Reversible ON/OFF Nanoswitches for Organo- and Photo-Catalysis

Soumen De, Susnata Pramanik, and Michael Schmittel*

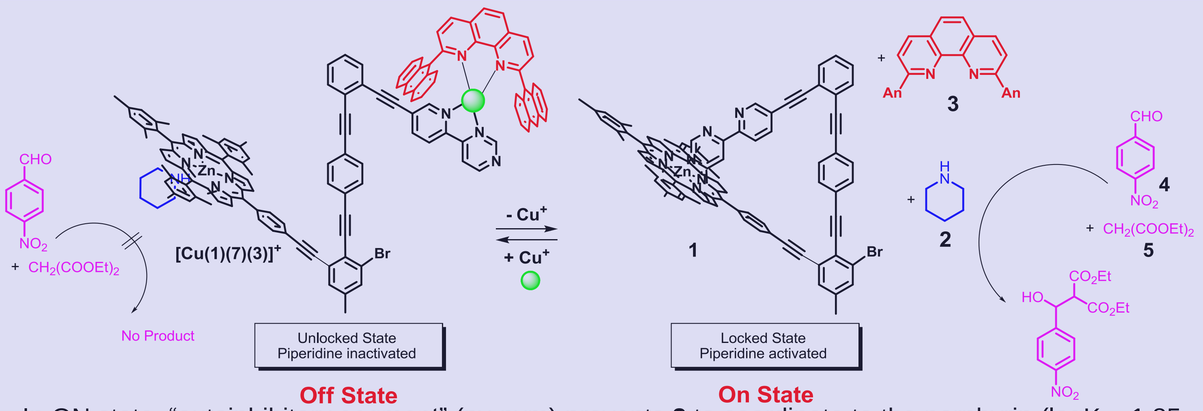
Universität Siegen

Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany

E-mail: *schmittel@chemie.uni-siegen.de*

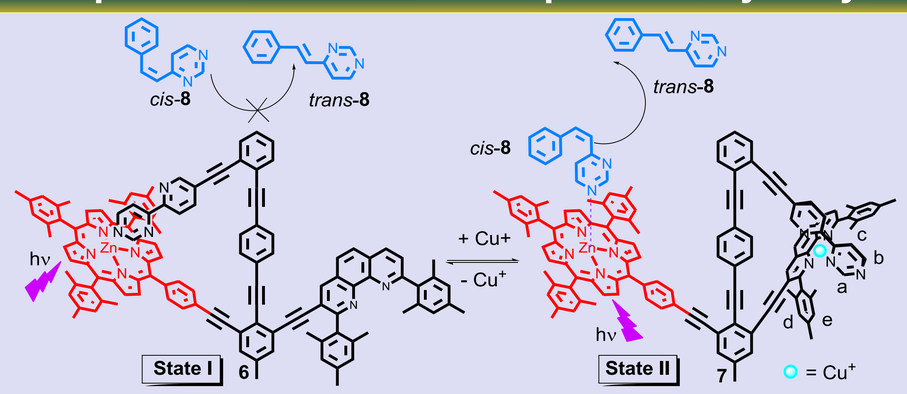
Introduction: Using chemical inputs, nanoswitches are commanded to trigger ON/OFF catalysis at the zinc porphyrin unit using piperidine and prophyrin itself as catalyst. For switch **1**, while in self-locked[1] state, the catalysis is ON, in unlocked-state the same is OFF as the piperidine is engaged in strong coordination to the porphyrin. The process has been run fully reversibly over three cycles without loss of activity.[2] Similarly, ligand **6** was utilized for the reversible photosensitized *cis* to *trans* isomerization irradiating at the porphyrin station.[3] In OFF state, intramolecular coordination prevents guest binding at porphyrin station and thus no isomerization was observed. However, in ON state, generates on Cu^+ binding, removes the intramolecular coordinating unit from the porphyrin station and thus affecting the guest binding which initiates the photocatalysis.

Representation of ON/OFF organocatalytic cycle[2]



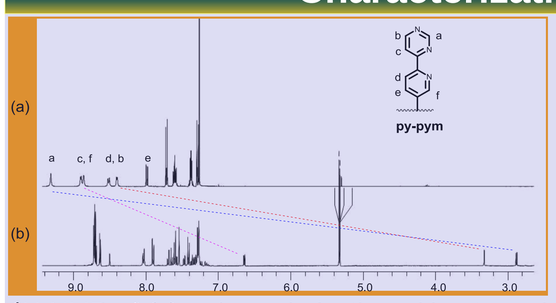
In ON state, “autoinhibitory segment” (py-pym) prevents **2** to coordinate to the porphyrin (logK = 1.85 0.15 at 55 C) and hence catalyzed the Knoevenagel reaction. In contrast, OFF state dose not catalyze as after adding [Cu(**3**)]$^+$, py/pym unit is engaged in forming heteroleptic[4] HETPHEN complex and drives its release from the docking station and allowing **2** to bind tightly even at 55 °C (logK = 5.15 0.04 at 25 °C).

Representation of ON/OFF photocatalytic cycle[3]

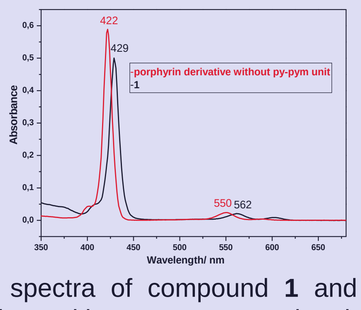


In **State I**, “autoinhibitory segment” (py-pym) prevents **8** to coordinate to porphyrin and hence triplet sensitization is no longer be possible. However, in **State II**, *cis*-**8** can bind with the porphyrin and affecting the photoisomerization on irradiation the porphyrin at 419 nm.

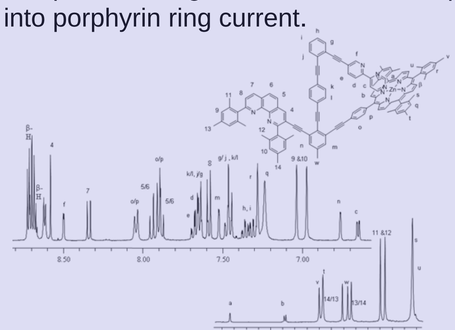
Characterization of 1 and 6



^{1}H NMR of (a) py/pym derivative without porphyrin and (b) compound **1**: the shifting of peaks of py-pym unit from aromatic to aliphatic region in compound **1** signifies immersion of py-pym unit into porphyrin ring current.



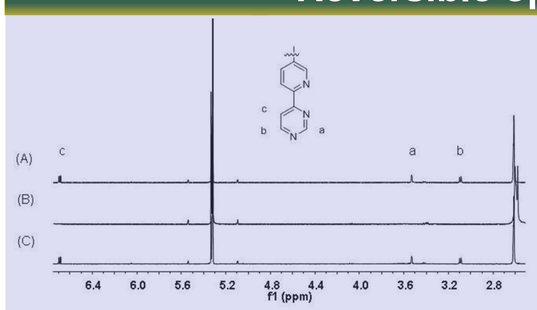
UV-vis spectra of compound **1** and porphyrin derivative without py-pym unit: the spectra shows 7 nm bathochromic shift of the Soret band which attributes to axial coordination to zinc porphyrin.



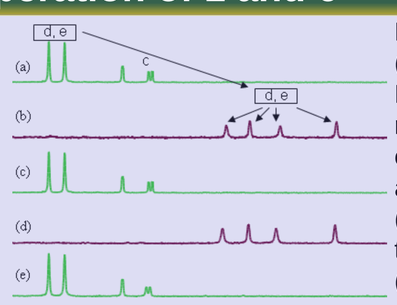
The ^{1}H NMR of the ligand **6** appears to be similar as we have seen for the ligand **1**, particularly, for the py-pym protons. a- and b- protons of py-pym unit are observed at aliphatic region suggesting coordination of py-pym unit to porphyrin.

The intramolecular coordination was proved from concentration dependent NMR and UV-vis studies. Concentration independent resonance positions of a, b and c protons in ^{1}H NMR and Soret absorption band in UV-vis imply intramolecular coordination.

Reversible operation of 1 and 6

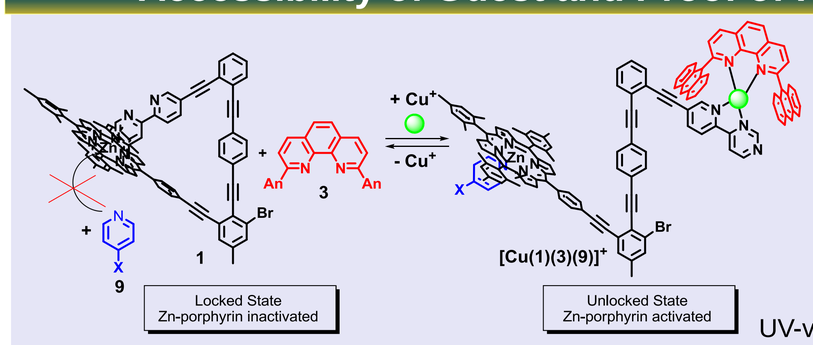


Partial ^{1}H NMR of (A) **1**; (B) after adding [(**3**)Cu]$^+$ to **1** produce unlocked state; (C) addition of cyclam which removes Cu^+ from [Cu(**1**)(**3**)]$^+$ and reproduce locked state confirmed from reappearance of a and b protons in aliphatic region.



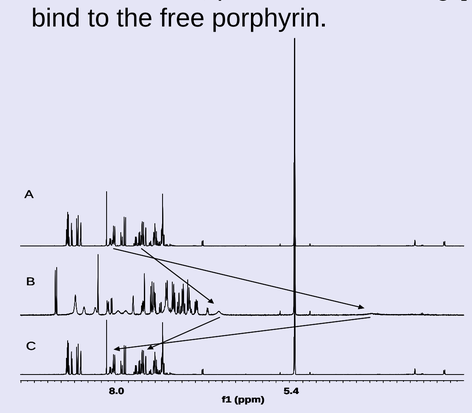
Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) depicting the reversibility of 4 cycles of switching between **6** and **7** (1.2 mM). (a), (c), (e) and (g) correspond to **6** (state I) whereas (b), (d), (f) and (h) represent **7** (state II), obtained after successive addition of Cu^+ and cyclam (d and e: mesityl protons of the phenanthroline; c: c-proton at the pyrimidine ring). The four cycles start with (a)

Accessibility of Guest and Proof of Reversibility



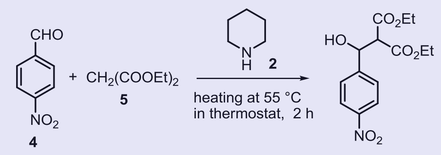
Schematic representation of reversible locking-unlocking and guest binding. In locked state guest binding is prohibited by the locking unit where as in unlocked state, produced on adding [Cu(**3**)]$^+$, guest can bind to the free porphyrin.

UV-vis titration of [(**1**)(**3**)Cu]$^+$ (10^{-4} M) against **9** (10^{-2} M). Titration of unlocked state (λ_{max} = 550 nm at Q band) with **9** shifts the absorption by 12 nm.

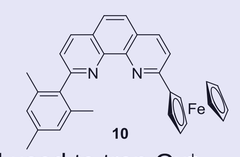


Partial ^{1}H NMR of (A) **1**, **3** and **9**; (B) [(**1**)(**3**)(**9**)Cu]$^+$ (C) after addition of cyclam to (B). Locked state restricts **9** to dock into porphyrin but addition of Cu^+ generates unlocked state allowing guest binding. Cyclam with strong affinity towards Cu^+, withdraws the metal ion and originates locked state rendering guest releasing.

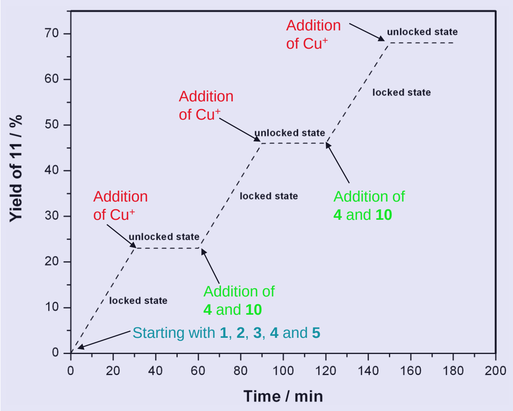
Efficiency and Reversibility of Organocatalysis with 1



Schematic representation of Knoevenagel reaction



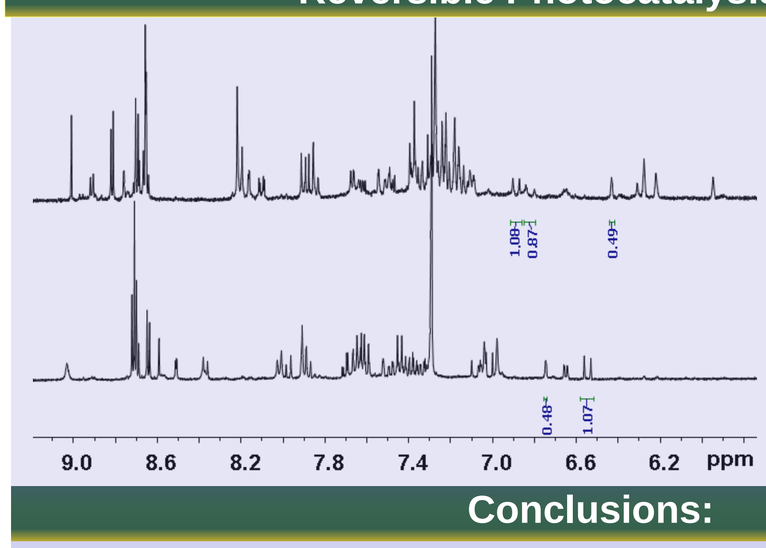
Ligand used to trap Cu^+



Representation of efficiency and reversibility of organocatalysis

Catalysis was started with mixture of **1**, **2**, **3**, **4** and **5** at 1:1:1:10:1000 ratio. After heating at 55 °C NMR was measured indicating 23% of product formation. To stop the reaction, catalyst **2** was needed to trap which was achieved by addition of Cu^+. The catalysis was switched to ON by removing Cu^+. Cyclam was not used to abstract Cu^+ as [Cu(cyclam)]$^+$ complex was found to be active for the catalysis. To overcome this problem, we designed a new ligand **10** which form strong homoleptic complex [Cu(**10**)$_2$]$^+$ thus removing Cu^+ from the unlocked state. After each of the catalytic cycle, consumed aldehyde was added to maintain the reaction kinetics. The reversibility was performed over three cycles and was proved to be efficient regeneration of the catalytic activity.

Reversible Photocatalysis with 6



Partial ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of experiments checking for reversibility with *cis*-**8**; (top) after irradiation for 20 min in presence of **7** and (bottom) after irradiation for 20 min in presence of **6** after addition of cyclam, both at 419 nm in DCM.

Conclusions:

- Ligand **1** and **6** were synthesized and fully characterized by NMR, ESI-MS, and UV-vis spectroscopies.
- Ligand **1** and **6** are completely self-locked system with respect to binding of selected guest.
- Reversible quantitative switching between locked state and unlocked state was performed using copper(I) ions/**3** and cyclam in case of **1**. However, for the ligand **6**, only Cu^+ and cyclam was required as phenanthroline is now intramolecularly attached as a second arm to the switch.
- Self-locked molecule **1** is providing a docking station which can trap or release the catalyst. Modulating the docking station, organocatalysis was switched ON/OFF and run over the three cycles reversibly without loss of activity.
- The switch **6** was also effective for the photoinduced isomerization of cis-azastilbene and was found to be reversible.

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References: (1) T. Muraoka, K. Kinbara, T. Aida, *J. Am. Chem. Soc.* **2006**, *128*, 11600; (2) M. Schmittel, S. De, S. Pramanik, *Angew.Chem. Int. Ed.* **2012**, *51*, 3832; (3) M. Schmittel, S. Pramanik, S. De, *Chem. Commun*. **2012**, *48*, 11730; (4) S. De, K. Mahata, M. Schmittel, *Chem. Soc. Rev.* **2010**, *39*, 1555.