Dynamic Combinatorial Chemistry: Substrate H-Bonding Directed Assembly of Receptors Based on Bipyridine-Metal Complexes

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The functionalized ligands **1** and **2** bearing hydrogen-bonding recognition groups have been synthesized. Their assembly by metal ions such as Cu^I and Pd^{II} having different coordination geometries generates different receptor architectures for the binding of suitable substrates. Addition of the complementary bis(imide) Janus molecules (**4**–**7**) to [**1a**, **2a**, CuTf] or to [**1b**, **2b**, $Pd(BF_4)_2$] mixtures leads to a moderate selective increase of the fraction of the $[(\mathbf{1a})_2Cu]^+$ or $[(\mathbf{1b})_2Pd]^{2+}$ complex depending on the Janus substrate used. Largest enhancements are observed for those Janus substrates that may be expected to display highest geometrical complementarity with the two complexes. These results represent a process directed by target binding based on dynamic combinatorial chemistry.

Introduction

The reversible connection of molecular building blocks generates potentially a set of molecular or supramolecular entities containing in principle all possible combinations of the constituents whose proportions are controlled by thermodynamic equilibria. This process may be considered as defining a dynamic combinatorial chemistry (DCC) that gives access to virtual combinatorial libraries (VCLs). In the presence of a species that binds one of the (real or virtual) members of such a library, a selective increase of the amount of this specific constituent may be expected, amounting to a target-directed enhancement of a member of the library. This is the case in the selective self-assembly of a pentameric circular helicate induced by the strong binding of a chloride ion, which led us to the DCC/VCL concept.[1] The latter was formulated in detail and extended to the recognition-induced assembly of an enzyme inhibitor.[2a] A major aspect of DCC is the search for suitable reversible processes.

Dynamic combinations of building blocks have made use of covalent linkages, such as the reversible formation of imines,[2] esters,[3] disulfides,[4] or the photoisomerization of alkenes[5] for the generation of equilibrating combinatorial libraries of receptor or substrate molecules. They may also be based on non-covalent linkages such as metal coordination,[1][6] hydrophobic effects,[7] or hydrogen bonding.[8] In the present work, we have taken advantage of the reversible assembly of ligands bearing recognition groups on a transition metal center for generating dynamic mixtures of artificial receptors.

The coordination of organic ligands to metal ions has proved an efficient approach to create cavities of defined shape and size and to preorganize recognition groups in space to generate binding cavities.[9] The combination of different ligands or the formation of coordination isomers has led to the construction of libraries of self-assembled receptors, in systems where each receptor was studied as a separate entity.[10] The use of *reversible* coordination to metal centers for assembling receptors has also been reported. It was shown that an appropriate guest can act as a template for the preferential formation of the receptor.[11]

In the present study, we take advantage of this phenomenon to identify, in a dynamic mixture of coordination receptors bearing hydrogen-bonding units, those presenting best complementarity to a particular substrate molecule of Janus type,[12] i.e. a molecule having two recognition faces. As depicted in Scheme 1, the mixture is based on the *reversible* coordination of pairs of ligands to a transition metal ion. Using two different ligands, a mixture of three different complexes can be generated. Each complex is defined by a recognition capability, which results from the combination of the recognition elements of its ligands. Thus, a complex made of two ligands possessing hydrogen-bonding functions with a Donor-Acceptor-Donor (DAD) pattern, potentially has an enhanced affinity for Janus molecules having twice the complementary ADA hydrogen-bonding pattern. Indeed, this complex may form six hydrogen bonds with the two faces of a Janus molecule, whilst the free ligand or a complex bearing only one such ligand can only form three hydrogen bonds with one face. Thus, a better recognition may be achieved by a combination of the recognition elements of two ligands than from one ligand only.

The main consequence of the involvment of two ligands from the same complex in the recognition event is the selective stabilization of the complex since the Janus molecule bridges the ligands through noncovalent interactions. The equilibria should thus be shifted towards the formation of the complex displaying the best complementarity to the Janus molecule. The free energy associated with this equilibrium shift corresponds to the differential binding energy of

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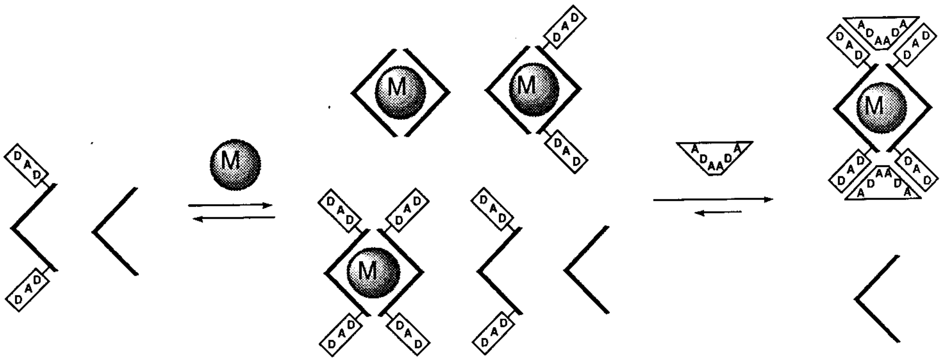


Scheme 1. Dynamic mixture of ligands and complexes formed upon coordination of two different ligands to a transition metal; stabilization of a receptor complex (molding) with a complementary Janus substrate molecule; one ligand bears two recognition groups with DAD hydrogen-bonding pattern; the Janus-type substrate presents two complementary ADA patterns

the Janus molecule to one complex with respect to the other components of the mixture.

Another consequence of the equilibrium shift is the release of the other ligand from the complexes. Using an appropriate stoichiometry of ligands, metal ion, and Janus substrate molecule, this may ultimately lead to a situation where only one ligand participates to the coordination, the other remaining free in solution (Scheme 1). A good receptor is thus identified simply from the fact that it becomes more abundant in the presence of its complementary substrate.

Ligand Components

As metal coordination components, 2,2′-bipyridine units bearing diacylaminopyridine DAD hydrogen-bonding motifs in position 4 and 4′ were used (Figure 1). Molecules such as **1** possess one bidendate metal-binding center and can hydrogen-bond to two imide functions via a complementary DAD/ADA array of three hydrogen bonds.[13] Ligands **2** also have 4,4′-carboxamide groups, but lack the diacylaminopyridine moiety. This should confer on them electronic properties and affinities for transition metals

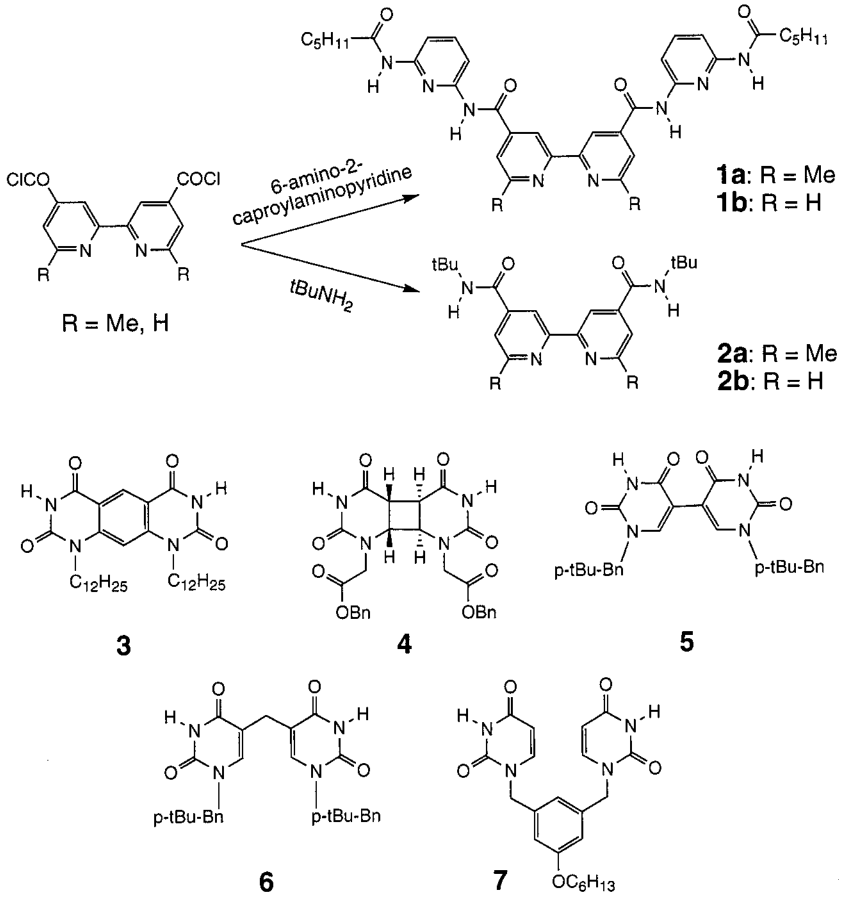


Figure 1. Functionalized ligands and substrate Janus molecules

similar to that of **1**, while keeping low hydrogen-bonding capacity to imide functions. Ligands **1** and **2** were prepared from the coupling of a 2,2′-bipyridine-4,4′-dicarbonyl chloride and either *t*BuNH$_2$ or 6-amino-2-caproylaminopyridine.

Janus molecules **3**−**7** all possess two hydrogen-bonding ADA imide functions as prime recognition elements. They thus all belong to the same interactional space and only differ by their geometrical properties. In **3** and **4**, the imide groups are rigidly held in parallel planes. In **5**, **6**, and **7** the imides are separated by an increasing number of single bonds, a feature that goes along with reduced preorganization and larger conformational freedom.

Copper(I) Complexes

Formation

Cu^I ions coordinate two bipyridine ligands in a distorted tetrahedral geometry, thus holding them in an approximately perpendicular arrangement ($\Phi \approx 90°$ in Figure 2). The 2,2′-bipyridine ligands **1a** and **2a** having methyl groups in the 6,6′ positions were preferred to **1b** and **2b** because their complexes with Cu^I are less labile, and less sensitive to oxidation by air. In pure chloroform at room temperature, the ligands exchange slowly on the NMR time scale. The signals observed in the ^{1}H-NMR spectrum of a solution of **1a**, **2a** (1 mM each) and CuTf (0.5 mM) can be assigned to a mixture of the five possible species by comparison with the individual spectra of **1a**, **2a**, (**1a**)$_2$CuTf, and (**2a**)$_2$CuTf. A series of six singlets is seen at $\delta = 2-2.8$, that correspond to the signals of the methyl substituents *ortho* to the bipyridine nitrogen atom (Figure 3A): one singlet for each free ligand, one singlet for each homocomplex, and two singlets of equal intensity for the mixed complex (**1a**)(**2a**)CuTf. Integration of these signals allows to measure the proportion of each species in the mixture. Due to a slightly higher intrinsic affinity of **2a** for Cu^I, (**2a**)$_2$CuTf is more abundant than (**1a**)$_2$CuTf, and **2a** and **1a**, respectively, represent 27% and 73% of the free ligands.

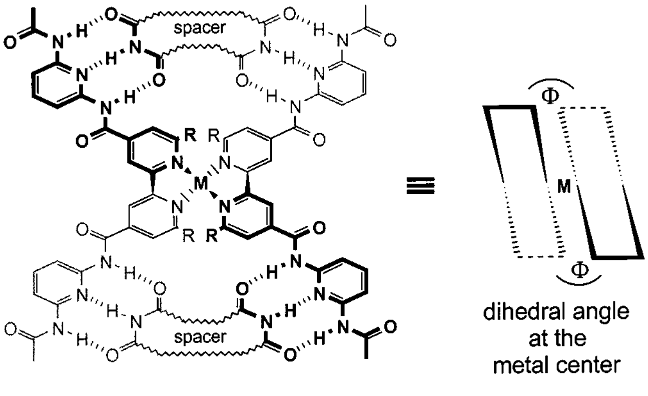


Figure 2. Schematic representation of the bridging of two ligands of a transition metal complex through hydrogen bonding to Janus molecules; the coordination sphere of the metal center determines the relative orientation of the aminopyridine moieties (Φ); the degree of complementarity of the Janus molecules is set by their spacer

Binding of Substrate Molecules

When a substrate **3**, **4**, **5**, or **7** (1 mM) is added to the mixture of complexes and ligands, the ratios [**1a**]/[**2a**] and [(**1a**)$_2$CuTf]/[(**2a**)$_2$CuTf] remained unchanged (Figure 3B). The signals assigned to **1a**, (**1a**)$_2$CuTf, and (**1a**)(**2a**)CuTf shifted upon the formation of hydrogen-bonded complexes, while those corresponding to **2a** and (**2a**)$_2$CuTf did not shift. This indicates that hydrogen bonding occurs between the imide and the diacylaminopyridine groups without specificity. None of these Janus molecules is capable of bridging two ligands on a same complex. On the other hand, hydrogen bonding of the Janus molecules to **2a** and (**2a**)$_2$CuTf is negligible. These results also indicate that hydrogen bonding to **1a** does not enhance its affinity for copper through any electronic effect.

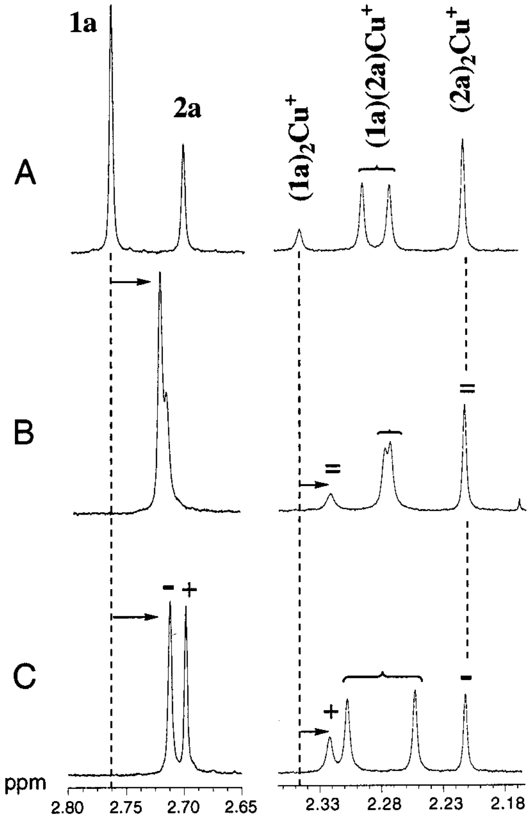


Figure 3. Part of the 500-MHz ^{1}H-NMR spectrum of a CDCl$_3$ solution of **1a**, **2a** (1 mM each) and CuTf (0.5 mM) at 298 K; the region at $\delta = 2.36-2.65$ is omitted for clarity; arrows indicate some of the shifts observed upon the addition of bis(imide) Janus substrate; A: no substrate added; B: **5** added (1 mM); C: **6** added (1 mM)

When the bis(imide) **6** (1 mM) was added to the mixture, similar shifts were observed, but the proportions between the different species were also modified (Figure 3C). The amount of (**1a**)$_2$CuTf was multiplied by a factor 2.3, and the proportions of **1a** in the free ligand decreased from 73 to 52%. Concomitantly the amount of (**2a**)$_2$CuTf decreased whilst the proportion of **2a** in the free ligands increased from 27 to 48%. The free energy difference between the two entities formed may be estimated to be about 4 kJ/mol.

The diacylaminopyridine groups of two different ligands in a Cu^I complex are more or less perpendicular. The capability of a Janus molecule to stabilize (**1a**)$_2$CuTf upon forming simultaneously hydrogen bonds with both ligands of the complex is thus linked to its ability of positioning its imide groups perpendicularly to each other. The results indicate that only **6** is able to do so at sufficiently low entropic and enthalpic costs. Thus, these experiments allowed to identify one Janus molecule to which (**1a**)$_2$CuTf binds selectively. However, the affinity for **6** remained small, and we searched for larger effects by changing the geometry of the complex. This was achieved by using Pd^{II} instead of Cu^I.

Palladium(II) Complexes

Formation

Pd^{II} can coordinate two 2,2′-bipyridines such as **1b** and **2b** which have no substituents in the 6 and 6′ positions in a square-planar arrangement ($\Phi \approx 0°$ in Figure 2). As a consequence, within a complex with **1b**, the aminopyridine moieties are held in the same plane. To form hydrogen bonds to both ligands of this complex, a Janus molecule should thus have coplanar imides diverging at an angle of ca. 120°, such as in **3** and **4**.

The bis(bipyridine)−Pd(BF$_4$)$_2$ complexes are not readily soluble in pure chloroform. In the following experiments this was circumvented by adding small amounts of DMSO (5%) to the mixtures, resulting in a satisfactory solubility whilst keeping competing hydrogen-bonding to the solvent low. In this solvent however, the ligand exchange is fast on the NMR time scale. For a mixture of **1b**, **2b**, and Pd(BF$_4$)$_2$, each ligand appears as one set of signals in the ^{1}H-NMR spectrum. The chemical shift of each signal is an average of its value for the free ligand and for the ligand complexed to Pd^{II}. From the chemical shift, one can access the proportion of free and complexed ligand, as illustrated by the titration experiment shown in Figure 4.

Increasing amounts of Pd(BF$_4$)$_2$ were added to a solution of **1b** and **2b** (1 mM each). Coordination to Pd^{II} causes a downfield shift of the bipyridines 3-H/3′-H, and amide NH signals. It is interesting to note that the 3-H/3′-H signal of **2b** shifts more at the beginning of the titration before reaching its limit value, whilst the 3-H/3′-H signal of **1b** follows a sigmoidal curve. As with Cu^I, this arises from a slightly larger affinity of ligand **2b** for Pd^{II}. During the titration, **1b** is involved in the complexes only in a second step, when the amount of free **2b** becomes smaller. When [Pd(BF$_4$)$_2$] = 0.5 mM, 65% of **2b** and 35% of **1b** are coordinated to Pd^{II}.

Substrate Binding

The effect of the presence of the Janus molecules on the ^{1}H-NMR signals was first evaluated on **1b**, (**1b**)$_2$Pd(BF$_4$)$_2$, **2b**, (**2b**)$_2$Pd(BF$_4$)$_2$ individually. For **1b** and (**1b**)$_2$Pd(BF$_4$)$_2$ the introduction of imide units resulted in shifts similar to those observed for **1a** and (**1a**)$_2$CuTf: downfield shift of the amide NH signals, and upfield shift of the bipyridine 3-H/3′-H signals. Since shifts occur both upon hydrogen bonding of **1b** to imides and upon its coordination to metal centers, these signals cannot be used as reliable probes for either phenomenon. However, the presence of the Janus molecules had no effect on the spectra of **2b** and (**2b**)$_2$Pd(BF$_4$)$_2$, as was also the case for **2a** and (**2a**)$_2$CuTf. Thus, a shift of the signals of **2b**, and in particular of the signals of 3-H/3′-H, can be assigned directly to its coordination to Pd^{II}.

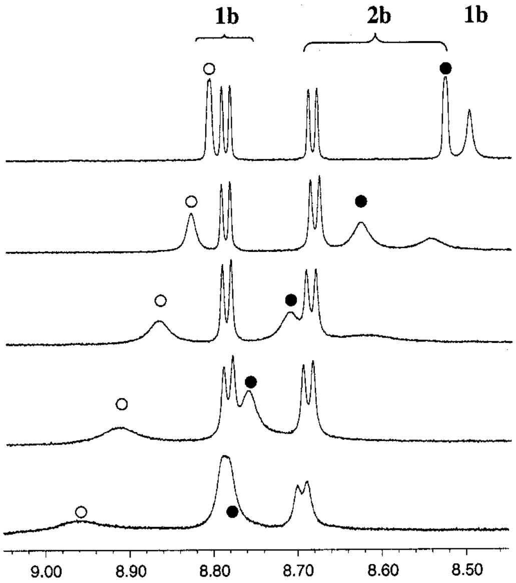


Figure 4. Part of the 500-MHz ^{1}H-NMR spectrum of a 95:5 CDCl$_3$/[D$_6$]DMSO solution of **1b**, **2b** (1 mM each) and Pd(BF$_4$)$_2$ (0, 0.25, 0.5, 0.75 and 1 mM from top to bottom) at 298 K; the circles mark the signals assigned to the bipyridine 3-H and 3′-H of **1b** (o) and **2b** (•); these signals shift upon the formation of bipyridine−palladium complexes; the doublets at δ = 8.79 and 8.69 were assigned to **1b** and **2b**, respectively (bipyridine 5-H and 5′-H); the singlet at δ = 8.50 (top spectrum) was assigned to **1b** (pentyl−CON*H*−)

In a last series of experiments, we measured the effect of the addition of Janus molecules (1 mM) on a dynamic mixture of **1b**, **2b** (1 mM each) and Pd(BF$_4$)$_2$ (0.5 mM). The results are summarized in the Table 1. They show that Janus molecules cause a release of **2b** from the Pd^{II} complexes, and therefore an increase of the coordination of **1b** to Pd^{II}. This is best explained by a selective stabilization of (**1b**)$_2$Pd(BF$_4$)$_2$ upon formation of hydrogen-bonded bridges between these Janus molecules and the ligands. This occurs despite the presence of DMSO in the solvent. The effect can be enhanced upon cooling the mixture down to 273 K (Figure 5): association becomes stronger, and the proportion of **2b** involved in coordination to Pd^{II} drops below 5% in the case of **3**.

Nevertheless, the selectivity for **3** remains low, and despite their structural differences, all the Janus molecules have some effectiveness to shift the equilibrium towards a better coordination of **1b** to Pd^{II}. One possible explanation is a flexibility in the positioning of the ligands about the metal center. The angle Φ (Figure 2) may deviate substan-

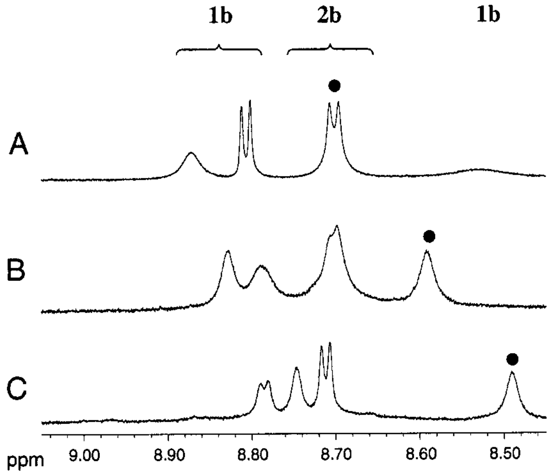


Figure 5. Part of the 500-MHz ^{1}H-NMR spectrum of a 95:5 $CDCl_3$/[D_6]DMSO solution of **1b**, **2b** (1 mM each), and $Pd(BF_4)_2$ (0.5 mM) at 298 K; A: no wedge added; B: **3** added (1 mM); C: same as B at 213 K; the circle marks the bipyridine 3-H and 3′-H of **2b**; in A, this signal overlaps with the bipyridine 5-H and 5′-H of **2b**

tially from zero, thus allowing $(\mathbf{1b})_2Pd(BF_4)_2$ to accommodate imides at various distances and orientations.

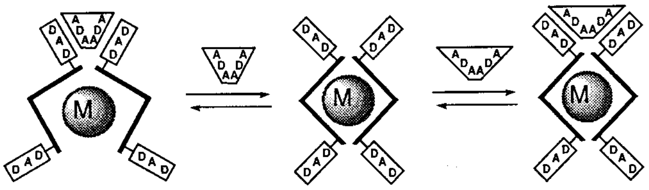
Table 1. Proportions (± 5%) of **1b** and **2b** involved in the coordination with Pd^{II} in a mixture of **1b**, **2b** (1 mM each), $Pd(BF_4)_2$ (0.5 mM), and various Janus molecules (1 mM)[a]

	Janus molecule						
	none	3	3[b]	4	5	6	7
Proportion (%) of **1b** coordinated to Pd^{II}	35	70	95	65	55	60	65
Proportion (%) of **2b** coordinated to Pd^{II}	65	30	5	35	45	40	35

[a] At 298 K. The proportion of the different complexes was calculated from the chemical shift of the bipyridine 3-H/3′-H signal in **2b**. – [b] At 273 K.

Cooperativity

The metal complexes involving two ligands **1** have two binding sites for Janus molecules (Scheme 2). The experiments above were performed using two equivalents of Janus molecule (1 mM) with respect to the metal. We looked for the conceivable presence of some degree of cooperativity between these two binding sites by examining the effect of *a single equivalent* (0.5 mM) of Janus molecule on the same dynamic mixtures as above ([**1**] = [**2**] = 1 mM, [metal] = 0.5 mM). In the case of a strong negative cooperativity between the binding sites, one equivalent of Janus molecule should be as effective as two for the stabilization of complexes $(\mathbf{1})_2$(metal) (Scheme 2). In the case of a strong positive cooperativity, one equivalent of Janus molecule should have a stabilizing effect of exactly half the effect of two equivalents. In none of our systems, however, we observed a clear cooperativity, and the results were always between these ideal cases.



Scheme 2. Negative (left) and positive (right) cooperativity; the binding of a Janus molecule to the complex may favor or disfavor the binding of a second Janus molecule

Conclusion

The present results demonstrate a selective enhancement of a constituent of a dynamic combinatorial set of metal complexes acting as receptors for the binding of a complementary substrate species. They are based on the simultaneous operation of reversible metal ion coordination for the exploration of the combinatorial space and of substrate binding through hydrogen bonding, for the amplification of a given constituent of the dynamic library.

A variety of other reversible molecular or supramolecular processes may be envisaged for gaining access to dynamic combinatorial libraries, real or virtual, adapted to the molecular recognition of specific partners.

Experimental Section

General: ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker WM-200 (200 MHz) or a Bruker 500 (500 MHz) spectrometer at 298 K. Chemical shifts are reported as δ values relative to the residual solvent peak. – Yields are calculated on isolated compounds and are unoptimized. The following compounds were prepared according to literature procedures: 2,2′-bipyridine-4,4′-dicarbonyl chloride,[14] 6,6′-dimethyl-2,2′-bipyridine-4,4′-dicarbonyl chloride,[15] 2-amino-6-caproylaminopyridine,[16] Janus molecule **3**,[12] uracil photodimer **4**,[17] 5,5′-diuracil and methylene 5,5′-diuracil.[18]

General Procedure for the Preparation of Ligands 1 and 2: 2,2′-Bipyridine-4,4′-dicarbonyl chloride (0.5 mmol) was dissolved in anhydrous toluene (5 mL), and either freshly distilled tBuNH$_2$ (5 equiv.) or 2-amino-6-caproylaminopyridine (2.1 equiv.) was added. The suspension was stirred at room temperature for 24 h under an anhydrous atmosphere. The solvent was then evaporated and the solid residue triturated in saturated aqueous $NaHCO_3$. The suspension was filtered and the solid was washed thoroughly with saturated aqueous $NaHCO_3$ and water, and finally dried under vacuum. Recrystallization from EtOAc/EtOH afforded analytically pure **1a**, **1b**, **2a**, and **2b**.

4,4′-Bis[(6-caproylamino-2-pyridyl)carboxamido]-2,2′-bipyridine (1b): White solid m.p. 260°C. – ^{1}H NMR ($CDCl_3$, 10% [D_6]DMSO, 200 MHz): δ = 10.87 (br, s, 2 H, NH), 10.21 (br, s, 2 H, NH), 8.94 (d, 2 H, J = 5 Hz, 6-H, 6′-H bipy), 8.88 (d, 2 H, J = 1.5 Hz, 3-H, 3′-H bipy), 7.97 (dd, 2 H, J = 5 Hz, J = 1.5 Hz, 5-H, 5′-H bipy), 7.90–7.76 (m, 6 H, H py), 2.41 (t, 4 H, J = 7.2 Hz, CH_2–NH), 1.59 (q, 4 H, J = 7.2 Hz, CH_2–CH_2–NH), 1.29 (m, 8 H, CH_3–CH_2–CH_2-), 0.87 (t, 6 H, J = 7.2 Hz, CH_3). – ^{13}C NMR ([D_6]DMSO, 50 MHz): d = 172.2, 164.4, 155.2, 150.6, 150.0, 149.6, 142.7, 139.9, 122.3, 118.7, 110.6, 110.0, 35.9, 30.7, 24.6, 21.8, 13.7. – $C_{34}H_{38}N_8O_4$ (622.73): calcd. C 65.57, H 6.15, N 17.99; found C 65.14, H 6.16, N 17.86.

4,4′-Bis[(6-caproylamino-2-pyridyl)carboxamido]-6,6′-dimetyl-2,2′-bipyridine (1a): White solid m.p. 225°C. − ^{1}H NMR ([D$_6$]DMSO, 200 MHz): δ = 10.80 (br, s, 2 H, NH), 10.20 (br, s, 2 H, NH), 8.64 (s, 2 H, 3-H, 3′-H bipy), 7.87−7.78 (m, 8 H, H py and 5-H, 5′-H bipy), 2.69 (s, 6 H, CH$_3$), 2.44 (t, 4 H, J = 7.2 Hz, CH_2−NH), 1.57 (q, 4 H, J = 7.2 Hz, CH_2−CH$_2$−NH), 1.29 (m, 8 H, CH$_3$−CH_2−CH_2−), 0.87 (t, 6 H, J = 7.2 Hz, CH$_3$). − ^{13}C NMR ([D$_6$]DMSO, 50 MHz): δ = 172.2, 158.7, 154.8, 150.6, 149.7, 143.0, 139.9, 121.5, 115.9, 110.5, 110.0, 35.9, 30.7, 24.5, 24.1, 21.7, 13.7. − High Resolution MS; $C_{36}H_{43}N_8O_4^+$: calcd. 651.3407; found 651.3414.

4,4′-Bis(*tert*-butylcarboxamido)-6,6′-dimethyl-2,2′-bipyridine (2a): White solid m.p. 287.2°C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 8.35 (d, 2 H, J = 0.8 Hz, 3-H, 3′-H), 7.54 (dd, 2 H, J = 4.4 Hz, J = 0.8 Hz, 5-H, 5′-H), 6.18 (br, s, 2 H, NH), 2.67 (s, 6 H, CH_3 bipy), 1.48 (s, 18 H, CH$_3$). − ^{13}C NMR ([D$_6$]DMSO, 50 MHz): δ = 165.1, 158.0, 154.7, 144.5, 121.1, 115.6, 51.0, 28.3, 24.1. − High Resolution MS; $C_{22}H_{31}N_4O_2^+$: calcd. 383.2447; found 383.2436. − The crystal structure of this compound was determined and will be reported elsewhere.

4,4′-Bis(*tert*-butylcarboxamido)-2,2′-bipyridine (2b): White solid, m.p. 272°C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 8.80 (d, 2 H, J = 4.4 Hz, 6-H, 6′-H), 8.58 (d, 2 H, J = 0.8 Hz, 3-H, 3′-H), 7.76 (dd, 2 H, J = 4.4 Hz, J = 0.8 Hz, 5-H, 5′-H), 6.18 (br, s, 2 H, NH), 1.51 (s, 18 H, CH$_3$). − ^{13}C NMR ([D$_6$]DMSO, 50 MHz): δ = 164.7, 155.2, 149.6, 144.2, 122.0, 118.3, 51.1, 28.3. − High Resolution MS; $C_{20}H_{27}N_4O_2^+$: calcd. 355.2134; found 383.2135.

Cu(2a)$_2$Tf: Red crystals. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 8.60 (s, 2 H, 3-H, 3′-H), 7.76 (s, 2 H, 5-H, 5′-H), 7.09 (br, s, 2 H, NH), 2.21 (s, 6 H, CH$_3$ bipy), 1.54 (s, 18 H, CH$_{3\ \mathrm{tert}}$-butyl). − ^{13}C NMR ([D$_3$]MeCN, 50 MHz): δ = 165.0, 159.1, 152.9, 146.2, 125.0, 118.7, 53.0, 28.8, 25.3. − The crystal structure of this compound was determined and will be reported elsewhere.

Pd(2b)$_2$[BF$_4$]$_2$: Yellow crystals. − ^{1}H NMR (CDCl$_3$, 200 MHz, 10% [D$_6$]DMSO, 200 MHz): δ = 8.81 (s, 2 H, 3-H, 3′-H), 8.70 (d, 2 H, J = 5.5 Hz, 6-H, 6′-H), 8.18 (d, 2 H, J = 5.5 Hz, 5-H, 5′-H), 7.69 (br, 2 H, NH), 1.43 (s, 18 H, CH$_{3\ \mathrm{tert}}$-butyl). − ^{13}C NMR ([D$_3$]MeCN, 50 MHz): δ = 163.6, 158.2, 153.3, 149.9, 127.7, 124.1, 53.9, 29.1.

Acknowledgments

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