^{1}H NMR spectrum (Figure 2). No detectable ^{1}H NMR signals of the homodimers **1·1** and **3·3** were observed from the ^{1}H NMR spectrum. Considering the sensitivity of the ^{1}H NMR method, a lower limit of the yield of heterodimer **1·3** was estimated to be 97%. Within the temperature range of -50 to $55\,^\circ$C, no signals of homodimers **1·1** and **3·3** were observed in the ^{1}H NMR spectra, whereas the signals of homodimer **1·1** or **3·3** were displayed when a pure sample of **1** or **3** was added to the 1:1 mixture of solutions in CDCl$_3$. These observations clearly demonstrate that the additional donor–acceptor interaction between the bis(*p*-phenylene)-[34]crown-10 moiety of **1** and the NDI unit of **3** remarkably stabilizes the hydrogen-bonded heterodimer **1·3** in chloroform within the temperature range investigated.

In order to quantitatively assess the promoting behavior of the additional donor–acceptor interaction on the binding ability of the hydrogen bonding motif, the binding constants of all four homodimers and heterodimers were measured in varying CDCl$_3$/[D$_6$]DMSO solvent systems [14] (Table 1).

Homodimers **1·1**, **2·2**, and **3·3** exhibit very similar binding stability in all the solvent systems. This indicates that the donor and acceptor groups do not have a pronounced influence on the hydrogen-bonding stability of the homodimers. However, the binding constants of heterodimers **1·3** are always greater than those of homodimers **1·1** and **2·2**, which is especially obvious in 3% and 4% [D$_6$]DMSO of CDCl$_3$. This demonstrates that the additional donor–acceptor interaction can increase the stability of the hydrogen-bonding heterodimers.

Heterodimers **1·2** and **1·3** also represent a novel class of pseudo[2]rotaxanes. UV/Vis spectroscopy was used to investigate the promoting effect of the hydrogen-bonding moiety
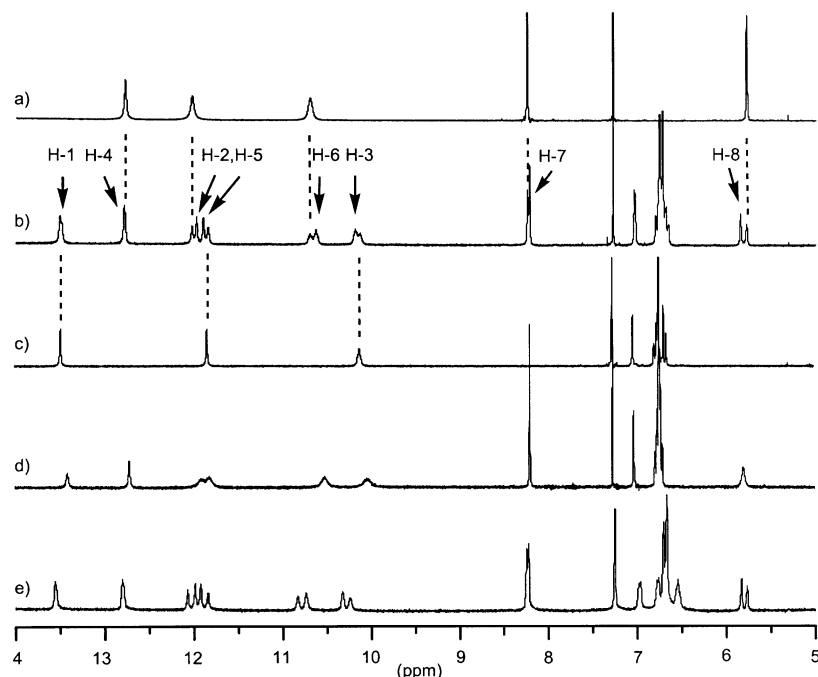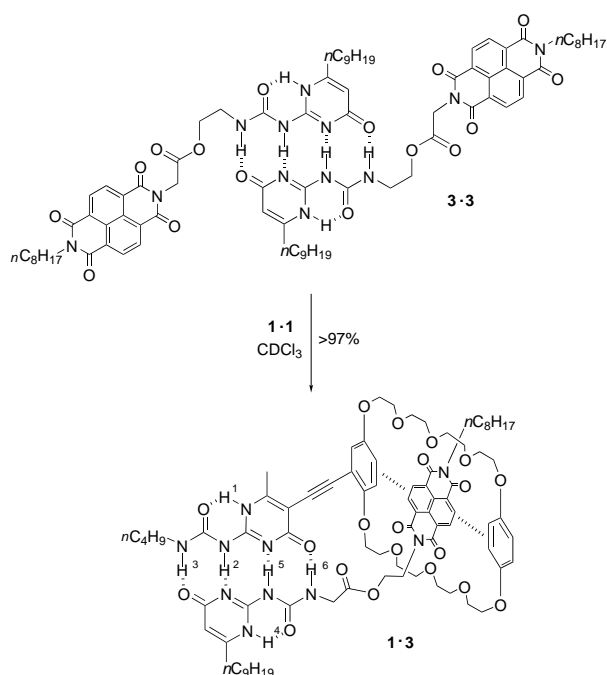

Figure 1. Partial 400 MHz ^{1}H NMR spectra of dimers (10 mм) in CDCl$_3$: a) **2·2** at 25 °C; b) **1·2** at 25 °C; c) **1·1** at 25 °C; d) **1·2** at 55 °C; e) **1·2** at -50 °C.

Scheme 5. The self-assembly of heterodimer $1 \cdot 3$ from homodimers $1 \cdot 1$ and $3 \cdot 3$.

absorption bands could be observed between **9** and *N,N'*-dioctyl PDI **27** or NDI **28** within the above concentration range. The binding constants between **9** and **27** or **28** were determined to be only ≈ 10 and $35\,\mathrm{M}^{-1}$, respectively, by the ^{1}H NMR titration method, also indicating the donor–acceptor interactions between **9** and **27** or **28** are very weak.[14]
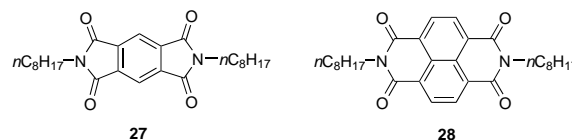
The addition of 2 equiv of **29** to the solution of 1 equiv of heterodimer $1 \cdot 2$ in CDCl$_3$ led to the disappearance of the orange color of the solution. The UV/Vis spectrum did not exhibit the charge-transfer absorption band of heterodimer $1 \cdot 2$, suggesting that the donor–acceptor interaction in the dimer was completely destroyed. ^{1}H NMR (Figure 3) also revealed that dimer $1 \cdot 2$ disassociates completely and two new, more robust, heterodimers $1 \cdot 29$ and $2 \cdot 29$, both with the new ADDA–DAAD binding mode, were generated selectively (Scheme 6).[7e] The signals of heterodimers $1 \cdot 29$ and $2 \cdot 29$ in
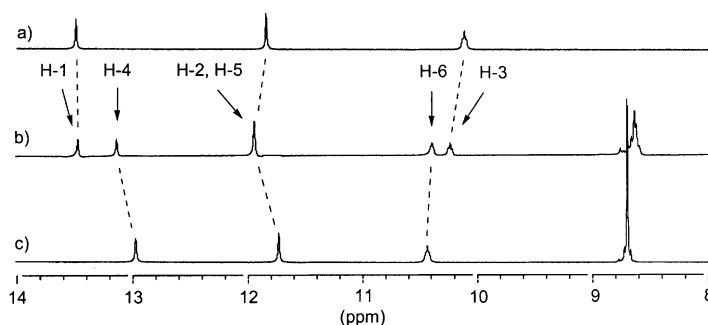

Figure 2. Partial 400 MHz ^{1}H NMR spectra of dimers a) $1 \cdot 1$, b) $1 \cdot 3$, and c) $3 \cdot 3$ in CDCl$_3$ at room temperature.

Figure 3. Partial ^{1}H NMR spectra (400 MHz) of a) $1+29$ (1:1); b) $2+29$ (1:1); c) $1+2$ (1:1); d) $1+2+29$ (1:1:2); e) $1+2+29$ (1:2:3) in CDCl$_3$. In all the cases, the concentrations of **1** were kept at 10 mM. The numbering of protons is given in Scheme 6.

on the donor–acceptor interaction of the pseudo[2]rotaxane moiety. As described above, a typical charge-transfer absorption band was observed for dimers $1 \cdot 2$. Actually, heterodimer $1 \cdot 3$ exhibited an even stronger charge-transfer absorption in chloroform ($\lambda_{\mathrm{max}} = 475$ nm, $\varepsilon = 429\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$). These values of molar absorption coefficients are rather high to be comparable to that observed in a [2]catenane system.[15] Moreover, within the measurable concentration range of 50–0.5 mM, the ε values are concentration-independent, which also proves their extremely high stability that is reminiscent of an intramolecular interaction. In contrast, no charge-transfer
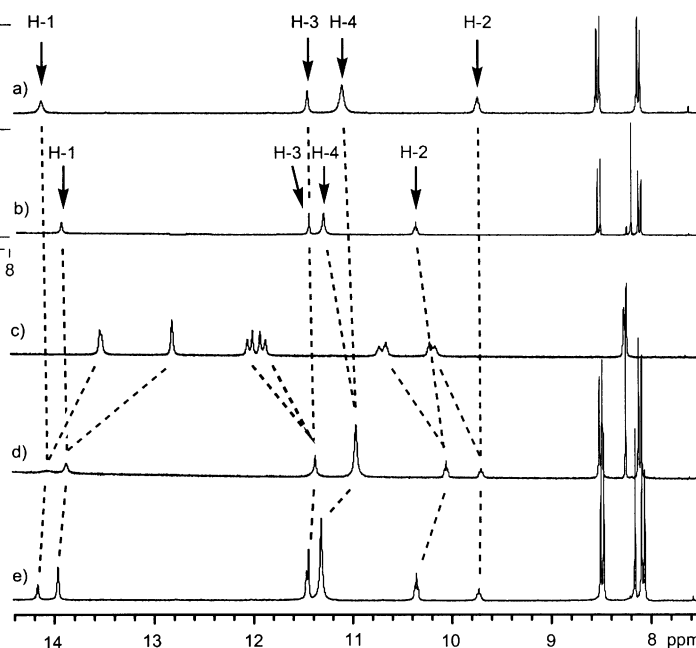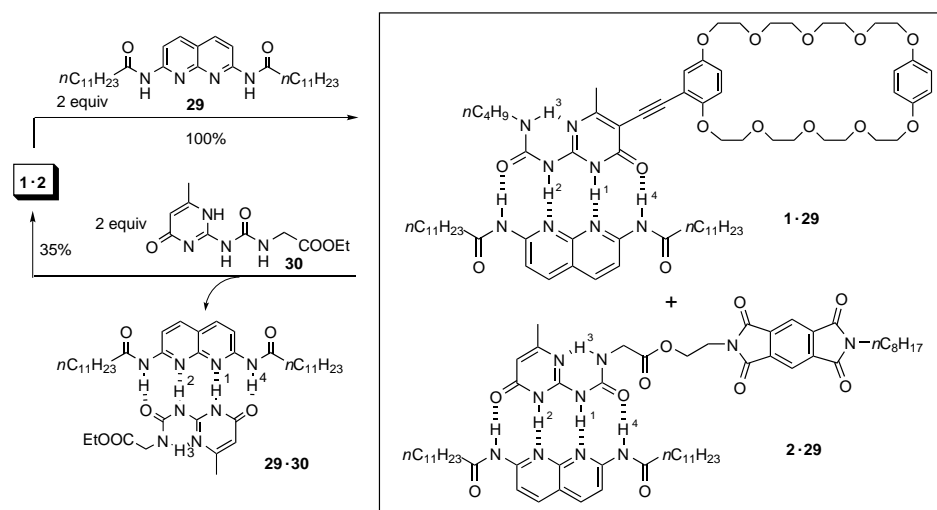
Table 1. Binding constants K_a [M^{-1}] of dimers in CDCl$_3$ with different amount of [D$_6$]DMSO (*v/v*) at room temperature.

[D$_6$]DMSO	$1 \cdot 1$	$2 \cdot 2$	$3 \cdot 3$	$1 \cdot 3$
0.5	9.3 (± 1.8) × 10^5	9.5 (± 2.0) × 10^5	8.9 (± 1.6) × 10^5	1.0 (± 0.19) × 10^6
1.0	1.6 (± 0.26) × 10^5	1.8 (± 0.32) × 10^5	1.5 (± 0.21) × 10^5	2.8 (± 0.36) × 10^5
2.0	2.8 (± 0.25) × 10^4	2.4 (± 0.30) × 10^4	2.5 (± 0.33) × 10^4	6.3 (± 0.42) × 10^4
3.0	1.6 (± 0.18) × 10^4	1.5 (± 0.16) × 10^4	1.7 (± 0.22) × 10^4	4.2 (± 0.45) × 10^4
4.0	6.6 (± 0.81) × 10^3	7.1 (± 0.95) × 10^3	6.8 (± 0.53) × 10^3	3.7 (± 0.52) × 10^4

Scheme 6. The dissociation and reassociation of heterodimer **1·2** in chloroform.

1·29 or **3·29** in CDCl$_3$, which could lead to strengthening of the signals of dimer **1·29** or **3·29**. Based on the relative integrated intensity of H1 of **3·29** and H4 of **1·3** in the mixture, it was estimated that $\approx 90\%$ of **1·3** was dissociated when 2 equiv of **29** was added (Figure 4c). The result is consistent with the UV/Vis measurement, which afforded a ε value of $\approx 40\,\text{M}^{-1}\text{cm}^{-1}$ ($\lambda_{max} = 474$ nm) for the mixture system, corresponding to a 91% dissociation of dimer **1·3**. The signals of dimer **1·3** could be detected ($\approx 3\%$, based on the integrated ^{1}H NMR intensity) even after 4 equiv of **30** was added to the 1:1:2 solution of **1**, **3**, and **29** in CDCl$_3$, revealing greater stability of dimer **1·3** relative to dimer **1·2**. Treatment of the 1:1:2 solution of **1**, **3**, and **29** with 2 equiv of **30** caused $\approx 45\%$ recovery of dimer **1·3** by forming the new heterodimer **29·30**, as estimated by the integrated intensities of the corresponding N–H signals (Figure 4e). A similar result was also obtained from UV/Vis measurement, which gave 42% regeneration of dimer **1·3** (180 M^{-1}cm^{-1}, $\lambda_{max} = 430$ nm). The signals of heterodimer **29·30** in the ^{1}H NMR spectrum of the solution of **1**, **3**, **29**, and **30** (Figure 4e) were established by adding 1 equiv of dimer **29·30** to the solution, which accordingly induced the signals of dimer **29·30** in the mixture to strengthen (Figure 4f). For comparison, the ^{1}H NMR spectrum of dimer **29·30** is provided as Figure 4g.

In theory, the stability of heterodimers **1·29**, **2·29**, **3·29**, and **29·30** should be comparable in chloroform. The above results reveal the following sequence of stability: heterodimers **1·29**, **2·29**, **3·29**, **29·30** > heterodimers **1·2**, **1·3** > homodimers **1·1**, **2·2**, **3·3**. The extremely high stability of heterodimers **1·29**, **2·29**, **3·29**, and **29·30**, relative to that of

the solution of **1**, **2**, and **29** in CDCl$_3$ were assigned by adding a 1:1 mixture of **1** and **29** or **2** and **29** to the solution. This induced strengthening of the corresponding signals of heterodimer **1·29** or **2·29**. The latter result is provided in Figure 3e.
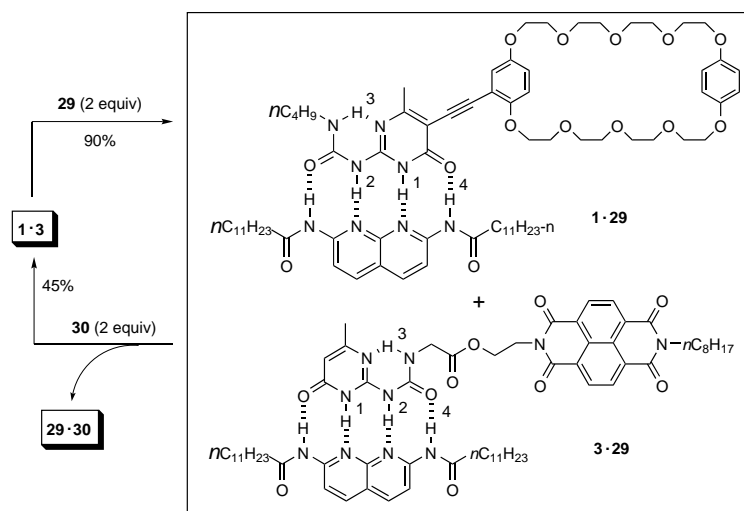
It was found that in CDCl$_3$, homodimer **30·30** could dissociate and bind with **29** to selectively afford heterodimer **29·30**, as indicated by the ^{1}H NMR spectrum (Figure 4, see below). Therefore, compound **30** was used to explore the possibility of recovering heterodimer **1·2** from the mixture solution of **1**, **2**, and **29**. Addition 2 equiv of **30**, which also exists as stable homodimer in CDCl$_3$, to the above solution of **1**, **2**, and **29** induced the solution to turn to pale orange again, suggesting that heterodimer **1·2** had been regenerated. However, no quantitative data could be obtained from the ^{1}H NMR spectrum because of its low resolution, which suggests that extensive exchanges might exist within the mixture of the heterodimers. A ε value of $\approx 38\,\text{M}^{-1}\text{cm}^{-1}$ ($\lambda_{max} = 428$ nm) was determined based on the UV/Vis measurement, which represents regeneration of $\approx 35\%$ heterodimer **1·2**, relative to the content of **1·2** in the above solution of **1**, **2**, and **29**.

Further ^{1}H NMR studies were then performed to investigate the "rearrangement reactions" of heterodimer **1·3** with **29** and **30** (Scheme 7, Figure 4). Thus, the continuous addition of **29** (0.5, 1.0, 1.5, and 2.0 equiv) to the solution of heterodimer **1·3** in CDCl$_3$ caused the signals of dimer **1·3** to gradually weaken while the signals of new heterodimers **1·29** and **3·29** gradually strengthened. The signals of **1·29** and **3·29** in the solution had been inferred by adding a solution of

Scheme 7. The dissociation and reassociation of heterodimer **1·3** in chloroform.
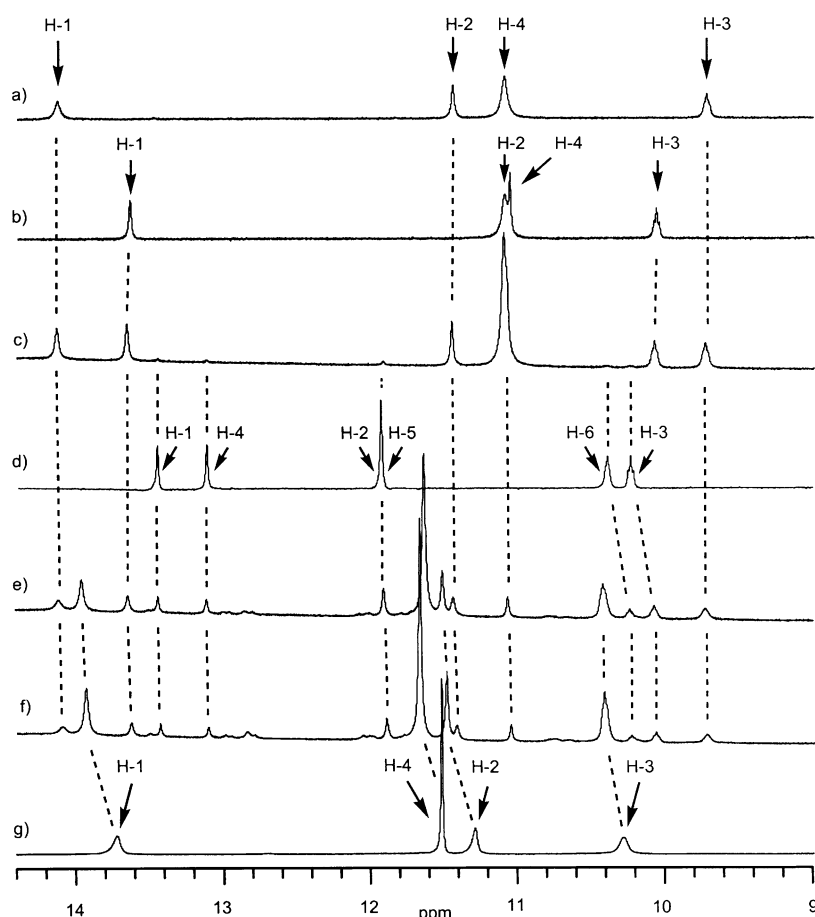
Figure 4. Partial ^{1}H NMR spectra (400 MHz) of a) **1**+**29** (1 equiv); b) **3**+**29** (1 equiv); c) **1**+**3**+**29** (2 equiv); d) **1**+**3** (1:1); e) **1**+**3**+**29** (2 equiv)+**30** (2 equiv); f) **1**+**3**+**29** (3 equiv)+**30** (3 equiv), and g) **29** + **30** (1:1) in CDCl$_3$. In all the cases, the concentrations of **1** and **3** were kept at 10 mM. The numbering of the protons is given in the corresponding schemes.

demonstrate the great potential of the cooperative interactions of different noncovalent forces for assembling a novel class of well-defined artificial supramolecular species. In principle, this cooperative concept may be utilized to achieve selective switching between more complicated hydrogen-bonded supramolecular oligomers and polymers, and to construct a new generation of supramolecular systems that are being investigated with vigor in our laboratory.

Experimental Section

General procedures: Melting points are uncorrected. All reactions were performed under an atmosphere of dry nitrogen. The ^{1}H NMR spectra were recorded on 600, 400, or 300 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million relative to the residual solvent protons as internal standards. Chloroform ($\delta = 7.26$) was used as an internal standard for CDCl$_3$. Mass spectra (EI, ESI) were obtained on a Varian SATURN 2000 spectrometer. Elemental analysis was carried out at the SIOC analytical center. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. All solvents were dried before use following standard procedures. Compounds **4**,[16] **5**,[17] **10**,[18] **20**,[7f], **21**,[19] **27**,[20] and **28**[20] were prepared according to reported procedures.

16-Bromo-2,5,8,11,14,19,22,25,28,31-decaoxa-tricyclo[30.2.2.2^{15,18}]octatriaconta-1(35),15(38),16,18(37),32(36),33-hexaene (6): A solution of compound **4** (4.60 g, 6.00 mmol) in acetonitrile (50 mL) was added at 60 °C to a stirred suspension of compound **5** (1.14 g, 6.00 mmol) and sodium hydroxide (0.49 g, 12.3 mmol) in acetonitrile (100 mL). The reaction mixture was then heated under reflux for 24 h. After cooling to room temperature, the resulting solid was filtered off and washed with chloroform. The combined filtrates were concentrated and the residue was dissolved in methylene chloride (200 mL). This solution was washed with water, brine, and dried over sodium sulfate. After removal of the solvent, the oily residue was purified by column chromatography (EtOAc/CH$_3$OH 50:1), to afford compound **6** as a yellow oil (1.60 g, 43 %). ^{1}H NMR (CDCl$_3$): $\delta = 3.69 – 4.04$ (m, 32 H), 6.73 – 6.79 (m, 6 H), 6.95 (m, 1 H); EI-MS: m/z: 616 [M]$^+$; elemental analysis calcd (%) for C$_{28}$H$_{39}$BrO$_{10}$ (615.51): C 54.64, H 6.39; found: C 54.63, H 6.34.

4-(2,5,8,11,14,19,22,25,28,31-Decaoxa-tricyclo[30.2.2.2^{15,18}]octatriaconta-1(35),15(38),16,18(37),32(36),33-hexaen-16-yl)-2-methylbut-3-yn-2-ol (8): Compound **6** (0.31 g, 0.50 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (30.0 mg, 0.040 mmol, 8 %), CuI (10.0 mg, 0.050 mmol, 10 %), and 2-methylbut-3-yn-2-ol (**7**) (65.0 mg, 0.75 mmol) were added to iPr$_2$NH (15 mL). The reaction mixture was stirred under reflux for 18 h and then cooled to room temperature. The solvent was evaporated in vacuo and the residue was triturated with methylene chloride (50 mL). The organic phase was washed with 1N hydrochloride (10 mL), water (10 mL), brine (10 mL), and dried over sodium sulfate. After removal of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/CH$_3$OH

homodimers **1·1**, **2·2**, **3·3**, and **30·30** is consistent with a similar heterocyclic motif reported by Zimmerman et al. and may reflect the inherent strong binding feature of these kind of heterodimers.[7e]

Conclusion

We have developed two new useful quadruple hydrogen-bonding assembling monomers based on Meijer's AADD quadruply hydrogen-bonded motif and, for the first time, realized the selective rearrangement or secondary assembly of this kind of homodimer by introducing an additional donor–acceptor interaction. The new heterodimers assembled from this kind of rearrangement represent one class of new pseudo[2]rotaxanes with a new unique structural feature. It has been revealed that the intermolecular hydrogen-bonding and donor–acceptor interactions in these supramolecular systems are capable not only of promoting each other to a remarkable effect, but they can also fully regulate each other in chloroform. The rearrangement, dissociation, and reassociation processes of the newly assembled heterodimers displayed in this work may, to some extent, be regarded as new kinds of "supramolecular reactions". The results clearly

50:1). Compound **8** was obtained as a yellow oil (0.23 g, 75 %). ^{1}H NMR (CDCl$_3$): δ = 1.53 (s, 6H), 3.70–4.04 (m, 32H), 6.68–6.78 (m, 6H), 6.88 (m, 1H); EI-MS: m/z: 618 $[M]^+$; elemental analysis calcd (%) for C$_{33}$H$_{46}$O$_{11}$ (618.71): C 64.06, H 7.49; found: C 63.79, H 7.35.

16-Ethynyl-2,5,8,11,14,19,22,25,28,31-decaoxa-tricyclo[30.2.2.2^{15,18}]octatriaconta-1(35),15(38),16,18(37),32(36),33-hexaene (9): Sodium hydroxide (52.0 mg, 1.30 mmol) was added to a solution of compound **8** (0.61 g, 1.00 mmol) in benzene (10 mL). The mixture was heated under reflux for 12 h and cooled to room temperature, washed with water (2 × 10 mL), brine (10 mL), dried over sodium sulfate. The solvent was then removed in vacuo and the resulting residue was chromatographed on silica (EtOAc/CH$_3$OH 50:1), to afford compound **9** as a white solid (0.53 g, 95 %). M.p. 73–75 °C; ^{1}H NMR (CDCl$_3$): δ = 3.29 (s, 1H), 3.29–4.10 (m, 32H), 6.73–6.79 (m, 6H), 6.95–6.96 (m, 1H); EI-MS: m/z: 560 $[M]^+$; elemental analysis calcd (%) for C$_{30}$H$_{40}$O$_{10}$ (560.63): C 64.27, H 7.19; found: C 64.23, H 7.32.

1-Butyl-3-(5-iodo-6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)-urea (11): A solution of compound **10** (3.00 g, 12.0 mmol) and butyl isocyanate (2 mL, 20.2 mmol) in dry pyridine (200 mL) was heated at 90 °C for 24 h. After removal of the solvent in vacuo, the resulting residue was thoroughly washed with diethyl ether and purified by column chromatography (dichloromethane/methane 30:1), to give compound **11** (3.78 g, 90 %) as a white solid. M.p. 212–214 °C; ^{1}H NMR (CDCl$_3$): δ = 0.98 (t, 3H), 1.43 (m, 2H), 1.63 (m, 2H), 2.55 (s, 3H), 3.30 (m, 2H), 9.85 (s, 1H), 11.69 (s, 1H), 13.45 (s, 1H); FAB-MS: m/z: 351 $[M+H]^+$; elemental analysis calcd (%) for C$_{10}$H$_{15}$IN$_4$O$_2$ (350.16): C 34.30, H 4.32, N 16.00; found: C 34.54, H 4.33, N 15.91.

1-Butyl-3-[5-(2,5,8,11,14,19,22,25,28,31-decaoxa-tricyclo[30.2.2.2^{15,18}]octatriaconta-1(35),15,17,32(36),33,37-hexaen-16-ylethynyl)-6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl]-urea (1): Compounds **9** (0.28 g, 0.50 mmol), **11** (0.21 g, 0.60 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (30 mg, 6 %), and CuI (10 mg, 10 %) were added to a solution of THF (30 mL) and Et$_3$N (1.5 mL). The mixture was stirred for 5 h at room temperature and then concentrated under reduced pressure. The residue was triturated with methylene chloride (100 mL). After workup, the residue was purified by column chromatography on silica gel (CH$_2$Cl$_2$/CH$_3$OH 20:1). Compound **1** (118 mg, 30 %) was obtained as a white solid. M.p. 158–159 °C; ^{1}H NMR (CDCl$_3$): δ = 0.95 (t, 3H), 1.39 (m, 2H), 1.63 (m, 2H), 2.55 (s, 3H), 3.29 (m, 2H), 3.68–4.09 (m, 32H), 6.67–6.80 (m, 6H), 7.04 (m, 1H), 10.12 (m, 1H), 11.85 (s, 1H), 13.49 (s, 1H); ESI-MS: m/z: 805 $[M+Na]^+$; elemental analysis calcd (%) for C$_{40}$H$_{54}$O$_{12}$N$_4$ (782.88): C 61.37, H 6.95, N 7.16; found: C 60.96, H 6.94, N 6.99.

2-(2-Hydroxyethyl)-6-octylpyrrolo[3,4-f]isoindole-1,3,5,7-tetraone (15): A solution of compounds **12** (4.40 g, 20.0 mmol), **13** (2.60 g, 20.0 mmol) and **14** (1.20 g, 20.0 mmol) in DMF (40 mL) was stirred at 120 °C for 4 h and then cooled to room temperature. The insoluble materials were filtered off and the solution was poured into water (250 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 × 150 mL) and the organic phase was washed with 1N aqueous NaHCO$_3$ solution and water, and then dried (MgSO$_4$). After removal of the solvent under reduced pressure, the crude product was subjected to flash chromatography (hexane/EtOAc 1:1), to afford compound **15** as a white solid (2.30 g, 31 %). M.p. 185.5–187.5 °C; ^{1}H NMR (CDCl$_3$): δ = 0.83–0.87 (m, 3H), 1.24–1.31 (m, 10H), 1.66–1.68 (m, 2H), 1.88 (s, 1H), 3.69–3.74 (t, J = 7.2 Hz, 2H), 3.89–3.96 (m, 4H), 8.26 (s, 2H); EI-MS: m/z: 372 $[M]^+$; elemental analysis calcd (%) for C$_{20}$H$_{24}$N$_2$O$_4$ (372.42): C 64.50, H 6.50, N 7.52; found: C 64.31, H 6.53, N 7.61.

tert-**Butoxycarbonylaminoacetic 2-(6-octyl-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl) ethyl ester (17)**: DCC (105 mg, 0.51 mmol) was added to a solution of compounds **15** (186 mg, 0.50 mmol) and **16** (88 mg, 0.51 mmol) and DMAP (5 mg) in methylene chloride (50 mL) at 0 °C. The solution was stirred for 0.5 h at room temperature and the precipitate was filtered off. After workup, the solvent was evaporated. The resulting residue was subjected to flash chromatography (CH$_2$Cl$_2$/MeOH 75:1) to give compound **17** as a white solid (224 mg, 85 %). M.p. 167–169 °C; ^{1}H NMR (CDCl$_3$): δ = 0.85–0.89 (m, 3H), 1.26–1.33 (m, 10H), 1.41 (s, 9H), 1.68–1.72 (m, 2H), 3.72–3.77 (t, J = 7.8 Hz, 2H), 3.86–3.88 (d, J = 5.4 Hz, 2H), 4.02–4.06 (t, J = 9.9 Hz, 2H), 4.42–4.45 (t, J = 10.2, 2H), 4.98 (s, 1H), 8.29 (s, 2H); EI-MS: m/z: 530 $[M]^+$; elemental analysis calcd (%) for C$_{27}$H$_{35}$N$_3$O$_8$ (529.58): C 61.23, H 6.66, N 7.99; found: C 61.22, H 6.41, N 7.94.

Isocyanato-acetic 2-(6-octyl-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl) ethyl ester (18): Boron trifluoride etherate (0.4 mL) was added with a syringe at room temperature to a solution of compound **17** (180 mg, 0.34 mmol) in acetic acid (15 mL). The solution was stirred for 15 min and then poured into aqueous ammonia solution (1N, 50 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic phases were washed with water (3 × 20 mL) and then poured into a 250 mL flask. A saturated solution of Na$_2$CO$_3$ (15 mL) was added. After stirring for 5 min, a solution of triphosgene (1N) in CH$_2$Cl$_2$ (5 mL) was added and the mixture was stirred vigorously for 15 min. The organic phase was separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (30 mL). The combined organic phases were dried and concentrated to afford compound **18**, which was used for next step without further purification.

[3-(6-Methyl-4-oxo-1,4-dihydro-pyrimidin-2-yl)-ureido]-acetic 2-(6-octyl-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl) ethyl ester (2): A suspension of compound **18**, obtained above, and pyrimidine **19** (50 mg, 0.40 mmol) in THF (50 mL) was heated under reflux for 20 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was washed with diethyl ether (30 mL) and then recrystallized from CH$_2$Cl$_2$ and MeOH. Compound **2** was obtained as a white solid (108 mg, 64 %). M.p. 197–195 °C; ^{1}H NMR (CDCl$_3$): δ = 0.85–0.89 (m, 3H), 1.26–1.32 (m, 10H), 1.66–1.70 (m, 2H), 2.24 (s, 3H), 3.69–3.74 (t, J = 7.2 Hz, 2H), 3.97–3.99 (d, J = 5.4 Hz, 2H), 4.02–4.06 (t, J = 5.1 Hz, 2H), 4.41–4.45 (t, J = 4.8 Hz, 2H), 5.77 (s, 1H), 8.24 (s, 2H), 10.69 (s, 1H), 12.02 (s, 1H), 12.77 (s, 1H); FAB-MS: m/z: 580 $[M]^+$; elemental analysis calcd (%) for C$_{30}$H$_{42}$O$_{12}$ (580.59): C 57.92, H 5.56, N 14.48; found: C 57.58, H 5.70, N 14.53.

1-(2-Benzyloxy-ethyl)-3-(6-nonyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (22): Saturated aqueous NaHCO$_3$ (280 mL) was added to a solution of benzoxyethylamine hydrochloride (2.62 g, 14.0 mmol) in methylene chloride (280 mL). The biphasic mixture was cooled to 0 °C and stirred for 10 min. Stirring was stopped and the layers were allowed to separate. A solution of triphosgene (2.80 g, 9.43 mmol) in methylene chloride (30 mL) was added to the organic phase by means of a syringe. The mixture was cooled for 0.5 h in an ice bath with stirring. The layers were allowed to separate and the aqueous phase was extracted with methylene chloride (3 × 100 mL). The combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated to give compound **21**, which was used immediately in the next step. The crude isocyanate was dissolved in dry pyridine (100 mL), and **20** (3.37 g, 14.0 mmol) was added. The solution was heated under reflux for 4 h, the solvent was removed and the residue was thoroughly washed with Et$_2$O and then purified by column chromatography (CH$_2$Cl$_2$/MeOH 30:1), to afford compound **22** as a white solid (4.13 g, 71 %). M.p. > 190 °C; ^{1}H NMR (CDCl$_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.24–1.32 (m, 12H), 1.64 (d, J = 7.4 Hz, 2H), 2.46 (t, J = 7.7 Hz, 2H), 3.49–3.55 (q, J = 5.4 Hz, 2H), 3.65 (t, J = 5.7 Hz, 2H), 4.57 (s, 1H), 5.81 (s, 1H), 7.24–7.37 (m, 5H), 10.36 (s, 1H), 11.97 (s, 1H), 13.09 (s, 1H); EI-MS: m/z: 414 $[M]^+$; elemental analysis calcd (%) for C$_{23}$H$_{34}$N$_4$O$_3$ (414.54): C 66.64, H 8.27, N 13.52; found: C 66.61, H 8.06, N 13.52.

1-(2-Hydroxyethyl)-3-(6-nonyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (23): 10 % Pd/C (0.15 mg) was added to a mixture of **22** (2.07 g, 5.00 mmol) and NH$_4$HCO$_3$ (7.0 g) in methanol (150 mL). The mixture was stirred under reflux for 1.5 h, and then filtered to remove the catalyst. The solvent was evaporated and the crude product was recrystallized from methanol and acetone to afford compound **23** (1.37 g, 84 %) as a gel. ^{1}H NMR (CDCl$_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.31–1.33 (m, 12H), 1.64 (q, 2H), 2.47 (t, J = 7.7 Hz, 2H), 3.44 (t, J = 4.5 Hz, 2H), 3.72 (t, 1H), 3.81 (m, 2H), 5.82 (s, 1H), 10.29 (s, 1H), 11.81 (s, 1H), 13.06 (s, 1H); EI-MS: m/z: 293 $[M - CH_3O]^+$; elemental analysis calcd (%) for C$_{16}$H$_{28}$N$_4$O$_3$ (324.42): C 59.23, H 8.70, N 17.27; found: C 59.29, H 8.55, N 17.01.

(7-Octyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydro-1H-benzo[lmn][3,8]phenanthrolin-2-yl) acetic acid (25): A solution of compounds **24** (2.68 g, 10.0 mmol), **13** (1.30 g, 20.0 mmol), and glycine (0.62 g, 20.0 mmol) in DMF (40 mL) was stirred at 120 °C for 4 h. After the mixture had cooled to room temperature, the insoluble solid was filtered off and the solution was poured into water (100 mL) The precipitate was filtered, washed with water (15 mL), methanol (15 mL), and CH$_2$Cl$_2$ (15 mL), and then purified by column chromatography (CHCl$_3$/MeOH 50:1). Compound **25** was obtained as a pink solid (1.33 g, 29 %). M.p. 154–155 °C; ^{1}H NMR (CDCl$_3$): δ = 0.83–0.87 (m, 3H), 1.25–1.32 (m, 10H), 1.62–1.65 (m, 2H), 4.00–4.05 (t,

$J = 7.8$ Hz, 2H), 4.74 (s, 2H), 8.62–8.68 (m, 4H); EI-MS: m/z: 454 $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{24}N_2O_6 \cdot H_2O$ (436.46): C 63.52, H 5.76, N 6.06; found: C 63.97, H 5.78, N 5.56.

(7-Octyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydro-1H-benzo[lmn][3,8]phenanthrolin-2-yl) acetic 2-[3-(6-nonyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido]ethyl ester (3): Compound **25** (0.30 g, 0.66 mmol) was added to oxalyl chloride (5 mL) at room temperature, and the suspension was refluxed until the mixture had turned clear (6 h). The solution was then concentrated in vacuo and the oily residue **26** was used for the next step without further purification. To a solution of compound **23** (0.15 mg, 0.70 mmol), NEt$_3$ (0.5 mL), and DMAP (10 mg) in chloroform (50 mL) was added a solution of the above compound **26** in chloroform (10 mL) with stirring at room temperature. The mixture was refluxed for 20 h and cooled to room temperature. It was washed with water and brine, and then dried over sodium sulfate. The solvent was removed in vacuo, and the residue was subjected to flash chromatography (CH$_2$Cl$_2$/EtOAc 3:1) to afford compound **3** as a pink solid (15 %). M.p. 192–193 °C; ^{1}H NMR (CDCl$_3$): $\delta =$ 0.82–0.86 (m, 6H), 1.23–1.37 (m, 18H), 1.70–1.75 (m, 4H), 2.46–2.51 (t, $J = 7.8$ Hz, 2H), 3.57–3.59 (d, $J = 5.1$ Hz, 2H), 4.14–4.19 (t, $J = 7.8$ Hz, 2H), 4.38–4.41 (t, $J = 5.1$ Hz, 2H), 5.02 (s, 2H), 5.81 (s, 1H), 8.69–8.72 (m, 4H), 10.43 (s, 1H), 11.72 (s, 1H), 12.96 (s, 1H); ESI-MS: m/z: 743 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{32}N_2O_8$ (742.86): C 64.67, H 6.78, N 11.31; found: C 64.60, H 6.85, N 11.23.

Dodecanoic (7-dodecanoylamino[1,8]naphthyridin-2-yl)amide (29): Triethylamine (5 mL), N-dimethylaminopyridine (DMAP, 61 mg, 5 %), and lauroyl chloride (5.48 g, 25.0 mmol) were added to a stirred suspension of 2,7-diamino-1,8-naphthyridine[21] (1.60 g, 10.0 mmol) in chloroform (200 mL). The mixture was then heated at reflux for 48 h and cooled to room temperature. The solid was filtered off and the organic phase washed with 1N hydrochloride solution (2 × 50 mL), 1N sodium carbonate solution (2 × 50 mL), water (30 mL), brine (50 mL) and was then dried (MgSO$_4$). After removal of the solvent in vacuo, the resulting residue was purified by column chromatography (CH$_2$Cl$_2$/ethyl acetate 5:1), to afford the title compound as a colorless solid (65 %). M.p. 130–132 °C; ^{1}H NMR (CDCl$_3$): $\delta = 8.44$ (d, 2H), 8.18 (s, 2H), 8.16 (d, 2H), 2.43 (t, 4H), 1.75 (m, 4H), 1.42–1.20 (m, 16H), 0.86 (m, 3H); FAB-MS: m/z: 525 $[M+H]^+$; elemental analysis calcd (%) for $C_{32}H_{52}N_4O_2$ (524.78): C 73.24, H 9.99, N 10.68; Found: C 73.19, H 10.01, N 10.70.

[3-(6-Methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido]acetic ethyl ester (30): A mixture of 2-amino-4-hydroxy-6-methylpyrimidine (0.50 g, 4.00 mmol) and ethyl 2-isocyanatoglycinate[22] (0.50 g, 3.91 mmol) in dried pyridine (20 mL) was stirred under reflux for 3 h. The solvent was removed under reduced pressure and the residue was thoroughly washed with Et$_2$O and then subjected to flash chromatography (CH$_2$Cl$_2$/MeOH 10:1), to give compound **30** as a white solid (0.77 g, 78 %). M.p. 197.5–199 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.25$–1.30 (t, 3H), 2.22 (s, 3H), 3.98–4.00 (d, 2H), 4.12–4.25 (m, 2H), 5.82 (s, 1H), 10.76 (s, 1H), 12.13 (s, 1H), 12.87 (s, 1H); EI-MS: m/z: 254 $[M]^+$; anal. calcd (%) for $C_{10}H_{14}N_4O_4$ (254.24): C 47.24, H 5.55, N 22.03; found: C 47.17, H 5.50, N 22.26.

^{1}H NMR binding studies: All ^{1}H NMR binding studies were carried out at 25 °C. The CDCl$_3$ used in these studies was passed through a short column of dry, activated, basic alumina prior to use. [D$_6$]DMSO was used as provided without further purification. Volumetric flasks and syringes used in preparing solutions were washed with dried CDCl$_3$ and dried in vacuum before use. Samples (usually 0.6 mL) were prepared from stock solutions, transferred to the NMR tubes and diluted accordingly with syringes.

For one series, usually 10–15 samples were prepared and binding constants reported are the average of two or three experiments, which were obtained by fitting the data of the changes in the chemical shifts to 1:1 binding isotherms with standard nonlinear curve-fitting procedures.[14] The nonlinear equations, used in dilution (self-association) and 1:1 dilution or titration (complexation) studies, were derived from mass-balance equations and the relationship between the concentrations of free and complexed samples and the weighted chemical shifts under the condition of rapid exchange.[14] Detailed methods and typical examples are available as Supporting Information.

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