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Introduction

Hydrogen is one of the best energy carriers owing to its high energy density and non-polluting consumption process.^{1–3} Harvesting hydrogen from water using solar and electrical energy has received enthusiastic attention as this solution would result in an inexhaustible feedstock and sustainable energy source.^{4–10} To achieve efficient hydrogen evolution, water reduction catalysts (WRCs) are indispensable, and transition metal complexes have undergone intensive and extensive exploration as homogeneous molecular WRCs. The diverse choice of metal centers, coupled with the rich and tailorable ligands, make them particularly suitable, not only for improving the hydrogen evolution efficiency, but also for understanding the reasons behind this.^{11–14} Among all these complexes, cobalt-based complexes show a high catalytic

Polypyridyl Co complex-based water reduction catalysts: why replace a pyridine group with isoquinoline rather than quinoline?†

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The electronic effect of the substituent has been fully leveraged to improve the activity of molecular water reduction catalysts (WRCs). However, the steric effect of the substituents has received less attention. In this work, a steric hindrance effect was observed in a quinoline-involved polypyridyl Co complex-based water reduction catalyst (WRC), which impedes the formation of Co(m)–H from Co(n), two pivotal intermediates for H₂ evolution, leading to significantly impaired electrocatalytic and photocatalytic activity with respect to its parent complex, [Co(TPA)Cl]Cl (TPA = tris(2-pyridinylmethyl)-amine). In sharp contrast, two isoquinoline-involved polypyridyl Co complexes exhibited significantly improved H₂ evolution efficiencies compared to [Co(TPA)Cl]Cl, benefitting mainly from the more basic and conjugated features of isoquinoline over pyridine. The dramatically different influences caused by the replacement of a pyridine group in the TPA ligand by quinoline and isoquinoline fully demonstrates the important roles of both the electronic and steric effects of a substituent. Our results may provide novel insights for designing more efficient WRCs.

activity and excellent stability,^{15–20} and polypyridyl-based tetradentate and pentadentate ligands can even translate these properties into pure water environments by virtue of their unique stabilization of the metal center.^{21–27}

Although the efficiencies of the studied cobalt complexes differentiate from each other remarkably, their hydrogen evolution has been identified to follow the same mechanism, that is the sequential formation of Co(1) and Co hydride species (Co (III)-H) as key intermediates prior to H-H bond formation.²⁸ Based on this common mechanism, it is expected that ligand modification by either electron withdrawing- or electron donating- groups might lead to an activity enhancement because the former may improve the electron accepting ability of the Co center and therefore facilitate the formation of Co(I), while the latter may increase the pK_a values of both Co(1) and Co(11)-H and therefore favor the protonation processes. This intriguing feature has inspired detailed structure-function relationship studies of Co complex-based WRCs, and it was indeed observed that the introduction of electron-withdrawing groups improved the catalytic activity in some cases,²⁹⁻³¹ but caused the opposite result in other cases.^{32–34}

Although the electronic effect of the substituents has been the focus in ligand modification, the steric effect of substituents has received less attention.³⁵ Very recently, Zhao, Webster and co-workers demonstrated for the first time an unexpected steric effect in Co complex-based WRCs.³⁶ As shown in

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[†]Electronic supplementary information (ESI) available: ¹H-NMR, ESI-MS spectra, UV-visible absorption spectra, photochemistry, electrochemistry, Stern-Volmer plots and computational details. CCDC 2053060 and 2053061. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c9dt04767k



Scheme 1 Co complex-based WRCs reported by Zhao and Webster.³⁶

Scheme 1, they replaced the axial pyridine group with a more basic and conjugate isoquinoline group of a pentadentate ligand and found that the photocatalytic hydrogen evolution efficiency of complex **B** was markedly improved, but that of complex **C** was remarkably impaired with respect to that of complex **A**. The reduced activity of complex **C** is attributed to the nonplanar structure between the isoquinoline moiety and the pyridine group directly linked to it, which on the one hand results from the steric hindrance of the C8–H of isoquinoline and C3–H of pyridine, and on the other hand results in a reduced electron donating ligand, that is unfavorable for proton binding processes.

Interestingly, unlike isoquinoline, which is a more basic and conjugate ligand compared to pyridine, quinoline is a more conjugated, but less basic ligand with respect to pyridine. On the basis of the above discussion, a less basic ligand may assist the formation of the Co(i) intermediate. Will this benefit give rise to enhanced hydrogen evolution efficiency? The improved activity was clearly observed in the Co complexbased electrocatalytic and photocatalytic reduction of CO_2 to $CO.^{37}$ Lu, Zhong and co-workers found that the replacement of one or two pyridine groups of a tetradentate ligand, TPA (tris (2-pyridinylmethyl)-amine), with quinoline could significantly increase the CO_2 catalytic activity. The resultant Co complexes were reported to be highly specific in CO production. Does this mean that they are poor WRCs? Does the electronic effect, or the steric effect, or both, play a decisive role?

Bearing these questions in mind and in light of the excellent hydrogen evolution³⁸ and CO_2 reduction³⁹ activity of [Co (TPA)Cl]Cl, we herein systematically explored the effects of the substitution of a pyridine group of TPA by either quinoline or isoquinoline on the hydrogen evolution activity. To this end, four Co complexes **C1–C4** (Scheme 2), based on TPA (**L1**), BPQA (**L2**, *N*,*N*-bis(2-pyridinylmethyl)-quinoline-6-methana-



Scheme 2 Chemical structures of ligands L1–L4 and the corresponding Co complexes C1–C4.

mine), DPA-3-IQA (L3, *N*,*N*-bis(2-pyridinylmethyl)-isoquinoline-3-methanamine), and DPA-1-IQA (L4, *N*,*N*-bis(2-pyridinylmethyl)-isoquinoline-1-methanamine), respectively, were prepared and compared in detail. The electrocatalytic and photocatalytic experiments, as well as density functional theory (DFT) calculations show that the influences of the extra benzene group are highly dependent on the position in which it is fused onto the pyridine group of TPA. For complexes C3 and C4, isoquinoline replacement improves the hydrogen evolution activity to some extent, mainly owing to the electronic effect. In the case of C2, the steric effect is observed to overturn the electronic effect, fully demonstrating the important role of the steric interaction in designing efficient WRCs.

Results and discussion

Synthesis and characterization

Complexes **C1–C4** were synthesized in two steps, as previously reported.³⁸ The identity of the corresponding ligands and complexes have been characterized using ¹H NMR (Fig. S1–S4†), electron spray ionization mass spectrometry (ESI-MS) (Fig. S5– S12†), UV-vis absorption spectra, cyclic voltammetry, singlecrystal X-ray diffraction and elemental analysis. Interestingly,



Fig. 1 Single-crystal X-ray structures of complexes C3 (a) and C4 (b). C atoms (gray), N atoms (blue), Co atoms (yellow), Cl atoms (blue), H atoms are omitted for clarity. The bond lengths of Co-Cl are given in Å.

the single crystal structures of C3 and C4 adopt a distorted octahedral geometry with two chlorido ligands as presented in Fig. 1, instead of the common trigonal-bipyramidal geometry of the TPA ligand-based $Cu(\pi)$ and $Co(\pi)$ complexes, including C1 and C2.^{24,37,40,41} We found the extra chlorido ligand on the equatorial position has a much longer Co-Cl bond distance than the axial one (2.446 Å vs. 2.364 Å in C3, 2.444 Å vs. 2.358 Å in C4). The subsequent DFT calculations (Fig. S30[†]) confirm that the dissociation of the equatorial chloride ions could result in a five-coordinate configuration with lower energy in the solvent sphere for both complexes. Additionally, there should be 14 groups of aromatic proton signals for C3 owing to the un-equivalent pyridine groups of TPA in an octahedral coordination geometry, however, its ¹H NMR spectra in D₂O (Fig. S13[†]) only showed 10 groups of aromatic proton signals, consistent with a five-coordinate configuration. All of these suggest that both C3 and C4 may readily form a similar trigonal-bipyramidal geometry to C1 and C2 once dissolved in a solvent. The subsequent calculations and discussion of C1-C4 all begin from this solution configuration.

The UV-vis absorption spectra of C1–C4 were recorded in CH₃CN (Fig. S14†) and the spectrum of C1 is in good agreement with the previously published literature.^{39,42} The absorption bands that occurred in the region of 450–700 nm may be attributable to the d–d transitions of C1–C4. Their molar extinction coefficients fall in the range of 150–210 M^{-1} cm⁻¹ (Table S1†), in line with the character of a Co complex with a five-coordinate configuration in acetonitrile.⁴²

The optimized structures of C1–C4 in H₂O are shown in Fig. 2, all of them adopted a distorted trigonal-bipyramid geometry, in which ligands L1–L4 act as tetradentate ligands with the aliphatic N atom occupying an apex and a chloride ion occupying the other apex of the bipyramid. The optimized structures of C1 and C2 are in very good agreement with the single crystal structures determined by Wang and co-workers (CCDC numbers 1529343: [Co(TPA)Cl]ClO₄ and 1529345: [Co (BPQA)Cl]ClO₄·CH₃OH†).³⁷ The Co–N bond lengths listed in Table 1 are in good agreement with a high spin Co(II) complex.^{29,43,44}



Fig. 2 Optimized structures of C1–C4 (a)–(d) in H_2O . C atoms (gray), N atoms (blue), Co atoms (yellow), Cl atoms (blue), H atoms are omitted for clarity.

Table 1Selected bond lengths (Å) and angles (°) from the optimizedstructures of C1-C4 in H2O and single crystal data from CCDC numbers1529343 ([Co(TPA)Cl]ClO4) and 1529345 ([Co(BPQA)Cl]ClO4·CH3OH)†

Selected bond lengths (Å) and angles (°)					
	Co-N1	Co-N2	Co-N3	N1-Co-Cl	
	$\begin{array}{c} 2.11370\\ 2.18561\\ 2.10349\\ 2.10800\\ 2.056\\ 2.111\end{array}$	2.11321 2.13541 2.11435 2.11575 2.069 2.078	2.11432 2.14365 2.11631 2.11903 2.060 2.075	$103.45674 \\114.51847 \\103.54262 \\104.66401 \\104.46 \\111.18$	

It is worth noting that the Co-N1 lengths of the optimized structures follow the order $C2 \gg C1 > C4 > C3$. A similar trend may also be found from the crystal data of [Co(TPA)Cl]ClO₄ and [Co(BPQA)Cl]ClO₄·CH₃OH. Generally, a more basic ligand tends to bind a metal center more strongly. The Co-N1 lengths of C1-C4 have a clear correlation with the pK_a values of the related N donors, that is, quinoline (4.85) < pyridine (5.17) < isoquinoline (5.45).⁴⁵ The more basic character of isoquinoline leads to the shorter Co-N1 lengths of C3 and C4. It also suggests that the proton binding processes of the Co(1) and Co(11)-H intermediates might be more favorable in C3 and C4 than in C1 and C2.³⁶ In the case of C2, the significantly lengthened Co-N1 bond may not result from the less basic features of quinoline alone, the effects of steric hindrance are also expected to make a contribution. As shown in Table 1, the N1-Co-Cl angle of C2 from either the optimized structure or crystal data is much larger than those of C1, C3 and C4, suggesting a strong repulsion between the axial chloride ion and the H atom at the C8 position of quinoline. This steric hindrance may have a large impact on its catalytic activity (vide post).

Electrochemical properties

The electrochemical properties of C1–C4 were studied using cyclic voltammetry in anhydrous CH₃CN under an argon atmo-

Table 2 Reduction potentials (V vs. SCE) of C1–C4 in 0.1 M TBAPF₆ anhydrous MeCN (Ar, scan rate 100 mV s⁻¹) and their potential catalytic wave values upon the addition of 2.5 mM acetic acid

	$\mathrm{Co}^\mathrm{II} \to \mathrm{Co}^\mathrm{I}$	$\mathrm{Co^{I}} \rightarrow \mathrm{Co^{0}}$	Potential of catalytic wave
C1	-1.57	-1.79	-1.61
C2	-1.43	-1.82	-1.68
C3	-1.53	-1.69	-1.60
C4	-1.55	-1.74	-1.62

sphere (Table 2 and Fig. S15[†]). Upon the cathodic scan, all complexes showed quasi-reversible Co^{II/I} and irreversible Co^{I/0} events.³⁷⁻³⁹ The peak current of the Co^{II/I} couple for all the complexes were raised linearly with the square root of the scan rate, which indicates the processes are diffusion controlled (Fig. S16–S19 \dagger). For C2, the reduction potential of the Co^{II/I} couple is much more positive than that of C1, implying the Co center of C2 is easier to reduce. This finding is in good agreement with that of Wang and co-workers,³⁷ and may be ascribed to the weaker electron donating ability of quinoline, as well as the much longer Co-N1 length of C2. Both reasons may decrease the electron density on the Co center and facilitate its reduction. There is also a small positive shift observed for the Co^{II/I} couples of C3 and C4. Similar results were also observed for the Co complexes B and C, and are attributed to the more conjugate feature of isoquinoline with respect to pyridine.⁴⁶

We used acetic acid as a mild proton source to evaluate the electrocatalytic hydrogen evolution activities of C1-C4. Upon the addition of acetic acid (Fig. S21[†]), a significant current enhancement was observed over the Co^{II/I} couples, indicative of the immediate formation of a Co(III)-H species followed by hydrogen evolution. In the absence of Co complexes, a negligible current increase was recorded (Fig. S24[†]), confirming the catalytic hydrogen evolution stems from these complexes. Interestingly, in contrast to its most positive Co^{II/I} reduction potential, C2 showed a catalytic wave at the most negative potential (Table 2 and Fig. S20[†]). It seems that C2 encounters an obstacle in proton binding, though it can obtain electrons from the cathode more efficiently than the other three complexes. Considering the abovementioned steric hindrance between the axial chloride ion and the C8-H of quinoline, it may be anticipated that proton binding to the Co center may also experience a similar hindrance, leading to the lower electrocatalytic hydrogen evolution efficiency of C2.

The controlled potential electrolysis (CPE) experiments of the Co complexes (1 mM) were performed in CH₃CN solutions (10 mL) containing 140 mM acetic acid as a proton source and 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) as a supporting electrolyte. The charge accumulation and current changes during 1 h of electrolysis at -2.0 V are displayed in Fig. S22.[†] The stable currents in all cases demonstrate the stability of the catalysts. After the CPE experiments, the GC (glass carbon) electrode was rinsed with water and used again in CH₃CN-acetic acid-TBAPF₆ solutions without further polishing. A negligible catalytic current was found (Fig. S23[†]), indicating that the electrocatalytic reaction are homogeneous and



Fig. 3 Controlled potential electrolysis at -2.0 V versus SCE of 1 mM C1-C4 and blank in 0.1 M TBAPF₆ MeCN with 140 mM acetic acid under an argon atmosphere.

no active materials were deposited on the electrode. All complexes revealed near quantitative faradaic efficiency for hydrogen evolution (Table S2†). For C3, 0.0446 mmol of hydrogen was obtained and the hydrogen generated by C4, C1, and C2 decreased in sequence (Fig. 3). Obviously, the substitution of pyridine by the more basic and conjugate isoquinoline promotes electrocatalytic hydrogen evolution. Similar effects were also observed in the cases of complexes **A**, **B**, and **C**,³⁶ suggesting such a replacement may be a general strategy for hydrogen evolution and can be leveraged in other pyridineinvolving ligands. In sharp contrast, replacement by quinoline impairs the hydrogen evolution activity. In light of the opposite effect that the quinoline replacement aroused during CO₂ reduction,³⁷ the underlying mechanisms deserves investigation.

Photocatalytic H₂ evolution

The photocatalytic experiments of C1-C4 were performed in a multi-component system, in which [Ir(ppy)2(dtbpy)]Cl (ppy = 2-phenylpyridine, dtbpy = 4,4'-di-tert-butyl-2,2'-bipyridine) was used as a photosensitizer (PS) and triethylamine (TEA) as a sacrificial electron donor (SD). After optimization (Fig. S25 and S26[†]), we selected conditions of 0.2 mM PS, 0.3 M SD, and 10 µM cobalt complexes in CH₃CN/H₂O (8:2, v/v) for photocatalytic reactions. The control experiments shown in Table S3[†] indicate that all three components (PS, WRC, and SD) and light are necessary for efficient hydrogen evolution. No significant decay was observed during the Hg poisoning experiments (Fig. S27[†]), suggesting the active catalysts are the Co complexes rather than Co metal. The H₂ production rates slowed down after 1.5 h of irradiation. In our attempt to restore the H₂ production activity, PS, SD, or the cobalt complexes were, respectively, added to the solution. Only the addition of PS was found to recover the H2 evolution (Fig. S28[†]) indicating that the decomposition of the PS is responsible for the loss of activity.

Under optimal conditions, the photocatalytic activities of the complexes follow the order C3 > C4 > C1 > C2 (Fig. 4), a



Fig. 4 Photocatalytic H₂ production of C1–C4 after 6 h of irradiation. Conditions: 0.2 mM [Ir(ppy)₂(dtbpy)]Cl, 0.3 M TEA, and 10 μ M catalyst in MeCN/H₂O (8 : 2), 455 nm 40 W LED.

trend identical to that observed in the electrocatalytic hydrogen evolution experiments. The TONs (turnover numbers *vs.* catalyst) of **C3** and **C4** reached 10234 and 8849, higher than that of **C1** (7851). Surprisingly, **C2** only achieved a turnover number (TON) of 1043, far lower than that of **C1**. Clearly, the introduction of an isoquinoline group to replace a pyridine group of the TPA ligand also facilitates the photocatalytic activity of the resultant complexes, but the structurally similar quinoline group results in a totally opposite effect, even worse than the case of electrocatalytic hydrogen evolution.

The main difference between both types of hydrogen evolution lies in the reduction pathways of the Co-based WRCs to form the Co(1) intermediate. In electrocatalytic cases, the electrons come from the cathode. In contrast, the electrons are provided by either the excited PS (PS*) or the reduced PS (PS⁻). To elucidate the mechanism, we measured the luminescence quenching of the Ir-based PS by C1-C4 and SD. As shown in Fig. S29 and Table S4,† the quenching rate constants follow the order $C3 > C1 > C4 > C2 \gg$ SD. However, owing to the significantly higher concentration of SD (0.3 M) over that of the complexes (10 µM), the PS* is reduced by SD first, followed by donation of an electron to a Co complex. Although the quenching of PS* by the catalyst did not dominate in the photocatalytic reactions, it is very surprising that the quenching rate constant of C2 is the lowest one among the examined complexes. In contrast, the most efficient quenching by C2 is expected to result from C2, which exhibits a more positive reduction potential for the Co^{II/I} couple than the other three complexes. A possible explanation is that C2 has some difficulty in accepting electrons from PS⁻, and the reason for this most likely originates from some type of steric hindrance which does not exist in the electrode reactions. As a result, the dual steric hindrance in both the reduction and proton binding leads to the dramatically diminished photocatalytic activity of C2.

Mechanism discussion

The mechanism for the catalytic H_2 evolution of cobalt complexes has been established through a decade of research.^{47–52}



Scheme 3 Proposed mechanism of hydrogen evolution catalyzed by the cobalt complexes C1–C4.

For our Co complexes, a possible photocatalytic mechanism is presented in Scheme 3. Upon irradiation, the excited PS (PS*) is quenched by SD first to form PS⁻. Then, the Co^{II}–Cl–L complex (L denotes our tetradentate ligand) gains an electron from PS⁻, and is reduced to the unstable Co^I–Cl–L species, which carries a longer Co–Cl bond and a larger Cl–Co–N1 angle, as shown in Fig. S31 and Table S5,† the subsequential Co–Cl bond dissociation reduces the energy while the dissociation of other Co–N bonds does not (Table S6†). The subsequent protonation of Co^I–L generates another key intermediate, Co^{III}–H–L. Further reduction and protonation complete the entire hydrogen evolution cycle.

In most cases, both Co(1) and Co(11)–H are the most pivotal intermediates in the H₂ evolution reactions. Accordingly, we performed DFT calculations for **C1–C4** to gain insights into their optimized structures and energies, as well as the free energy changes of their transformations. After dissociation of the chloride ligand, all Co(1) intermediates of **C1–C4** show a very similar coordination geometry, as evidenced by their similar Co–N bond lengths and N–Co–N angles (Table S7 and Fig. S32†). This result confirms that the steric effect present in **C2** results from the repulsion of the chloride ligand and the C8–H atom of quinoline. Interestingly, the formation of the Co (1) and Co(1)–C1 intermediate of **C2** shows the largest Gibbs free energy reduction among the four complexes (Fig. 6), which seems to be in line with the most positive reduction potential of the Co^{II/I} couple of **C2**.

The optimized structures of the Co(III)-H intermediates could also provide critical information. We found that the triplet Co(m)-H states present a trigonal-bipyramidal geometry, which has a lower energy than that of the singlet Co(III)-H states with a pseudo-octahedron geometry (Fig. 5, S33 and Table S8[†]). For these lowest-lying triplet Co(III)-H states, the H-Co-N1 angle of C2 is 98.81°, larger than that of C1 (96.83°), C3 (96.29°) and C4 (96.65°). It is not hard to find that the C8-H of quinoline is only 1.968 Å away from the hydride coordinated with the cobalt atom, as shown in Fig. 5b, much closer than the corresponding atoms from other intermediates of C1, C3 and C4. In this case, the repulsion between both the H atoms may result in an unstable Co(III)-H intermediate, leading to a more positive Gibbs free energy change for the transformation from Co(I) to Co(III)-H as presented in Fig. 6 and accounting for the poor performance of C2.

In contrast to C2, the catalytic performance of complexes C3 and C4 was improved. Looking deep into the spin density



Fig. 5 Optimized structures for the triplet Co(m)-H intermediates of C1-C4 (a)-(d), the N-Co-H bond angles (given in °) are shown in the corresponding positions. The distance between selected H atoms is given in Å.



Fig. 6 DFT-calculated free energy profile for the formation of the key intermediates of complexes C1 to C4.

distributions of their triplet Co(m)-H intermediates, as shown in Fig. S34,† we found that the spin population values on the cobalt atoms of C1 to C4 are 2.292, 2.381, 2.262, 2.275 separately. The higher degree of delocalization of the unpaired electrons on cobalt atoms stabilizes the Co(m)-H intermediates of C3 and C4. As a result, an easier transformation from Co(i) to Co(m)-H, as evidenced by their less positive Gibbs free energy changes (Fig. 6 and Table S8†), may correlate with their higher H₂ evolution activity.

If the poor H_2 evolution catalytic activity of C2 is ascribed to the steric effect, several questions naturally arise. Owing to its much bigger size, will a CO₂ molecule face a much larger repulsive force when approaching the Co(1) species of C2? How to better understand the fact that C2 is more efficient in CO₂ reduction than C1,³⁷ but less efficient in proton reduction than C1? Both questions may also be translated in another way, why is C2 so specific to CO₂ reduction when both CO₂ and H₂O are present. We surmise the oxygen atoms of CO₂ may have somewhat attractive interactions with the C8–H atom of the quinoline.⁵³ Additionally, as CO₂ is a neutral molecule, a significantly reduced electrostatic repulsion is expected compared to the case of a proton when approaching a positively charged complex.

Conclusions

By fusing an extra benzene ring onto the pyridine group of the TPA ligand (L1), we obtained ligands L2–L4 and their Co complexes C2–C4. Compared to their parent complex C1, C3 and C4 can catalyze H₂ evolution either electrocatalytically or photocatalytically more efficiently. The more basic and conjugate isoquinoline structure may facilitate stabilization of the key intermediate Co(m)–H and is therefore responsible for the improved catalytic activity of C3 and C4. In the case of C2, the effect of steric hindrance between the axial hydride and the C8–H atom of the quinoline group would be averse to the transformation from Co(1) to Co(m)–H. These results contribute to a better understanding of the electronic and steric effects that occur in catalytic H₂ evolutions reactions, and may provide novel insights into the design of more efficient WRCs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Dalton Transactions

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