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Redox and photocatalytic properties of a Ni^{II} complex with a macrocyclic biquinazoline (Mabiq) ligand†‡

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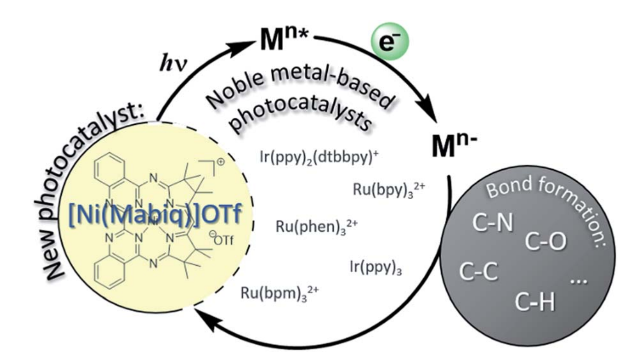
We present a late, first row transition metal photosensitizer that promotes photocatalytic C–C bond formation. The title compound, [Ni(Mabiq)]OTf, as well as its one-electron reduced form, Ni(Mabiq), were synthesized and molecular structures of both were obtained. The electronic structure of the reduced complex additionally was characterized by spectroscopic and DFT computational methods. Notably, [Ni^{II}(Mabiq)]OTf is photoactive: reduction of the compound was achieved photochemically upon irradiation at $\lambda = 457$ nm and reductive quenching by NEt_3. 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 $[Ru(bpy)_3]^{2+}$ in terms of efficiency (turnover number) and chemoselectivity. Studies using a series of sacrificial donor amines indicate that the excited state redox potential of $[Ni(Mabiq)]^{+}*$ is ≥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.

Introduction

Photoredox catalysis offers nascent opportunities to shift conventional chemical production methods to light-driven processes.[1] 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).[2] With very few exceptions, photoredox catalysis relies on the use of noble metal containing photosensitizers, mainly Ru- or Ir-polypyridyl complexes;[3] other heavy metal complexes (*e.g.* Os^{II}, Re^{I}, Mo^{0}, W^{0}) also have occasionally been employed.[4,5] $[Ru(bpy)_3]^{2+}$ – with its long lived, charge separated excited state ($[Ru^{III}(bpy^{\bullet -})(bpy)_2]^{2+}*$) – is the classic and universal photocatalyst for a plethora of applications.[2]

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,[6] though the use of an added photosensitizer (commonly Ir) still is required in all of these tandem systems. A class of Ni^{II} ligand-to-ligand charge transfer complexes recently were shown to possess advantageous properties as photosensitizers, but applications have not yet been demonstrated.[7] In fact, reports describing catalytic applications or reactivity of systems using only non-noble metal photosensitizers are exceedingly scarce.[8–10]



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.

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† Dedicated to the memory of Inge Grübel.

‡ Electronic supplementary information (ESI) available: CIF files, synthetic procedures, spectroscopic, electrochemical and DFT computational data. CCDC 1538675, 1538676 and 1586948. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc05320g

We now report a Ni^{II} complex with a macrocyclic biquinazoline (Mabiq) ligand,[11,12] [Ni(Mabiq)]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, [Ni(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 $Ni(OTf)_2$ 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 ($\varepsilon \approx 10^4\ M^{-1}\ cm^{-1}$) in the visible light region ($\lambda_{max} = 414$, 435, and 457 nm; $\varepsilon = 13.6, 16.4, 22.3 \times 10^3\ M^{-1}\ cm^{-1}$; Fig. 2 inset). Similar features were observed in the spectra of other M-Mabiq complexes, notably in the spectrum of Zn(Mabiq)Cl.[12a] The Zn^{II}-complex displayed two strong absorption bands at 471 and 502 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 $Ni^{II/I}$ redox couple at -1.05 V *vs.* $Fc^{+/0}$ (Fc = ferrocene; $Fc^{+/0} = 0.4$ V *vs.* SCE). Additional, seemingly reversible, reductive processes appear at potentials <−1.5 V.

The one-electron reduced Ni(Mabiq) (**2**) was subsequently generated from **1** using $CoCp_2$ as the reductant (Scheme 2). The molecular structure of **2** (Fig. 1) reveals shorter Ni–N bond distances ($Ni–N_{avg} = 1.874$ Å *vs.* $Ni–N_{avg} = 1.882$ Å in **1**), as well as the hallmark changes in the diketiminate 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 $g_{iso} = 1.995$ (Fig. S4‡). Low energy features at $\lambda_{max} = 641$, 711 and 801 nm ($1.4, 3.5, 5.4 \times 10^3\ M^{-1}\ cm^{-1}$) are apparent in the electronic spectrum of **2** in THF (Fig. 2 inset), accounting for the vibrant green color of the complex in solution. The spectrum again closely resembles that of the one-electron reduced Zn complex, $Zn^{II}(Mabiq^{\bullet -})$.[12a] The spectroscopic data thus point to ligand-centered reduction of **1**, such that the electronic structure of **2** corresponds to $Ni^{II}(Mabiq^{\bullet -})$. Indeed, DFT calculations (B3LYP) on **2** further support this conclusion.

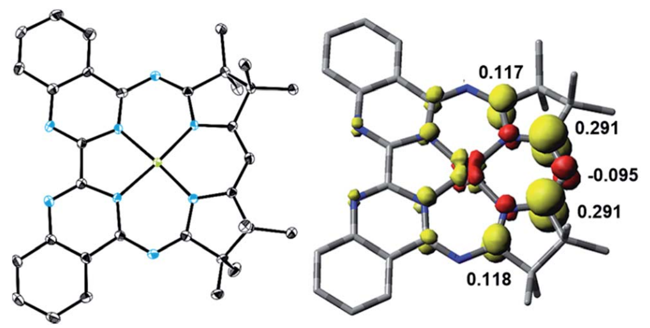


Fig. 1 Left: Molecular structure of **2** (50% probability ellipsoids; hydrogen atoms omitted for clarity). Right: DFT-derived (B3LYP) spin density plot for **2** based on Löwdin population analysis (isosurface value = ±0.005).

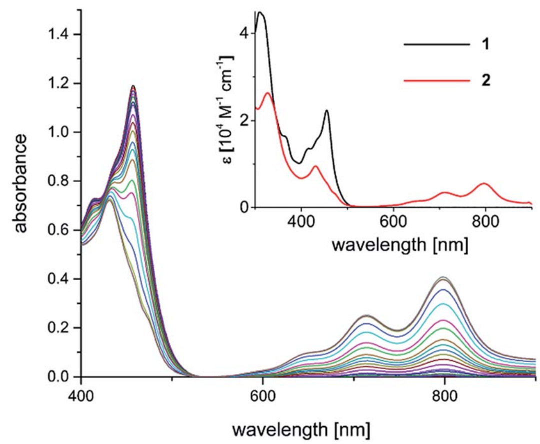
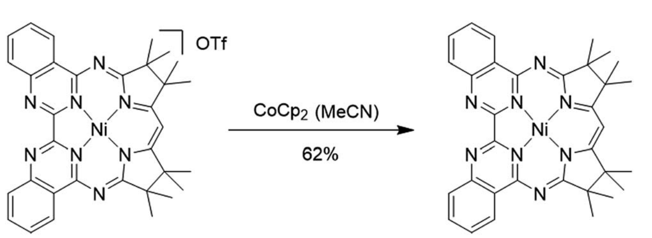


Fig. 2 Spectral evolution during photoconversion of **1** to **2** [c (**1**) = 0.05 mM; c (NEt_3) = 1.4 M; $\lambda = 457$ nm, DMF]. Inset: electronic spectra of **1** (black trace; CH_2Cl_2) and **2** (red trace; THF).

The DFT-derived (B3LYP) spin density plot (Fig. 1) describes a diamagnetic d^8 Ni^{II} center with an unpaired electron localized primarily on the diketiminate 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 π^* orbital (Fig. S5‡). The latter molecular orbital is antibonding with respect to the diketiminate 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.[12]

The well-behaved redox chemistry of [Ni(Mabiq)]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



[Ni(Mabiq)]OTf (**1**) [Ni(Mabiq)] (**2**)

Scheme 2 Reaction of **1** with $CoCp_2$ (Cp = cyclopentadienyl) yields the one-electron reduced **2**.

multi-structured absorption band with a maximum at λ = 457 nm (ε = 22 300 M^{-1} cm^{-1}), 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 λ = 457 nm, in the presence of NEt_3 (7.5 mM to 1.4 M), leads to a color change from yellow to green and to the formation of complex **2**.

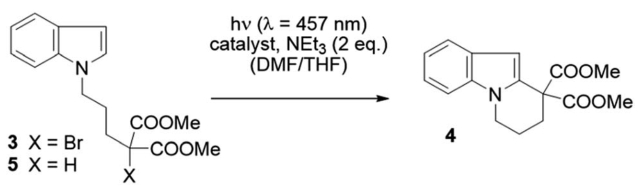
The formation of the reduced compound was complete after 15 minutes (using 1.4 M NEt_3; c (**1**) = 0.05 mM), as verified spectroscopically (Fig. 2). The photoconversion of **1** to **2** occurs on a much faster timescale in MeCN/THF or DMF/THF mixtures (the solvent combination solubilizes both forms), under identical conditions. The quantum yield for the photoconversion is $\approx 10^{-4}$ (THF : DMF 4 : 1), and correlates with the Et_3N concentration (14–56 mM; Table S3 and Fig. S29‡). From the data, the lifetime of the excited state form that reacts with the Et_3N 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 [$\lambda \cong 510$ nm, $E_0 \leq 235$ kJ mol^{-1} (2.4 V)] of compound **1** to estimate the redox potential of photoexcited complex **1***, a value of $\leq$+1.35 V (*vs.* $Fc^{+/0}$) is obtained.[13]

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 π* orbital (Fig. S7‡). Other, less intense, transitions in the vicinity possess d–d (Ni $d_{z^2} \rightarrow$ Ni $d_{x^2-y^2}$) and MLCT (Ni $d_{z^2} \rightarrow L_{\pi^*}$) 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*-(ω-bromoalkyl)-substituted indole **3** was chosen as a test reaction.[14] 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.[15] 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 $[Ru(bpy)_3]Cl_2$ as the catalyst (1 mol%) and NEt_3 (2 equiv.) in DMF solution and gave product **4** in 60% yield.[15]

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_3 as the quencher (Table 1, entry 1).[16] 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^{II} complex $[Ru(bpy)_3](PF_6)_2$ 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[a]	Catalyst[a]	mol%	DMF/THF [v/v]	Conv.[b] [%]	Yield[c] [%]	**4**/**5**[d]
1	**1**	2	1/2	93	84	95/5
2	**1**	2	1/4	94	86	95/5
3	$[Ru(bpy_3)(PF_6)_2$	2	1/4	73	46	95/5
4	**1**	1	1/4	95	84	95/5
5	$[Ru(bpy_3)(PF_6)_2$	1	1/4	59	23	95/5
6	**1**[e]	2	1/4	n.d.	—	—
7	—[f]	—	1/4	12	12	55/45
8	**1**[g]	2	1/4	<5	<5	—

[a] 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. [b] The conversion was calculated from recovered starting material. [c] Total yield of isolated products **4** and **5**. [d] Ratio of cyclized to hydro-de-brominated product as determined by ^1H-NMR. [e] Attempted reaction without irradiation. [f] No catalyst was added. [g] No NEt_3 was added. n.d. = not detected.

loading was further decreased to 1 mol%: while the performance of Ni^{II} catalyst **1** remained unchanged (entry 4) the reaction with the Ru^{II} 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^{II} catalyst,[17] 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_3 (reductive quenching cycle)[1] 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 ^{1}H-NMR (Fig. S8 and S41‡).

To experimentally verify the estimated photoexcited state redox potential of **1***, 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** ($E_{ox} = 1.41$ V *vs.* SCE) and **6e** ($E_{ox} = 1.59$ 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_3 (Table 1, entry 7). The results confirm that the excited state redox potential of **1*** is at least 1.25 V (*vs.* SCE). Thus, our new Ni-Mabiq complex is a more powerful oxidant than $[Ru(bpy)_3]^{2+}$ ($E_{1/2}$ [Ru^{2+*}/Ru^{+}] 0.78 V *vs.* SCE),[18] and comparable to $[Ir(dF(CF_3)ppy)_2(dtbbpy)]^{+}$ ($E_{1/2}$ [Ir^{3+*}/Ir^{2+}] 1.21 V *vs.* SCE).[19]

We additionally generated a sterically hindered amine, $N(CH_2Mes)Cy_2$ (**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 intramolecular electron transfer from a coordinated amine to the 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_3N (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_3N (**6a**) and **6b–6e** as sacrificial donors.

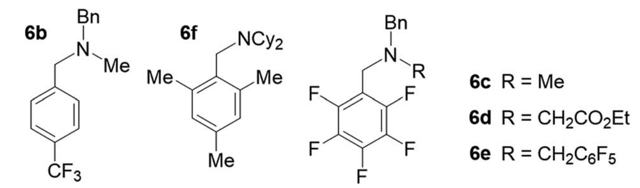


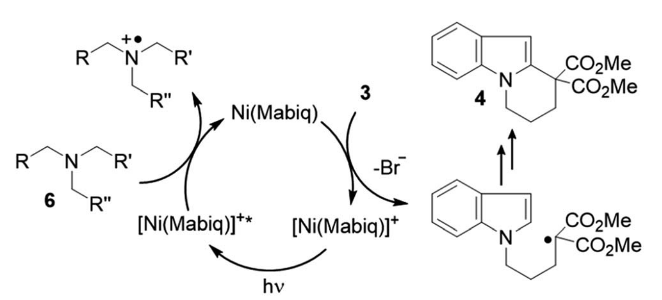
Table 2 Comparison of the oxidation potentials for different sacrificial donors **6** with the yields obtained for the catalytic reaction of **3** to **4** and **5**

Amine[a]	E_{ox} (*vs.* SCE)	Yield[b] [%]
Et_3N (**6a**)	0.83	84
6b	1.05	97
6c	1.25	95
6d	1.41	40
6e	1.59	20[c]
6f	0.78	84

[a] 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. [b] Total yield of isolated products **4** and **5**, with a 95 : 5 ratio of cyclized to hydro-de-brominated product as determined by ^{1}H-NMR. [c] Average of two runs. $Fc^{+/0} = 0.4$ V *vs.* SCE. Cy = cyclohexyl.

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*** 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.

Acknowledgements

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