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# Rearranging spin electrons by axial-ligand-induced hybridization state transition to boost the activity of nickel single-atom-catalysts for electrochemical CO<sub>2</sub> reduction†

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Single-atom catalysts (SACs) with M–N<sub>4</sub> active sites show great potential to catalyze the electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) toward CO. The activity and selectivity of SACs are determined by the local coordination configuration of central metal atoms in M–N<sub>4</sub> sites, which is readily tuned by axial ligands. In this work, we construct axial ligands *in situ* on two Ni–N<sub>4</sub>-type model SACs, NiPc and Ni–N–C, by adding Cl<sup>−</sup> into the electrolyte taking advantage of the strong chemisorption of Cl<sup>−</sup> over Ni–N<sub>4</sub>. Cl axial ligand lowers the energy barrier of the potential-determining step for the eCO<sub>2</sub>RR due to a hybridization state transition of Ni orbitals and the resulting rearrangement of spin electrons. Consequently, both NiPc and Ni–N–C with axial Cl exhibit superior activity for the eCO<sub>2</sub>RR toward CO. Finally, we propose the magnetic moment of Ni as a universal descriptor for the eCO<sub>2</sub>RR toward CO on Ni–N<sub>4</sub> with various axial ligands.

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## Introduction

The electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) yielding value-added chemicals and fuels, coupled with renewable electricity, offers a sustainable solution to achieve carbon neutrality.<sup>1</sup> The products of the CO<sub>2</sub>RR vary from C1 (CO, CH<sub>4</sub>, HCOOH, CH<sub>3</sub>OH, *etc.*) to C2+ (CH<sub>3</sub>CH<sub>2</sub>OH, C<sub>2</sub>H<sub>4</sub>, *etc.*).<sup>2</sup> The high energy barrier for C–C coupling, which is the key step to form C2+ products, generally leads to high overpotential and low selectivity for the eCO<sub>2</sub>RR toward C2+.<sup>3</sup> In contrast, C1 products with fewer electrons transferred (*e.g.*, CO and HCOOH) are economically favorable due to their low overpotential,<sup>3</sup> high selectivity, and enhanced energy efficiency.<sup>4</sup> CO constitutes a crucial raw material in industrial production processes.<sup>5</sup> Particularly, CO and H<sub>2</sub> (the by-product of the eCO<sub>2</sub>RR) with a tunable ratio co-produced by the eCO<sub>2</sub>RR can be readily used

as a feedstock for syngas.<sup>6</sup> In addition, cascade eCO<sub>2</sub>RR systems, which integrate two consecutive steps of CO<sub>2</sub>-to-CO and CO-to-C2+ either within one CO<sub>2</sub> electrolyzer using a bifunctional cathode or in two tandem CO<sub>2</sub> and CO electrolyzers,<sup>7–9</sup> have been reported to boost the current density and faradaic efficiency (FE) for the eCO<sub>2</sub>RR toward C2+. Thus, extensive efforts have been devoted to exploring catalysts for the eCO<sub>2</sub>RR toward CO with outstanding activity and tunable selectivity in the past decades.<sup>10,11</sup>

Single-atom catalysts (SACs) with unique electronic and geometric structures exhibit superior activity and selectivity for the eCO<sub>2</sub>RR toward CO.<sup>12,13</sup> The M–N<sub>4</sub> (M = Fe, Co, Ni, Cu, *etc.*) moieties, in both macrocyclic metal complexes (metal porphyrins, metal phthalocyanines (MPc), *etc.*) and their analogous metal–nitrogen–carbon (M–N–C) materials, are widely accepted as active sites.<sup>14,15</sup> Particularly, nickel SACs deliver extraordinary performance with a FE >90% at a wide potential range.<sup>16,17</sup> However, nickel SACs still suffer from insufficient activity in practical CO<sub>2</sub> electrolyzers, leading to a significantly reduced selectivity of the eCO<sub>2</sub>RR toward CO at high current densities (*e.g.*, >200 mA cm<sup>−2</sup>).<sup>17</sup> Thus, it is pivotal to further boost the activity of Ni SACs for the eCO<sub>2</sub>RR toward CO to promote their feasible implementation in large-scale CO<sub>2</sub> electrolyzers. It is reported that the symmetric D<sub>4h</sub> square-planar geometry of Ni–N<sub>4</sub> is unfavorable for adjusting the spatial distribution of electrons and, consequently impedes the electron transfer during electrochemical reactions.<sup>17–20</sup> Hence, breaking the D<sub>4h</sub> symmetry of Ni–N<sub>4</sub> *via* geometric distortion modulates their

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electronic structures, leading to accelerated electron transfer and enhanced activity of nickel SACs for the eCO<sub>2</sub>RR toward CO.<sup>21</sup>

Regulating the planar and axial ligands are two major strategies for tuning the geometric and electronic structures of M–N<sub>4</sub>.<sup>22–25</sup> Planar ligand regulation includes doping with heteroatoms,<sup>26,27</sup> engineering surface vacancies,<sup>28,29</sup> adjusting coordination numbers,<sup>30</sup> and constructing multi-atom sites.<sup>6</sup> For example, S. Ji *et al.*<sup>31</sup> incorporated P heteroatoms in the second coordination shell of Fe–N<sub>4</sub> to break the local symmetry of electron distribution, leading to excellent activity and stability for oxygen reduction and evolution reactions. S. Chen *et al.*<sup>32</sup> doped sulfur in the second coordination shell of Fe–N<sub>4</sub>, which induces a pronounced proton-feeding effect to boost the eCO<sub>2</sub>RR. However, it remains a great challenge for the precise and site-specific manipulation of the first and/or secondary coordination shell of central metal atoms, resulting in heterogeneous structures of planar coordination particularly for M–N–Cs obtained by high-temperature pyrolysis.<sup>33,34</sup> In contrast, M–N<sub>4</sub> sites with axial ligands constitute a well-defined proximal coordination configuration with tunable geometric and electronic structures.<sup>22</sup> M. Li *et al.*<sup>35</sup> reported an electronic localization enhancement of Ni–N<sub>4</sub> induced by the Cl axial ligand, accounting for the superior HER activity of Ni–N<sub>4</sub>–Cl. However, electronic-level insights into the axial effect in tuning the eCO<sub>2</sub>RR activity of M–N<sub>4</sub> moieties are still lacking, which is crucial for designing highly efficient SACs for the eCO<sub>2</sub>RR.

Herein, we systematically investigated the electronic structures and eCO<sub>2</sub>RR activities of two Ni–N<sub>4</sub>-type model SACs, namely NiPc and Ni–N–C, with and without the axial ligand. The axial ligand is introduced *in situ* by adding Cl<sup>–</sup> into the electrolyte taking advantage of the strong chemisorption of Cl<sup>–</sup> on Ni–N<sub>4</sub>. The Cl axial ligand induces a transition in hybridization states of Ni orbitals and a rearrangement of spin electrons, leading to the low energy barrier for the formation of key intermediate COOH\*. As a result, Ni–N<sub>4</sub> SACs with Cl axial ligands exhibit an enhanced CO partial current density. The magnetic moment of Ni is proposed as a universal descriptor for the eCO<sub>2</sub>RR toward CO on Ni–N<sub>4</sub> with various axial ligands. This study provides a feasible strategy for screening highly efficient M–N<sub>4</sub>-type SACs with axial ligands for the eCO<sub>2</sub>RR toward CO.

## Results and discussion

There are two typical classes of SACs extensively investigated for the eCO<sub>2</sub>RR: macrocyclic metal complexes (*e.g.*, MPc) with a well-defined square-planar M–N<sub>4</sub> coordination configuration<sup>36</sup> and their analogous M–N–Cs consisting of isolated metal atoms anchored on nitrogen-doped carbon.<sup>37</sup> M–N–Cs derived from high-temperature pyrolysis generally show heterogeneous structures, with well-recognized structures of bulk-hosted M–N<sub>4</sub>–C<sub>10</sub> moieties embedded within a graphene sheet (denoted as MN<sub>4</sub> hereafter) and edge-hosted M–N<sub>2+2</sub>–C<sub>4+4</sub> bridging two adjacent graphene sheets (denoted as MN<sub>2+2</sub> hereafter).<sup>38–40</sup> Taking into consideration the superior activity and selectivity of Ni–N<sub>4</sub> moieties,<sup>17,36</sup> we focus on Ni SACs and exploit NiPc, NiN<sub>4</sub> and NiN<sub>2+2</sub> as representative model structures (Fig. 1a–c) to

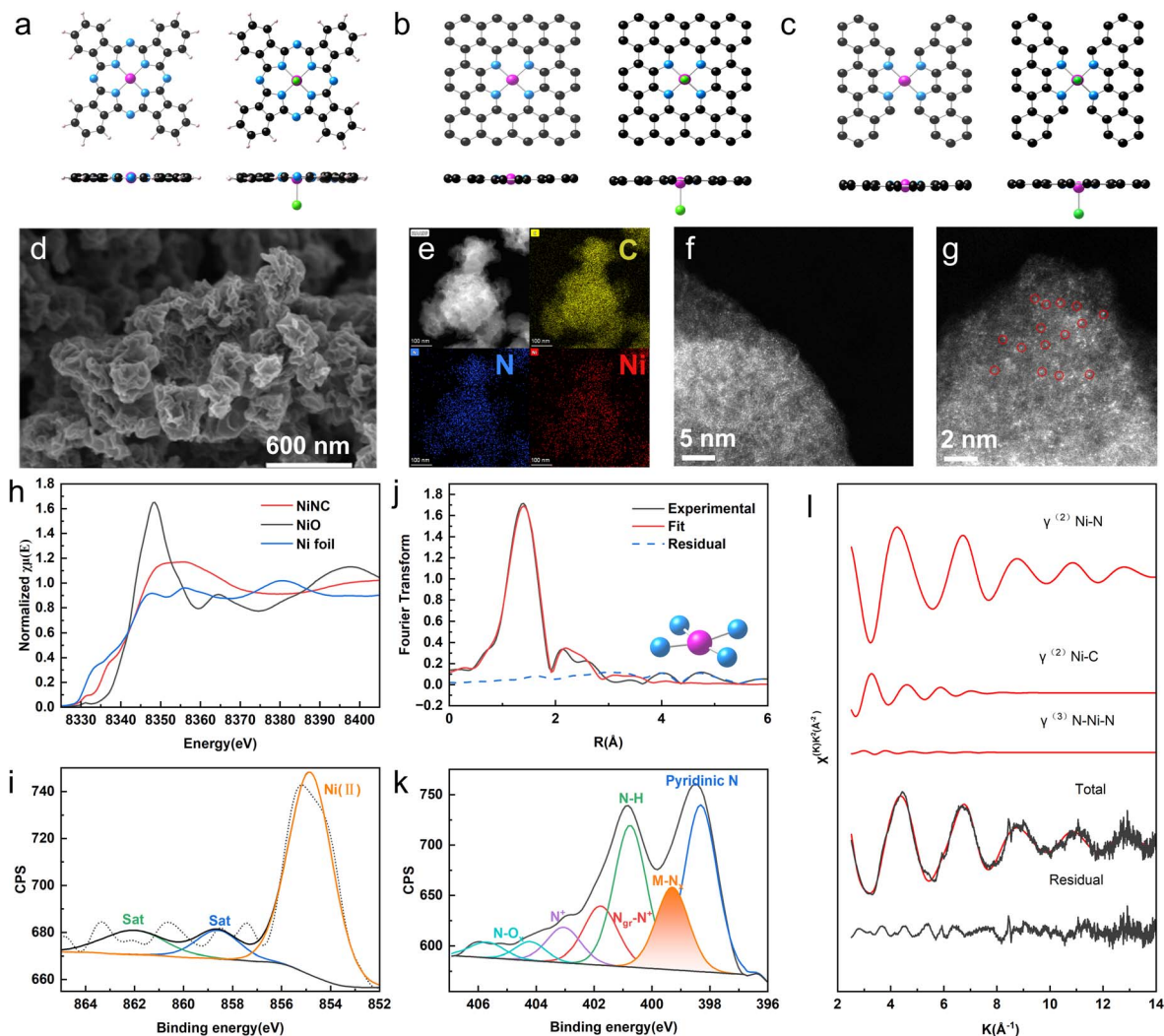
investigate the effect of axial ligands on their electrocatalytic activity for the eCO<sub>2</sub>RR toward CO *via* density functional theory (DFT) simulations.

We then utilized NiPc and Ni–N–C as model catalysts to verify the positive effect of Cl axial ligand on the electrolytic activity of Ni–N<sub>4</sub> for the eCO<sub>2</sub>RR toward CO. NiPc was loaded on carbon supports *via* ball milling to enhance the electronic conductivity, followed by a heat treatment under milder conditions (300 °C) to stabilize NiPc on carbon without altering its structure.<sup>41,42</sup> A Ni–N–C material consisting of atomically dispersed nickel sites was synthesized according to our previous work.<sup>43</sup> The X-ray diffraction (XRD) pattern of Ni–N–C reveals two characteristic peaks of disordered carbon (Fig. S1a†), and the defective structure of carbon is further supported by the high intensity of D band at 1350 cm<sup>–1</sup> in the Raman spectrum (Fig. S1b†). The scanning electron microscopy (SEM) image indicates a porous structure of Ni–N–C (Fig. 1d), which consists of abundant micropores and mesopores (Fig. S1c and d†). The Brunauer–Emmett–Teller surface area of Ni–N–C is 223 m<sup>2</sup> g<sup>–1</sup> (Table S1†). The highly microporous and defective structure of the carbon matrix is favorable to anchor single atoms of transition metals.<sup>44</sup> The energy-dispersive X-ray spectroscopy (EDX) mappings show a uniform distribution of Ni, N, and C elements in Ni–N–C (Fig. 1e). No metallic particle is observed after an extensive evaluation of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 1f), in good agreement with the absence of characteristic peaks arising from nickel-based agglomerates in XRD (Fig. S1a†). The isolated nickel atoms are distinctly visible (highlighted by red circles) in the abbreviation-corrected STEM image (Fig. 1g), confirming that nickel in Ni–N–C is present as single atoms.

The atomically dispersed nature of nickel in Ni–N–C is further supported by X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) (Fig. 1h–l). The Ni 2p X-ray photoelectron spectroscopy (XPS) spectrum of Ni–N–C delivers only one main peak arising from Ni<sup>2+</sup> accompanied by several satellite peaks, and Ni<sup>0</sup> species is not detected (Fig. 1i).<sup>45</sup> The XANES spectrum of Ni–N–C significantly deviates from that of NiO (Fig. 1h), suggesting that the Ni<sup>2+</sup> species detected in XPS is not in the form of oxide. Meanwhile, the Fourier transform of extended X-ray absorption fine structure (EXAFS) exhibits negligible signals at ~2.1 and ~2.4 Å attributed to the Ni–Ni backscattering in metallic nickel and nickel oxide (Fig. 1j and S3†), indicating the absence of nickel-based agglomerates. Thus, XPS, EXAFS, XRD and STEM characterization studies unambiguously demonstrate the atomic dispersion of nickel in Ni–N–C. The nickel content in Ni–N–C is 0.22 at% according to XPS (Table S2†).

Then we elucidate the coordination environment of atomically dispersed nickel sites in Ni–N–C with detailed analysis of N 1s XPS and EXAFS spectra. Five nitrogen species are identified in the N 1s XPS spectrum of Ni–N–C, namely, N in M–N<sub>x</sub>, pyrrolic N (labeled as N–H), pyridinic N, graphitic N (including N<sub>gr</sub> and N<sup>+</sup>), and N–O<sub>x</sub> (Fig. 1k and Table S3†).<sup>43</sup> The presence of abundant M–N<sub>x</sub> suggests that nickel coordinates with nitrogen defects in the carbon matrix. Thus, we fit the Fourier transform





**Fig. 1** The morphology and structure of Ni–N–C. Top views (upper panel) and side views (lower panel) of model structures for (a) NiPc, (b) NiN<sub>4</sub> and (c) NiN<sub>2+2</sub> with and without Cl axial ligand. The black, blue, purple, green, and white balls represent C, N, Ni, Cl, and H atoms, respectively. (d) SEM image. (e) HAADF-STEM image and the corresponding EDX mappings. (f and g) Abbreviation-corrected STEM images with different magnifications. (h) Ni K-edge XANES spectrum. The spectra for nickel foil and nickel oxide powders are also presented as references. (i) Ni 2p XPS spectrum. (j) The Fourier transform of experimental and best fit Ni K-edge EXAFS spectra. Inset is the schematic model for the best fit, with nickel and nitrogen atoms represented by purple and blue balls, respectively. No phase-shift correction was applied to the Fourier transforms. (k) N 1s XPS spectrum. (l) Ni K-edge EXAFS analysis: Ni–N, Ni–C  $\gamma(2)$  two-body signals and the N–Ni–N  $\gamma(3)$  three-body signal included in the fit, the total signal (red line) superimposed on the experimental one (black line).

of the experimental EXAFS spectrum of Ni–N–C with a variable number of in-plane nitrogen atoms binding the Ni<sup>2+</sup> center (inset of Fig. 1j), and the best-fit result shows a coordination number of 4.3 and a Ni–N bond distance of 1.92 Å (Table S4†). The dominant contribution is given by Ni–N first shell coordination (Fig. 1l), leading to the major peak at 1.5 Å in the Fourier transform of the EXAFS spectrum (Fig. 1j). In contrast, Ni–C second shell coordination contributes to the minor peak in the range of 2–3 Å (Fig. 1j and l).<sup>40</sup> The intensity of the N–Ni–N signal is insufficient to determine the bond angle and, consequently, the geometric structure of the Ni–N<sub>4</sub> moiety. Therefore, the nickel single atoms in Ni–N–C are mainly present in the form of Ni–N<sub>4</sub> moieties, with either square-planar or distorted geometry.

The eCO<sub>2</sub>RR toward CO undergoes four elementary steps (written for acidic solutions): (1) CO<sub>2</sub>(g) + \* → CO<sub>2</sub>\*, (2) CO<sub>2</sub>\* + H<sup>+</sup> + e<sup>−</sup> → COOH\*, (3) COOH\* + H<sup>+</sup> + e<sup>−</sup> → CO\* + H<sub>2</sub>O(g), and (4) CO\* → CO(g) + \*,<sup>46</sup> with a debatable potential-determining step (PDS) of either COOH\* formation or CO<sub>2</sub>\* adsorption.<sup>46,47</sup> The configurations of all elementary steps on NiPc, NiN<sub>4</sub> and NiN<sub>2+2</sub> models are shown in Fig. S3†. The free energy (*G*) diagrams for the eCO<sub>2</sub>RR toward CO over three models show that the Gibbs free energy change ( $\Delta G$ ) of COOH\* formation is the highest among four elementary steps (Fig. 2a–c and Table S5†). Thus, we can infer that the first proton coupled electron transfer to form COOH\* is the potential-determining step (PDS) for the eCO<sub>2</sub>RR toward CO over Ni–N<sub>4</sub>. The changing current densities with pH on an absolute scale (*vs.* normal hydrogen



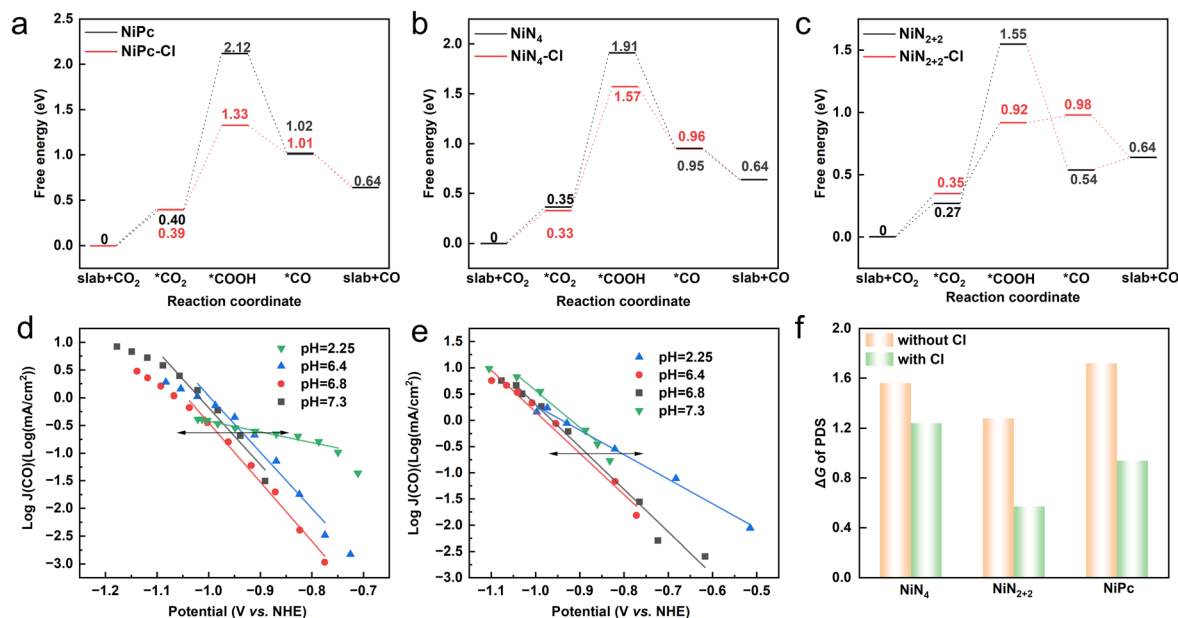


Fig. 2 The effect of Cl axial ligand on the energy barrier of PDS for the eCO<sub>2</sub>RR toward CO over Ni-N<sub>4</sub>. Free energy diagrams of the eCO<sub>2</sub>RR to CO for (a) NiPc, (b) NiN<sub>4</sub> and (c) NiN<sub>2+2</sub> with and without the Cl axial ligand. Experimental current densities plotted against potential vs. NHE for (d) NiPc and (e) Ni-N-C. (f) Comparison of the ΔG of PDS for NiPc, NiN<sub>4</sub> and NiN<sub>2+2</sub> with and without the Cl axial ligand.

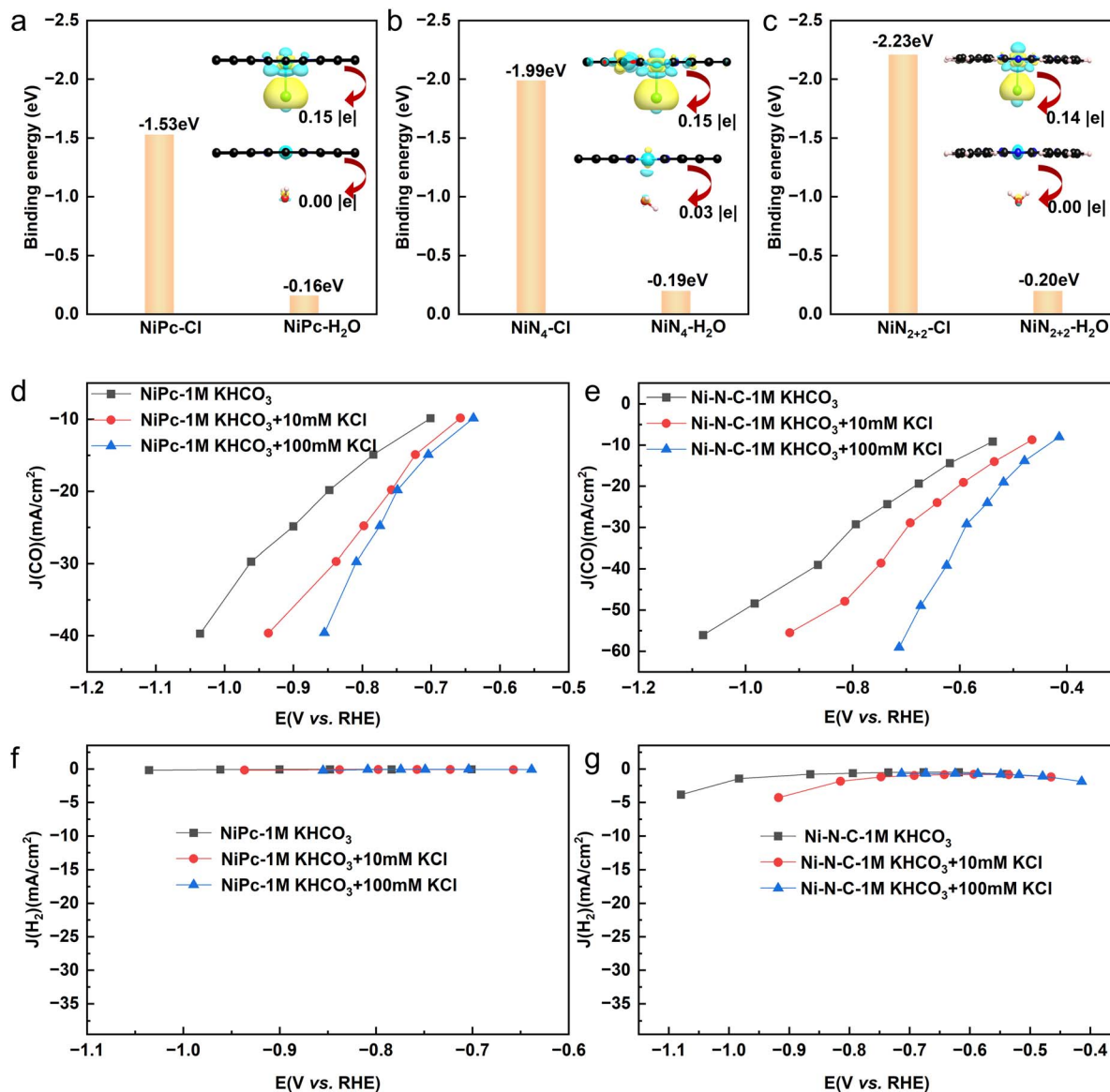
electrode (NHE)) over NiPc and Ni-N-C (with NiN<sub>4</sub> and NiN<sub>2+2</sub> structures) indicate that proton participates in the PDS (Fig. 2d and e), further confirming COOH\* formation as PDS for the eCO<sub>2</sub>RR toward CO. Pinpointing Cl axial ligand on Ni-N<sub>4</sub> does not alter the PDS (Fig. 2a-c), but lowers its energy barrier for all three model structures (Fig. 2f). Moreover, NiN<sub>2+2</sub> exhibits the lowest ΔG among three models without the axial ligand due to the strong adsorption of \*COOH. However, the strong adsorption of \*CO over NiN<sub>2+2</sub> as a consequence of linear scaling relationship<sup>48</sup> leads to an uphill \*CO desorption (ΔG > 0), in contrast to the spontaneous \*CO desorption over Ni-N<sub>4</sub> and NiPc (ΔG < 0). Interestingly, Cl axial ligand not only strengthens \*COOH adsorption over NiN<sub>2+2</sub>, but also weakens the adsorption of \*CO, leading to a reduced energy barrier of PDS and a downhill \*CO desorption. Thus, Cl axial ligand breaks the linear scaling relationship over NiN<sub>2+2</sub>,<sup>48</sup> probably due to the synergistic effect of the axial ligand and defects in the edges. Overall, the Cl axial ligand lowers the energy barrier of PDS for the eCO<sub>2</sub>RR toward CO over Ni-N<sub>4</sub>, boosting the catalytic activity of Ni single atoms.

We then measured the activity and selectivity of the eCO<sub>2</sub>RR toward CO over NiPc and Ni-N-C, and evaluated the effect of Cl axial ligand by adding KCl in the electrolyte. The metal center in the M-N<sub>4</sub> site tends to be occupied by a H<sub>2</sub>O molecule in the backside axial position,<sup>49–51</sup> and Cl<sup>-</sup> in the electrolyte replaces H<sub>2</sub>O due to the significantly higher binding energy of Cl than that of H<sub>2</sub>O adsorbed on Ni-N<sub>4</sub> (including NiPc, NiN<sub>4</sub> and NiN<sub>2+2</sub>) according to DFT simulations (Fig. 3a-c). Further charge analysis shows that Cl atoms transfer 0.14–0.15|e| charges to Ni atoms, indicative of a strong chemisorption of Cl on Ni-N<sub>4</sub> (insets of Fig. 3a-c). In contrast, the charge transfer from H<sub>2</sub>O molecules to Ni atoms is only 0.00–0.03|e|, suggesting

a physisorption of H<sub>2</sub>O on Ni-N<sub>4</sub> (insets of Fig. 3a-c). Thus, we can infer that Ni-N<sub>4</sub> binds with the Cl axial ligand by simply adding Cl<sup>-</sup> in the electrolyte.

The CO and H<sub>2</sub> partial current densities vs. potential (*iR*-corrected) over NiPc and Ni-N-C catalysts in electrolytes measured in 1 M KHCO<sub>3</sub> electrolyte with 0, 10 and 100 mM KCl are presented in Fig. 3d-g. CO<sub>2</sub> electrolysis was conducted for 30 minutes at constant current densities from 10 mA cm<sup>-2</sup> to 60 mA cm<sup>-2</sup> in a flow cell with Ag/AgCl as the reference electrode. The total faradaic efficiencies (FEs) of CO and H<sub>2</sub> for NiPc and Ni-N-C are ~100% (Fig. S4†), indicating negligible liquid products formed during the eCO<sub>2</sub>RR. Thus, we didn't measure liquid products for this study. Both NiPc and Ni-N-C exhibit enhanced CO partial current densities in a wide potential range after adding trace amount of Cl<sup>-</sup> (10 mM), and the enhancement increases with an increasing Cl<sup>-</sup> concentration (Fig. 3d and e). The improvement in the catalytic activity of Ni-N<sub>4</sub> for the eCO<sub>2</sub>RR toward CO induced by the Cl axial ligand is consistent with the reduced energy barrier of PDS (Fig. 2a-c). In contrast, the H<sub>2</sub> partial current densities of NiPc and Ni-N-C are not affected by the addition of Cl<sup>-</sup> (Fig. 3f and g). The above results demonstrate that the Cl axial ligand enhances the intrinsic activity of Ni-N<sub>4</sub> for the eCO<sub>2</sub>RR toward CO without altering its HER activity, leading to an increase in the total current density (Fig. S5†). Moreover, during the 8-hour chronoamperometry (CA) tests in 1 M KHCO<sub>3</sub> electrolyte with 100 mM KCl, both Ni-N-C and NiPc maintained stable CO faradaic efficiency (FE) and current density, as shown in Fig. S6.† The Cl 2p spectra of the Ni-N-C and NiPc after stability tests exhibit a characteristic peak at ~198.0 eV attributed to Ni-Cl species (Fig. S7†),<sup>52</sup> with Cl as the axial ligand considering the absence of high-temperature required to form planar coordinated Cl.<sup>24</sup> In addition, a new





**Fig. 3** The effect of Cl axial ligand on the activity of Ni-N<sub>4</sub> for the eCO<sub>2</sub>RR toward CO. The binding energies of Cl and H<sub>2</sub>O adsorbed on the Ni center in (a) NiPc, (b) NiN<sub>4</sub>, and (c) NiN<sub>2+2</sub>. The insets are the charge density differences of Cl and H<sub>2</sub>O on Ni-N<sub>4</sub> sites. The cyan and yellow regions represent loss and accumulation of charge density, respectively, and the isosurface value is ±0.002 e bohr<sup>-3</sup>. CO partial current densities vs. potential (*iR*-corrected) for (d) NiPc and (e) Ni-N-C. H<sub>2</sub> partial current densities vs. potential (*iR*-corrected) for (f) NiPc and (g) Ni-N-C. The above electrochemical characterization is measured in 1 M KHCO<sub>3</sub> electrolyte with 0, 10 and 100 mM KCl (the data shown in (d-g) are the average of three repeated experiments).

peak at 858.3 eV assigned to Ni<sup>3+</sup> emerges in the Ni 2p XPS spectra of Ni-N-C and NiPc after stability tests (Fig. S8<sup>†</sup>), further confirming the formation of Ni-N<sub>4</sub>-Cl with Cl as the axial ligand.<sup>53</sup> The postmortem XPS studies unambiguously demonstrate the successful introduction and high stability of the Cl axial ligand. Approximately 37% and 18% of Ni<sup>3+</sup> species are detected in Ni-N-C and NiPc after the stability tests (Fig. S8<sup>†</sup>), suggesting that Ni-N<sub>4</sub> is partially coordinated with axial Cl ligands.

Strong chemisorption of the axial ligand on M-N<sub>4</sub> sites pulls single metal atoms away from the carbon plane, which breaks the D<sub>4h</sub> symmetry of square-planar M-N<sub>4</sub>, and consequently

promotes the electron transfer during electrochemical reactions.<sup>19,20</sup> The distance of Ni atom from the carbon plane ( $d_{\text{Ni}}$ ) and the Ni-N bond distance ( $d_{\text{Ni-N}}$ ) (insets in Fig. 4a and b) describe the degree of geometric distortion of Ni-N<sub>4</sub> sites upon adsorption of Cl axial ligand. Thus, we explore the relationship between the energy barrier of PDS ( $\Delta G_{\text{p}}$ ) for the eCO<sub>2</sub>RR and  $d_{\text{Ni}}/d_{\text{Ni-N}}$  (Fig. 4a and b). For comparison, weak adsorption of H<sub>2</sub>O axial ligand on three models are considered (Fig. S9, S10 and Table S6<sup>†</sup>). In contrast to H<sub>2</sub>O molecules ( $d_{\text{Ni}} = 0.02\text{--}0.08$  Å), Cl atom with a strong binding energy on Ni-N<sub>4</sub> pulls Ni atom further away from the carbon plane ( $d_{\text{Ni}} = 0.10\text{--}0.33$  Å), resulting in a larger  $d_{\text{Ni-N}}$  (Fig. 4a, b and Table S7<sup>†</sup>). There is a positive



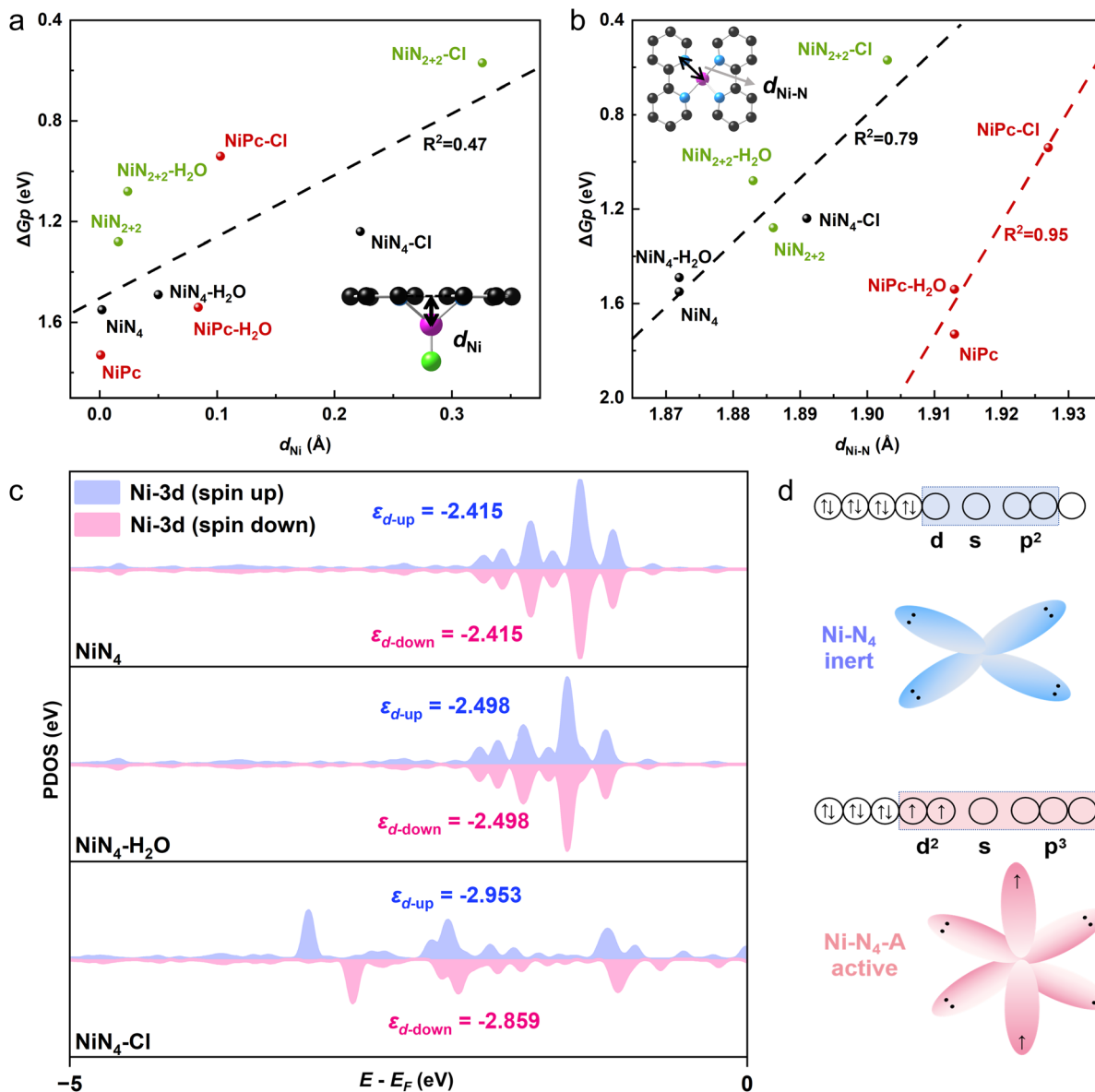


Fig. 4 The effect of Cl axial ligand on the geometric and electronic structure of Ni-N<sub>4</sub>. The relationship between  $\Delta G_p$  and (a)  $d_{Ni}$ , (b)  $d_{Ni-N}$ . (c) The partial density of states and d-band center of Ni atoms in NiN<sub>4</sub>, NiN<sub>4</sub>-Cl, and NiN<sub>4</sub>-H<sub>2</sub>O. (d) Schematic diagram of orbital hybridization of Ni atoms in Ni-N<sub>4</sub> with and without axial ligands.

correlation between  $d_{Ni}$  and  $\Delta G_p$ : the further away the Ni atoms are from the carbon plane, the lower the  $\Delta G_p$  (Fig. 4a). The relationship between  $d_{Ni-N}$  and  $\Delta G_p$  falls into two linear lines for NiPc and Ni-N-C (NiN<sub>4</sub> and NiN<sub>2+2</sub>), respectively (Fig. 4b). It is noteworthy that both the change of  $d_{Ni}$  and  $d_{Ni-N}$  of NiPc-Cl are smaller than those of NiN<sub>4</sub>-Cl and NiN<sub>2+2</sub>-Cl due to the more rigid structure of NiPc (Fig. 4a and b). Moreover, the periodic boundary conditions on the xy plane of molecular NiPc and periodic NiN<sub>4</sub>/NiN<sub>2+2</sub> are different for DFT simulations. Thus, it is reasonable that the linear coefficient for the correlation between the geometric parameters and  $\Delta G_p$  of NiPc differs from that of Ni-N-C. In summary, Cl axial ligand induces geometric distortion of Ni-N<sub>4</sub> sites, and the geometric parameters,  $d_{Ni}$  and  $d_{Ni-N}$ , are strongly correlated with the

energy barrier of PDS, and consequently the electrocatalytic activity for the eCO<sub>2</sub>RR toward CO.

Then we evaluate the effect of Cl axial ligand on the electronic structures of Ni atoms in Ni-N<sub>4</sub>. The partial density of states (PDOS) show that the up and down spin images of Ni 3d orbitals of NiN<sub>4</sub> and NiPc (with/without H<sub>2</sub>O ligands) are symmetrical (Fig. 4c and S11a†), indicating the symmetrical arrangement of the up and down spin electrons of 3d orbitals for Ni-N<sub>4</sub> without geometric distortion (Fig. 4d). In contrast, the geometric distortion induced by Cl axial ligand results in the asymmetric up and down spin electron arrangement of Ni 3d orbitals, and thus the magnetic properties of NiN<sub>4</sub>-Cl (Fig. 4c, d and S11a†). The empty 3d, 4s and two 4p orbitals of Ni undergo dsp<sup>2</sup> hybridization to interact with the sp<sup>2</sup> orbitals of



the four-coordinated N ligands in Ni-N<sub>4</sub> with square planar geometry,<sup>54</sup> whereas Ni-N<sub>4</sub> with Cl axial ligand exhibits a d<sup>2</sup>sp<sup>3</sup> hybridization with an octahedral coordination environment (Fig. 4d). The d<sup>2</sup>sp<sup>3</sup> hybridization of Ni leads to the rearrangement of spin electrons, which activates Ni-N<sub>4</sub> sites and boosts their intrinsic activity for the eCO<sub>2</sub>RR.<sup>54</sup> Particularly, the up and down spin PDOS image of Ni 3d orbitals in NiN<sub>2+2</sub> is asymmetric (Fig. S11b†), leading to a lower energy barrier for PDS of NiN<sub>2+2</sub> than those of NiPc and NiN<sub>4</sub> (Fig. 2f). The Cl axial ligand further intensifies the degree of asymmetry for the PDOS image of Ni 3d orbitals in NiN<sub>2+2</sub>-Cl (Fig. S11b†), indicating the enhanced activity of NiN<sub>2+2</sub>-Cl for the eCO<sub>2</sub>RR toward CO.

We then analyzed the d-electron distribution of Ni atoms in NiPc, NiN<sub>4</sub> and NiN<sub>2+2</sub> with/without the Cl axial ligand (Fig. S12†). For all three models without Cl axial ligand, the peak of partial density of states (PDOS) below the Fermi level is mainly contributed by the d orbital components containing the z-axis direction (such as d<sub>yz</sub>, d<sub>xz</sub>, and d<sub>z<sup>2</sup></sub>), indicating that the electrons involved in the eCO<sub>2</sub>RR are mainly provided by the d orbitals in the z-direction. Stronger the electron donating capability of

d orbitals, better the eCO<sub>2</sub>RR activity we achieve. NiPc only provides electrons through d<sub>z<sup>2</sup></sub> and d<sub>xz</sub>, while all the d<sub>yz</sub>, d<sub>xz</sub>, and d<sub>z<sup>2</sup></sub> of NiN<sub>4</sub> donate electrons. Moreover, the structural symmetry of NiN<sub>2+2</sub> has been disrupted, enabling d<sub>xy</sub> to donate electrons in addition to d<sub>yz</sub>, d<sub>xz</sub>, and d<sub>z<sup>2</sup></sub>. The above results are in good agreement with the superior eCO<sub>2</sub>RR activity of Ni-N-C to that of NiPc. Introducing Cl axial ligands further breaks the structural symmetry of NiPc, NiN<sub>4</sub> and NiN<sub>2+2</sub>, which not only leads to asymmetric up and down spin images, but also brings the peak of d orbital components containing the z-axis direction closer to the Fermi level (Fig. S12†). As a result, the introduction of Cl axial ligands induces the strong electron donating capability and, consequently, enhances the eCO<sub>2</sub>RR activity of Ni-N<sub>4</sub>.

Since the asymmetric up and down spin electron arrangements of Ni 3d orbitals in Ni-N<sub>4</sub>-Cl are crucial for their enhanced eCO<sub>2</sub>RR activity, we then explore the relationship between  $\Delta G_p$  and  $\Delta \epsilon_d$  (the difference in the d-band center of Ni between down and up spin).  $\Delta \epsilon_d$  delivers a good linear relationship with  $\Delta G_p$  (Fig. S13a†). The change of  $\Delta \epsilon_d$  induced by Cl axial ligands for three model structures follows the trend of

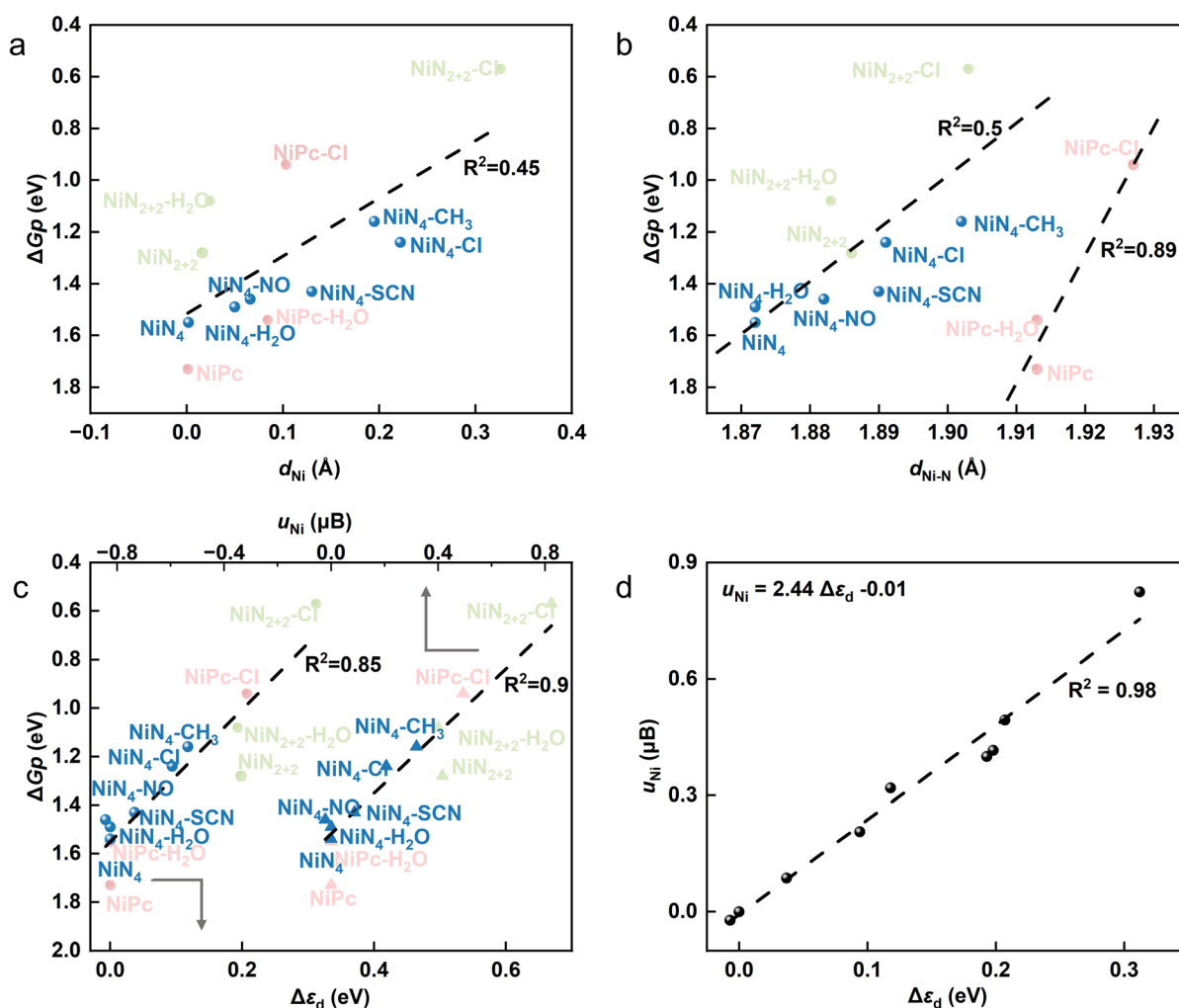


Fig. 5 Universal descriptors for the eCO<sub>2</sub>RR activity of Ni-N<sub>4</sub> with various axial ligands. The relationships between  $\Delta G_p$  and (a)  $d_{Ni}$ , (b)  $d_{Ni-N}$ , (c)  $\Delta \epsilon_d$ ,  $u_{Ni}$  (the circular symbol represent  $\Delta \epsilon_d$ , and the triangular symbol represents  $u_{Ni}$ ). (d) The relationship between  $\Delta \epsilon_d$  (the difference in the d-band center of Ni between down and up spin) and  $u_{Ni}$  (the magnetic moment of Ni atoms).



NiPc (0.207 eV) > NiN<sub>2+2</sub> (0.114 eV) > NiN<sub>4</sub> (0.094 eV), perfectly matching the trend for the change of  $\Delta G_p$  induced by Cl axial ligands (NiPc > NiN<sub>2+2</sub> > NiN<sub>4</sub>). Therefore, although the effect of axial ligands on the geometric structure of NiPc is the lowest among all three model structures due to its rigid structure, that on the electronic structures is the highest, resulting in the most significant decrease in  $\Delta G_p$  for NiPc induced by Cl axial ligands. Since  $\Delta \epsilon_d$  is directly correlated with the electronic asymmetry of Ni–N<sub>4</sub> as discussed above, we can safely conclude that the electronic symmetry breaking, which originates from the geometric symmetry breaking, is the primary factor in enhancing the eCO<sub>2</sub>RR activity.

Furthermore, the asymmetric up and down spin electron arrangements of Ni 3d orbitals will cause changes in the magnetic moment of Ni atoms ( $u_{Ni}$ ), and the linear relationship between  $\Delta \epsilon_d$  and  $u_{Ni}$  is shown in Fig. 5d. Therefore, we further investigate the relationship between  $\Delta G_p$  and  $u_{Ni}$ , which also exhibit a good linear correlation: larger the  $u_{Ni}$ , lower the  $\Delta G_p$  (Fig. S13b†). Thus,  $u_{Ni}$  and  $\Delta \epsilon_d$  are possible descriptors of the eCO<sub>2</sub>RR activity of Ni–N<sub>4</sub>-type SACs with axial ligands. The separate linear relationships for NiPc and Ni–N–C systems are unified when using  $\Delta \epsilon_d$  and  $u_{Ni}$  as descriptors since electronic properties circumvent the fundamentally different geometries of NiPc and Ni–N–C.

To demonstrate the universality of the above geometric and electronic descriptors, we further extend axial ligands over NiN<sub>4</sub> from Cl<sup>−</sup> to −NO, −SCN, and −CH<sub>3</sub>, and investigate the relationship between  $\Delta G_p$  and geometric/electronic parameters ( $d_{Ni}$ ,  $d_{Ni-N}$ ,  $u_{Ni}$ ,  $\Delta \epsilon_d$ ). The configurations of all elementary steps on NiN<sub>4</sub> models are shown in Fig. S14.† The free energy diagrams indicate that all axial ligands over NiN<sub>4</sub> investigated exhibit reduced  $\Delta G_p$ , and thus promote the electrocatalytic CO<sub>2</sub>RR to CO (Fig. S15, S16 and Table S7†). There are linear correlations between  $\Delta G_p$  and  $d_{Ni}$ ,  $d_{Ni-N}$ ,  $u_{Ni}$ ,  $\Delta \epsilon_d$  for NiN<sub>4</sub> with various ligands (Fig. S17†), which fit well in the linear lines we have described in Fig. 4a, b and S13† (Fig. 5). Therefore,  $u_{Ni}$  and  $\Delta \epsilon_d$  are universal descriptors for evaluating the eCO<sub>2</sub>RR activity of Ni–N<sub>4</sub>-type SACs with a variety of axial ligands, and, most probably, can be extended to other M–N<sub>4</sub>-type SACs. The spin electron rearrangement in M–N<sub>4</sub> SACs induced by axial ligands is the key for boosting eCO<sub>2</sub>RR activity.

## Conclusions

In summary, we investigated the effect of axial ligand on the eCO<sub>2</sub>RR activity of two Ni–N<sub>4</sub>-type model catalysts (NiPc and Ni–N–C), and both theoretical and experimental studies demonstrate that Cl axial ligand is beneficial for the eCO<sub>2</sub>RR. The Cl axial ligand induces a hybridization state transition of nickel orbital from dsp<sup>2</sup> to d<sup>2</sup>sp<sup>3</sup> and, consequently, a rearrangement of spin electrons, accounting for the superior activity of Ni–N<sub>4</sub>–Cl for the eCO<sub>2</sub>RR. The low energy barrier of PDS for the eCO<sub>2</sub>RR exhibits a strong correlation with the geometric ( $d_{Ni}$  and  $d_{Ni-N}$ ) and electronic ( $\Delta \epsilon_d$  and  $u_{Ni}$ ) parameters of Ni–N<sub>4</sub>. Furthermore, we propose the magnetic moment of Ni as a universal descriptor for the eCO<sub>2</sub>RR toward CO on Ni–N<sub>4</sub> with various axial ligands (−H<sub>2</sub>O, −Cl, −NO, −SCN, and −CH<sub>3</sub>). Our

work provides valuable insights on regulating the geometric configuration and electronic structure of SACs to boost their electrocatalytic activities for various energy and environmental applications.

## Data availability

All experimental and computational procedures and associated data are provided in the ESI.†

## Author contributions

M. P., K. H., and J. L. conceived the project. M. P. prepared materials, performed measurements and analysed the data. K. H. performed the DFT calculations. X. H. and A. Z. helped with some of the experiments and characterization. All authors discussed the results and commented on the manuscript. M. P., K. H., and J. L. wrote the draft, revised and finalized the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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