

Cite this: *Chem. Sci.*, 2018, 9, 3313Redox and photocatalytic properties of a Ni<sup>II</sup> complex with a macrocyclic biquinazoline (Mabiq) ligand†‡

Michael Grübel, Irene Bosque, Philipp J. Altmann, Thorsten Bach \* and Corinna R. Hess

We present a late, first row transition metal photosensitizer that promotes photocatalytic C–C bond formation. The title compound, [Ni(Mabiq)]OTf, as well as its one-electron reduced form, Ni(Mabiq), were synthesized and molecular structures of both were obtained. The electronic structure of the reduced complex additionally was characterized by spectroscopic and DFT computational methods. Notably, [Ni<sup>II</sup>(Mabiq)]OTf is photoactive: reduction of the compound was achieved photochemically upon irradiation at  $\lambda = 457$  nm and reductive quenching by NEt<sub>3</sub>. The performance of [Ni(Mabiq)]OTf as a photoredox catalyst was examined in the cyclization of a bromoalkyl-substituted indole. In this reaction, the first-row transition metal compound is comparable if not superior to [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in terms of efficiency (turnover number) and chemoselectivity. Studies using a series of sacrificial donor amines indicate that the excited state redox potential of [Ni(Mabiq)]<sup>•+</sup> is  $\geq 1.25$  V vs. SCE. This value is similar to the excited state potential of commonly employed noble metal based photocatalysts. The Ni-Mabiq compound thus provides a rare example of an earth-abundant photoredox catalyst.

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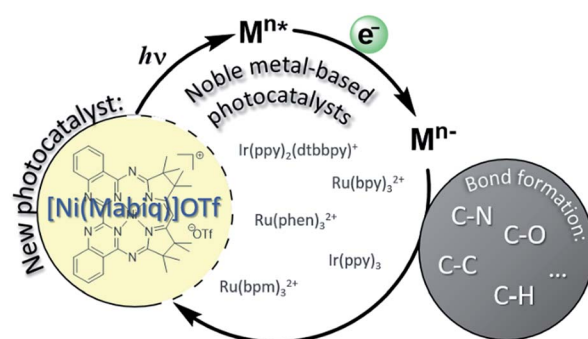
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## Introduction

Photoredox catalysis offers nascent opportunities to shift conventional chemical production methods to light-driven processes.<sup>1</sup> The design of new photoactive metal compounds is key to the development of new catalytic transformations. Chromophores can effect a wide array of functional group transformations and C–C bond formation reactions *via* the generation of active radical species, originating from excited state electron transfer processes (Scheme 1).<sup>2</sup> With very few exceptions, photoredox catalysis relies on the use of noble metal containing photosensitizers, mainly Ru- or Ir-polypyridyl complexes;<sup>3</sup> other heavy metal complexes (*e.g.* Os<sup>II</sup>, Re<sup>I</sup>, Mo<sup>0</sup>, W<sup>0</sup>) also have occasionally been employed.<sup>4,5</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> – with its long lived, charge separated excited state ([Ru<sup>III</sup>(bpy<sup>•−</sup>)(bpy)<sub>2</sub>]<sup>2+\*</sup>) – is the classic and universal photocatalyst for a plethora of applications.<sup>2</sup>

The use of less expensive, more abundant, late first row transition metal alternatives is generally precluded by their

inherently short excited-state lifetimes. In the first row, nickel complexes have been used in photocatalytic cross coupling reactions,<sup>6</sup> though the use of an added photosensitizer (commonly Ir) still is required in all of these tandem systems. A class of Ni<sup>II</sup> ligand-to-ligand charge transfer complexes recently were shown to possess advantageous properties as photosensitizers, but applications have not yet been demonstrated.<sup>7</sup> In fact, reports describing catalytic applications or reactivity of systems using only non-noble metal photosensitizers are exceedingly scarce.<sup>8–10</sup>



**Scheme 1** Photoredox catalysis commonly relies on noble metal complexes for organic transformations, initiated by single electron transfer upon excitation of Ru or Ir compounds. The [Ni(Mabiq)]OTf catalyst offers an earth-abundant photosensitizer.

Department of Chemistry, Catalysis Research Center (CRC), Technische Universität München, 85747 Garching, Germany. E-mail: thorsten.bach@ch.tum.de; corinna.hess@ch.tum.de

† Dedicated to the memory of Inge Grübel.

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We now report a  $\text{Ni}^{\text{II}}$  complex with a macrocyclic biquinazoline (Mabiq) ligand,<sup>11,12</sup>  $[\text{Ni}(\text{Mabiq})]\text{OTf}$  (**1**), providing a rare example of a non-noble metal based photosensitizer. The divalent complex **1** can be photochemically reduced and the electronic structure of the product,  $[\text{Ni}(\text{Mabiq})]$  (**2**), is described herein. Using a series of synthesized sacrificial donor molecules, the photo-excited state redox potential of **1** was assessed and compared to common noble-metal photocatalysts. We demonstrate the photoredox catalytic ability of **1** in a radical-based cyclization of a bromoalkyl-substituted indole. The reaction relies solely on the Ni-Mabiq photocatalyst, without the need for an additional noble metal photosensitizer.

## Results and discussion

The yellow diamagnetic **1** (Scheme 2) was readily prepared by complexation of the ligand with  $\text{Ni}(\text{OTf})_2$  in ethanol solution (see ESI† for further details). The Ni ion adopts the expected square planar geometry in the solid state (Fig. S1†). The electronic spectrum of **1** in DCM exhibits intense absorption bands ( $\epsilon \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the visible light region ( $\lambda_{\text{max}} = 414, 435$ , and  $457 \text{ nm}$ ;  $\epsilon = 13.6, 16.4, 22.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ; Fig. 2 inset). Similar features were observed in the spectra of other M-Mabiq complexes, notably in the spectrum of  $\text{Zn}(\text{Mabiq})\text{Cl}$ .<sup>12a</sup> The  $\text{Zn}^{\text{II}}$  complex displayed two strong absorption bands at  $471$  and  $502 \text{ nm}$  that were assigned as Mabiq  $\pi \rightarrow \pi^*$  transitions. However, d-d or metal-to-ligand charge transfer (MLCT) processes may additionally contribute to the corresponding absorptions of **1**. The cyclic voltammogram of **1** in MeCN (Fig. S9†) exhibits a reversible, formally  $\text{Ni}^{\text{II/I}}$  redox couple at  $-1.05 \text{ V vs. Fc}^{+/0}$  ( $\text{Fc}$  = ferrocene;  $\text{Fc}^{+/0} = 0.4 \text{ V vs. SCE}$ ). Additional, seemingly reversible, reductive processes appear at potentials  $< -1.5 \text{ V}$ .

The one-electron reduced  $\text{Ni}(\text{Mabiq})$  (**2**) was subsequently generated from **1** using  $\text{CoCp}_2$  as the reductant (Scheme 2). The molecular structure of **2** (Fig. 1) reveals shorter Ni-N bond distances ( $\text{Ni}-\text{N}_{\text{avg}} = 1.874 \text{ \AA}$  vs.  $\text{Ni}-\text{N}_{\text{avg}} = 1.882 \text{ \AA}$  in **1**), as well as the hallmark changes in the diketimate C-N bonds that signify reduction of the Mabiq ligand (Table S8†). The  $S = 1/2$  ground state of the complex was verified by EPR spectroscopy. The spectrum is consistent with a ligand-centered radical, with  $g_{\text{iso}} = 1.995$  (Fig. S4†). Low energy features at  $\lambda_{\text{max}} = 641, 711$  and  $801 \text{ nm}$  ( $1.4, 3.5, 5.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) are apparent in the electronic spectrum of **2** in THF (Fig. 2 inset), accounting for the



Fig. 1 Left: Molecular structure of **2** (50% probability ellipsoids; hydrogen atoms omitted for clarity). Right: DFT-derived (B3LYP) spin density plot for **2** based on Löwdin population analysis (isosurface value =  $\pm 0.005$ ).

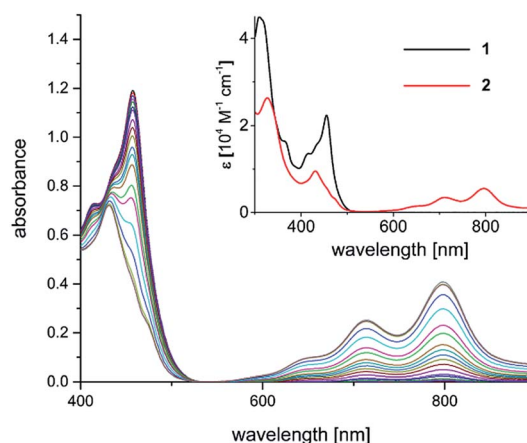


Fig. 2 Spectral evolution during photoconversion of **1** to **2** [ $\text{c}$  (**1**) =  $0.05 \text{ mM}$ ;  $\text{c}$  ( $\text{NEt}_3$ ) =  $1.4 \text{ M}$ ;  $\lambda = 457 \text{ nm}$ , DMF]. Inset: electronic spectra of **1** (black trace;  $\text{CH}_2\text{Cl}_2$ ) and **2** (red trace; THF).

vibrant green color of the complex in solution. The spectrum again closely resembles that of the one-electron reduced Zn complex,  $\text{Zn}^{\text{II}}(\text{Mabiq}^{\cdot-})$ .<sup>12a</sup> The spectroscopic data thus point to ligand-centered reduction of **1**, such that the electronic structure of **2** corresponds to  $\text{Ni}^{\text{II}}(\text{Mabiq}^{\cdot-})$ . Indeed, DFT calculations (B3LYP) on **2** further support this conclusion.

The DFT-derived (B3LYP) spin density plot (Fig. 1) describes a diamagnetic  $d^8 \text{ Ni}^{\text{II}}$  center with an unpaired electron localized primarily on the diketimate unit of the Mabiq ligand. Four doubly occupied d-orbitals can be identified, while the SOMO possesses only *ca.* 4% d-orbital character and otherwise depicts a ligand  $\pi^*$  orbital (Fig. S5†). The latter molecular orbital is antibonding with respect to the diketimate C-N p-orbital interactions, which explains the lengthening of these bonds in the structure of **2**. It is noteworthy that ligand-centered reduction appears to prevail across the series of metal-Mabiq compounds we have examined thus far.<sup>12</sup>

The well-behaved redox chemistry of  $[\text{Ni}(\text{Mabiq})]\text{OTf}$  (**1**), its high absorbance in the visible region and its relatively high reduction potential warranted a study of its photoredox properties. As mentioned above, the compound exhibits a strong



Scheme 2 Reaction of **1** with  $\text{CoCp}_2$  ( $\text{Cp}$  = cyclopentadienyl) yields the one-electron reduced **2**.



multi-structured absorption band with a maximum at  $\lambda = 457$  nm ( $\epsilon = 22\,300$  M<sup>-1</sup> cm<sup>-1</sup>), which invites excitation with a visible light source and quenching studies with a suitable reductant. Gratifyingly, it was indeed found that irradiation of a DMF solution of **1** at  $\lambda = 457$  nm, in the presence of NEt<sub>3</sub> (7.5 mM to 1.4 M), leads to a color change from yellow to green and to the formation of complex **2**.

The formation of the reduced compound was complete after 15 minutes (using 1.4 M NEt<sub>3</sub>;  $c$  (**1**) = 0.05 mM), as verified spectroscopically (Fig. 2). The photoconversion of **1** to **2** occurs on a much faster timescale in MeCN/THF or DMF/THF mixtures (the solvent combination solubilizes both forms), under identical conditions. The quantum yield for the photoconversion is  $\approx 10^{-4}$  (THF : DMF 4 : 1), and correlates with the Et<sub>3</sub>N concentration (14–56 mM; Table S3 and Fig. S29†). From the data, the lifetime of the excited state form that reacts with the Et<sub>3</sub>N can be estimated as  $\approx 1 \times 10^{-8}$  s (see ESI† for details). Steady-state emission spectra recorded at ambient temperature and at 77 K did not reveal any luminescence. Thus, we currently cannot comment in detail on the nature of the excited state processes involved in the photo-reduction of **1**. If one takes the longest wavelength absorption [ $\lambda \approx 510$  nm,  $E_0 \leq 235$  kJ mol<sup>-1</sup> (2.4 V)] of compound **1** to estimate the redox potential of photoexcited complex **1**<sup>\*</sup>, a value of  $\leq +1.35$  V (vs. Fc<sup>+/0</sup>) is obtained.<sup>13</sup>

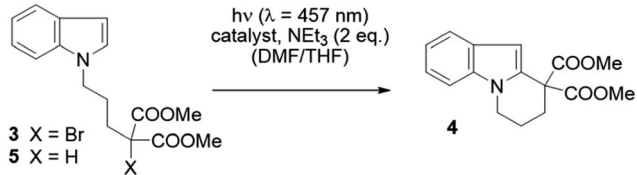
TDDFT (B3LYP) computational studies provide some insight into the nature of the absorptions in the visible region. The calculated transitions correlate well with the experimentally obtained absorbance spectrum of **1** (Fig. S6†). The absorptions at 400–500 nm include a prominent LL/CT transition that corresponds to the HOMO to LUMO transition. The HOMO is localized on the bipyrimidine moiety of the MabiQ ligand, while the LUMO is a diketiminate based  $\pi^*$  orbital (Fig. S7†). Other, less intense, transitions in the vicinity possess d–d (Ni d<sub>z<sup>2</sup></sub> → Ni

d<sub>x<sup>2</sup>-y<sup>2</sup></sub>) and MLCT (Ni d<sub>z<sup>2</sup></sub> → L $\pi^*$ ) character. These states may contribute to the unique photochemical properties of **1**. However, a detailed investigation regarding the photochemistry and excited state kinetics of this compound is warranted, and will be the subject of future investigations.

We examined whether the photochemical properties of **1** might render it a suitable photoredox catalyst for C–C bond formation reactions. The radical cyclization of the *N*-( $\omega$ -bromoalkyl)-substituted indole **3** was chosen as a test reaction.<sup>14</sup> The reaction had been previously studied by the Stephenson group and was found to produce mainly product **4** by C–C bond formation under optimized conditions.<sup>15</sup> Under non-optimized conditions, hydro-de-bromination was a competing side reaction and varying product ratios of **4** and **5** were observed. Optimal conditions were reported to include the use of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as the catalyst (1 mol%) and NEt<sub>3</sub> (2 equiv.) in DMF solution and gave product **4** in 60% yield.<sup>15</sup>

Given the limited solubility of **2** in DMF, the reaction was initially attempted in a DMF/THF mixture (v/v = 1/2) with 2 mol% of catalyst **1** and 2 equiv. NEt<sub>3</sub> as the quencher (Table 1, entry 1).<sup>16</sup> We were pleased to find that the desired cyclization proceeded smoothly and delivered with high chemoselectivity the desired product **4**. The inseparable hydro-de-brominated by-product **5** was detectable in minor quantities but the ratio of products was 95/5 in favor of cyclization product **4**. When increasing the relative volume of THF in the solvent mixture both conversion and yield improved slightly (entry 2). The selectivity towards the desired reaction was high with a yield of 86% at 94% conversion, *i.e.* 91% yield based on conversion. For comparison, the Ru<sup>II</sup> complex [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> was employed under identical conditions (entry 3). Although the ratio 4/5 was identical with this catalyst, the reaction suffered from a lower conversion and a lower chemoselectivity (63% yield based on conversion). Similar observations were made when the catalyst

**Table 1** Photoredox-catalyzed cyclization of bromide **3** to tricyclic product **4** and reduction to hydro-de-brominated product **5**; influence of the catalyst and the reaction parameters on the yield and chemoselectivity

						
Entry <sup>a</sup>	Catalyst <sup>a</sup>	mol%	DMF/THF [v/v]	Conv. <sup>b</sup> [%]	Yield <sup>c</sup> [%]	4/5 <sup>d</sup>
1	<b>1</b>	2	1/2	93	84	95/5
2	<b>1</b>	2	1/4	94	86	95/5
3	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2	1/4	73	46	95/5
4	<b>1</b>	1	1/4	95	84	95/5
5	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	1	1/4	59	23	95/5
6	<b>1</b> <sup>e</sup>	2	1/4	n.d.	—	—
7	— <sup>f</sup>	—	1/4	12	12	55/45
8	<b>1</b> <sup>g</sup>	2	1/4	<5	<5	—

<sup>a</sup> All reactions were performed on a scale of 0.08 mmol ( $c = 25$  mM) with a LED lamp (3 W power output) as light source. Irradiation time: 13 h. <sup>b</sup> The conversion was calculated from recovered starting material. <sup>c</sup> Total yield of isolated products **4** and **5**. <sup>d</sup> Ratio of cyclized to hydro-de-brominated product as determined by <sup>1</sup>H-NMR. <sup>e</sup> Attempted reaction without irradiation. <sup>f</sup> No catalyst was added. <sup>g</sup> No NEt<sub>3</sub> was added. n.d. = not detected.

loading was further decreased to 1 mol%: while the performance of Ni<sup>II</sup> catalyst **1** remained unchanged (entry 4) the reaction with the Ru<sup>II</sup> catalyst was sluggish and a decrease in yield was observed (entry 5).

The above reaction is induced by visible light as no conversion occurs without irradiation (entry 6). In the absence of the Ni<sup>II</sup> catalyst,<sup>17</sup> only 12% of a product mixture was obtained, which was composed of the cyclized product **4** and the reduced product **5** in a 55/45 ratio (entry 7). In the absence of the reductant, no reaction was observed (entry 8). The free HMabiq ligand is not photocatalytically active. The quantum yield for the [Ni(Mabiq)]OTf catalysed cyclization reaction was determined to be  $\Phi = 0.006$ .

Mechanistically, it is suggested that the photoreduction of complex **1** by NEt<sub>3</sub> (reductive quenching cycle)<sup>1</sup> generates complex **2**, which may engage in SET to the bromide **3** (Scheme 3). Complex **2** was shown to be competent to reduce **3**. We note that modification of the Ni-Mabiq complex during the cyclization reaction was not observed, as verified by ESI-MS and <sup>1</sup>H-NMR (Fig. S8 and S41†).

To experimentally verify the estimated photoexcited state redox potential of **1**<sup>\*</sup>, we synthesized a series of amines with oxidation potentials in the range of 0.78–1.59 V (vs. SCE; Tables 2 and S1†), as determined by CV. The amines were employed as sacrificial donors in the cyclization reaction. Excellent yields of **4** were obtained using the donor molecules with oxidation potentials up to 1.25 V (Table 2, amines **6a–6c**), whereas a drastic decrease in yield was observed using those with higher redox potentials. Only 40% and 20% product yields were obtained with **6d** ( $E_{\text{ox}} = 1.41$  V vs. SCE) and **6e** ( $E_{\text{ox}} = 1.59$  V vs. SCE), respectively. The product yield in the control reaction using **6e** in the absence of photocatalyst **1** was 7%, a result that is comparable to that obtained using NEt<sub>3</sub> (Table 1, entry 7). The results confirm that the excited state redox potential of **1**<sup>\*</sup> is at least 1.25 V (vs. SCE). Thus, our new Ni-Mabiq complex is a more powerful oxidant than [Ru(bpy)<sub>3</sub>]<sup>2+</sup> ( $E_{1/2}$  [Ru<sup>2+\*/</sup>Ru<sup>+</sup>] 0.78 V vs. SCE),<sup>18</sup> and comparable to [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]<sup>+</sup> ( $E_{1/2}$  [Ir<sup>3+\*/</sup>/Ir<sup>2+</sup>] 1.21 V vs. SCE).<sup>19</sup>

We additionally generated a sterically hindered amine, N(CH<sub>2</sub>Me)<sub>2</sub>Cy<sub>2</sub> (**6f**), to assess whether coordination of the sacrificial donor molecules influences the reactivity of **1**. In contrast to the bpy- and phen-based photosensitizers, the Ni-Mabiq complexes are coordinatively unsaturated and intra-molecular electron transfer from a coordinated amine to the

**Table 2** Comparison of the oxidation potentials for different sacrificial donors **6** with the yields obtained for the catalytic reaction of **3** to **4** and **5**

Amine <sup>a</sup>	$E_{\text{ox}}$ (vs. SCE)	Yield <sup>b</sup> [%]
Et <sub>3</sub> N ( <b>6a</b> )	0.83	84
<b>6b</b>	1.05	97
<b>6c</b>	1.25	95
<b>6d</b>	1.41	40
<b>6e</b>	1.59	20 <sup>c</sup>
<b>6f</b>	0.78	84

<sup>a</sup> All reactions were performed on a scale of 0.08 mmol ( $c = 25$  mM) with a 457 nm LED lamp (3 W power output) as the light source. Irradiation time: 13 h. <sup>b</sup> Total yield of isolated products **4** and **5**, with a 95 : 5 ratio of cyclized to hydro-de-brominated product as determined by <sup>1</sup>H-NMR. <sup>c</sup> Average of two runs.  $\text{Fc}^{+/0} = 0.4$  V vs. SCE. Cy = cyclohexyl.

divalent metal center could potentially occur. The molecular structure of **6f** (Fig. S3†) suggests that coordination of this amine group to the Ni center is unlikely; the cyclohexyl and mesityl groups encapsulate the nitrogen atom rendering the lone pair inaccessible. Whereas noticeable changes in the absorption spectrum of **1** were observed upon addition of Et<sub>3</sub>N (400 equiv.) to a solution of the complex in THF/DMF, the addition of **6f** has no effect (Fig. S30 and S31†). However, the yield of the catalytic reaction using **6f** as sacrificial donor was found to be 84%, a value that is comparable to the one obtained using Et<sub>3</sub>N (**6a**) and **6b–6e** as sacrificial donors.

## Conclusions

In summary, we have discovered a new photoredox catalyst, [Ni(Mabiq)]OTf (**1**) that is based on the earth-abundant metal nickel. The diamagnetic, bench-stable compound was readily prepared, its redox properties were studied and the one-electron reduced form Ni(Mabiq) (**2**) likewise was isolated. Further studies to elucidate the detailed photophysical properties of **1**<sup>\*</sup> are warranted. However, we have already demonstrated that the photoexcited complex is a strong oxidant, with the capacity to induce C–C bond formation in an initial test reaction. The Ni-Mabiq compound may offer an alternative to noble metal photosensitizers for other synthetic transformations in organic photoredox chemistry, as well as for energy conversion processes. The Mabiq ligand also features a second metal binding site that could be exploited for tandem catalysis. Thus, the macrocycle represents a new type of platform for the development of photoactive systems. With evidence of the ability of **1** to act as a photosensitizer and photoredox catalyst, the broader photocatalytic applications of our system subsequently will be investigated.



**Scheme 3** Proposed catalytic cycle for the cyclization of **3** to give **4**.





## Conflicts of interest

There are no conflicts to declare.

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