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# A photoactive basket-like metal–organic tetragon worked as an enzymatic molecular flask for light driven $H_2$ production†

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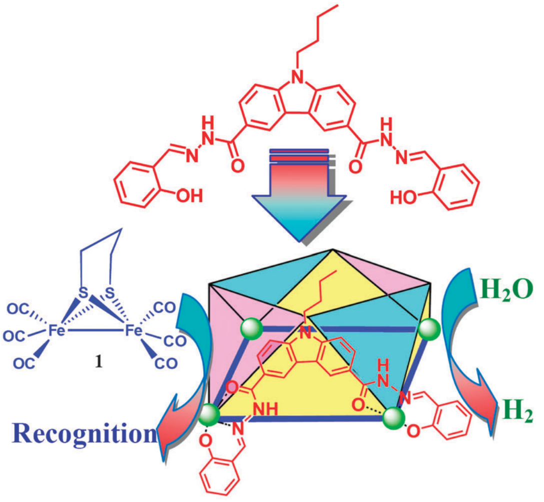
**A photoactive basket-like metal–organic tetragon Ce–ZL that contained a carbazole photosensitizer was developed to capture the biomimetic [FeFe]-$H_2$ases for light driven $H_2$ production. The system exhibited enzymatic behaviour and its activity was inhibited by the encapsulation of ATP.**

Photocatalytic hydrogen production from water represents an important process in sustainable solar energy conversion for the future. Inspired by photosynthetic complexes in nature, this process was realized by a homogeneous reaction environment toward optimal availability of active catalytic sites for solar hydrogen production.[1] With the structural elucidation of [FeFe]-$H_2$ases,[2] scientists are working hard to develop long-lived homogeneous artificial photo-synthetic systems that, in their excited states, can reduce [FeFe]-$H_2$ases directly and efficiently for $H_2$ generation.[3] The naturally engineered pockets that bond the catalytic centres of metalloenzymes impart stability to unusual molecular structures to facilitate molecular transformation.[4] The construction of host–guest photosynthetic systems enforcing the electron transfer process in a local microenvironment might be a promising approach to increase the $H_2$ production efficiency.

Metal–organic macrocycles represent a unique class of functional molecular containers that display interesting recognition properties and fascinating reactivity reminiscent of natural enzymes.[5] The architectures that generate well-defined cavities with gated pores provide specific inner environments for the selective uptake and bonding of guest molecules and the catalysis of their reactions.[6] Without doubt, the major challenge for well-confined systems applied to photocatalytic $H_2$ production goes beyond achieving molecular recognition of the [FeFe]-$H_2$ases, but includes the modification of the excited state potential of the photo-sensitizer to match the reduction potential of [FeFe]-$H_2$ases, and the relative positions between the photosensitizer and the [FeFe]-$H_2$ases to avoid unwanted energy-transfer.[7]

By incorporating a carbazole fragment[8] as the photosensitizer within linear bridged bistridentate amide-containing chelating systems, we report herein a basket-like tetragon Ce–**ZL** for encapsulating a [FeFe]-$H_2$ases model compound **1**. This molecular basket had a robust framework with a gated flexible hydrophobic cavity, modelled on the naturally engineered pockets that potentially interacted with **1** directly. We envisioned that the imparted stability to the host–guest system would benefit photocatalytic $H_2$ production in aqueous solution. The reduction potential of the excited carbazole moiety (*ca.* −2.3 V) would be negative enough to make photo-induced electronic transfer from the sensitizer to **1** possible,[9] and the confinement of the cavity would enforce the proximity between the carbazole groups and the substrate, ensuring the enhancement of the PET efficiency to avoid unwanted energy-transfer or reverse-ET reactions (Scheme 1).[10]

Ligand $H_4$**ZL** was obtained by a simple Schiff-base reaction of salicylaldehyde with 9-butyl-3,6-dicarbohydrazidecarbazole in a methanol solution. Evaporating a DMF solution of $H_4$**ZL** with



**Scheme 1** Schematic representation of the fragment of the photoactive basket-like metal–organic tetragon and host–guest complexation species for photocatalytic $H_2$ production. The green balls represent the cerium ions.

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$Ce(NO_3)_3·6H_2O$ in air led to the formation of crystalline solids of Ce–**ZL** in a yield of about 52%. Elemental analysis and powder X-ray diffraction indicated the pure phase of the sample. Magnetic susceptibility measurements (1.8–300 K) showed the diamagnetic behaviour of the bulk sample, suggesting the presence of four $Ce^{IV}$ ions in Ce–**ZL**. The X-ray photoelectron spectroscopy spectrum of Ce–**ZL** exhibited a distinct band at 916 eV assignable to the $4f^0$ orbital transitions of the $Ce^{IV}$ atom.[11]

Single crystal X-ray structural analysis of compound Ce–**ZL** revealed the formation of a basket-like molecular structure. Each molecule of Ce–**ZL** comprised six deprotonated ligands and four cerium ions. The cerium ions each coordinated to three tridentate chelating sites and were positioned at the corners of a square. Four of the six ligands were positioned at the edge of the square, and each bridged two cerium centers alternately. The bridged Ce···Ce separation in one edge was about *ca.* 12.6 Å. The alkyl rings of the four ligands positioned in the same direction interacted with each other and acted as the handle of the basket. The other two ligands positioned at the other side of the square acted as the bottom of the basket. As shown in Fig. 1, the height of the basket is approximately 5.74 Å (from the center of the $Ce_4$ square to the $N_4$ square formed by the four carbazole N atoms), allowing guests with suitable sizes to ingress and egress. The four flexible handles afford the possibility for the modulation of the cavity size to match the geometries of guest molecules. As the opening of the basket is about 16.9 × 8.9 $Å^2$, which is larger than the size of **1** (7.5 × 6.1 $Å^2$), Ce–**ZL** thus was able to encapsulate compound **1** within the cavity. The Ce–O (phenol) and Ce–O (amide) distances of 2.17 and 2.45 Å, respectively, and the Ce–N distance of 2.64 Å were in good agreement with relative compounds,[12] with valences of cerium centers calculated as 3.9 and 4.0 for Ce(1) and Ce(2), respectively.[13]

Ce–**ZL** (15 μM) exhibited a characteristic absorption band for the carbazole moiety at 395 nm (log ε = 5.07) and an emission band (quantum yield *ca.* 0.013) at about 470 nm, when excited at 335 nm. The energy difference between the LUMO and HOMO of the carbazole group was calculated as 3.10 eV.[14] Electrochemical measurements exhibited a redox potential of $E_{1/2}$(Ce–**ZL**$^+$/Ce–**ZL**) at 0.79 V (*vs.* SCE), assignable to the redox potential of the carbazole moiety.[8] The redox potential of the excited state species $E_{1/2}$(Ce–**ZL**$^+$/Ce–**ZL***), calculated as −2.3 V, was negative enough to reduce **1** (−1.7 V)[9] forming the $[Fe^IFe^0]$ intermediate for electro- and photochemical $H_2$ generation.

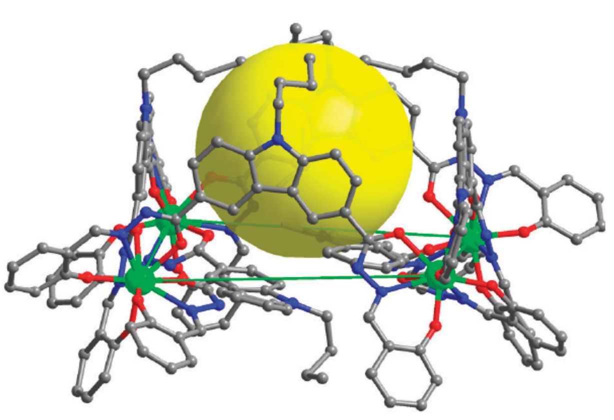

**Fig. 1** Crystal structure of the Ce-based supramolecular host Ce–**ZL**. Solvent molecules and anions are omitted for clarity. The metal, oxygen, nitrogen and carbon are drawn in green, red, blue and grey respectively.

The ESI-MS spectrum of Ce–**ZL** exhibited an intense peak at *m*/*z* = 1914.08 with isotopic distribution patterns separated by 0.5 Da, assignable to the species $[Ce_4(HZL)_6]^{2-}$, demonstrating the formation of $M_4L_6$ species in solution. Upon the addition of **1**, the ESI-MS spectrum exhibited two new peaks at *m*/*z* 2354.06 and 2372.50, assignable to $[Ce_4(HZL)_6 \supset 1_2·DMF·2H_2O]^{2-}$ and $[Ce_4(HZL)_6 \supset 1_2·DMF·4H_2O]^{2-}$, suggesting the formation of a 1 : 2 stoichiometric host–guest complexation species in solution. The addition of **1** (up to 0.50 mM) caused the emission quenching of Ce–**ZL** (30 μM) with an intensity decrease to 5% of its original intensity. The quenching behaviour, assignable to the photo-induced electron transfer (PET) process from the excited state of Ce–**ZL*** to **1**, provided the possibility of Ce–**ZL** to activate **1** for $H_2$ production in solution.[15]

The light-driven $H_2$ production of the Ce–**ZL**/**1** system was carried out in the presence of $N^iPr_2EtH·OAc$ as the sacrificial electron donors.[16] The thermostatic solutions were continuously irradiated with light from a 500 W Xe lamp, using a water filter to absorb the heat. As shown in Fig. 2, the turnover number (TON) of $H_2$ evolution (based on Ce–**ZL**) with Ce–**ZL**/**1** in a 1 : 2 stoichiometry was up to 30 in 4 h with the initial turnover frequency (TOF) about 11 $h^{-1}$ for the first hour. The TON of our system was comparable with the previously reported non-covalently connected supramolecular systems.[16] Control experiments with either the free photoactive host Ce–**ZL** or free **1** demonstrated that both of them together are essential for $H_2$ generation. The absence of either of them yielded unobservable to insignificant amounts of $H_2$.

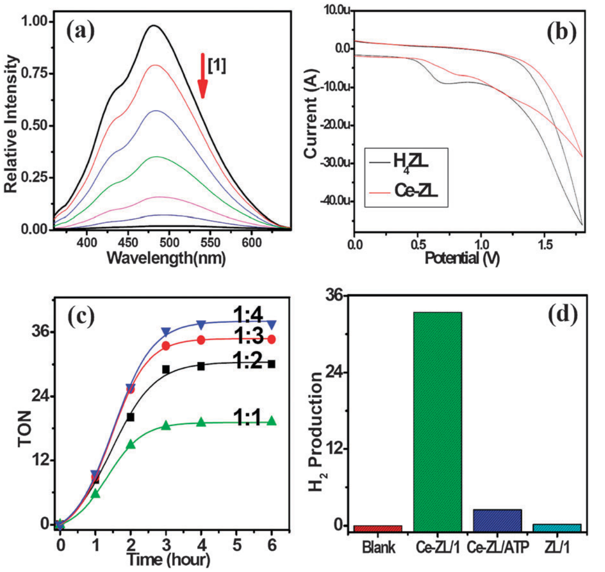

**Fig. 2** Family of emission spectra for Ce–**ZL** (30 μM) upon the addition of **1** (up to 0.50 mM) (a); cyclic voltammograms of Ce–**ZL** in a DMF solution containing *n*-$Bu_4NClO_4$ (0.1 mol $L^{-1}$) with a scan rate of 50 $mVs^{-1}$ (b); photoinduced $H_2$ evolution (TON, based on Ce–**ZL**) of Ce–**ZL** (0.2 mM) over time with different **1** concentrations of 0.2 (green), 0.4 (black), 0.6 (red) and 0.8 (blue) mM (c); photoinduced $H_2$ production of the Ce–**ZL**/**1** systems and other control systems. The red, green, blue and cyan bars show the TON value after irradiation for 3 hours of the blank, Ce–**ZL**/**1**, with the ATP and the ligand with **1** systems, respectively (d).

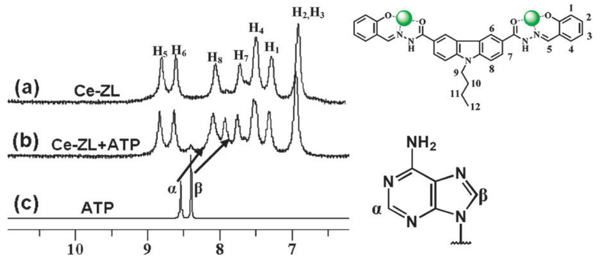

**Fig. 3** ${}^1$H NMR spectra (aromatic region) of free Ce–**ZL** (0.1 mM) (a), free ATP (0.2 mM) (c) and of Ce–**ZL** and ATP (b) in a 1 : 2 molar ratio in $d_6$-DMSO/$D_2O$, respectively.

On the other hand, using ligand $H_4$**ZL** as the photosensitizer instead of Ce–**ZL** in the presence of **1** in same condition caused a little $H_2$ production. This result might be one of the indicators for the fact that the formation of a host–guest complexation species was essential to photo-activate **1**. The small but significant blue shift of the $\nu$(CO) vibration signals in the IR spectra gave further proof for the formation of a host–guest complexation species.

Importantly, experiments carried out with different Ce–**ZL** : **1** mole ratios showed that the initial rate in first hour of $H_2$ production increased with increasing Ce–**ZL** : **1** mole ratio, until it reached 1 : 2. Almost the same TOF in the case of the Ce–**ZL** : **1** ratio over 1 : 2 suggested that the main species for the catalytic reaction possibly was the 1 : 2 stoichiometric host–guest Ce–**ZL** $\supset$ $\mathbf{1}_2$. In fact, the linear fitting of the fluorescence titration curve of Ce–**ZL** upon addition of **1** demonstrated the 1 : 2 stoichiometric host–guest behaviour and the associative constant $K_{ass}$ was calculated as $1.15 \times 10^8$ dm$^6$ mol$^2$. In the presence of excess **1** (more than 10 equivalent), our system exhibited a pseudo-zeroth-order kinetic behaviour. It seems that the production of $H_2$ is enzymatic-like, governed by the Michaelis–Menten mechanism,[17,18] in which substrate binding is a first equilibrium prior to the rate-limiting step of the reaction.

To validate whether the photoinduced $H_2$ production either occurred within the cavity of Ce–**ZL** or was just displayed through a normal homogeneous system, the inhibition of the photocatalytic reaction was displayed through the addition of a nonreactive species, ATP.[18] As shown in Fig. 3, the presence of the molecular host Ce–**ZL** led to significant upfield shifts of the aromatic protons in the Adenosine ring, suggesting the presence of $\pi\cdots\pi$ stacking interactions between the adenosine aromatic rings and the benzene rings of the host. Emission titration of Ce–**ZL** upon the addition of ATP also induced the quenching process and suggested the formation of a 1 : 2 stoichiometry of host–guest complexation with the association constant calculated as $1.23 \times 10^8$ dm$^6$ mol$^2$. This value is a little larger than that of the Ce–**ZL**/**1** system. Since ATP does not exhibit any suitable redox potential for $H_2$ production, in this case, the important biomolecule ATP was chosen as the inhibitor for our enzymatic system. As can be expected, in the presence of 0.8 mM of ATP, photo-catalytic $H_2$ production by the Ce–**ZL**(0.2 mM)/**1** (0.4 mM) system was stopped. The competitive inhibition behaviour thus was enzymatic-like and suggested that the $H_2$ production occurred within the cavity of Ce–**ZL**.[18] In the case of $[Ru(bpy)_3]^{2+}$ as the photosensitizer, the TON value in a modulated system was comparable to the literature work,[19] but the addition of 10 mole equivalent of ATP (2 mM) did not cause any significant change in the TON value. All these complete experiments demonstrated that molecules of ATP were true competitive inhibitors. The inhibition was reversible, as upon addition of excess **1** to the above mentioned ATP inhibiting system, photo-induced $H_2$ production was recovered. These results gave further proof that Ce–**ZL** is an interesting molecular flask, within which **1** was activated.

In summary, a photoactive metal–organic basket comprising an artificial protein environment and a chromophore was achieved for the encapsulation of the [FeFe]-hydrogenase model. The host–guest system displayed light-driven $H_2$ production in aqueous media with characteristic enzymatic dynamic behaviour and was inhibited by the presence of ATP, demonstrating the bright future of metallcycles acting as artificial molecular flasks for solar-driven splitting of water for $H_2$ production.

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