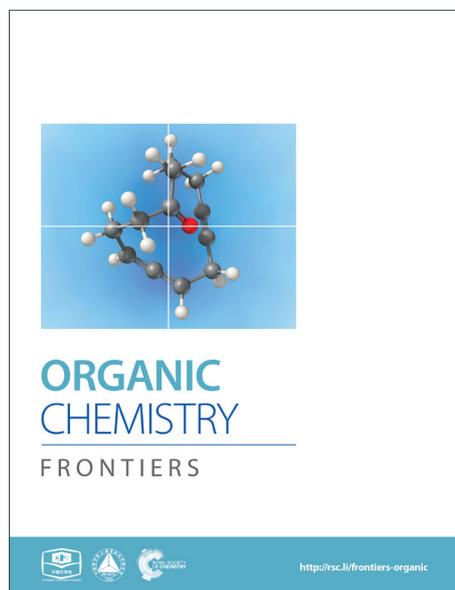
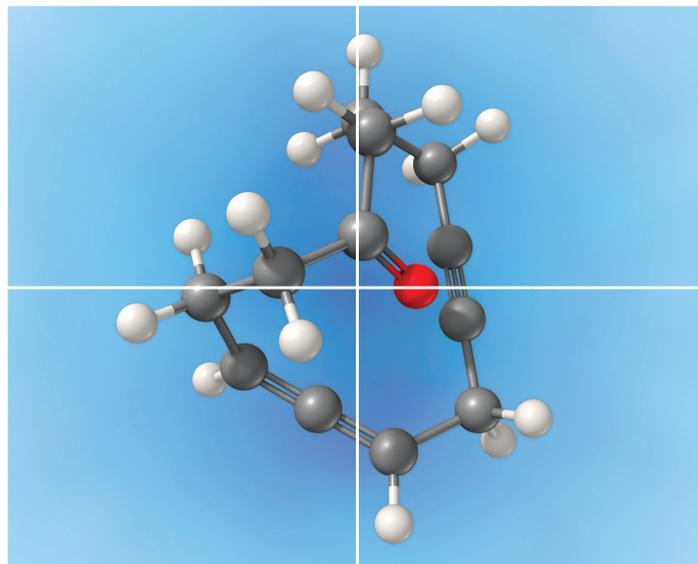


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ARTICLE

Synthesis and Characterization of N-2-Aryl-1,2,3-Triazole Based Iridium Complexes as Photocatalysts with Tunable Photoredox Potential

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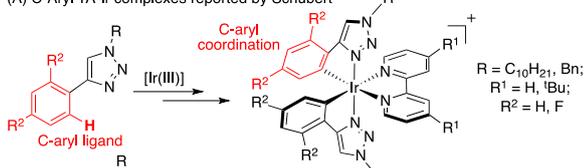
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N-2-Aryl chelated 1,2,3-triazole-Ir(III) complexes with various substituents were prepared for the first time. These photoactive Ir(III) complexes were characterized by X-ray crystallography and their redox potentials were evaluated. This study revealed a new class of photocatalysts with tunable photoredox potentials.

The cationic Ir(III) polyimine complexes have been widely applied in various areas,¹ including live cell imaging,² electroluminescent materials,³ water oxidation etc.⁴ Recently, [Ir(ppy)₂(bpy)]⁺ and [Ir(ppy)₂(dtbbpy)]⁺ have gained tremendous attention as efficient photocatalysts in promoting organic transformations.^{5,6} The fast growth of photocatalytic research led to strong needs for new systems with structural novelty and potentially new reactivity. Herein, we report the application of N-2-aryl-1,2,3-triazoles as ligands for the synthesis of novel N-aryl chelated Ir(III) photocatalysts with tunable redox potentials.

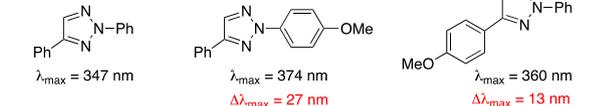
(A) C-Aryl TA-Ir complexes reported by Schubert



(B) Strong substituent influence at N-aryl position revealed from fluorescence emission

Reaction scheme (B) showing the synthesis of N-aryl TA-Ir complexes. An N-aryl ligand (1,2,3-triazole with an aryl group at the 1-position) reacts with Ir(III) to form a complex. The N-aryl ligand is highlighted in blue. The Ir(III) complex is shown with two other ligands (R₁ and R₂). The text indicates "no desired complex isolated" and "poor complex stability and formation of by-products" due to "less controlled binding, formation of side products".

(C) Proposed new TA-Ir complexes using N-2-aryl-TA to achieve N-aryl coordination



Hypothesis:
Avoid -N₂ decomposition;
Tunable photoredox potential via substitution on both aryl rings

Concerns:
Selectivity (H_a vs H_b/H_c)

Scheme 1. New Ir(III) complexes with 1,2,3-triazole ligands.

After the discovery of “click chemistry”, 1,2,3-triazole (TA) became one of the most important heterocycles in chemical research.⁷ However, the studies regarding the binding ability of N-2-substituted triazole toward metal cation are relatively rare. During the past several years, our group has been working on developing new synthetic methods toward triazole functionalization⁸ while investigating coordination ability of various triazole derivatives.⁹ Inspired by recent success on Ir(III) promoted photocatalysis, we become interested in studying TA binding ability with Ir(III) cations and hope to develop a new class of photoactive complexes with the potential to further extend the reaction scope of photocatalysis.

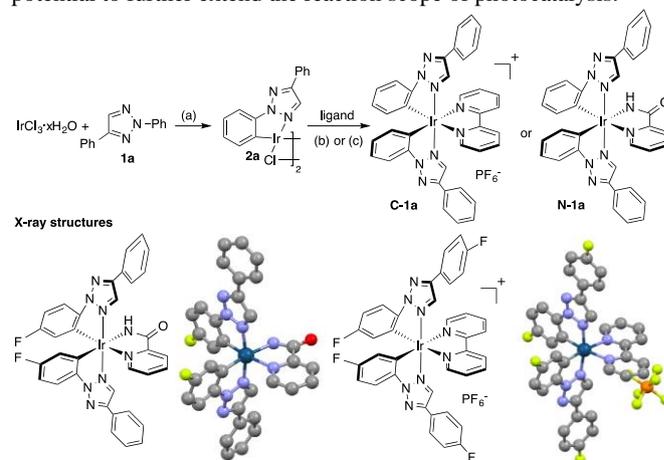


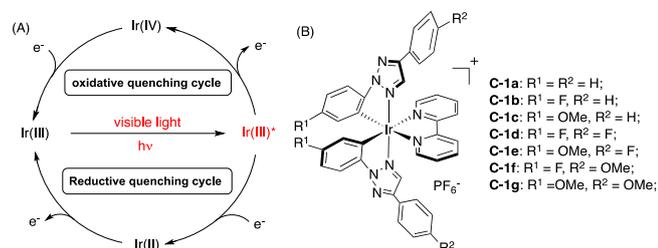
Figure 1. General synthetic route and X-ray crystal structures of N-aryl-chelated TA-Ir complexes: (a) 2-Ethoxyethanol, 140°C, N₂, 24h; (b) 2,2'-bispyridine (bpy, 2.5 eq.), 1,2-ethanediol, 120°C, N₂, 20h, followed by anion exchange with NH₄PF₆; (c) 2-picolinamide (2.6 eq.), Na₂CO₃ (11 eq.), 2-ethoxyethanol, 140°C, N₂, 20h.

In 2009, Schubert and co-workers reported the first triazole coordinated Ir(III) complexes using N1-substituted 1,2,3-triazole as the C^N ligand.¹⁰ Later, De Cola and co-workers reported the electroluminescent properties of similar Ir(III) complexes (Scheme 1A).¹¹ Although these and other pioneering work¹² revealed good coordination ability of TA ligands with Ir(III), no photocatalytic reactivity has been reported. More importantly, as mentioned by

Schubert, only C-aryl-TA chelated Ir(III) complexes could be produced. The attempts to form N-aryl-TA chelating complexes were unsuccessful due to either poor complex stability or the formation of unidentified byproducts.

Among various triazole derivatives, one particularly interesting compound is the fluorescence active N-2-aryl triazoles (NATs).^{7b} As revealed by the crystal structures, the N-2-aryl group holds a perfect co-planar conformation with the triazole ring, resulting in a strong fluorescence emission, whereas the N-1-isomer exhibits no emission.¹³ Moreover, substitution on the N-2-aryl group exhibited strong influence on fluorescence emission wavelength and intensity (Scheme 1B). Based on these results, we postulated that the N-2-aryl-triazole may be used as the ligand to prepare novel N-aryl-chelated Ir(III) complexes, by avoiding the potential triazole decomposition (via loss of N₂) and providing specific coordination sites.¹⁴ To test our hypothesis, N-2-aryl-triazoles were prepared and used for Ir(III) complex formation. The general synthetic route is summarized in Figure 1.¹⁵

As expected, treating triazole **1** with IrCl₃·xH₂O gave the corresponding chloro-bridged iridium(III) dimer **2** in excellent yields (generally > 80%). Subsequent reaction with either a neutral N[^]N ligands (condition b) or an anionic N[^]N ligand (condition c) gave the corresponding cationic TA-Ir (C-1) or neutral TA-Ir (N-1) complexes. Both complexes were characterized by X-ray crystallography. Notably, unlike N-1-aryl triazoles, the N-2-aryl triazoles indicated strong coordination ability, forming stable Ir(III) complexes, which could be easily purified by column chromatography without decomposition. With this synthetic method, various TA-Ir complexes were prepared. Good to excellent yields were obtained in most cases, which warranted further applications of N-2-aryl triazoles as the C[^]N ligand for iridium photocatalysts.



Scheme 2. (A) The general mechanism for Ir(III) photocatalysis; (B) TA-Ir complexes prepared from N-2-aryl triazoles.

As shown in Scheme 2A, the general mechanism of Ir-photocatalysis is initiated from the promotion of Ir(III) to excited state Ir(III)* by visible light, followed by oxidative or reductive quenching through single-electron transfer. The resulting Ir(IV) or Ir(II) will be reduced or oxidized to regenerate the ground state Ir(III). The redox potential for each step is a crucial factor in catalyst design, simply because oxidation/reduction reactions require good matching of the redox potentials between catalysts and substrates. Compared to 2-phenylpyridine (ppy) ligands, N-2-aryl triazoles are more electron-deficient. Thus, higher oxidation potentials of the corresponding iridium complexes are expected.^{5d} To evaluate the photophysical properties of these new TA-Ir complexes, UV-Vis absorption and fluorescence emission were examined.

Similar to other literature reported systems^{13a}, the neutral complex N-1a (with anionic N[^]N ligand) gave very weak fluorescence emission and almost no photocatalytic reactivity. On the other hand, compared with [(ppy)₂Ir(bpy)]PF₆, the TA-Ir cationic complexes [(tapy)₂Ir(bpy)]PF₆ indicated better absorption of blue light and stronger fluorescence emission in the visible light region (Figure 2, see detailed spectra comparison in supporting information).

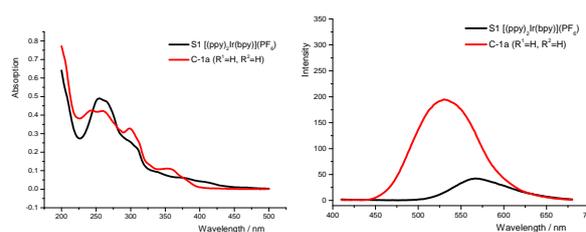


Figure 2. UV-Vis (left) and fluorescence (right) spectra comparison

The fluorescence emission and redox potentials of some representative TA-Ir complexes are summarized in Table 1.

Table 1. Redox Potentials of selected Iridium complexes^{a,b}

	R ¹	R ²	λ_{em} (nm)	Φ^c	τ^d (ns)	$E_{1/2}$ (V)			
						(Ir ^{4+/3+})	(Ir ^{4+/3+*})	(Ir ^{3+/2+})	(Ir ^{3+*/2+})
S1	-	-	566			1.28	-0.91	-1.38	0.81
C-1a	H	H	530	0.32	266	1.54	-0.80	-1.34	1.00
C-1b	F	H	503	0.39	358	1.67	-0.80	-1.33	1.14
C-1c	OMe	H	550	0.02	30	1.37	-0.88	-1.35	0.90
C-1d	F	F	501	0.29	270	1.66	-0.82	-1.33	1.15
C-1e	OMe	F	554	0.02	32	1.37	-0.87	-1.35	0.89
C-1f	F	OMe	508	0.21	172	1.61	-0.83	-1.32	1.12
C-1g	OMe	OMe	558	0.01	18	1.25	-0.90	-1.37	0.85

^a **S1** = [(ppy)₂Ir(bpy)]PF₆; All potentials are given versus saturated calomel electrode (SCE). Measurements were performed at room temperature in acetonitrile using an internal standard Fc/Fc⁺ redox couple (0.40V vs. SCE). ^b PF₆⁻ is used as the counter anion. ^c The quantum yields were calculated relative to Ru(bpy)₃(PF₆)₂ ($\Phi = 0.062$ in ACN). ^d Excited-state lifetime.

The data in Table 1 revealed a clear substituent effect on the Ir^{4+/3+} redox potential. First, with more electron-deficient phenyl-triazole (pta) ligand, **C-1a** gave higher Ir^{4+/3+} redox potential (1.54V) than [Ir(ppy)₂(bpy)]PF₆ (**S1**, 1.28 V). The introduction of electron withdrawing groups (such as F, **C-1b**) at R¹ position (N-2 aryl) further increased the E_{1/2} (Ir^{4+/3+}) to 1.67 V. In contrast, complex **C-1c** (with electron donating OMe) gave lower Ir^{4+/3+} redox potential (1.37 V), which was still higher than ppy complex **S1**. A similar trend was also observed in the Ir^{3+*/2+} redox potential, though with a smaller variation. However, substitution at R² position indicated little influence to the redox potential (eg. **C-1b**, 1.67 V vs **C-1d**, 1.66 V), suggesting that the electronic effect influence from the ring that is directly touching the metal center is much more important. Similarly, introducing EWG at R¹ position (**C-1b**) helped to increase the excited-state lifetime and quantum yield while introducing EDG (**C-1c**) impaired the excited-state lifetime and quantum yield.

The reduction potential E_{1/2} (Ir^{3+/2+}) of all tested **C-1** TA-Ir complexes were almost the same even with different C[^]N ligands. This is likely due to the fact that Ir(III) reduction is more related to the metal-ligand charge transfer (MLCT) through the π^* orbital of the N[^]N ligand (bpy).¹ To fully elucidate the ligand effect on redox potential, we prepared triazole-pyridine (tapy)¹⁶ as a new type of N[^]N ligands to coordinate with Ir cations. The reaction between the chloro-bridged iridium dimer **2a** and N-2 tapy gave messy mixtures with no desired complex isolated. Interestingly, a much cleaner reaction was obtained with N-1-tapy. Although growing a single crystal is unsuccessful at this moment, the TA-Ir complexes with N-1-tapy as N[^]N ligand have been successfully prepared and characterized (by ¹H, ¹³C, ¹⁹F NMR and HRMS). The fluorescence emission and redox potentials of these complexes were then determined as shown in Table 2.

Interestingly, compared to complex **S1** (with ppy N[^]N ligand), complex **C-2** (with tapy N[^]N ligand) resulted in a clear increase of Ir^{3+/2+} reduction potential, from 1.38 V to 1.48 V, similar to complex **S2** (with dtbbpy N[^]N ligand). Notably, the Ir^{3+/2+} reduction potential

remained almost the same when changing the C^N ligand to pta. These results highlighted the excellent viability of these new triazole based Ir photocatalysts: using pta as the C^N ligand to adjust the Ir^{4+/3+} oxidation potential while using tapy as the N^N ligand to tune the Ir^{3+/2+} reduction potential.

Table 2. Redox Potentials of Iridium complexes formed from tapy ligand^{a,b}

R ¹	λ _{em} (nm)	Φ ^c	τ ^d (ns)	E _{1/2} (V)				
				(Ir ^{4+/3+})	(Ir ^{4+/3+})	(Ir ^{3+/2+})	(Ir ^{3+/2+})	
S1	-	566	1.28	-0.91	-1.38	0.81		
S2	-	560	0.20	175 ^d	1.25	-0.96	-1.48	0.73
C-2	-	546	0.12	110	1.37	-0.90	-1.48	0.79
C-3a	H	462, 486	0.06	217	1.61	-0.94	-1.45	1.10
C-3b	F	458, 482	0.07	375	1.75	-0.82	-1.41	1.16
C-3c	OMe	508	0.01	108	1.37	-1.07	-1.43	1.01

^a S1 = [(ppy)₂Ir(bpy)]PF₆; S2 = [(ppy)₂Ir(dtbbpy)]PF₆. ^{b, c, d} Same conditions as Table 2 applied.

Two typical photocatalytic reactions^{6c, 17} were performed to prove the feasibility of these new TA-Ir complexes and good catalytic reactivity were observed as shown in **Figure 3**.

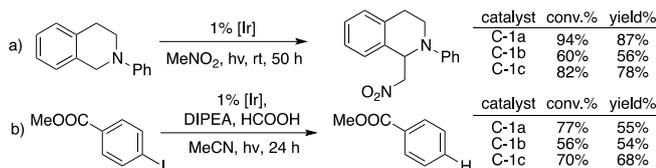


Figure 3. TA-Ir as effective new photocatalysts

In conclusion, we herein report the synthesis and characterization of N-2-aryl-1,2,3-triazole-Ir(III) complexes (TA-Ir). Various complexes have been prepared and their photophysical properties were evaluated. Tunable redox potentials were achieved through varying substituents on either pta C^N ligand or tapy N^N ligand, which indicated promising future of these new photocatalysts. Investigation on challenging photocatalytic reactions using this new class of photocatalysts is currently undergoing in our lab.

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† Electronic Supplementary Information (ESI) available: NMR, UV, fluorescence spectra, cyclic voltammetry and X-ray data with CCDC numbers. See DOI: 10.1039/c000000x/

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