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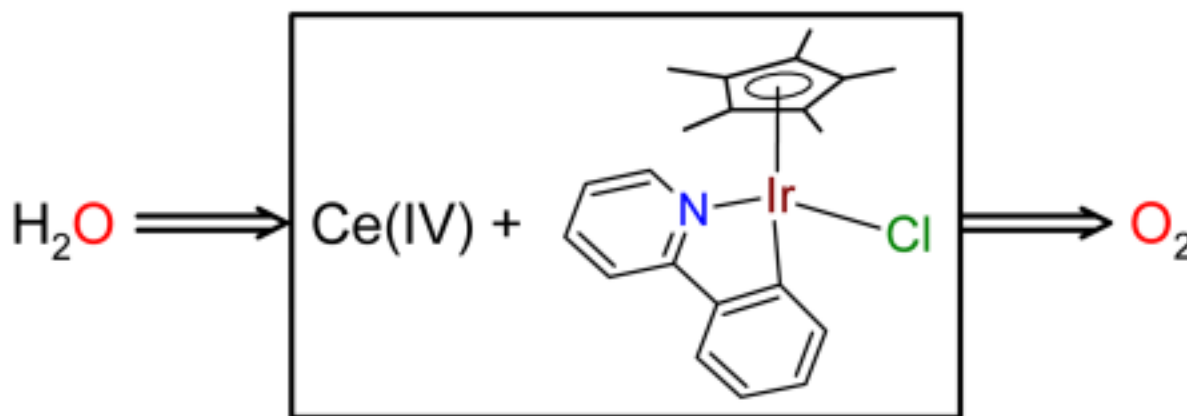
Highly Active and Robust Cp* Iridium Complexes for Catalytic Water Oxidation

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Abstract



A series of Cp*Ir catalysts are the most active known by over an order of magnitude for water oxidation with Ce(IV). DFT calculations support a Cp*Ir=O complex as active species.

Catalytic water oxidation (Eq. 1) is of fundamental importance to natural and artificial photosynthesis,¹ as well as photochemical energy storage and fuel production.



Few homogeneous water oxidizing catalysts are known. Ones that contain Ru, Mn or Ir have been reported,² but high activity and stability are often lacking. A few are only active with the 2e[−] primary oxidants, such as oxone or OCl[−]. Ones active with Ce(IV) are more significant, being more relevant to the 4 × 1e[−] process of photosynthesis. We now describe several robust

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Supporting Information: Synthesis and characterization of compounds **1a–b** and **2**, and crystal parameters. Experimental details for oxygen evolution and kinetic measurements, CV and homogeneity tests. Optimized geometries and energies of the singlet and triplet states of [(Cp*)Ir(O)(ppy)]⁺. Frontier molecular orbitals of the singlet. This material is available free of charge via the Internet at <http://pubs.acs.org>.

water oxidation catalysts using Ce(IV) as the primary oxidant that are the most active yet reported, achieving an initial rate of 54 t.o./min., and are active beyond seven hours.

Bernhard et al.²ⁱ have recently reported a robust homogeneous Ir catalyst, **3** in Fig. 1, that maintains activity with Ce(IV) for one week. Having confirmed this result, we moved to complexes with much more strongly donating ligand sets to look for improved activity, and now report **1a–b** and **2** as highly active catalyst precursors for water oxidation, easily accessible from commercially available [Cp*IrCl₂]₂.³ The crystal structure of **2**, shown in Fig. 2, confirms the expected atom connectivity.

Complex **1a** dissolves in water (50 mM), but only on addition of excess Ce(IV) in the form of CAN (cerium ammonium nitrate), and gas bubbles are observed within one minute. For oxygen detection by the Clark electrode, bubble formation has to be avoided, so rate data for the reaction was obtained under the dilute conditions noted in Figure 3 by adding catalyst (10 μ L, 38 nmol) dissolved in a MeCN/H₂O mixture to the Ce(IV) solution (7 mL, 78 mM). This shows initial oxygen evolution rates for **1a**, **2** and **3** in water with CAN and no lag time is observed upon injection of the catalyst. Complex **1a** (54 t.o./min) and **2** (17 t.o./min) are significantly more active than the known **3** (3 t.o./min), and more active by at least an order of magnitude than those shown in Table 1. Because reaction is so fast, measurements using the Clark electrode are limited to 1 min., dilatometry was used for measurements over longer periods (see SI). No catalyst deactivation is observed after 7.5 hours.⁴ The rate over seven hours is lower (0.1 s⁻¹) than the initial rate, consistent with most catalysts reported in Table 1.

Cyclic voltammetry (CV) of the chloro complex **1a** in MeCN shows three irreversible oxidation waves in contrast to triflate complex **1b** which only shows two peaks. This, together with the much greater rate seen for **1a** versus **1b** (see SI) suggests that chloride oxidation may accelerate O₂ evolution via oxidation to OCl⁻,⁵ or Cl₂.⁶ This is consistent with previous reports of an accelerating effect of Cl⁻ ion.⁷ However, we see 11.9 t.o./min from the triflate complex **1b**, so Cl⁻ is not required for activity. The [Cp*IrCl₂]₂ dimer also evolves O₂, albeit at a much slower rate (8 t.o./min). The formation of IrO₂ or other heterogeneous catalyst is unlikely: the catalyst can be fully recovered from the reaction mixture (NMR), no lag phase is seen, no dark deposit is formed, evolution is reproducible and the reaction is 1st order in **1b**. Furthermore, the reported reaction rate catalyzed by IrO₂ is very slow (Table 1, Entry 8). Other homogeneity tests are reported in the SI. Water was confirmed as the source of O by the detection of ³⁶O₂ in ¹⁸O labeling experiments.

Assuming the chelate remains bidentate, **1–2** only have one labile site. If so, this limits the mechanistic possibilities and the steric bulk present may inhibit μ -oxo dimer formation or other bimolecular deactivation processes.

Moving from the pyridine complex **1a** to the pyrimidine complex **2** causes a rate decrease. Pyrimidines are less donor than pyridines and at low pH they can also protonate at the distal N. The need for strong donor ligands is consistent with a requirement for easy attainment of a high oxidation state intermediate, plausibly an Ir^V oxo. A 2e⁻ oxidation from Ir^{III} is also consistent with the presence of two oxidation waves in the CV for **1b** in MeCN (see SI).

The minimum number of metal atoms required for water oxidation is debated, but several reports^{2c,2i,2k,2l} suggest that a single metal is sufficient. The reaction is first order with respect to **1b** in the 1–80 μ M range (see SI). This makes [(Cp*)Ir(O)(ppy)]⁺ a plausible intermediate. DFT calculations⁸ show that the electronic structure of this pseudo-octahedral (t_{2g})⁴ complex can be understood by the formal combination of the [(Cp*)Ir(ppy)]³⁺ and O²⁻ fragments (Figure 4).⁹ The electrons on the metal are localized in the non-bonding d_{x²-y²} orbital, which does not interact with O p orbitals. The Ir d orbitals oriented towards N, d_N, and C, d_C, make d _{π} /p _{π} interactions with the O p orbitals, yielding two bonding π (Ir=O) orbitals, π_N and π_C , and

two anti-bonding $\pi^*(\text{Ir}=\text{O})$ orbitals, π^*_N and π^*_C . In the singlet state, π^*_N is doubly occupied and π^*_C is empty, whereas in the triplet both orbitals are half occupied. The presence of low-lying $\pi^*(\text{Ir}=\text{O})$ orbitals, which have significant O contribution, may promote the formation of an O-O bond by nucleophilic attack to the oxo group, which is the key step in water oxidation.^{10,11} The singlet state is only 3.7 kcal mol⁻¹ above the triplet, due to the similar energies of the π^*_N and π^*_C orbitals. The accessibility of the singlet state may also facilitate the O-O bond formation, because the addition of the nucleophile will yield a diamagnetic Ir^{III} octahedral complex. The electronic structure of $[(\text{Cp}^*)\text{Ir}(\text{O})(\text{ppy})]^+$ is consistent with this complex being the active species of the catalytic system. A thorough experimental and theoretical investigation is now in progress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- (a) Alstrum-Acevedo JH, Brennaman MK, Meyer TJ. *Inorg Chem* 2005;44:6802. [PubMed: 16180838] (b) Yagi M, Kaneko K. *Chem Rev* 2001;101:21. [PubMed: 11712192] (c) Cady CW, Crabtree RH, Brudvig GW. *Coord Chem Rev* 2008;252:444.
- (a) Gersten SW, Samuels JG, Meyer TJ. *J Am Chem Soc* 1982;104:4029. (b) Liu F, Concepcion JJ, Jurss JW, Cardolaccia T, Templeton JL, Meyer TJ. *Inorg Chem* 2008;47:1727. [PubMed: 18330966] (c) Concepcion JJ, Jurss JW, Templeton JL, Meyer TJ. *J Am Chem Soc* 2008;130:16462. [PubMed: 19554681] (d) Limburg J, Vrettos JS, Liable-Sands LM, Rheingold AL, Crabtree RH, Brudvig GW. *Science* 1999;283:1524. [PubMed: 10066173] (e) Limburg J, Vrettos JS, Chen H, de Paula JC, Crabtree RH, Brudvig GW. *J Am Chem Soc* 2001;123:423. [PubMed: 11456544] (f) Tagore R, Crabtree RH, Brudvig GW. *Inorg Chem* 2008;47:1815. [PubMed: 18330972] (g) Sens C, Romero I, Rodriguez M, Llobet A, Parella T, Benet-Buchholz J. *J Am Chem Soc* 2004;126:7798. [PubMed: 15212526] (h) Nagoshi K, Yamashita S, Yagi M, Kaneko M. *J Mol Catal A* 1999;144:71. (i) McDaniel ND, Coughlin FJ, Tinker LL, Bernhard S. *J Am Chem Soc* 2008;130:210. [PubMed: 18062690] (j) Zong R, Thummel RP. *J Am Chem Soc* 2005;127:12802. [PubMed: 16159265] (k) Deng Z, Tseng HW, Zong R, Wang D, Thummel RP. *Inorg Chem* 2008;47:1835. [PubMed: 18330974] (l) Tseng HW, Zong R, Muckerman JT, Thummel RP. *Inorg Chem* 2008;47:11763. [PubMed: 19006384] (m) Geletii YV, Botar B, Kogerler P, Hillesheim DA, Musaev DG, Hill CL. *Angew Chem Int Ed* 2008;47:3896. (n) Morris ND, Suzuki M, Mallouk TE. *J Phys Chem A* 2004;108:9115.
- See Supporting Information for synthetic procedures.
- Measurements over longer periods are now in progress using a headspace oxygen detector.
- Yagi M, Sukegawa N, Kaneko M. *J Phys Chem B* 2000;104:4111.
- Gilbert JA, Eggleston DS, Murphy WR Jr, Geselowitz DA, Gersten SW, Hodgson DJ, Meyer TJ. *J Am Chem Soc* 1985;107:3855.
- Yagi M, Tomita E, Kuwabara TJ. *Electroanal Chem* 2005;579:83.
- DFT(B3LYP) calculations are carried out with Gaussian03 (full reference in the SI). The geometry of $[(\text{Cp}^*)\text{Ir}(\text{O})(\text{ppy})]^+$ is fully optimized for each spin state with basis set I (Stuttgart-Bonn scalar relativistic ECP with associated basis set for Ir and the 6-31G** for O, N, C and H). The zero-point and entropy energy corrections are obtained from gas phase frequency calculations with basis set I, as the difference between the potential and free energies, $(G - E)_\text{g}$. The energies in solution, G_sol , are obtained from single-point CPCM(H₂O) calculations with basis set II (the same as I but with 6-311 +G** for O, N, C and H). The energies given in the text are obtained by adding G_sol to $(G - E)_\text{g}$.

9. (a) Schilling BER, Hoffmann R, Faller JW. *J Am Chem Soc* 1979;101:592. (b) Kiel WA, Lin GY, Constable AG, McCormick FB, Strouse CE, Eisenstein O, Gladysz JA. *J Am Chem Soc* 1982;104:4865.
10. Lundberg M, Blomberg MRA, Siegbahn PEM. *Inorg Chem* 2004;43:264. [PubMed: 14704076]
11. Yang X, Baik MH. *J Am Chem Soc* 2008;130:16231. [PubMed: 18998636]

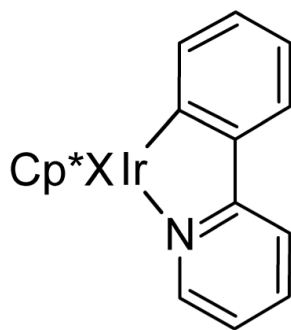
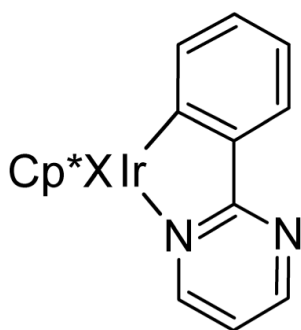
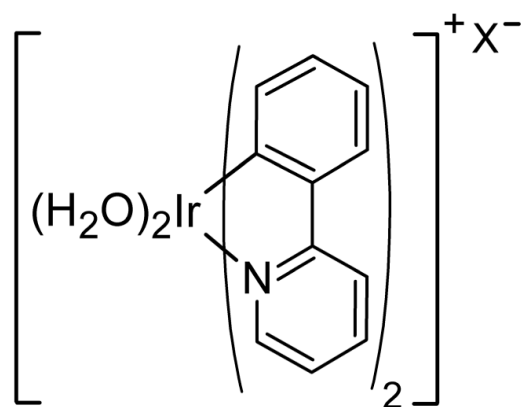
**1a**, X = Cl**1b**, X = OTf**2**, X = Cl**3**, X = OTf

Figure 1.
Iridium catalysts for water oxidation.

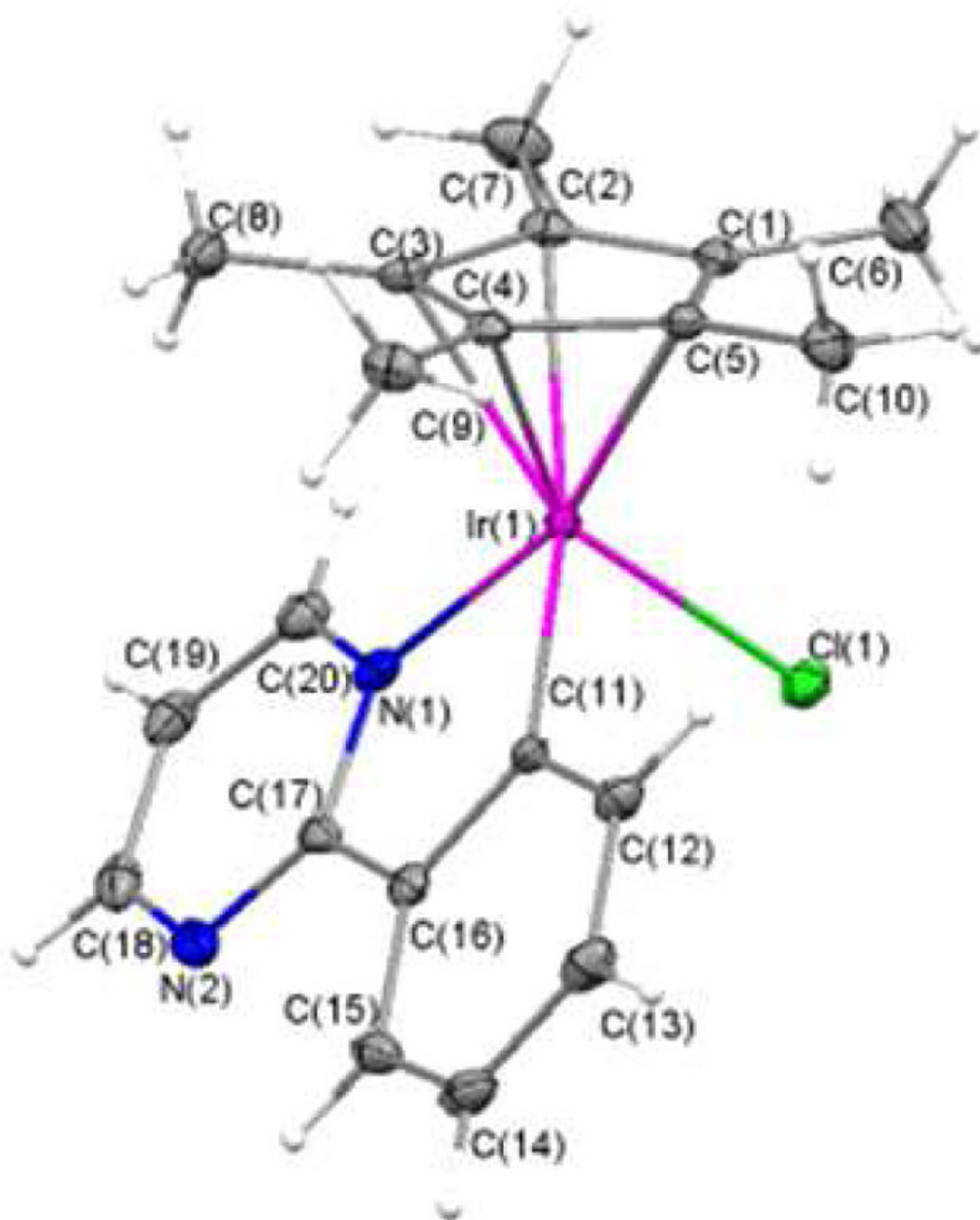


Figure 2.
ORTEP diagram of **2** (see SI for XRD data).

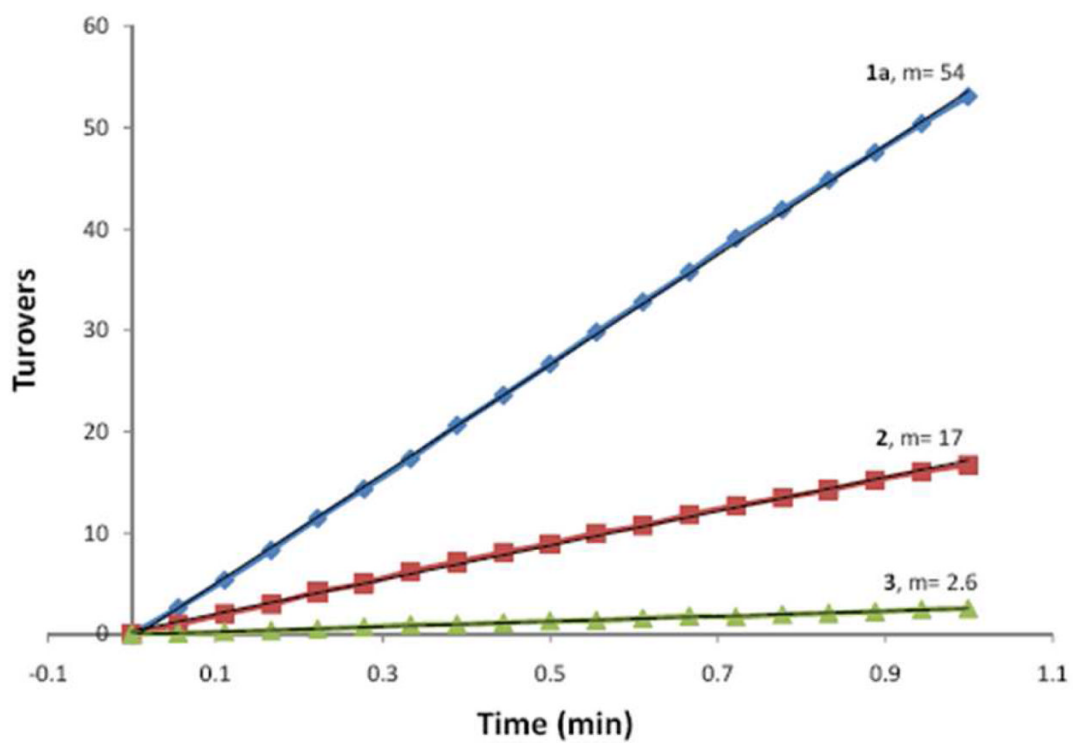


Figure 3. Initial rates for catalysts **1a**, **2** and **3** as measured by a Clark electrode using 38 nmol (5.43 μ M) catalyst and 0.55 mmol (78 mM) CAN in H₂O (7 mL) at 25°C.

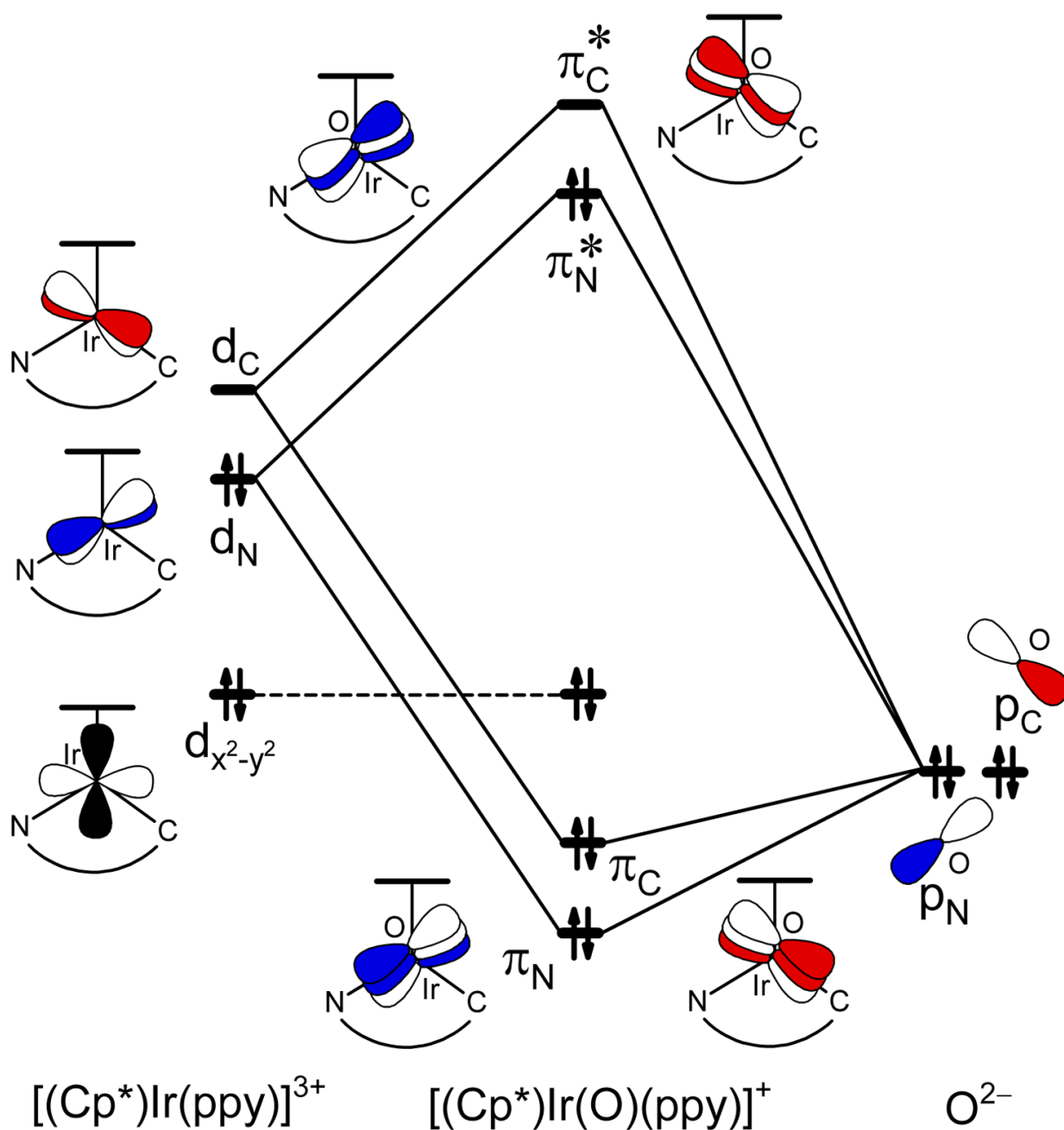


Figure 4. Qualitative interaction diagram for the molecular orbitals of $[(\text{Cp}^*)\text{Ir}(\text{O})(\text{ppy})]^+$ with Ir d and O p contributions.

Table 1
Dioxygen evolution rates for reported homogeneous water oxidation catalysts that use Ce(IV) as oxidant.

Catalyst	Rate ^a	t.o./h ^b	C ^c	Ref.
1a	9100	>1500/5.5 ^d	5.4	this work
2	2800	213/2.5 ^e	5.4	this work
3	50 ^f	2490/168	300	2i
[Ru ₂ (bpy) ₄ (H ₂ O) ₂ O] ⁴⁺	42	5/2	300	2a,2h
[Ru ₂ (bpy)(trpy) ₂ (H ₂ O) ₂] ³⁺	140	19/48	914	2g
[Ru ₂ (npp)(4-Me-py) ₄ Cl] ³⁺	7.7	3200/15	333 ^g	2j
[[Ru(tpy)(pynap)Cl] ⁺	340 ^g	1170/20	67	2l
IrO ₂ (heterogeneous)	14	na	na	2h

^aInitial rate in (t.o./s)×10⁴;

^bTotal t.o./time (h);

^cCatalyst concentration (μM);

^dBy dilatometry using 1.15 M Ce(IV) and 2.90 μM **1a**. See text and SI for details;

^eBy dilatometry using 1.15 M Ce(IV) and 3.09 μM catalyst;

^fWe find 0.042 t.o./s with 5.4 μM catalyst;

^gCalculated from ref. using our scale.