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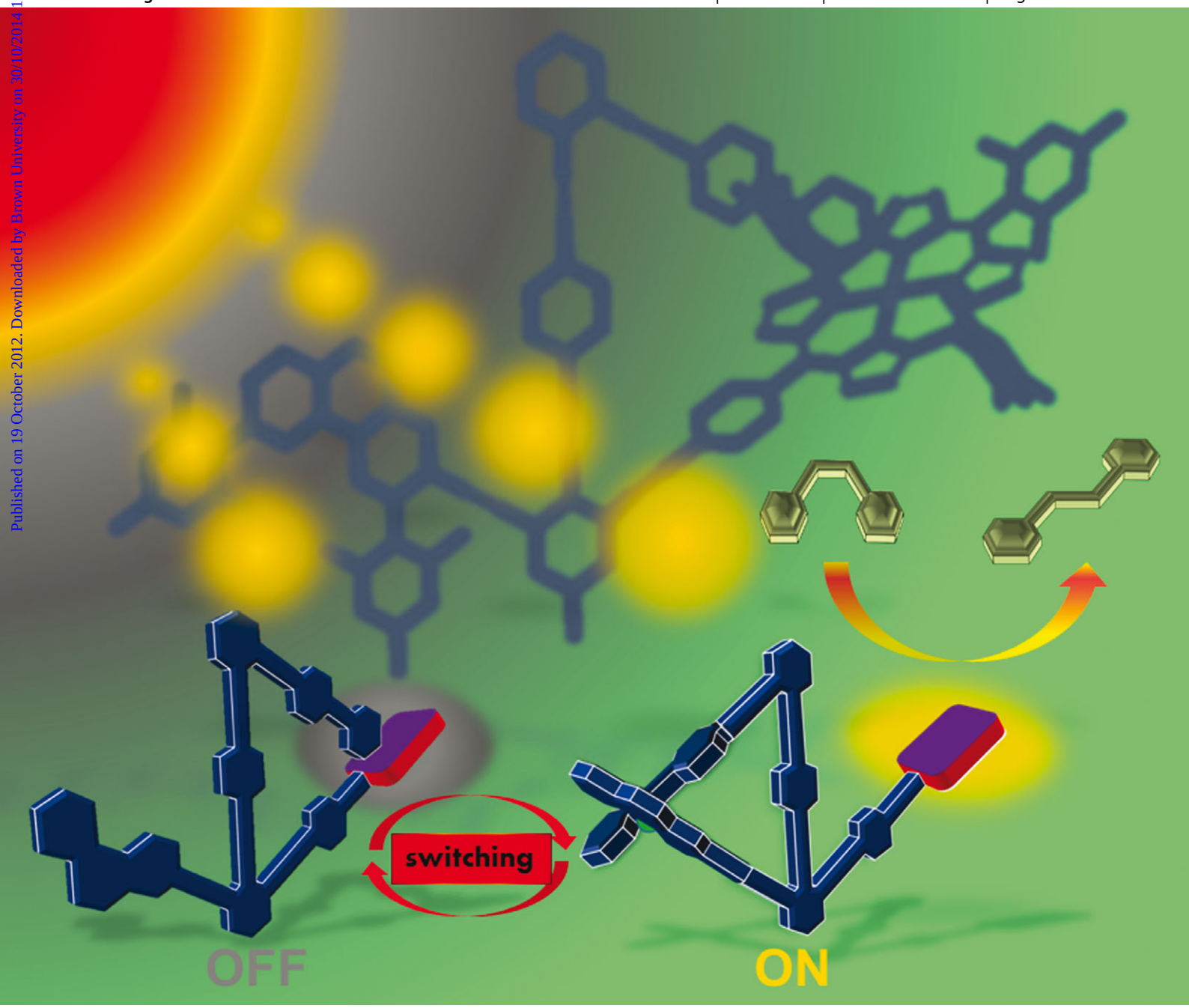

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A reversible nanoswitch as an ON–OFF photocatalyst†

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The two states of a new nanomechanical switch were quantitatively and reversibly populated in several subsequent switching cycles using either Cu^+ or cyclam as chemical inputs. State II was demonstrated to *cis–trans* isomerise diazastilbene upon irradiation selectively in the presence of stilbene, and even to operate as a photocatalyst.

The ease at which intricate and intertwined biological machines perform multifarious tasks with supreme efficiency has inspired researchers worldwide to design and investigate artificial molecular machines, switches and devices[1–4] that are controlled by external input signals. As a notable subcategory in this wide field, molecular switches[5] that trigger chemical processes[6] have recently gained importance, among them in particular nanomechanical switches with their fascinating modes of action. A nanomechanical switch, here called a nanoswitch, operates *via* significant amplitude motions, thus entailing large geometric and often electronic changes. In one recent example, Rebek and coworkers[7] have described a light-responsive cavitand–piperidinium complex that is used to catalyse a Knoevenagel condensation. Although the rate of reaction is well modulated using the light-triggered isomerisation of an azobenzene arm, switching does not operate in ON–OFF mode. The switchable organocatalyst based on a rotaxane design as presented lately by Leigh fulfills much better the criteria of an ON–OFF switch, but the ON mode requires both an alternate switching state and an activation of the nucleophile.[8] Already these two examples demonstrate that a nanomechanical switch with distinct ON–OFF[9] functions for catalysis requires a clear-cut OFF state, while the ON state should simply lead to a significantly accelerated reaction with regard to that of the OFF state. In this context, we presented lately the chemical-stimuli responsive nanoswitch **4** for reversible ON–OFF Knoevenagel organocatalysis.[10] In the ON state of catalysis, an "autoinhibitory segment" precludes the catalyst to bind to a zinc porphyrin unit of the switch while in the presence of [Cu(2,9-di(9-anthryl)phenanthroline)]$^+$ as input the zinc porphyrin becomes active for binding of the catalyst, resulting in an OFF state.

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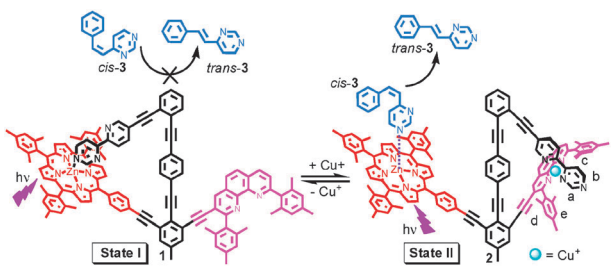
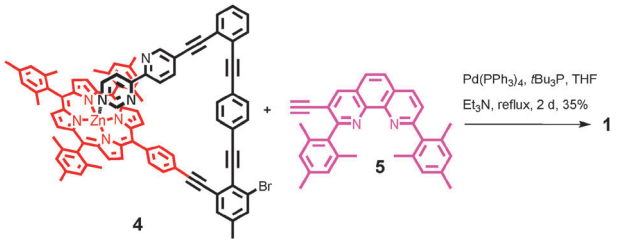
In the present communication, we describe the synthesis, characterisation and *modus operandi* of an improved nanoswitch architecture: a fixed two-state conformational nanomechanical switch. The switch works reversibly and quantitatively in the presence of Cu^+ as a chemical stimulus liberating a zinc porphyrin unit in the ON state that acts as a photosensitiser and even a photocatalyst in the isomerisation of an alkene (Scheme 1). To the best of our knowledge, there is no report on any nanoswitch that is operated reversibly and quantitatively by a chemical stimulus and allows to control a photoreaction in an ON–OFF manner.

In extending our previous design and to more readily effect formation of both switching states, we attach a sterically encumbered phenanthroline as a second intramolecular station to nanomachine **4**[10] (Scheme 2). The so formed fixed two-state nanoswitch **1** (Scheme 1) requires only one single chemical input for switching between the two states as relocation of the arm is intramolecular. In state I, the pyridyl-pyrimidine (py-pym) subunit coordinates to the zinc porphyrin thus diminishing its propensity to coordinate to added substrates. Upon switching to state II triggered by Cu^+ addition, the zinc porphyrin, a well-known triplet photosensitiser,[11] should be liberated and be available for photosensitized isomerisation reactions of properly chosen substrates.

Nanoswitch **1** was synthesised using a Sonogashira reaction between **4**[10] and **5** (Scheme 2), the latter being prepared following a synthetic protocol reported earlier.[12] ESI-MS, ^{1}H and ^{13}C NMR, UV-Vis, and elemental analysis techniques were used to characterise switch **1**. ESI-MS data show a molecular ion peak at m/z 1736.5 that is attributed to **1**·H$^+$ with the experimental isotopic distribution matching the theoretical values (Fig. S21, ESI†). In the ^{1}H NMR, protons a-H, b-H and c-H of the pyrimidine unit appear as sharp signals at 3.32, 2.87 and 6.63 ppm, respectively (Fig. S7, ESI†), indicating that they are immersed into the shielding region of



Scheme 1 Nanoswitching controls a photosensitised isomerisation.



Scheme 2 Synthesis of nanoswitch **1** from **4**.[10]

the porphyrin ring current. The diagnostic shifts and their concentration independence (Fig. S2, ESI†) indicate that the py-pym unit is intramolecularly coordinated to the zinc porphyrin. The UV-Vis spectrum of **1** displays an absorption maximum at 429 nm of the Soret band that is typical for a mono-coordinated porphyrin. Like for the self-locked molecule **4**,[10] the combined ^{1}H NMR and UV-Vis data unambiguously support intramolecular coordination between the pyrimidine and the zinc porphyrin units in **1**, representing state I.

Switching to state II was achieved by addition of 1 equiv. of $[Cu(CH_3CN)_4]PF_6$ as an external stimulus to furnish complex **2** (Scheme 1). **2** was fully characterised by ESI-MS, NMR, UV-Vis, and elemental analysis. The peak at m/z 1798.4 in the ESI-MS (Fig. S22, ESI†) strongly supports formation of **2** with the experimental isotopic distribution neatly matching the computed one. The ^{1}H NMR spectrum is informative in two ways with regard to establishing switching state II. Firstly, the downfield shifts of the pyrimidine protons a-, b- and c-H (Fig. S7, ESI†) from 3.32, 2.87, and 6.63 to 7.31, 7.31 and 7.67 ppm, respectively, clearly indicate formation of **2**. Likewise, the characteristic upfield shifts and splitting of the mesityl protons at the phenanthroline (d- and e-H) from 6.97 and 7.03 to 5.93, 6.16, 6.26 and 6.37 ppm, respectively, are comprehensibly diagnostic of the formation of heteroleptic[13] complex **2**. Thus, spectroscopic evidence suggests a clean toggling of the pyridyl-pyrimidine unit from the porphyrin station (state I) to the phenanthroline station (state II).

To further investigate the switching process, a UV-Vis titration of a solution of **1** (10^{-4} M) against $[Cu(CH_3CN)_4]PF_6$ (2.5×10^{-3} M) was carried out in dichloromethane. The UV-Vis absorption maximum at 563 nm, characteristic for a mono-coordinated porphyrin, completely shifts to 550 nm upon addition of only 1 equiv. of Cu^+ (Fig. S23, ESI†). To further corroborate the switching to state II, *i.e.* **2**, an ^{1}H-NMR titration of a solution of **1** (1.05 mM) was performed with $[Cu(CH_3CN)_4]PF_6$. The results clearly indicate full switching to state II upon addition of one equiv. of Cu^+ (Fig. S8, ESI†), because the upfield shifted mesityl protons of **2** (due to shielding by the py-pym ring current) appear, while at the same time the original downfield shifted mesityl protons of **1** disappear completely.

To assess reversibility of the switching process, we choose cyclam[10,14] to remove Cu^+. Because $[Cu(cyclam)]PF_6$ is insoluble in the reaction mixture, it precipitates and sedimentates; thus, the removal of the copper salt as waste in each repeating step is quite convenient. The ensuing reversal of the switching, *i.e.* a change from state II to I, was confirmed by UV-Vis and NMR spectroscopic data. Firstly, a UV-Vis titration with **2** (10^{-4} M) and cyclam (2.5×10^{-3} M) in DCM demonstrates that upon addition of one equiv. of cyclam the band at 550 nm completely shifts to 563 nm (Fig. S24, ESI†). This change indicates convincingly that the py-pym unit is now again coordinated to the zinc porphyrin. Secondly, after addition of one equivalent of cyclam to **2**, similarly the ^{1}H NMR titration showed protons a-H and b-H (Scheme 1) of the py-pym unit to reappear in the aliphatic region at 3.33 and 2.88 ppm, respectively, proposing its coordination to the zinc porphyrin. Moreover, the peaks at 5.93, 6.16, 6.26 and 6.37 ppm of protons d-H and e-H disappear and regenerate at 6.97 and 7.03 ppm (Fig. S9, ESI†). Thus, both UV-Vis and NMR titration data unambiguously provide evidence for quantitative switching from state II to state I, a result that is still rare for nanoswitches. Reversibility of this process was checked up to four cycles and monitored by ^{1}H NMR (Fig. 1).

After proving quantitative reversible switching between states I and II, we considered to use **2** (state II) with its liberated zinc porphyrin to command a chemical process. As a reference reaction we envisaged the photoinduced *cis–trans* isomerisation of azastilbenes, reported by Whitten.[11] However, azastilbene already binds weakly to the intramolecularly bound zinc porphyrin of state I ($\log K = -1.09 \pm 0.01$, Fig. S27, ESI†) thus partly displacing the intramolecular arm. It is thus not suited to keep state I, our chosen OFF state for photochemical activity, intact. In contrast, 1 equiv. of the weaker binding diazastilbene *trans*-**3** (at 0.18 mM) (Fig. S10, ESI†) does not displace the arm and likewise *cis*-**3** (Scheme 1) should have suitable binding properties.[15]

To probe for its photochemical suitability, *cis*-**3** was subjected to isomerisation using Zn**TPP** as a photosensitiser at a 1 : 1 ratio. Irradiation at 419 nm (λ_{max} = 422 nm) in DCM for 30 min led to 72(±3)%[16] of *trans*-**3** (at 0.10 mM concentration, Fig. S12, ESI†). As a control, we made sure that *cis*-**3** is stable to unsensitised irradiation at 419 nm for 30 min. In contrast,

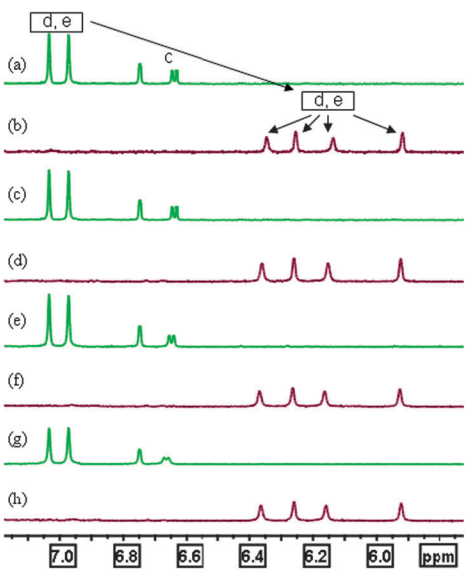


Fig. 1 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) depicting the reversibility of 4 cycles of switching between **1** and **2** (1.2 mM). (a), (c), (e) and (g) correspond to **1** (state I) whereas (b), (d), (f) and (h) represent **2** (state II), obtained after successive addition of Cu^+ and cyclam (d and e: mesityl protons of the phenanthroline; c: c-H protons at the pyrimidine ring). The four cycles start with (a).

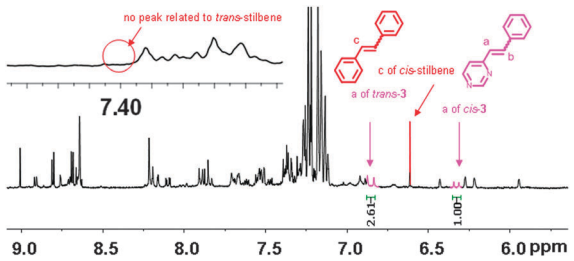


Fig. 2 Partial ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of a mixture of *cis*-**3** and *cis*-stilbene after irradiation in presence of **2** with 419 nm light for 30 min in DCM producing 72% of *trans*-**3**.

cis-stilbene does not isomerise at all under both conditions (Fig. S13, ESI†).

To evaluate the nanoswitch's properties to act as an ON–OFF photosensitiser, the 1 : 1 mixture of pure *cis*-**3** and **1** (0.10 mM) was irradiated at 419 nm for 30 min in DCM resulting in no isomerisation. Thus, state I is suitable as an OFF state (Fig. S14, ESI†). Upon addition of stoichiometric amounts of $[Cu(CH_3CN)_4]B(C_6F_5)_4$, the nanoswitch is moved to state II,[17] thus freeing the zinc porphyrin of **2** for coordination with *cis*-**3** ($\log K = 3.13 \pm 0.04$; Fig. S28, ESI†). Rewardingly, isomerisation was then readily effected yielding a mixture of *cis* and *trans*-**3** (28 : 72 (±4)) upon irradiation at 419 nm for 30 min (at 0.10 mM; Fig. S15, ESI†).

Clearly, the system **1/2** acts as an ON and OFF photoisomerisation nanoswitch. Besides, both states are found to be inactive in photoisomerising *cis*-stilbene (Fig. S16 and S17, ESI†). In a competition experiment, both states of the nanoswitch were evaluated for their ability to differentiate *cis*-**3** in the presence of *cis*-stilbene. State I, *i.e.* **1**, is found to be inactive for both alkenes (Fig. S18, ESI†), whereas state II selectively isomerises 72(±4)% of *cis*-**3** to *trans*-**3** without any isomerisation of *cis*-stilbene. Thus, nanoswitch **1/2** is not only an ON–OFF toggle for photoisomerisation, but additionally selective in isomerising *cis*-**3** in the presence of *cis*-stilbene (Fig. 2).

The results so far, *i.e.* reversible and quantitative switching of a nanoswitch and ON–OFF photoisomerisation, motivated us to check for reversible and catalytic ON–OFF photoisomerisation in DCM. When *cis*-**3** (4 equiv.) was irradiated at 419 nm for 20 min in the presence of **2** (1 equiv.; with $B(C_6F_5)_4^-$ as the counter ion), 45% of **3** isomerises to *trans*-**3** as determined by ^{1}H NMR (Fig. S20, ESI†). Addition of one equivalent of cyclam generates state I, *i.e.* **1**, with the effect that irradiation for 20 min does not yield any further isomerisation. As a consequence, nanoswitch **1/2** acts not only as a photosensitiser but alike Zn**TPP**, as described by Whitten earlier,[11] as a photocatalyst.

In conclusion, we illustrate the design, synthesis and characterisation of a fixed two-state nanomechanical switch acting as a photocatalyst. Switching is accomplished quantitatively and reversibly using Cu^+ and cyclam as input signals. Catalytic photosensitised isomerisation of *cis*-**3** is achieved in state II (free zinc porphyrin station), while state I is photochemically inactive. It is truly remarkable to see the photoefficiency of state II closely match that of the parent Zn**TPP**. Both show under identical and standardised conditions a yield of ≈72% isomerisation. Moreover, the reversibly operating nanoswitch can discriminate between stilbene and diazastilbene in the photoisomerisation. These results demonstrate that even complex structures such as **1/2** may be operated as ON–OFF photosensitisers.

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