

Catalytic Properties of Luminescent Tris-Homoleptic Cyclometalated Iridium(III) Complexes in the Oxidation of Morin in Visible Light

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ABSTRACT

The photo-oxidation of Morin, 2',3,4',5,7-pentahydroxyflavone by six luminescent homoleptic tris-cyclometalated iridium(III) complexes was investigated with the aim of evaluating the catalytic properties of the complexes. The Iridium complexes were synthesized using 2-(1-naphthyl)-pyridine (npy) ligand and its derivatives such as npy-OMe, npy-CF₃ and npy-Me to form Tris-homoleptic cyclometalated complexes; Ir(npy)₃, Ir(npy-OMe)₃, Ir(npy-CF₃)₃, Ir(npy-Me)₃, Ir(Me-npy-Me)₃, and Ir(Me-npy)₃ with substitution at para position relative to nitrogen. The ligand substitution positions were found to influence the excited state lifetimes, where the complexes exhibited long lifetimes, τ , 1.4 – 3.6 μ s, ensuring time for substrates to react before relaxation to ground state. All the six complexes displayed reversible or pseudo reversible redox processes with ground state oxidation potential range of 0.57 to 0.93V compared to Standard Calomel Electrode in CH₂Cl₂. The complexes degraded morin with rate constants k_{obs} between 0.023-0.036 s⁻¹ within a timescale of 12 minutes. The Ir(npy-Me)₃ complex was found to have a high degradation with a rate constant of $k_{obs} = 0.036$ s⁻¹. Degradation reactions using all the six Iridium (III) complexes photoredox catalysts were found to follow first order kinetics and ca. 10-fold faster compared to similar oxidative reactions.

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1. Introduction

In the recent years, pollution by organic dyes from textile, food, pharmaceutical and cosmetics industries, has increased exponentially. These dyes lead pollute both land and water bodies [1,2,3] and are toxic to microorganisms, aquatic life and humans [4,5]. It is therefore, imperative that remediation techniques are developed such as photodegradation, electrochemical methods, adsorption and catalytic oxidation in the removal of these dyes from the environment [6]. This implies that industrial bleaching is of both environmental and economic importance and utilizes oxidants such as O₂ and H₂O₂ with transition metals for activation of oxidants for enhanced performance. Photocatalysts in degradation reactions of dyes, do activate O₂ by transforming it to reactive oxygen species (ROS) that include

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superoxide anion radical, hydrogen peroxide, singlet oxygen and hydroxy radicals, which are oxidants in many organic reactions [7].

Morin, 2',3,4',5,7-pentahydroxyflavone, is a non-toxic flavonoid polyphenolic dye, that is present in tea, fruits and vegetables. It is used in industries as a test dye for first stage screening of potential laundry bleach catalyst as it can react with O₂ in the presence of light and other catalysts [8,9]. The degradation reaction of Morin has been studied under heterogeneous conditions using manganese oxide [10], Au [9], and Pd- dendrimer-encapsulated nanoparticles (NPs) [4], a series of divalent manganese complexes [MII(HL1–6)Cl₂] with the 1,3-bis(2'-Ar-imino) isoindolines [11] and γ -Al₂O₃ supported AuNPs [12] catalysts with H₂O₂ as the oxidant. Oxidation of Morin using manganese NPs and O₂ as a terminal oxidant has also been reported [13]. However, investigation of Morin oxidation with Ir(III) complexes under visible light with O₂ has not been studied.

Luminescent cyclometalated complexes of transition metals such as Pt(II), Pd(II), Ru(II) and Ir(III) have been found to exhibit properties that make them suitable for use as organic light emitting diodes (OLEDs), dye sensitized solar cells, oxygen sensing, therapeutics, photocatalysts and photosensitizers [14,15,16,17]. The *d*⁶ *tris* cyclometalated Ir(III) complexes are stable in their ground state owing to the spin orbit coupling (SOC) of the Ir(III) metal centre and upon excitation, the excited singlet state initially produced, rapidly relaxes via spin forbidden intersystem crossing to the long-lived triplet state where metal- to-ligand charge transfer (³MLCT) and spin forbidden *d-d* transitions are observed. Triplet quantum yields, phosphorescence properties and reversible redox behaviour are characteristic of these complexes, making them ideal for photoredox catalysis [18,19, 9].

Photoredox catalysis has evolved to be a powerful route for organic synthesis [20] that utilizes electron transfer processes initiated by absorption of a photon by a transition metal complex or organic dyes leading to single electron transfer (SET) processes with organic substrates. Polypyridyl Ru(II) and Ir(III) complexes have been utilized as catalysts in these reactions in presence of visible light [21,22] due to their ability to form charge transfer excited states after absorbing visible light and have long lifetimes [23].

The determining step in photoredox catalysis is the absorption of light by catalysts, leading to formation of intermediate excited states (photoexcited complex), that participates in the chemical reaction. The intermediate excited state is a charge-separated electron-hole pair formed when an excited electron is promoted from the photocatalyst's HOMO to its LUMO. It is both a stronger oxidant and reductant than its corresponding ground state and acts as an electro shuttle that interacts with sacrificial electron-rich donors (D) or acceptors (A) to yield oxidizing or reducing catalyst towards organic substrates [24,25]. This study aims to evaluate the photocatalytic properties of six homoleptic *tris*-cyclometalated Ir(III) complexes using Morin as a model reaction with dioxygen as a terminal oxidant under blue lights (470nm).

2. Materials and Methods

Synthesis of *tris-cyclometalated* homoleptic iridium(III) complexes. Six *tris*-cyclometalated homoleptic iridium complexes; Ir(npv-H)₃ **C1**, Ir(npv-OMe)₃ **C2**, Ir(npv-CF₃)₃ **C3**, Ir(npv-Me)₃ **C4**, Ir(Me-npv-Me)₃ **C5**, and Ir(Me-npv)₃ **C6**, were synthesized through cyclometalation of IrCl₃.xH₂O with 2-(1-naphthyl)-pyridine moiety based ligands. These complexes, C1 to C6 were synthesized through specified novel routes with b separate characterization of ligands and complexes as reported in our previous work [26].

Catalytic Oxidation of Morin. The properties of the complexes **C1** to **C6** was studied through the catalytic oxidation of Morin by monitoring the maximum absorbance using time-resolved UV-VIS. The complexes were prepared by weighing 0.3 mg and dissolving in 10 cm³ of a pH 10 buffer solution of sodium bicarbonate and sodium carbonate which was sonicated for 10 minutes. The reaction was initiated by mixing the complex of a volume of 500 µl, 0.1 mM with an equal amount of freshly prepared Morin solution of 500 µl. Morin displays poor aqueous solubility and sensitive to pH and solvent used, hence carbonate buffer system at pH10 was used to prepare the measurement solutions. Time resolved UV/Vis spectra was taken at minute 0, then at interval of 1 minute for 12 minutes. Before each measurement, the air equilibrated solutions in the cuvette would be illuminated with 470nm visible light first. Control experiments were done by adding 100 µl H₂O₂ into the reaction mixture with 500 µl **C1** and 500 µl 0.1 mM Morin solution and the spectra taken from 0-90 minutes at a 10-minute interval in absence of visible light. Concentration studies were done for **C1** at 1 x10⁻⁵ M, 3 x10⁻⁵ M, 1 x10⁻⁴ M and 2 x10⁻⁴ M to determine the optimum catalytic loading for the experiment.

3. Results and discussion

***Tris-cyclometalated* homoleptic iridium(III) complexes**

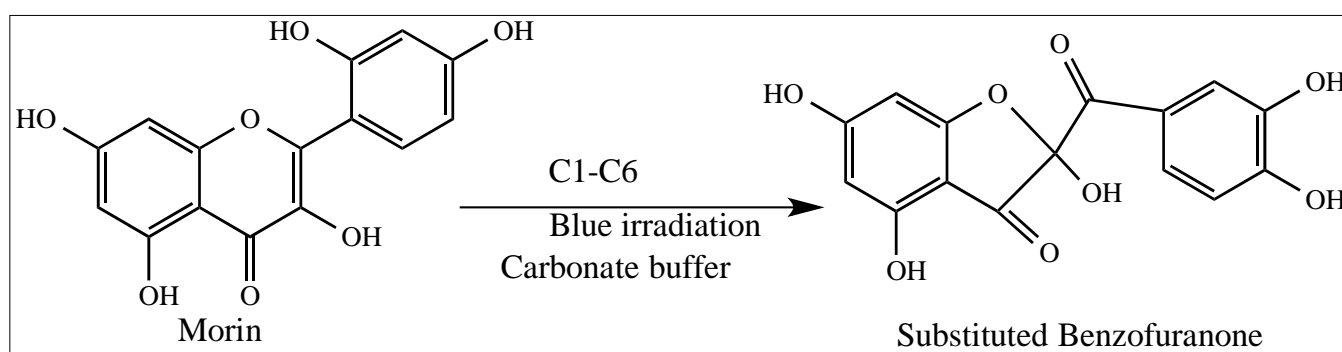
The six homoleptic *tris*-cyclometalated complexes **C1** to **C6** exhibited photoluminescence of 591 nm, 610 nm, 603 nm, 588 nm, 603 nm and 602 nm respectively. Complex **C4** was the most energetic with an emission of 588nm and a corresponding 10Dq value of 25000 cm⁻¹. The complexes were found to emit phosphorescence, long-lived emissions, of lifetimes, τ, 1.5 µs, 3.0 µs, 3.7 µs, 2.6 µs, 1.4 µs and 2.6 µs respectively. Emission lifetimes acts as an intrinsic timer for photoredox reactions hence excited state of the complex should be long enough in order for the reaction to take place. Essentially, long lifetimes ensure adequate time for substrates to react before relaxation to ground state occurs [22]. The oxidation potentials E_{ox}½, were determined to be 0.74V, 0.68V, 0.96V, 0.65V, 0.60V and 0.66V for **C1** to **C6** respectively with corresponding anodic and cathodic peak potential separation ΔE_p = 50-70 mV, which is consistent with pseudo or reversible oxidation processes. Reversibility of complexes is important in order to maintain their viability in the catalytic cycle.

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In this case, reversibility was due to SET event at the Ir^{III}/Ir^{IV} oxidation couple [27,23]. This pointed to the ability of the synthesized complexes to serve as single electron oxidants in photoredox catalysis.

Catalytic Oxidation of Morin

The photocatalytic properties of the complexes **C1** to **C6** were studied through the reaction with Morin as shown in Scheme 1 by monitoring the maximum absorbance using time-resolved UV-VIS. At pH10 the reported maximum absorbance for Morin has been λ_{max} 410 nm [9]. When the complexes were placed in the air equilibrated solution and irradiated with blue light at wavelength 470nm, the maximum absorbance quickly decreased with time.



Scheme 1: Photodegradation of Morin with Ir(III) Complexes and Blue Light

Fig. 1 shows the catalytic oxidation of Morin with complex **C1** and blue light at $\lambda = 470$ nm with the time-resolved measurement taken every minute for 12 minutes in the air equilibrated samples. Three peaks and two isosbestic points were observed on the spectra. The maximum absorbance for Morin was observed at $\lambda = 410$ nm and decreased steadily along with that at $\lambda = 296$ nm while $\lambda = 321$ nm increased with time. The absorbance at 321 nm has been associated with the formation of the substituted benzofuranone [9,10], an intermediate product of catalytic oxidation of Morin shown in Scheme 1.

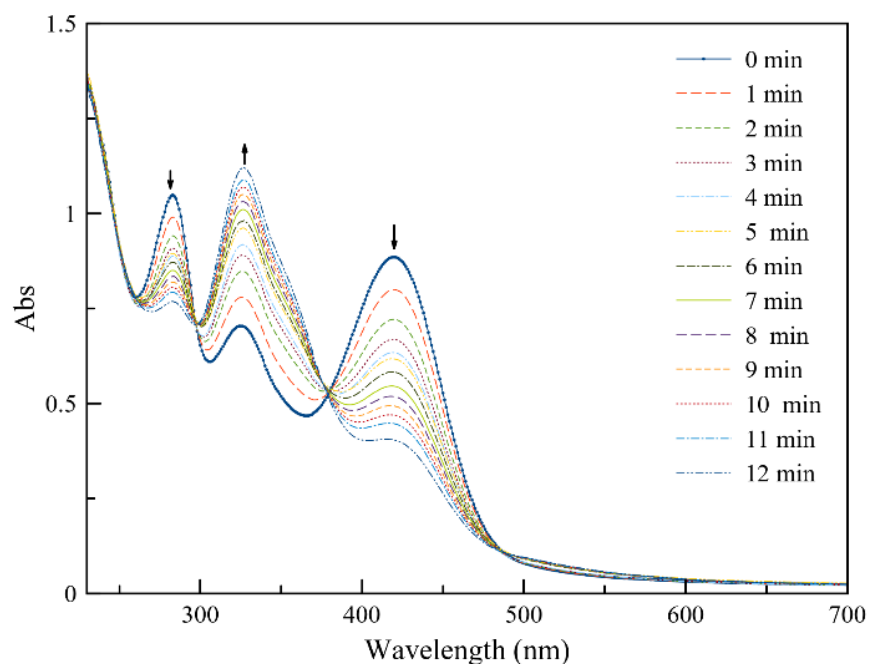


Figure 1: Time-resolved UV-VIS spectra of Morin solution with C1, O₂ and blue lights

Two isosbestic points were observed at $\lambda = 365$ and 290 nm indicating that only a single oxidation product was formed with no luminescent by-products in the reaction period, which is consistent with studies by Polzer and Co-workers [10] and Nemanashi & Meijboom (2015). [9] The peak at $\lambda = 321$ nm vanished after 30 minutes as shown in Fig. 2, with new formation of a new peak that undergoes a red shift to $\lambda = 332$ nm from 80-180 minutes. This is due to initiation of a secondary reaction which leads to further decomposition of the substituted benzofuranone into 2,4-dihydroxy benzoic acid and 2,4,6 trihydroxy benzoic acid. There are no well-defined isosbestic points in Fig. 2, indicative of the primary oxidation product undergoing further reaction to generate more than two species. Complexes C2 to C6 degraded Morin in a similar pattern as C1 for 12 minutes.

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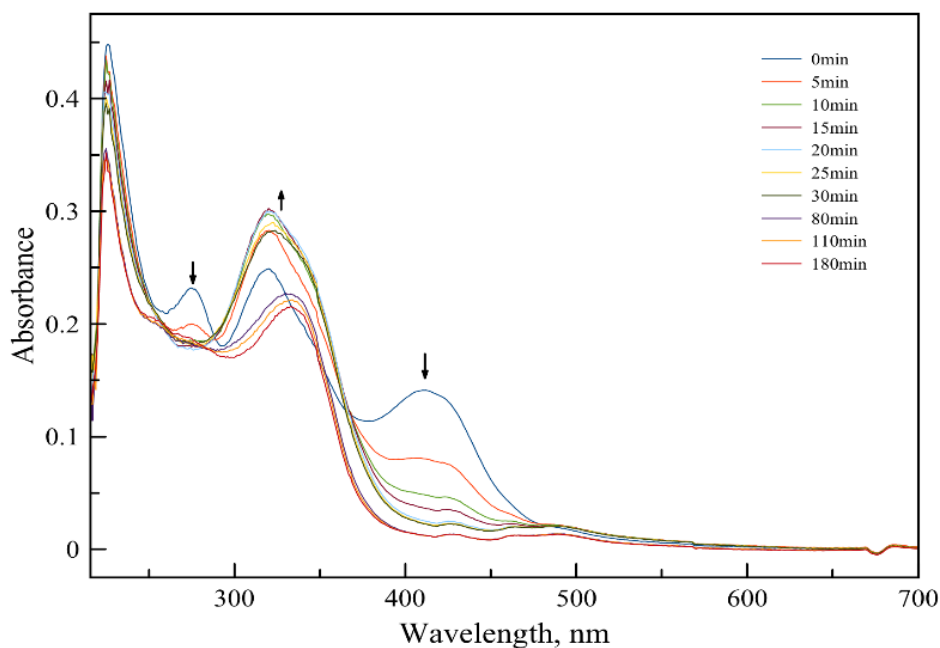


Figure 2: Time-resolved UV-VIS spectra of Morin solution with C1, O₂ and blue lights for 180 min

Control experiments carried out where the oxidation was done with complex C1 and H₂O₂ without the irradiation, had a similar pattern to that Fig. 1, but degradation took longer time, $t > 40$ minutes showing the oxidation process using H₂O₂ was slow. This was indicative of the critical role of the light and catalyst for the degradation in this case. Xiao and co-workers reported similar findings where oxidizing morin with H₂O₂ showed slow degradation of morin after 40 minutes [4], while morin degradation by O₂ as well as in purged solutions has been proven not to be significant in presence of H₂O₂ [9,10].

Concentration of morin is directly proportional to decrease in absorption at $\lambda = 410$ nm after irradiation hence, absorption at this wavelength can be used in determining the kinetics of the reaction since the proportionality constant, observed rate constants, k_{obs} , gives a direct measure for morin's decrease in concentration. The performance of the six complexes can thus be evaluated by direct comparison of their respective rate constants. K_{obs} was computed using Eq. 1, to give the degradation of morin with time at a fixed wavelength, $\lambda = 410$ nm, fitted to a three-parameter single exponential.

$$Abs_t = Abs_0 + (Abs_0 + Abs_\infty) * e^{-kt} \quad (1)$$

where Abs_t is the absorbance and Abs_0 and Abs_∞ are fitted parameters with the absorbance at time 0 and ∞ respectively.

Concentrations studies of C1 at 1×10^{-5} M, 3×10^{-5} M, 1×10^{-4} M and 2×10^{-4} M gave k_{obs} values of 0.22 s^{-1} , 0.026 s^{-1} , 0.019 s^{-1} and 0.015 s^{-1} respectively showing that low catalytic loading of the complexes, 3×10^{-5} M gave the best degradation rates.

The observed rate constants were 0.026 s^{-1} , 0.028 s^{-1} , 0.028 s^{-1} , 0.036 s^{-1} , 0.029 s^{-1} and 0.023 s^{-1} for C1 to C6 respectively. Complex C4 had the fastest k_{obs} of 0.036 s^{-1} hence was the most efficient in degrading morin. This could be attributed to it being the most energetic amongst the complexes, $\lambda = 588 \text{ nm}$, coupled with notable long $\tau = 2.6 \mu\text{s}$ and lower $E_{\text{ox}} = 0.65\text{V}$ thus readily oxidizable lending it the capability to serve as single electron oxidant or reductant with ease. Conversely, complex C6 had the lowest k_{obs} at 0.023 s^{-1} despite having comparable τ and E_{ox} values. The emission wavelength for this complex was observed at 603 nm making it have lower energy as compared to C4 hence the lower degradation rate. Both complexes C4 and C6 had -Me substitution. However, the positions of substitution differed in that the former had -Me substituted in the pyridyl ring while the later -Me substitution was in the naphthyl ring.

On plotting the logarithmic absorbance against time, a linear relationship was obtained as shown in Fig. 3, implying that Morin degradation is a first order reaction. This observation was consistent with Nemanashi and Meijboom (2015) findings. Based on the k_{obs} , the effectiveness of our catalysts compared well with other catalysts that have been reported with the oxidation under O_2 environment being faster than when H_2O_2 was utilized.

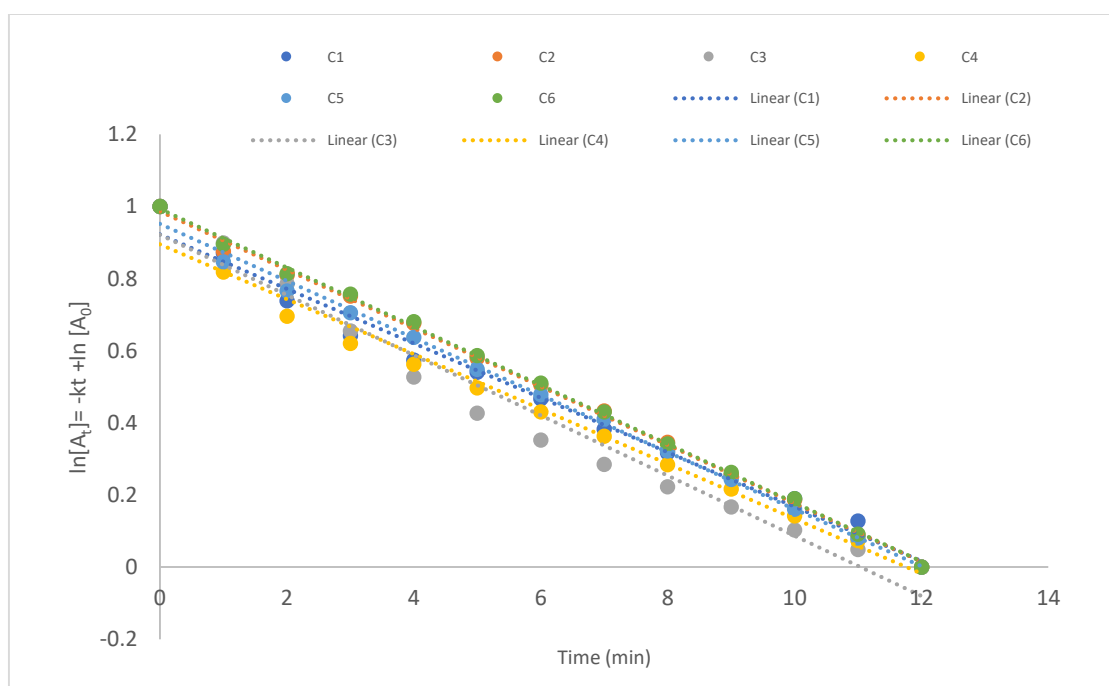


Figure 3: First-order plots for catalytic oxidation of Morin as a function of time for C1 to C6

Studies of morin degradation in presence of visible light with O_2 as a terminal oxidant are few since activation of O_2 with transition metals to yield a selective oxidation reaction is not common. Topalovic and co-workers were first to report the unprecedented ability of Manganese-triazacyclononane (MnTACN) catalysed oxidation of morin in presence of dioxygen as a terminal oxidant [13] whereas prior to this, catalysis with Mn proceeded in presence of H_2O_2 only. Studies conducted in air in absence of

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H₂O₂ with Au-DENs and Mn oxide NPs exhibited slow oxidation of morin, $k_{\text{obs}} = 1.1 \times 10^{-6} \text{ s}^{-1}$, concluding that in their case, the role of dioxygen in presence of H₂O₂ was insignificant [9,10].

Rapid oxidation degradation rates $k = 0.00627 \text{ s}^{-1}$ at pH 10.2 under ambient temperatures were reported for the case where dioxygen was used as a terminal oxidant. It was hypothesized that there was a stepwise formation of H₂O₂ i.e. both H₂O₂ and O²⁻ were operative in the oxidation of morin by the dioxygen with degradation rates similar to oxidation with H₂O₂ or KO₂ as terminal oxidants [13]. Abdolazadeh et al. [28] reported that Morin underwent metal catalyzed oxidative photoaccelerated degradation with dioxygen as a terminal oxidant as well. In their case they pointed the disadvantages of using Morin due to its photochemistry but this flavone has been used repeatedly and successfully by other researchers to study the catalytic properties of their complexes. For instance, Meena and Kaizer (2020) reported $k_{\text{obs}} = 0.541$ to 0.00623 s^{-1} for their Morin oxidation with Mn complexes and H₂O₂ [11]

4. Conclusions

The complexes exhibited luminescence at $\lambda = 588\text{-}610 \text{ nm}$ with **C4** at $\lambda = 588 \text{ nm}$, being the most energetic amongst the complexes having a 10Dq value of 25,000 cm⁻¹. The complexes displayed long-lived triplet phosphorescence lifetimes, $\tau = 1.4 - 3.7 \mu\text{s}$, which act as intrinsic timers for the reaction such that there is time for substrates to react before relaxation to ground state. These complexes displayed reversible or pseudo reversible redox couple processes with ground state oxidation potential 0.57 to 0.93V and vs Standard Calomel electrode in CH₂Cl₂ as reported in our previous work showing their ability to mediate single electron transfer processes as photocatalysts. They were found to catalyse the degradation of morin 1 in 12 minutes under ambient temperatures in O₂ environment at pH 10 with degradation rate constants, $k_{\text{obs}} 0.023 \text{ s}^{-1}$ to 0.036 s^{-1} . Ir(npy-Me)₃, **C4**, exhibited the highest $k_{\text{obs}} = 0.036 \text{ s}^{-1}$ while Ir(Me-ppy)₃, **C6**, degraded morin at the lowest rate with $k_{\text{obs}} = 0.023 \text{ s}^{-1}$. The degradation rates for all the complexes were ca. 10-fold faster than other studies that have used dioxygen ($k = 0.00627 \text{ s}^{-1}$) or H₂O₂ ($k_{\text{obs}} = 0.00623 \text{ s}^{-1}$) as oxidants. The photoredox catalytic degradation reaction of Morin dye was found to follow first order kinetics.

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References

[1] F. Han, V. S. R. Kambala, M. Srinivasan, D. Rajarathnam, and R. Naidu, "Tailored titanium dioxide

- photocatalysts for the degradation of organic dyes in wastewater treatment: A review," *Appl. Catal. A Gen.*, vol. 359, no. 1–2, pp. 25–40, May 2009.
- [2] J. Yin, Zhang, L., Jiao, T., Zou, G., Bai, Z., Chen, Y., Zhang, Q., Xia, M., Peng, Q., "Highly Efficient Catalytic Performances of Nitro Compounds and Morin via Self-Assembled MXene-Pd Nanocomposites Synthesized through Self-Reduction Strategy," *Nanomaterials*, vol. 9, no. 7, p. 1009, Jul. 2019.
- [3] M. J. Ndolomingo and R. Meijboom, "Kinetic analysis of catalytic oxidation of methylene blue over γ -Al₂O₃ supported copper nanoparticles," *Appl. Catal. A Gen.*, vol. 506, pp. 33–43, 2015.
- [4] H. Xiao, Wang, R., Dong, L., Cui, Y., Chen, S., Sun, H., Ma, G., Gao, D., Wang, L., "Biocompatible Dendrimer-Encapsulated Palladium Nanoparticles for Oxidation of Morin," *ACS Omega*, vol. 4, no. 20, pp. 18685–18691, Nov. 2019.
- [5] U. G. Akpan and B. H. Hameed, "Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: a review.," *J. Hazard. Mater.*, vol. 170, no. 2–3, pp. 520–9, Oct. 2009.
- [6] Y. Yun Lee, Moon, J. H., Choi, Y. S., Park, G. O., Jin, M., Jin, L. Y., Li, D., Lee, J. Y., Son, S. U., Kim, J. M. "Visible-Light Driven Photocatalytic Degradation of Organic Dyes over Ordered Mesoporous Cd x Zn 1-x S Materials."
- [7] W. Schilling, D. Riemer, Y. Zhang, N. Hatami, and S. Das, "Metal-Free Catalyst for Visible-Light-Induced Oxidation of Unactivated Alcohols Using Air/Oxygen as an Oxidant," *ACS Catal.*, vol. 8, no. 6, pp. 5425–5430, Jun. 2018.
- [8] T. Wieprecht, U. Heinz, J. Xia, G. Schlingloff, and J. Dannacher, "Terpyridine-manganese complexes: A new class of bleach catalysts for detergent applications," *J. Surfactants Deterg.*, vol. 7, no. 1, pp. 59–66, Jan. 2004.
- [9] M. Nemanashi and R. Meijboom, "Catalytic Behavior of Different Sizes of Dendrimer-Encapsulated Au Nanoparticles in the Oxidative Degradation of Morin with H₂O₂," *Langmuir*, vol. 31, no. 33, pp. 9041–9053, Aug. 2015.
- [10] F. Polzer, S. Wunder, Y. Lu, and M. Ballauff, "Oxidation of an organic dye catalyzed by MnO_x nanoparticles," *J. Catal.*, vol. 289, pp. 80–87, May 2012.
- [11] B. I. Meena and J. Kaizer, "Design and Fine-Tuning Redox Potentials of Manganese(II) Complexes with Isoindoline-Based Ligands: H₂O₂ Oxidation and Oxidative Bleaching Performance in Aqueous Solution," *Catalysts*, vol. 10, no. 4, p. 404, Apr. 2020.
- [12] M. J. Ndolomingo and R. Meijboom, "Kinetics of the catalytic oxidation of morin on γ -Al₂O₃ supported gold nanoparticles and determination of gold nanoparticles surface area and sizes by quantitative ligand adsorption," *Appl. Catal. B Environ.*, vol. 199, pp. 142–154, Dec. 2016.
- [13] Topalovic Tatjana, "Catalytic Bleaching of Cotton: Molecular and Macroscopic Aspects," University of Twente, the Netherlands, 2007.
- [14] K. Dedeian, J. Shi, N. Shepherd, E. Forsythe, and D. C. Morton, "Photophysical and electrochemical properties of heteroleptic tris-cyclometalated iridium(III) complexes.," *Inorg. Chem.*, vol. 44, no. 13, pp. 4445–7, Jun. 2005.
- [15] V. Cîrcu and M. Micutz, "X-Ray Structural Characterization of Cyclometalated Luminescent Pt (II) Complexes," vol. 2, no. li, 2011.
- [16] A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, and J. D. Weaver, "Facile synthesis and complete characterization of homoleptic and heteroleptic cyclometalated Iridium(III) complexes for photocatalysis," *J. Organomet. Chem.*, vol. 776, pp. 51–59, Jan. 2015.
- [17] T. Hofbeck and H. Yersin, "The Triplet State of fac -Ir (ppy) 3," *Inorg. Chem.*, vol. 49, no. 20, pp. 9290–9299, 2010.
- [18] Felici, M., Contreras-Carballada, P., Smits, J. M. M., Nolte, R. J. M., Williams, R. M., De Cola, L., Feiters, M. C. "Cationic heteroleptic cyclometalated iridium(III) complexes containing phenyl-triazole and triazole-pyridine clicked ligands.," *Molecules*, vol. 15, no. 3, pp. 2039–59, Mar. 2010.
- [19] Z. Li, P. Cui, C. Wang, S. Kilina, and W. Sun, "Nonlinear Absorbing Cationic Bipyridyl Iridium(III) Complexes Bearing Cyclometalating Ligands with Different Degrees of π -Conjugation: Synthesis, Photophysics, and Reverse Saturable Absorption," *J. Phys. Chem. C*, vol. 118, no. 49, pp. 28764–28775, Dec. 2014.

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- [20] M. Parasram and V. Gevorgyan, "Visible light-induced transition metal-catalyzed transformations: beyond conventional photosensitizers.," *Chem. Soc. Rev.*, vol. 46, no. 20, pp. 6227–6240, Oct. 2017.
- [21] C. K. Prier, D. A. Rankic, and D. W. C. MacMillan, "Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis," *Chem. Rev.*, vol. 113, no. 7, pp. 5322–5363, Jul. 2013.
- [22] D. M. Arias-Rotondo and J. K. McCusker, "The photophysics of photoredox catalysis: a roadmap for catalyst design," *Chem. Soc. Rev.*, vol. 45, no. 21, pp. 5803–5820, 2016.
- [23] J. R. Ochola and M. O. Wolf, "The effect of photocatalyst excited state lifetime on the rate of photoredox catalysis," *Org. Biomol. Chem.*, vol. 14, no. 38, pp. 9088–9092, 2016.
- [24] K. L. Skubi, T. R. Blum, and T. P. Yoon, "Dual Catalysis Strategies in Photochemical Synthesis," *Chem. Rev.*, vol. 116, no. 17, pp. 10035–10074, Sep. 2016.
- [25] D. M. Schultz and T. P. Yoon, "Solar synthesis: prospects in visible light photocatalysis.," *Science*, vol. 343, no. 6174, p. 1239176, Feb. 2014.
- [26] R.E.N., Njogu, Fodran, P., Tian, Y., Njenga, L.W., Kariuki, D.K., Yusuf, A.O., Scheblykin, I., Wendt, O.F., Wallentin, C.-J., "Electronically Divergent Triscyclometalated Iridium(III) 2-(1-naphthyl)pyridine Complexes and Their Application in Three-Component Methoxytrifluoromethylation of Styrene," *Synlett*, vol. 30, no. 7, 2019.
- [27] D. G. Rackus, M. H. Shamsi, and A. R. Wheeler, "Electrochemistry, biosensors and microfluidics: a convergence of fields.," *Chem. Soc. Rev.*, vol. 44, no. 15, pp. 5320–5340, Aug. 2015.
- [28] S. Abdolazadeh, N. M. Boyle, R. Hage, J. W. de Boer, and W. R. Browne, "Metal-Catalyzed Photooxidation of Flavones in Aqueous Media," *Eur. J. Inorg. Chem.*, vol. 2018, no. 23, pp. 2621–2630, Jun. 2018.