

Alternatives to Iridium: A Polyaza[7]helicene as a Strongly Reductive Visible Light Photoredox Catalyst

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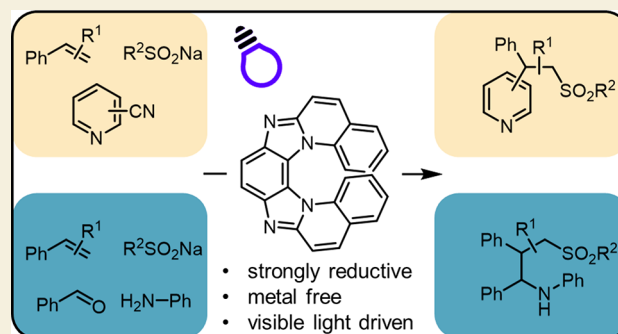
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ABSTRACT: The use of a readily accessible polyazahelicene as a strongly reducing metal-free alternative to the commonly used precious metal based photoredox catalysts is demonstrated. An improved two-step synthesis of the catalyst is described, and its photophysical properties with respect to its use as a photoredox catalyst are evaluated. Its activity under visible light irradiation is proven by application in two double radical light-driven multicomponent reactions. The azahelicene gave comparable results to an iridium-based catalyst originally used for the same transformations.

KEYWORDS: photochemistry, photoredox catalysis, helicenes, organocatalysis, multicomponent reactions, radicals, redox potential, photocatalysis, visible light



INTRODUCTION

Photoredox catalysis enables the generation of radicals under mild reaction conditions by single-electron transfer from a photoexcited catalytic species to a substrate. The resulting open shell intermediates enable transformations that are difficult or impossible to achieve with other means of chemical catalysis or thermal activation. Many of the commonly used photocatalysts (PCs) are complexes of iridium and ruthenium due to the favorable photophysical properties of these two transition metals (strong absorption, long-lived excited states, sufficient redox potential, tunability of redox potentials via ligand variation).¹ However, their versatility comes at a price as these precious metals are rare or even, in the case of iridium, exceedingly rare, which makes them very expensive. Iridium prices have increased from around 600 USD/oz in the early 2000s to over 2000 USD/oz in 2020, have skyrocketed to 6000 USD/oz in the last year, and remain at 5000 USD/oz to date.^{2,3} Apart from the economic burden, the mining and refining of precious metals can have a significant ecological impact.⁴ A more sustainable alternative to these metal-based catalysts is entirely organic PCs. While a wide variety of organic PCs has been reported and finds broad use in light driven transformations, most of the catalyst classes, including acridinium salts,^{5,6} benzophenones,^{7,8} quinones,^{9–11} cyanoarenes,⁵ and quinolinium salts,^{6,12,13} among others,¹⁴ are based on cationic or acceptor-substituted aromatic systems. Upon excitation, these catalysts tend to act as strong oxidants in a reductive quenching catalytic cycle. In contrast, reducing organic PCs that operate in oxidative quenching cycles are less common and only a few examples have an excited state

reduction potential comparable to that of metal-based PCs.¹⁵ These include phenothiazines, phenoxazines, and dihydrophe-nazines (examples are **1** and **2** in Table 1), which have been applied in a variety of chemical transformations,^{16–18} including organocatalyzed atom transfer radical polymerization of methacrylates^{19,20} and other monomers.²¹ An approach to tune the redox potential of the thermally activated delayed fluorescence (TADF) emitter 4-CzIPN **3** (Table 1) by modification of the donor substituents and the acceptor moiety also resulted in strongly reducing derivatives of this widely used catalyst by decorating the carbazolyl residues with methoxy substituents.²²

While the synthesis and functionalization of helical structures via photoredox catalysis has been a subject for research^{23–26} and the spectroscopic and photochemical properties of helicenes are well studied,^{27–30} the use of (hetero)helicenes as photoredox catalysts has been investigated only scarcely, including attempts to apply hexahelicene as an enantiodifferentiating fluorescence quencher.^{30–32} The complexity of the multistep procedures to obtain various helical structures often makes their use as catalysts unattractive despite their unique structural and optical properties.³³

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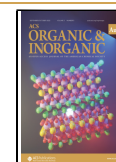
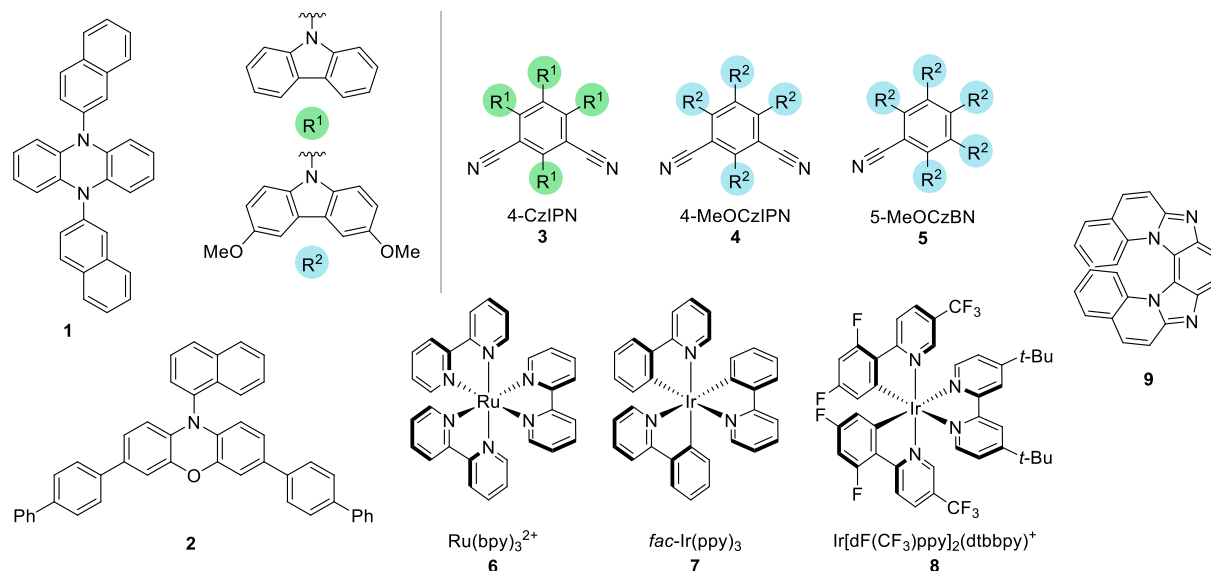


Table 1. Structure and Redox Potentials of Commonly Used Metal Based and Relevant Organic PCs^a

photocatalyst	excited state potentials		ground state potentials		$E_{0,0}/\text{eV}$	ref
	$E_{1/2}(\text{PC}^*/\text{PC}^{\bullet-})/\text{V}$	$E_{1/2}(\text{PC}^{\bullet+}/\text{PC}^{\bullet})/\text{V}$	$E_{1/2}(\text{PC}/\text{PC}^{\bullet-})/\text{V}$	$E_{1/2}(\text{PC}^{\bullet+}/\text{PC})/\text{V}$		
1		-1.69		+0.21	1.90	18
2		-1.80		+0.65	2.45	18
3	+1.43	-1.18	-1.24	+1.49	2.67	22
4	+1.27	-1.50	-1.34	+1.11	2.61	22
5	+1.15	-1.79	-1.66	+1.02	2.81	22
Ru(bpy) ₃ ²⁺ 6	+0.77	-0.81	-1.33	+1.29	2.10	1
fac-Ir(ppy) ₃ 7	+0.31	-1.73	-2.19	+0.77	2.50	1
Ir[dF(CF ₃)ppy] ₂ (dtbbpy) ⁺ 8	+1.21	-0.89	-1.37	+1.69	2.58	1
azahelicene 9		-1.87		+1.12	2.99	this work

^aAll potentials are given vs SCE.

Recently, the syntheses and photophysical properties of several polyazahelicenes were published^{34,35} and their structure and the ease of accessibility make them promising candidates as reducing organic PCs. Therefore, we investigated the photocatalytic potential of azahelicene **9** in self-developed^{36,37} photoredox-catalytic multicomponent reactions.

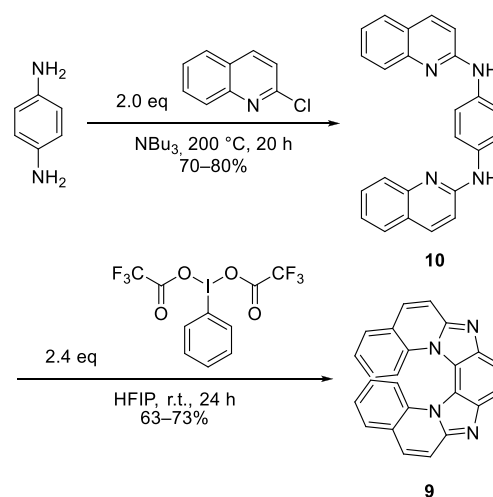
RESULTS AND DISCUSSION

Synthesis of the Azahelicene Catalyst

The synthesis of azahelicene **9** (Scheme 1) was performed in analogy to a recently published protocol,³⁵ where the yield could be improved to 58% over two steps by changing the solvent in the first step and the oxidation reagent from 4-iodoanisole/*m*CPBA to phenyliodine bis(trifluoroacetate) (PIFA) in the second step. *p*-Phenylenediamine and 2-chloroquinoline were reacted at 200 °C in tributylamine to yield *N,N'*-di(quinolin-2-yl)benzene-1,4-diamine (**10**) in up to 80% after recrystallization. Subsequent oxidative cyclization forms the tetraazahelicene **9** in 73% yield. As previously reported, the cyclization proceeds regioselectively to the helical structure, while formation of the S-shaped isomer is not observed.³⁵ The product can be purified by column chromatography and is obtained as a bench-stable solid. An absorption and emission spectrum of the catalyst is shown in Figure 1.

An estimation of the redox potentials of the azahelicene was made from cyclic voltammetry measurements and the excited

Scheme 1. Synthesis of Azahelicene Catalyst **9** from 2-Chloroquinoline in Two Steps



state energy which can be approximated from the absorption and fluorescence spectra.¹⁴ A reversible oxidation peak at +1.12 V (vs SCE) was observed in acetonitrile, and the midpoint between the absorption ($\lambda_{\text{abs,max}} = 376$ nm) and fluorescence ($\lambda_{\text{em,max}} = 454$ nm) maximum suggests an excited state energy of $E_{0,0} = 2.99$ eV. Using the equation for the Gibbs energy of photoinduced electron transfer while omitting the

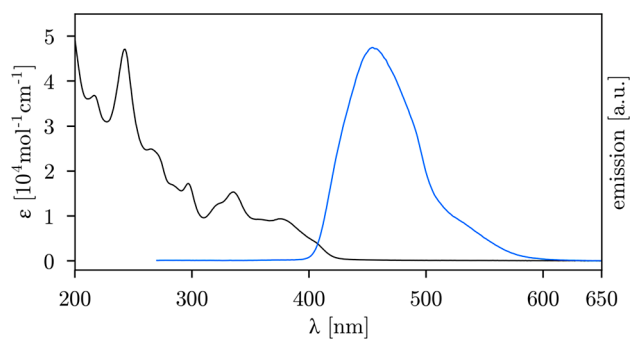


Figure 1. Absorption (black) and fluorescence (blue) spectra of tetraazahelicene **9** (MeCN, 2.3×10^{-5} M).

electrostatic work term, the potential of the excited state of the azahelicene can be calculated:

$$E_{\text{Ox}}^*(\text{PC}^{\bullet+}/\text{PC}^*) = E_{\text{Ox}}(\text{PC}^{\bullet+}/\text{PC}) - E_{0,0} = -1.87 \text{ V}$$

This compares favorably with the excited state potentials of commonly utilized metal-based photocatalysts like $\text{Ru}(\text{bpy})_3^{2+}$ (-0.81 V vs SCE), $\text{Cu}(\text{dap})_2^+$ (-1.43 V vs SCE), and *fac*- $\text{Ir}(\text{ppy})_3$ (-1.73 V vs SCE).¹ The reduction potential of the oxidized azahelicene $E_{1/2}(\text{cat}^{\bullet+}/\text{cat}) = +1.12$ V required to close the catalytic cycle when used as a photoredox catalyst also remains higher compared to the mentioned metal-based catalysts $\text{Cu}(\text{dap})_2^{2+}/\text{Cu}(\text{dap})_2^+$ ($+0.62$ V) and *fac*- $\text{Ir}(\text{ppy})_3$ ($+0.77$ V), but is 0.14 V lower than the reduction potential of $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ ($+1.29$ V).¹ To confirm the oxidation potential of the azahelicene catalyst, the well-known decarboxylative coupling of Boc-Pro-OCs ($E_{1/2} = +0.95$ V vs SCE)²² to 4-cyanopyridine was performed and the coupling product was obtained in 49% yield.

No peak in the reductive region of the cyclic voltammogram was observed, suggesting that a reduction of the catalyst does not occur under these conditions. Quenching studies of the catalyst with the easily oxidized reductive quencher triethylamine ($E_{1/2}(\text{cat}^{\bullet+}/\text{cat}) = +0.83$ V,³⁸ $+0.99$ V,³⁹ both vs SCE) showed no change in fluorescence intensity. This makes reductive quenching with other substrates unlikely, and all mechanistic considerations are therefore based on the assumption that an oxidative quenching cycle is taking place.

The solubility of **9** in various solvents was tested at 1 mM concentration, which is deemed to be sufficient for preparative use as a catalyst, and the absorption and fluorescence spectra in these solvents were recorded to assess the extent of solvatochromism that the azahelicene shows (Figure 2). Apart from poor solubility in hexane and water, the catalyst is soluble in low polarity solvents such as ethyl acetate, toluene, and dichloromethane as well as in the more polar solvents THF, acetonitrile, acetone, DMF, DMSO, ethanol, and methanol.

The position of the first absorbance maximum in different solvents ranges from 383 nm in hexane and toluene to 371 nm in methanol (the absorbance maximum in water could not be resolved due to the low solubility but may be further blue-shifted), while the fluorescence maximum shift from 447 nm in hexane to 461 nm in water. Overall, the effects of the solvent on absorbance and fluorescence maxima are small and the excited state energy $E_{0,0}$ is comparable in all solvents with ~ 3.0 eV. The exact values for each solvent are tabulated in the Supporting Information (Table S1).

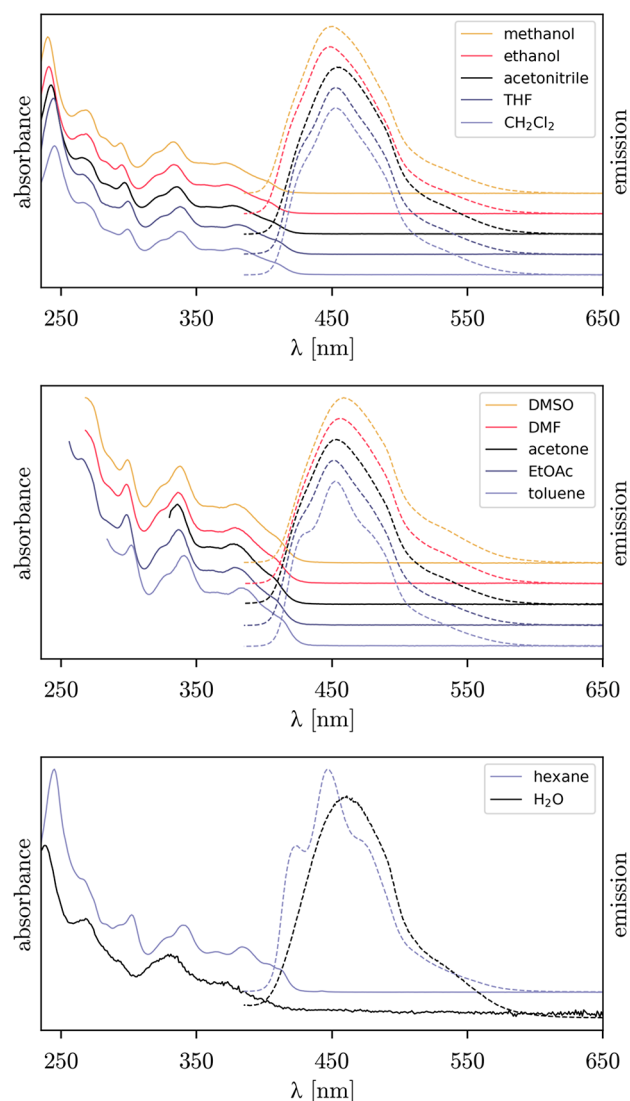
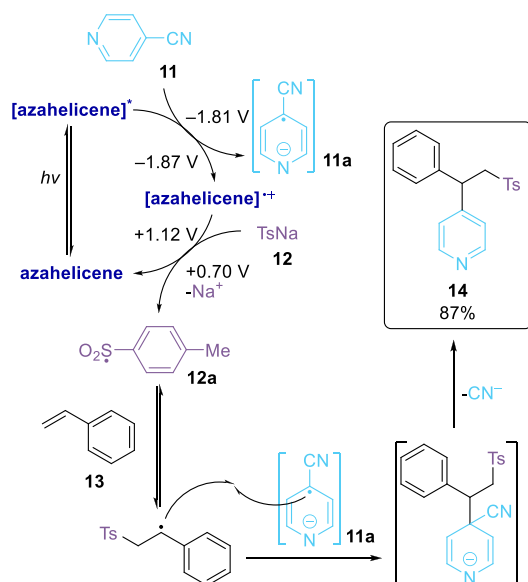


Figure 2. Absorption and normalized fluorescence spectra of **9** in various solvents. The spectra were separated in the graphs and offset for better clarity. Spectra were recorded at 1.0×10^{-5} M, except for hexane and water which were recorded in saturated solution. The absorbance spectrum in water was scaled to be comparable to that of hexane.

Application as a Photoredox Catalyst

Sulfonylation/Arylation of Styrenes. To test activity of the azahelicene as a photoredox catalyst and to verify the calculated potentials, we employed it in a three component reaction (3-CR) arylation/sulfonylation of styrenes, which has been developed earlier in our lab, in place of the $\text{Ir}(\text{ppy})_3$ catalyst originally used.³⁶ Reaction conditions similar to the optimized conditions with $\text{Ir}(\text{ppy})_3$ were initially chosen, but the catalyst loading was adjusted to 5 mol %. The proposed reaction mechanism (Scheme 2) of the reaction starts with an oxidative quenching of the excited catalyst by cyanopyridine **11** to form the corresponding radical anion **11a**. The catalyst regenerates by oxidation of sulfinate **12** to the sulfonyl radical **12a**, which attacks styrene **13**. The resulting benzylic radical recombines with the cyanopyridine radical anion **11a** and after elimination of cyanide furnishes the coupling product **14**. A complex formation of the catalyst with one of the substrates was not observed as no additional bands were found in the

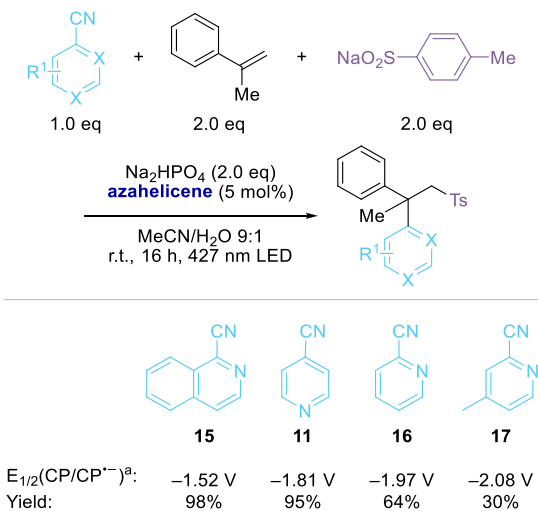
Scheme 2. Proposed Reaction Mechanism of 3-CR Sulfonylation/Arylation Reaction^a

^aPotentials are given vs SCE.

absorbance spectra of the combined reaction mixture compared to the separate reactants.

As the reduction of the cyanopyridines requires a strongly reducing catalyst, a screening of different substrates gives an indication of the reduction potential of the excited azahelicene. Four different cyanopyridines with decreasing electron affinity were used to scout the scope (Scheme 3). 1-Cyanoisquinoline

Scheme 3. Screening of Different Cyanopyridine Substrates and Correlation with Their Reduction Potentials



^aPotentials are given vs SCE. CP = cyanopyridine.

15 and 4-cyanopyridine 11 both gave high yields in the reaction which is in line with the calculated redox potential of the catalyst (-1.87 V). 2-Cyanopyridine 16 and 2-cyano-4-methylpyridine 17 have lower reduction potentials, and the catalyst failed to reduce these substrates to the radical anion efficiently, resulting in significantly lower yields.

A catalyst loading screening was performed and results are listed in Table S1. At 1 mol % loading, the yield of 18

decreased to 48%, yet already 3 mol % give a yield of 87% and an increase to over 5 mol % resulted in no further improvement. It should be noted that during the reaction, partial decomposition of the catalyst could be observed by TLC. While the decomposition products maintain fluorescent properties, it is uncertain whether catalytic activities are altered. The degradation pathway and the structure of the products are the subject of current investigations. Mass spectroscopy revealed several addition products of the catalyst and the styrene component in the reaction mixture so that reuse is not feasible. The addition of a second 5 mol % portion of catalyst to the reaction after 5 h was shown to increase the yield of 26 to 45%, suggesting premature catalyst deactivation in the case of inefficient quenching. This may also explain the higher yield of 26 that is attained with the Ir(ppy)₃ catalyst (80%)³⁶ due to its higher stability.

Control reactions to rule out light-independent catalysis were performed and no product formation was observed in the dark. To check for catalyst-independent background reaction under irradiation, the catalyst was omitted from the reaction medium which gave the product in 7% yield. The source of this background reaction might be a minor overlap of the absorption of the reaction mixture at with the emission spectrum of the lamp (Figure S4).

Apart from different cyanopyridines, four sulfonates and four styrenes were tested in the reaction to compare the performance of the azahelicene with the Ir(ppy)₃ catalyst on a broader scale (Scheme 4). Methane-, benzene- and 2-naphthalenesulfonate all gave comparable results to the iridium-catalyzed reaction.³⁶ With unsubstituted styrene and *p*-bromostyrene, the reaction proceeds with high yields, cinnamyl alcohol is less suitable as a substrate.

Sulfonylation/Aminoalkylation of Styrenes. To investigate the catalytic properties under acidic conditions, a related multicomponent reaction was chosen that uses protonated imines as electron acceptors to form α -amino radicals as the coupling component. The formation of sulfonyl radicals from sulfonates and the use of styrene are equivalent to the arylation/sulfonylation reaction performed with cyanopyridines. The catalytic cycle is proposed to be similar to that depicted in Scheme 2 and is shown in the Supporting Information (Scheme S2).

Reaction conditions (Scheme 5) were adopted from the original publication³⁷ apart from the catalyst loading, which was increased to 5 mol % and adjustment of the light source. Instead of the imines, the corresponding amines and aldehydes may be added separately during the reaction, without changing the reaction yield. Six different complex amines were synthesized from benzylideneaniline and three different sulfonates and styrenes, respectively. Again, the reaction was performed without catalyst and without irradiation to check for background reactions (Table 2).

CONCLUSION

An improved synthesis of azahelicene 9 was developed, and its photophysical and electrochemical properties were investigated. On the basis of the acquired data, the compound was successfully applied as a catalyst in two photoredox reactions. The catalytic properties of azahelicene 9 allow its use as a metal-free substitute for Ir(ppy)₃ in these reactions without compromising the yield or increasing the reaction time in most cases. A higher catalyst loading (5-fold higher molar loading, 2.7-fold higher mass loading relative to Ir(ppy)₃) was however

■ ABBREVIATIONS

4-CzIPN, 2,4,5,6-tetrakis(9*H*-carbazol-9-yl)isophthalonitrile

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