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Catalytic Three-Component Machinery: Control of Catalytic Activity by Machine Speed

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Abstract: Three supramolecular slider-on-deck systems **DS1-DS3** were created as two-component aggregates from the sliders **S1-S3** and deck **D** with its three zinc porphyrin (ZnPor) binding sites. The binding of the two-footed slider to the deck varies with the donor quality of and steric hindrance at the pyridine/pyrimidine (pyr) feet and was effected by two $N_{pyr} \rightarrow ZnPor$ interactions. Accordingly, the sliders move at different speed over the three zinc porphyrins in the deck: with 32.2, 220 and 440 kHz at room temperature. Addition of *N*-methylpyrrolidine as organocatalyst to **DS1-DS3** generates catalytic three-component machinery. Using a conjugate addition as a probe reaction, we observe a correlation between the operating speed of the slider-on-deck systems and the yields of the catalytic reaction. With decreasing thermodynamic binding of the slider, both the frequency of the sliding motion and yield of the catalytic reaction increase.

The connection of protein conformational dynamics and enzymatic activity is hotly debated,^[1,2] because both precise spatial arrangement and high dynamics have to work together synergistically for high turnover rates in enzymes.^[3] It is thus an appealing challenge to systematically use dynamic effects in artificial catalysts for speed-up.^[4,5] Herein we describe how a dynamic slider-on-deck system is coupled to an organocatalyst and how the sliding speed (machine speed) in this threecomponent aggregate impacts catalysis. The results show clearly the prevalence of kinetic over thermodynamic factors in the liberation of catalyst into solution and highlight the usefulness of dynamic multicomponent machinery.

Although most biological machine archetypes are multiprotein complexes, very few examples of artificial devices^[6-18] that arise from self-sorting of diverse components^[19-21] have been reported, quite in contrast to the large gamut of known covalently and topologically constructed machines.^[23-31]

For the present study we have chosen the two-component slider-on-deck systems **DS1-DS3** = **D**•(**S1-S3**) (Scheme 1) due to the following reasoning: (1) In **DS1-DS3** the two-footed slider **S1-S3** should move quickly on the D_{3h} -symmetric deck **D** with its three identical zinc porphyrin (ZnPor) binding sites. (2) The speed should be adjustable by changing the binding foot of **S1-S3**. (3) Addition of one equiv of an organocatalyst to **DS1-DS3** is expected to generate the catalytic three-component machinery **cat-D**•(**S1-S3**). (4) The slider's foot (various pyridine/pyrimidine derivatives: pyr) and the organocatalyst should have comparable affinity toward the binding sites of the deck, so that liberation of

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the catalyst into solution may be triggered by the motion of the slider. (5) The amount of catalyst in solution shall be quantifiable by a catalytic process. Thereby, significantly dissimilar sliding speeds of **DS1-DS3** should lead to divergent yields in the catalytic reaction.



Scheme 1. Molecular structures and cartoon representations of deck D, sliders S1-S3 and aggregates DS1-DS3.

Based on our recent work on rotors^[32] we decided to implement *meso*-protons (r-H) in the ZnPor units of deck **D**, because a kinetic analysis by ¹H NMR requires diagnostic changes upon formation of N_{pyr} \rightarrow ZnPor interactions. The sliders' feet were chosen after establishing enough distinct binding affinities for 4-iodopyridine (1), 4-iodopyrimidine (2) and 4-bromo-2-methylpyridine (3) toward zinc porphyrin 4, *i.e.* log K₁₊₄ = 4.31 ± 0.12 (Supporting Information = SI, Figure S72), log K₂₊₄ = 3.35 ± 0.15 (SI, Figure S73) and log K₃₊₄ = 2.72 ± 0.04 (SI, Figure S77).



In response to above considerations, we synthesized and fully characterized the symmetric deck **D** as well as the three two-footed sliders **S1-S3** with their different pyridyl/pyrimidyl binding sites (Schemes S1-S4 in SI). To prepare the slider-on-deck systems **DS1-DS3**, the slider units **S1-S3** were simply mixed with tris(zinc porphyrin) **D** in CDCl₃ in a 1:1 ratio. The aggregates **DS1-DS3** are furnished quantitatively and are fully characterized again by ¹H NMR, ¹H-¹H COSY, ¹H-¹H NOESY, ¹³C NMR, DOSY and elemental analysis (SI).

As expected, an upfield shift of *meso*-protons r-H from 10.33 ppm in **D** to 10.20 ppm in **DS1** is observable upon coordinating the pyridyl terminals of **S1** to the ZnPor units (Figure 1). Parallel, the pyridyl proton signals a_1 -H and b_1 -H are shifted upfield to 2.24 and 5.37 ppm in **DS1** from 8.61 and 7.40 ppm in **S1**,

respectively. The N_{py} \rightarrow ZnPor interaction was further validated by UV-vis investigations showing that the Q-band of **DS1** appears as a broad absorption at λ = 547 nm, in contrast to the Q-band signature of uncoordinated ZnPor in **D** (absorption at λ = 542 nm, SI, Figure S75). Finally, a single set of signals in the ¹H DOSY ($D = 2.70 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$, $r \sim 19.5 \text{ Å}$) confirms the clean formation of the sliding system (SI, Figure S54).

Analogous to **DS1**, ¹H NMR signals of *meso*-protons r-H in **DS2** are shifted to 10.22 ppm (Figure 1) while the pyrimidine protons a₂-H, a'₂-H and b₂-H are equally shifted upfield (SI). The Q-band absorption showing the N_{pym} \rightarrow ZnPor interaction is located at λ = 545 nm (SI, Figure S76). Likewise a single set of signals in the ¹H DOSY (D = 2.80 × 10⁻¹⁰ m²s⁻¹, r ~18.5 Å, SI, Figure S55) suggests the clean formation of the aggregate. Similar characteristic shifts are given in **DS3**.

First insights into the sliding dynamics of the slider-on-deck systems DS1-DS3 are already obtained from the ¹H NMR spectrum at 25 °C (Figure 1). The rapid motion of the slider across deck **D** is indicated by a single sharp ¹H NMR signal representing protons r-H at all three ZnPor units. In a static situation one would expect two sets of signals at a ratio 2:1. In order to quantify the sliding dynamics, the slider-on-deck aggregates DS1-DS3 were measured at various temperatures in toluene- d_8 (VT-¹H NMR). While all protons r-H of **DS1** appear as sharp singlet at 10.02 ppm at 25 °C, coalescence starts at -22 °C (Figure 2A). On further cooling, the signal starts to split and is completely separated at -75 °C, resulting in two singlets at 10.03 and 9.85 ppm at a ratio of 1:2. The first signal is assigned to free ZnPor and the second one to the pyridineloaded ZnPor units. The exchange frequency in DS1 is determined as k_{25} = 32.2 kHz and the free activation energy as ΔG_{25}^{\ddagger} = 47.3 kJ mol⁻¹. Alike, the ¹H NMR spectrum of **DS2** at 25 °C shows all protons r-H at 10.01 ppm in a single signal set while coalescence occurs around -35 °C (SI, Figure S60). At -75 °C the resonance for protons r-H is split into two signals at 10.00 and 9.86 ppm (1:2). The exchange frequency is k_{25} = 220 kHz and ΔG_{25}^{\ddagger} = 42.5 kJ mol⁻¹. **DS3** behaves analogously (SI, Figure S62) with k_{25} = 440 kHz and ΔG^{+}_{25} = 40.7 kJ mol⁻¹. All activation data are given in Figure 2B.

As expected, the weaker N_{pym} \rightarrow ZnPor interaction (log $K_{2\cdot4}$ = 3.35 ± 0.15) in **DS2** leads with k_{25} = 220 kHz to a faster sliding

Figure 1. Comparison of partial ¹H NMR spectra (CDCl₃, 400 MHz, 298 K) of (a) deck **D**, (b) **DS3** (**D** : **S3** = 1:1), (c) **DS2** (**D** : **S2** = 1:1) and (d) **DS1** (**D** : **S1** = 1:1).



Figure 2. (A) Experimental (left) and simulated (right) VT ¹H NMR spectra (toluene- d_{6} , 600 MHz) of proton signal r-H in **DS1**. (B) Experimental exchange frequency *k* at 25 °C and activation parameters of **DS1-DS3**.

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process compared to $k_{25} = 32.2$ kHz in **DS1** with the stronger N_{py} \rightarrow ZnPor binding (log $K_{1\cdot4} = 4.31 \pm 0.12$). Accordingly, the weakest N_{a-Me-py} \rightarrow ZnPor interaction (log $K_{3\cdot4} = 2.72 \pm 0.04$) results in the fastest exchange frequency (440 kHz at 25 °C). As shown by a control experiment, the exchange frequencies in Figure 2B are not affected by a bimolecular component (SI, Figure S82).

Mechanistically, one should consider two different alternatives: (1) complete dissociation of **DS1-DS3** and re-association of **D** and **S1-S3**, or (2) sliding based on disconnection/reconnection of only one foot of the slider. The first possibility demanding the complete dissociation of **S1-S3** and **D** is energetically incommensurate with the thermodynamic data. From a titration of **S1** to **D** the binding constant in **DS1** was determined as log $K_{D-S1} = 9.61 \pm 0.03$ ($\Delta G_{25} = 54.8$ kJ mol⁻¹; SI, Figure S75). As the activation barrier has to comply at least with the endergonicity of dissociation, a disconnection of **DS1** \rightarrow **S1** + **D** cannot be present since the experimental barrier for sliding in **DS1** ($\Delta G^{\dagger}_{25} = 47.3$ kJ mol⁻¹) is lower. This conclusion is confirmed by the fact that the barrier of a cognate rotor which is based on a single N_{py} \rightarrow ZnPor dissociation amounts to $\Delta G^{\ddagger}_{25} = 47.6$ kJ mol⁻¹.^[32]

This barrier may be compared to the activation energy for the N_{py} \rightarrow ZnPor dissociation in the simple complex **1**•4 (ΔG^{\dagger}_{25} = 32.4 kJ mol⁻¹, log $K_{1\cdot4}$ = 4.31; ΔG_{25} = 24.6 kJ mol⁻¹).^[32] Visibly, the sliding mechanism (2) that is based on a single N_{py} \rightarrow ZnPor bond cleavage in **DS1** has a barrier which is ca. 1.5-fold of that in the simple system **1**•4. The higher kinetic barrier possibly arises from intramolecular co-operative effects^[33] and the angular restrictions for N_{py} \rightarrow ZnPor dissociation in **DS1**. The same line of arguments can equally be given for **DS2** and **DS3**.

After preparing three slider-on-deck systems with different speed, we decided to interrogate whether distinct exchange frequencies would also influence the speed of a coupled catalytic reaction. Formally, in each slider-on-deck assembly **DS1-DS3** only two ZnPor units are occupied at any given time by the two-footed slider. The third ZnPor unit may therefore be used to bind a catalytically active nitrogen heterocycle, such as *N*-methylpyrrolidine (**5**). If the amine/slider-on-deck complexes, i.e. **DS1•5**, were static, we would expect no catalytic activity as the heterocycle **5** is firmly bound and thus not available for catalysis. For a dynamic system, however, we would expect a dynamic liberation of the catalyst.

To probe the concept of dynamic release of the catalyst from e.g. **5•DS1**, we have chosen the prototypical conjugate addition

reaction (1) of thiophenol (6) onto 2-cyclopentenone (7) with *N*-methylpyrrolidine (5) as catalyst (10 mol%) (Figure 3).^[34]

Before testing the slider-on-deck systems, we assessed the yields of model reaction **5** + **6** + **7** for reference purposes in the temperature range from 25 to 60 °C. After 4 h in each case, product yields were determined by ¹H NMR using tetrachloroethane (TCE) as internal standard (Figure 3). In presence of zinc porphyrin **4** and catalyst **5** (both 10 mol%) the reaction of **6** and **7** (both 13.4 mM) afforded no addition product **8** at a temperature below 50 °C. Clearly, product formation is precluded due to the strong interaction between porphyrin **4** and *N*-methylpyrrolidine (**5**) (log $K = 4.01 \pm 0.12$) (SI, Figure S74). Only at temperatures above 50 °C the equilibrium is shifted so much that liberated **5** causes perceptible product formation (Figure 3). Contrastingly, in absence of inhibitor **4**, at 50 °C the model reaction furnished (66 ± 2)% of product **8**.

Figure 3. Yields of the conjugate addition between **6** and **7** (both 1.34×10^{-2} M) with catalyst **5** (1.34×10^{-3} M) in presence of **4** (1.34×10^{-3} M) or **DS1-DS3** (1.34×10^{-3} M) after 4 hours.



Subsequently, the catalytic activity of the three-component machinery 5-D-(S1-S3) was evaluated under reference conditions. Hereunto we mixed 5, 6, 7 and the aggregates DS1, DS2 or DS3 in an NMR tube at 10:100:100:10 ratio in CDCI₃. Keeping the same conditions as for the model reaction (same concentrations, 4 h reaction time) we observed distinct yields for each individual slider-on-deck system with regard to the addition reaction. In presence of 5-DS1 the conjugate addition discernibly occurred already at 40 °C, while at 50 °C (taken as reference) it furnished (18 ± 2)% (Figure 3) of 8. For 5•DS2 the reaction already started at 35 °C; at 50 °C thiol adduct 8 was afforded in (32 ± 2)%. The catalytic machinery 5•DS3 led to an even faster acceleration of the conjugate addition reaction: the transformation started already at a temperature of 30 °C while at 50 °C it eventually exhibited (50 ± 2%) yield of 8 (Figure 3). All product yields are caused kinetically, as product 8 is formed irreversibly at 50 °C. A control experiment in absence of 5 shows that the aggregates DS1, DS2 or DS3 themselves are catalytically inactive (SI, Figure S69).

The present findings suggest that the dynamics of the catalytic three-component machinery **5**•**D**•**(S1-S3)** is correlated to the speed of the organocatalytic addition reaction. As the speeds of **D**•**S1** and **5**•**D**•**S1** are identical within error limits (SI, Figure S84), we use the kinetic data from Figure 2B for the three-component-machinery as well. As an indirect measure of the catalytic activity of **5**•**D**•**(S1-S3)** we use the temperatures T_{14%} at

which the yield of **8** is 14% after 4 h (Figure 4). $T_{14\%}$ can directly be extracted from the data furnished in Figure 3. In the reference reaction of **5+6+7+4**, thus with zinc porphyrin **4** inhibiting the activity of catalyst **5**, formation of product **8** in 14% yield requires a $T_{14\%}$ of 60 °C. When the binding of the catalyst at the ZnPor unit was reduced due to the increasing machine speed in **DS1**, **DS2** and **DS3** the $T_{14\%}$ dropped to 48, 37 and 33 °C, respectively. If one extrapolates the correlation shown in Figure 4 to infinite machine speed the lowest possible $T_{14\%}$ can be determined as 30.5 °C. This $T_{14\%}$ is very close to the temperature of 28 °C at which the unimpeded system **5+6+7** produces 14% of **8**!

Figure 4. Temperature $T_{14\%}$ (14% yield of product 8 is generated at $T_{14\%}$) depends on the sliding speed of the machinery.





Obviously temperatures $T_{14\%}$ are influenced by both the dynamic release and the inherent effect of the temperature on the catalytic reaction. To solely evaluate the effect of machine speed at a defined temperature, we determined the equilibrium amount of catalyst released into solution at 50 °C. As reference, we investigated the model reaction (catalyst **5** + substrates **6** + **7**) varying the amounts of **5** (2-10 mol%). As expected, the yield is almost linearly increased with augmented amounts of **5** (Figure 5A). A comparison with the yields that are obtained in the presence of **DS1-DS3** at 50 °C shows that 29% of **5** (with 10 mol% being the total amount) was available in solution with **DS1**, 48% with **DS2** and 76% with **DS3**. Thus with increasing speed the amount of liberated catalyst is largely increased at a given temperature (Figure 5B).

Figure 5. (A) Yields of the model reaction between 6 and 7 at 50 °C (4 h) using variable amounts of 5. The yields (18%, 32%, and 50%) are those of the corresponding reactions with the catalytic machinery **5**•(**DS1-DS3**). (B) Data for the catalytic machinery.



^{a)} Exchange frequencies k_{50} at 50 °C were calculated from the activation data.

From the data it is evident that, among the three machinery aggregates, **5**•**DS3** displays the highest catalytic activity due to the release of 76% of the available catalyst **5** from the ZnPor binding site into solution. The other ones **5**•**DS2** and **5**•**DS1** show lower yields of **8** and less release of **5** as a consequence of their reduced sliding speed. An interesting detail is the fact

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that the data allow us to extrapolate to both zero and infinite operating speed. At infinite exchange frequency the system would be expected to furnish the same yield as the model reaction at 50 °C in absence of porphyrin **4**, which would mean 66% of **8**. In contrast at zero sliding speed, the full inhibitory action of the ZnPor unit should be sensed, thus a yield of 0% is expected (0% yield was observed in the model reaction in presence of **4** at 50 °C). Remarkably, the release of catalyst is the more pronounced, the higher the sliding speed and the weaker the thermodynamic binding within the slider-on-deck systems.^[35] Thus liberation has to be a kinetic phenomenon!

The most likely explanation for the observed effect is a neighborgroup participation, analogous to the *proximity effect*. Due to the foot of the slider visiting all ZnPor stations on the deck, it displaces catalyst **5** bound to the third ZnPor unit of **DS1-DS3** in an S_N2-type reaction. Notoriously, ZnPor can only bind strongly to one additional ligand.^[36] This S_N2-displacement increases the dissociation speed (k_{diss}) of catalyst **5** from **DS1-DS3**. Reciprocally, the association (k_{ass}) of liberated **5** back to **DS1-DS3** should be slowed down due to the dynamic loading of all ZnPor platforms with the slider. In sum, both effects lower the binding constant $K_{5*(DS1-DS3)} = k_{ass}/k_{diss}$ and thereby increase the concentration of liberated catalyst **5** in solution.

In conclusion it can be stated that three two-component slideron-desk systems were presented, in which the adjustment of the binding strength of the slider's foot to the ZnPor determines the speed of the sliding motion. Addition of *N*-methylpyrrolidine (5) as organocatalyst to **DS1-DS3** generates catalytic machinery consisting of three components. In **5**•**D**•(**S1-S3**) the liberation of the catalyst and the yield of the organocatalytic reaction are unmistakably coupled to the machine speed. The liberation results from a *proximity effect* which is remotely related to the dynamic allosteric effect.^[37,38] Coupling of an output (catalysis) to the speed of a mechanical motion is a characteristic feature of machinery. As nature is using nanomechanical motions for some of its most demanding catalytic processes ^[39] it should be a great incentive to study further links between motion and catalytic activity in nanomechanical machinery.

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