Epitaxial Self-Assembly of Interfaces of 2D Metal–Organic Frameworks for Electroanalytical Detection of Neurotransmitters

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I. General Methods

Chemicals were purchased from Sigma Aldrich or TCI and used as received. Electrochemical experiments were run on an EmStat3MUX16 purchased from PalmSens. Electrodes and electrochemical cells were purchased from CH Instruments. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) were performed using a Hitachi TM3000 SEM (Tokyo, Japan) equipped for X-ray microanalysis with a Bruker Edax light element Si(Li) detector (Billerica, MA). Powder X-ray diffraction (PXRD) measurements were performed with a Rigaku sixth generation MiniFlex X-ray diffractometer with a 600 W (40 kV, 15 mA) CuKα (α= 1.54 Å) radiation source. X-ray photoelectron spectroscopy (XPS) experiments were conducted on Kratos Analytical AXIS Supra X-ray Photoelectron Spectrometer under ultrahigh vacuum (base pressure 10⁻⁷ Torr). The measurement chamber was equipped with a monochromatic Al (Kα) X-ray source. Both survey and high-resolution spectra were obtained using a beam diameter of 200 μm. AFM imaging was performed using an OmegaScope in non-contact mode. Tips were either uncoated silicon or Al coated silicon with tip radii <20 nm.

II. General Synthesis and Device Preparation Using MOF {001} and {100} Interfaces

\textit{Ni}_3(\textit{HHTP})_2 Hydrothermal Method

To prepare MOFs, 0.037 mmol hexahydroxytriphenylene (12 mg) and 0.074 mmol nickel (II) acetate tetrahydrate (18.4 mg) were added to a 20 mL scintillation vial. Deionized water (15 mL, 0.005 M [HHTP]) was added and the vial was loosely capped to
allow the exchange of air in the headspace. The reaction mixture was subjected to sonication (15 min) and then heated without stirring (85 °C) overnight (18–24 h). The resulting suspension was characterized by drop-casting onto silicon plates and imaging by SEM and PXRD. Suspensions were stored at 7 °C for up to 2 weeks. Rods were not isolated from the initial reaction mixture but were used as a suspension in the mother liquor.

**Co₃(HHTP)₂ Hydrothermal Method**

To prepare MOFs, 0.037 mmol hexahydroxytriphenylene (12 mg) and 0.074 mmol cobalt (II) acetate tetrahydrate (18.4 mg) were added to a 20 mL scintillation vial. Deionized water (15 mL, 0.005 M [HHTP]) was added and the vial was loosely capped to allow the exchange of air in the headspace. The reaction mixture was subjected to sonication (5 min) and then heated without stirring (85 °C) overnight (18-24 h). The resulting suspension was characterized by drop-casting onto silicon plates and imaging by SEM and PXRD. Suspensions were stored at 7 °C for up to 2 weeks. Rods were not isolated from the initial reaction mixture but were used as a suspension.

**Interfacial Synthesis of Ni₃(HHTP)₂**

Into a recrystallizing dish (ø = 8 cm) was added Ni(OAc)₂•4(H₂O) (56.5 mg, 0.227 mmol, 2 eq.) and 100 mL of DI water. Into a vial was added fully reduced HHTP (36.8 mg, 0.113 mmol, 1 eq.) and 20 mL of DI water. The vial was then sonicated for 10 min until a pink/grey suspension was formed. This suspension was poured into the recrystallizing dish containing the Ni(OAc)₂ solution. The reaction was left exposed to air but gently covered to prevent contamination from airborne particles. After 2 h, a thin film visually similar to an oil slick was observed on the surface of the reaction. After an additional 4 h, the film was uncovered and used. Finished films were mounted onto GCE using the Langmuir-Blodgett method.

**Interfacial Synthesis of Co₃(HHTP)₂**

Into a recrystallizing dish (ø = 8 cm) was added Co(OAc)₂•4(H₂O) (56.5 mg, 0.227 mmol, 2 eq.) and 100 mL of DI water that had been degassed with N₂ for 15 minutes before use. Into a vial was added fully reduced HHTP (36.8 mg, 0.113 mmol, 1 eq.) and 20 mL of DI water. The vial was then sonicated for 10 min until a pink/grey suspension was formed. This suspension was poured into the recrystallizing dish containing the Co(OAc)₂ solution. The reaction was left exposed to air but gently covered to prevent contamination from airborne particles. After 2 h, a thin film visually similar to an oil slick was observed.
on the surface of the reaction. After an additional 4 h, the film was uncovered and used. Finished films were mounted onto GCE using the Langmuir-Blodgett method.

**Preparation of Nanorods on Glassy Carbon Electrodes**

Onto a clean and polished glassy carbon disk electrode (GCE, ø = 3 mm) was drop cast 5 μL of the nanorod solution. The solution was allowed to dry under air at room temperature until dry to generate a thin film of nanorods on the surface of the electrode (MOF@GCE). After the nanorod film was dry the film had sufficient structural integrity to allow washing of the electrode. The electrode was washed alternatingly with water and acetone 5 times each. For each wash, the MOF@GCE was inverted into a vial containing 5 mL of fresh solvent. After the final wash, the electrode was allowed to air dry at room temperature under air. Once dry the electrode was ready to use. Electrodes were prepared immediately before use accounting for the time needed to wash the electrodes according to the washing regime determined.

**General Synthesis of Hexamethoxytriphenylene (HMTP) from Veratrole**

Into a 500 mL RBF was added 150 mL of dichloromethane, FeCl₃ (62 g, 0.39 mol, 3 eq.), and 1 mL of H₂SO₄ (cat.). In an addition funnel was combined 50 mL of dichloromethane and 18 g of veratrole (0.13 mol, 1 eq). Under an inert atmosphere, the dichloromethane/veratrole mixture was added to the reaction vessel dropwise over 4 hrs with vigorous stirring. The reaction was allowed to stir overnight. Once complete, the reaction was quenched by the slow addition of methanol to consume excess FeCl₃. Solids precipitated with the addition of methanol. The solids were collected by filtration and washed with methanol (3 x 100 mL) and dried to constant weight to yield (90 %) of a fluffy grey powder. No special precautions were needed for the storage of this product. Characterization by NMR matched previous reports.

**Synthesis of reduced hexahydroxytriphenylene (HHTP) from HMTP**

To a flame dried 250 mL RBF was added 50 mL of dichloromethane and HMTP (2.0 g, 4.89 mmol, 1 eq). The RBF was stirred until a consistent suspension was reached. To the RBF was slowly added 5.6 mL BBr₃ (24 eq.). The reaction was sealed and allowed to stir for 7 days. The reaction was quenched with dilute HCl (0.1 M) that had been degassed with N₂ and stirred under a flow of N₂ for an additional 5 hrs. The solids that precipitated were collected by filtration under an inert atmosphere and washed with degassed HCl (0.1 M, 3 x 50 mL), and degassed DI water (3 100 mL). Once dried, the
solids yielded 1.5 g (94% yield) of a light green powder that was brittle and had a chalky consistency. The product was stored under Ar at -22 °C Characterization by NMR matched previous reports.

The work-up for the deprotection of HMTP to HHTP was performed under an inert atmosphere to prevent the HHTP from reacting with O2 to produce HHTP in higher oxidation states. As synthesized, the product could be used in interfacial synthesis processes.
III. Scanning Electron Microscopy (SEM) of MOFs Synthesized by Hydrothermal and Interfacial Methods

SEM was used to determine the surface coverage, film thickness, and general morphology of materials. Materials were mounted for analysis on zero-diffraction silicon wafers in a manner similar to that used to mount the materials on GCE. To assess the thickness of films consisting of {001} and {100} interfaces, the sample stage of the SEM was tilted at 45° to obtain edge-on images. The images were digitally corrected to account for the angle of tilt to allow depth in the images to be directly measured using an unadjusted scale bar.

*SEM images of Ni$_3$(HHTP)$_2$ Grown by Hydrothermal Method*

**Figure S1.** Ni$_3$(HHTP)$_2$ rods drop cast on a flat Si plate were analyzed by SEM. Nanorods are seen in the image on the left to have good fidelity to the nanorod shape. Upon drying, the nanorods coalesced into a film averaging 400 nm in depth.
SEM images of Ni₃(HHTP)₂ Grown by Interfacial Method

Figure S2. Morphology of the growing edge of the Ni₃(HHTP)₂ having a {001} orientation is shown in the image on the left. The image on the right shows the broken edge of an extended film of {001} oriented nanorods. Highly oriented rods are aligned along their c-axis to present their basal plane {001} outward, while their edge surfaces {100} are blocked by adjacent nanorods. Nanorods like to cuddle. On the right is shown a contiguous film that has completely closed the space between rods to present a coherent surface consisting of highly orientated nanorod basal planes. The thickness of the film can be seen to be ~100 nm.

SEM images of Co₃(HHTP)₂ Grown by Hydrothermal Methods

Figure S3. Co₃(HHTP)₂ nanorods drop cast on a Si surface are shown to have rod-like morphologies (right image). In the left image, the nanorods are observed to coalesce into a thick film.
SEM images of Co₃(HHTP)₂ Grown by Interfacial Method

**Figure S4.** Co₃(HHTP)₂ grown by the interfacial method was observed to have oriented nanorod character similar to the Ni₃(HHTP)₂ synthesized by the same method. The growth of the individual Co₃(HHTP)₂ oriented rod-like components of the film appeared incomplete leading to hierarchical porosity across the surface of the film. The thickness of the film averaged ~100 nm.
Figure S5. SEM analysis of synthetic methods using increasing O\textsubscript{2} gradients. Hydrothermal synthesis (left) in which no gradient was present, a modified interfacial synthesis (center) in which a weak O\textsubscript{2} gradient was present, and the optimized interfacial synthesis (right) in which a large O\textsubscript{2} gradient directed the growth of oriented MOF films. Images were taken of materials on glassy carbon.

Statistical Analysis of the Size and Shape of Nanomaterials

To reliably correlate the electroanalytical properties of these materials with specific morphological features we rigorously measured the size, shape, and distribution of the MOF nanoparticles resulting from both the interfacial synthetic process and the hydrothermal synthesis. We established characteristic size and aspect ratio of the interfacially grown and hydrothermally grown MOF materials mounted on representative electrode materials (silicon die) used for electrochemical analysis. The measurements represent the size of the nanoparticles we observed by SEM and are not necessarily the size of crystallites or of coherently scattering domains. However, the measurements do represent the size of oriented nanoparticles and are therefore a relevant parameter for the sensing performance.
Figure S6. Statistical analysis of the two unique morphologies of Co₃(HHTP)₂ deposited on silicon wafers and imaged by SEM.

Figure S7. Statistical analysis of the two unique morphologies of Ni₃(HHTP)₂ deposited on silicon wafers and imaged by SEM.
IV. Atomic Force Microscopy (AFM) of Nanomorphologies of MOFs Synthesized by Hydrothermal and Interfacial Methods

Atomic force microscopy (AFM) was used to characterize fine features of the Ni$_3$(HHTP)$_2$ {001} nanomaterials. Materials synthesized according to the interfacial procedure were prepared for AFM analysis by sonicating for 5 minutes in acetone before being drop cast (1 drop) on silicon wafers and allowed to dry under air. The process of sonication and drop casting yielded samples of Ni$_3$(HHTP)$_2$ {001} nanomaterials where both the top-side (basal plane of material facing the air at the surface of the interfacial reaction) and bottom-side (side of material growing down into the interfacial reaction solution) were both observed. Observing both sides of the {001} nanomaterials allowed us to investigate the relative roughness of both sides and more clearly identify the highly-oriented nanorods that composed the nanosheet-like Ni$_3$(HHTP)$_2$ {001}. The bottom-side of the nanosheets showed significantly increased roughness compared to the top-side of the nanosheets (Figure S41-S42).

Figure S8. Profile scans of two nanosheets of Ni$_3$(HHTP)$_2$ grown by the interfacial synthesis method. The trace marked in green measures the profile of the bottom-side of a nanosheet while the red trace measures the profile of the top-side of a nanosheet.
Figure S9. Roughness data of nanosheets of Ni₃(HHTP)₂ top-side shown with red markers, and the bottom-side indicated with green markers.
V. Powder X-ray Diffraction (PXRD) Analysis of Nanoscale Morphologies and Orientations

Along with rigorous characterization of particle size and shape, we needed to determine how the particles were oriented at the heterogeneous interface. We used PXRD and Rietveld refinement, and Sherrer’s analysis to measure the prevalence of diffraction planes under specific orientations relative to the interfacial surface (e.g., GCE). Our observations of orientation by SEM allowed us to determine the orientation of crystalline planes relative to the particles, and relative to the interfacial system. Materials were mounted on zero diffraction PXRD plates. Nanomaterials were prepared on the PXRD plates by the same method used to mount the materials on the electrodes. That is, nanorods were drop-casted from a reaction solution then washed by submerging in alternating baths of acetone and water (water: 15 min, acetone: 15 min, water 15 min). Films consisting of \{001\} interfaces were mounted by lifting the PXRD plate through the film growing at the air-liquid interface. Washing of the mounted film followed the same routine as the mounted nanorods (above).

Rietveld Refinements

Refinements were performed on PXRD data gathered for each MOF and each MOF morphology. Each diffractogram was translated to a compatible file format using PowDLL (University of Ionnina, Greece). Next, refinements were performed using the Profex 5.0 user interface for the BGMN refinement program. Refinements started from the experimentally obtained crystal structure of $\text{Co}_3(\text{HHTP})_2$. The parameter GEWICHT represents the weighting of orientation along particular lattice vectors relative to the PXRD substrate. Orientations were quantified for the (004) and (100) peaks. The (004) diffraction peak was used to measure the alignment of the \{001\} family of plains, and the (100) was used to measure the orientation of the \{100\} family of plains.
Figure S10. Experimental PXRD and Rietveld refinement of Ni$_3$(HHTP)$_2$ synthesized via the interfacial method to provide Ni$_3$(HHTP)$_2$ \{001\}. 
**Figure S11.** Experimental PXRD and Rietveld refinement of Ni$_3$(HHTP)$_2$ synthesized via the interfacial method to provide Ni$_3$(HHTP)$_2$ \{100\}.
Figure S12. Experimental PXRD and Rietveld refinement of Co₃(HHTP)₂ synthesized via the interfacial method to provide Co₃(HHTP)₂ {001}.
Figure S13. Experimental PXRD and Rietveld refinement of Co$_3$(HHTP)$_2$ synthesized via the interfacial method to provide Co$_3$(HHTP)$_2$ \{100\}.
Figure S14. Scherrer's analysis of the (004) diffraction line for the MOFs synthesized by interfacial methods provided an assessment of the size of crystalline domains within the films. The close agreement between the values obtained by the Scherrer equation and those obtained by SEM analysis suggested that the films consisted of a single crystalline domain in the $c$ direction of the crystal habit. CSR: coherently scattering region.
VI. Elemental Analysis of the \{001\} and \{100\} Surfaces

**Figure S15.** $\text{Co}_3(\text{HHTP})_2$ materials examined by XPS. The morphologies were prepared for XPS in a manner conserving their epitaxial orientation or lack thereof. We designed the XPS experiments to mirror the material handling process utilized in SEM and PXRD experiments.
Figure S16. Ni₃(HHTP)₂ materials examined by XPS. The morphologies were prepared for XPS in a manner conserving their epitaxial orientation or lack thereof. We designed the XPS experiments to mirror the material handling process utilized in SEM and PXRD experiments.
Figure S17. Elemental mapping of the interfacially synthesized Ni₃(HHTP)₂ using Energy Dispersive X-ray Spectroscopy. Images were taken of materials on glassy carbon.
Figure S18. Elemental mapping of the \{100\} hydrothermally synthesized Ni$_3$(HHTP)$_2$ using Energy Dispersive X-ray Spectroscopy. Images were taken of materials on glassy carbon.
VII. Zeta-Potential Analysis of MOFs

It was important to understand if the nanoparticles in this study carried a charge in electrolyte solutions. Any charge carried by the particles would influence the interaction between analytes and the electrochemically active surface of the nanomaterial electrode. A zeta-sizer was used to determine the charged nature of the particles. Samples were prepared by suspending 1 mg of MOF powder (washed and dried) in 1 mL of the desired buffer solution (either KCl or PBS). The suspensions were loaded into a folded capillary cell (Malvern DTS1070) with a 5 mL Luer-Lock syringe.

| Zeta Potential (mV) | Co₃(HHTP)₂ | Ni₃(HHTP)₂ |
|---------------------|------------|------------|
| Electrolyte         |            |            |
| PBS (0.1 M)         | -27±1.1    | -27±1.0    |
| KCl (0.1 M)         | -18±0.8    | -29±0.9    |

**Figure S19.** Zeta potential results for Co₃(HHTP)₂ and Ni₃(HHTP)₂ were prepared by hydrothermal methods. The electrolyte (either PBS or 0.1 M KCl) was the same formulation used for electrochemical experiments.
VIII. Electrochemical Methods

Once structural characterization was complete, the electrochemical performance of the nanomaterial morphologies was assessed with a range of inorganic and organic probes. Inorganic probes were used to determine intrinsic physical properties. A variety of electrochemical methods were used to determine the performance of the electrode material in the role of active material for chemical sensing, to elucidate the mechanisms behind the ability of the materials to differentiate analyte signals, and to provide insight into the intrinsic electronic behavior in electrolyte solutions.

*Electrochemical experimental parameters*

*Cyclic Voltammetry*

**Inorganic Probes.** Electrochemical experiments were performed in 0.1 M KCl that had been degassed with N₂. Cyclic voltammograms were collected at nine scan rates starting from the fastest rate and proceeding to the slowest in the following order: 1000, 750, 500, 250, 100, 50, 25, 10, and 5 mV/s. The potential range applied in these experiments was -0.7–0.7 V, except for the case of K₃IrCl₆ where a potential range of -0.7–1.2 V was used to accommodate the higher oxidation potential of the iridium-based probe. 4 scans were collected at each scan rate and the 4th scan from each experiment was plotted on the same plot to characterize the reduction and oxidation events.

**Biologically Relevant Organic Probes (BRO).** Probes in this category were used to determine the performance of these materials in physiologically relevant conditions. Therefore, the electrolyte solution was chosen to be 0.1 M phosphate-buffered saline (1X PBS) at a pH of 7.4. Cyclic voltammograms were collected at nine scan rates starting from the fastest rate and proceeding to the slowest in the following order: 1000, 750, 500, 250, 100, 50, 25, 10, and 5 mV/s. 4 scans were collected at each scan rate and the 4th scan from each experiment was plotted on the same plot to characterize the reduction and oxidation events.
**Differential Pulse Voltammetry and Differential Pulse Anodic Stripping Voltammetry Methods**

DPASV was used to assess the sensitivity of our MOF@GCE electrodes towards targeted BROs. All DPASV experiments were performed in 0.1 M PBS at a pH of 7.4. Experiments consisted of two phases. The first phase consisted of a preparation phase where devices were electrochemically pretreated, and a measurement phase where analyte was added and DPASV traces were collected. **Phase 1.** To prepare electrodes modified with MOF@GCE materials for DPASV we first subjected the MOF@GCE devices to a series of electrochemical equilibration steps to obtain a stable baseline and reduce variability in the background electrochemical activity. This process consisted of first running 20 cycles using the cyclic voltammetry mode across the potential window of -0.7–0.7 V. After this process was completed, the electrode was then subjected to iterative scans under the DPASV conditions to be used in the data collection phase. Conditions: scans were run exactly two minutes apart. For DPASV experiments, the scan window was -0.6–0.7 V, the scan rate was 50 mV/s, the potential step was 1 mV, and the pulse width and time were 10 mV and 10 ms, respectively. The experiment was differentiated from a typical DPV experiment because a potential was applied to the cell between scanning experiments. The potential we chose was -0.1 V to optimize the adsorption of the analyte and avoid damage to the modified electrode layers. DPASV scans were repeated until a stable trace was obtained. The stable trace was then used as the background scan. **Phase 2.** DPASV scan conditions were maintained for the analysis portion of the experiment. Immediately after the end of a scan, a fresh aliquot of analyte was added to increase the [analyte] in the electrochemical cell. After allowing the remaining time to expire, another DPASV scan was recorded and analyzed. This process was repeated over a desired concentration range (typically 3 orders of magnitude in [analyte]).

**Data Analysis and Electrochemical Methods**

Raw traces were processed by subtracting from a background scan (from Phase 1). Once subtracted, traces were analyzed for the maximum peak current of the wave corresponding to analyte oxidation, and RMS noise by fitting to a fifth-order polynomial and determining the residuals. Significant signals were obtained when the maximum peak current was greater than 3×RMS noise. Finally, all statistically significant peak currents were plotted against their corresponding concentrations to give a response curve.
Electrochemical Transformations of Inorganic Probe Molecules

Figure S20. Redox transformations of the inorganic probes used in this study. The most widely reported and most likely transformation is shown for each probe.
Figure S21. List of biologically relevant organic analytes used in this study. Their most widely reported redox behavior is shown as well as the product of reduction/oxidation reactions at electrodes.
Intrinsic Electrochemical Activity of $\text{Co}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ {001} and {100} Materials Deposited on GCE

Figure S22. The change in intrinsic redox activity for the MOF@GCE shown for $\text{Ni}_3(\text{HHTP})_2$ (green traces) and $\text{Co}_3(\text{HHTP})_2$ (blue traces) for the {100} facet (closed lines) and the {001} facet (broken lines). Intrinsic redox activity was observed for the materials only on the first few scans of the cyclic voltammograms (1st scan shown). After 25 scans, the intrinsic redox activity was reduced to unobservable levels (25th scan shown).
**Figure S23.** Glassy carbon controls were taken for each analyte at 50 mV/s in PBS.
IX. Electrochemical Performance of Inorganic Probes on Co$_3$(HHTP)$_2$ {001} and {100} Interfaces

*Ru(NH$_3$)$_6$Cl$_3$ on Co$_3$(HHTP)$_2$ {001} and {100} Interfaces*

![Cyclic voltammograms of Co$_3$(HHTP)$_2$ materials against the inorganic probe Ru(NH$_3$)$_6$Cl$_3$. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.](image)

**Figure S24.** Cyclic voltammograms of the Co$_3$(HHTP)$_2$ materials against the inorganic probe Ru(NH$_3$)$_6$Cl$_3$. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

The response of the surface insensitive probe Ru(NH$_3$)$_6$Cl$_3$ was assessed on the {100} and {100} facets of Co$_3$(HHTP)$_2$ with cyclic voltammetry in an electrolyte solution of 0.1 M KCl. The response showed fast kinetics on both nanomaterials indicating the ability of the materials to adequately perform charge transfer through their bulk to analytes near their surface. The results provided a suitable control to allow the comparison of surface-sensitive probes on both the {100} and {100} interfaces, providing insight into surface-specific effects based on morphology. The similarity of response observed by CV
was borne out in the calculation of $k^0$ values for these two crystallographic orientations. We measured the $k^0$ of Ru(NH$_3$)$_3$Cl$_3$ on Co$_3$(HHTP)$_2$ {100} facet to be $2.1 \times 10^{-2}$ cm/s and $7.2 \times 10^{-2}$ cm/s on Co$_3$(HHTP)$_2$ {001} facets. The similarity of the response of Ru(NH$_3$)$_3$Cl$_3$ at the {100} and {100} facet confirmed that both surfaces were capable of electron transfer to surface-insensitive probes with a similar facility. To test if $k^0$ values, and thus electrochemical properties of the {100} and {001} facets, were tunable as a function of crystallographic orientations, a surface-sensitive probe was tested next.

$K_3$Fe(CN)$_6$ on Co$_3$(HHTP)$_2$ {001} and {100} Interfaces

**Figure S25.** Cyclic voltammograms of the Co$_3$(HHTP)$_2$ materials against the inorganic probe $K_3$Fe(CN)$_6$. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

The Ru-analyte showed diffusion-controlled characteristics on {100} facets but the {001} facet showed passivation of the electrode surface against the surface-sensitive probe.
No oxidation peaks were observed because of the electrode passivation and no assessment of the diffusional process could be made. The HETR constant, $k_0$, was determined to be $1.2 \times 10^{-5}$ cm/s at the {100} interface for the surface-sensitive analyte $K_3\text{Fe(CN)}_6$. The value at {001} facet could not be determined due to the lack of oxidation and reduction peaks in the CV. We interpreted this result as a lack of suitable surface chemistry to aid in the $[\text{Fe(CN)}_6]^{3-/4-}$ electrochemical transformation.

$K_3\text{IrCl}_6$ on $\text{Co}_3(\text{HHTP})_2$ {001} and {100} interfaces

![Image](image_url)

**Figure S26.** Cyclic voltammograms of the $\text{Co}_3(\text{HHTP})_2$ materials against the inorganic probe $K_4\text{IrCl}_6$. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

The transformation of the surface insensitive $[\text{IrCl}_6]^{4-/3-}$ anionic species were measured at the {100} facet and the {001} facets of $\text{Co}_3(\text{HHTP})_2$. The response at the {100} facet revealed a reversible process with oxidation and reduction peaks corresponding to the 1e- reduction and oxidation of $[\text{IrCl}_6]^{4-/3-}$ (Figure S26).
separation at 50 mV/s was 70 mV which was close to a Nernstian response (Figure S26). At the {001} facet of Co₃(HHTP)₂, the response towards K₄IrCl₆ was like that of the {100} facet. From the CVs, we calculated the HETR constant at the {100} interface to be 3.1×10⁻³ cm/s, at the {001} interface the HETR constant was measured to be 4.8×10⁻³.

X. Electrochemical Performance of Organic Probes on Co₃(HHTP)₂ {001} and {100} Interfaces

Ascorbic Acid on Co₃(HHTP)₂ {001} and {100} Interfaces

![Cyclic voltammograms of the Co₃(HHTP)₂ materials against the organic probe ascorbic acid (AA). Randles–Ševčik plots are shown to the right of their corresponding voltammograms.](image)

**Figure S27.** Cyclic voltammograms of the Co₃(HHTP)₂ materials against the organic probe ascorbic acid (AA). Randles–Ševčik plots are shown to the right of their corresponding voltammograms.
Ascorbic Acid at Co$_3$(HHTP)$_2$. CV experiments showed that the {100} of Co$_3$(HHTP)$_2$ provided an observable oxidation wave for AA while the {001} interface was passivating against AA. Even though the {100} of Co$_3$(HHTP)$_2$ showed an observable response, R–Š plots did not demonstrate linearity and the interaction was characterized as a complex mixture of adsorption and diffusion processes that could not be distinguished.

Dopamine on Co$_3$(HHTP)$_2$ {001} and {100} Interfaces

**Figure S28.** Cyclic voltammograms of the Co$_3$(HHTP)$_2$ materials against the organic probe dopamine (DA). Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

DA at Co$_3$(HHTP)$_2$. We first recorded the cyclic voltammograms of DA on the {100} facet (Figure 3f). The oxidation and reduction waves revealed a redox process we assigned to the 2e$^-$/2H$^+$ transformation of dopamine to dopamine quinone. We observed the oxidation peak potential at +327 mV against Ag/AgCl and an $i_p$ of 1.0 $\mu$A. The reduction wave displayed a weak reduction peak at -65 mV. We compared this response to
the response of DA on the {001} facet which showed a similar 2e/2H⁺ redox process with a strong oxidation peak at +225 mV and an \( I_p \) of 6 \( \mu \)A (Figure S19). Compared to the {100} facet, the response of DA at the {001} facet produced a stronger and less broad oxidation peak.

**Uric Acid on Co₃(HHTP)₂ {001} and {100} Interfaces**

![Cyclic voltammograms](image)

**Figure S29.** Cyclic voltammograms of the Co₃(HHTP)₂ materials against the organic probe uric acid (UA). Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

**UA at Co₃(HHTP)₂.** Similar to Ni₃(HHTP)₂-based materials, Co₃(HHTP)₂-based materials showed an enhanced response of UA on the {001} facet of Co₃(HHTP)₂ in both peak potential (+350 mV) and \( I_p \) (2.0 \( \mu \)A) compared to the {100} facet (+370 mV, \( I_p = 0.6 \) \( \mu \)A, Figure S29). UA showed a moderately linear response of the RS plots for both the
\{100\} and \{001\} interfaces. However, the asymmetry between the oxidation and reduction waves (no reduction wave observed) indicated that the oxidation of UA was irreversible on the modified electrodes.
**DOPAC on Co₃(HHTP)₂ {001} and {100} Interfaces**

![Cyclic voltammograms](image)

**Figure S30.** Cyclic voltammograms of the Co₃(HHTP)₂ materials against the organic probe 3,4-dihydroxyphenylacetic acid (DOPAC). Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

**DOPAC at Co₃(HHTP)₂.** DOPAC served as a valuable counterpoint to dopamine because its redox-active functionality is similar to that of DA (catechol group, 2e⁻/2H⁺) but the overall charge of the probe is opposite DA. At similar concentrations to DA (10 µM), the cyclic voltammetry experiments showed no response to DOPAC. We next tried a higher concentration of 100 µM which was similar to the concentration of other interferents studied by CV, such as UA and AA. At 100 µM DOPAC produced an observable oxidation peak at +420 mV with an \(i_p\) of 1.4 µA and a reduction wave with a maximum at -68 mV. At the {001} interface, the response was similar to that observed for the {100} interface. The oxidation peak of DOPAC shifted to +367 mV and with an \(i_p\) of 1.1 µA. The reduction wave shifted to lower oxidation potentials (-107 mV). DOPAC showed excellent linearity...
and was under diffusion-controlled kinetics. However, the peak-peak separation was too high to effectively determine a HETR $k^0$ for the process.
Figure S31. Cyclic voltammograms of the Co₃(HHTP)₂ materials against the organic probe 5-hydroxytryptamine (5-HT). Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

5-HT at Co₃(HHTP)₂. Both materials responded similarly to 10 µM 5-HT. The oxidation peak was observed at +347 mV for the {100} facet and +315 mV for the {001} facet. The $I_p$ values were similar for both materials as well, 1.0 µA for the {100} facet and 1.1 µA for the {001} facet. Neither material showed an appreciable reduction peak on the reverse scan corresponding to the 2e-/2H⁺ reduction of 5-HT but a broad peak at low potentials (-400 – -500 mV) was observed for both orientations.
XI. Electrochemical performance of inorganic probes on Ni₃(HHTP)₂ {001} and {100} Interfaces

*Ru(NH$_3$)$_6$Cl$_3$ on Ni₃(HHTP)$_2$ {001} and {100} Interfaces*

**Figure S32.** Cyclic voltammograms of the Ni₃(HHTP)$_2$ materials against the inorganic probe Ru(NH$_3$)$_6$Cl$_3$. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

The electrochemical response of Ru(NH$_3$)$_6$Cl$_3$ on Ni₃(HHTP)$_2$. The voltammetric response of Ni₃(HHTP)$_2$ {100} and {001} interfaces in 1 mM Ru(NH$_3$)$_6$Cl$_3$ were observed across a range of scan rates between 5–1000 mV/s. The CV of 1 mM Ru(NH$_3$)$_6$Cl$_3$ in 0.1 M aqueous KCl (Figure S23a) showed strong 1e$^-$ oxidation and reduction peaks corresponding to the [Ru(NH$_3$)$_6$]$^{3+/2+}$ redox couple on the {100} surface of Ni₃(HHTP)$_2$. The peak separation ($\Delta E_p$) at 50 mV/s was 110 mV, which was larger than a Nernstian response indicating a semi-reversible process. At slower scan rates, the highly asymmetric peak shape suggested that a catalytic process was possibly occurring at the surface of the electrode following the initial electrochemical faradaic process (EC$^\prime$). At
scan rates below 25 mV/s, multiple oxidation peaks were observed indicating contributions from surface-adsorbed species and freely diffusing species.

For the response of 1 mM Ru(NH$_3)_6$Cl$_3$ on the \{001\} facet of Ni$_3$(HHTP)$_2$ we observed oxidation and reduction peaks corresponding to the 1e$^-$ redox couple of [Ru(NH$_3)_6]^{3+/2}$. The $\Delta E_p$ at 50 mV/s was 116 mV (Figure 3a), which was similar to that found for \{100\} orientation. The asymmetric peak shape indicated a mixed EC' type mechanism which we also observed at \{100\} interfaces. The maximum reduction peak current was less for the \{100\} facet compared to the \{001\} facet. We anticipate this difference is due to the higher concentration of sites responsible for EC'-type catalytic activity (catechol moieties) decorating edge sites compared to the basal plane.

$K_3Fe(CN)_6$ on Ni$_3$(HHTP)$_2$ \{001\} and \{100\} Interfaces

**Figure S33.** Cyclic voltammograms of the Ni$_3$(HHTP)$_2$ materials against the inorganic probe $K_3Fe(CN)_6$. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

The electrochemical response of $K_3Fe(CN)_6$ on Ni$_3$(HHTP)$_2$. We measured the CV response of the Ni$_3$(HHTP)$_2$ \{100\} facet in 1 mM $K_3Fe(CN)_6$ across a range of scan...
rates (Figure S24a). Strong 1e\textsuperscript{−} oxidation and reduction events corresponding to the [Fe(CN)\textsubscript{6}]\textsuperscript{3−/4−} redox couple (Figure S24a) were observed with $E_{1/2}$ of 154 mV. The $\Delta E_p$ at 50 mV/s was 110 mV (Figure 3b) but was Nernstian at scan rates slower than 10 mV/s (Figure S24a).

For the Ni\textsubscript{3}(HHTP)\textsubscript{2} {001} facet, 1e\textsuperscript{−} oxidation and reduction events were observed (Figure S24b). However, the $\Delta E_p$ at 50 mV/s was 383 mV for the {001} facet (Figure 3b) which was significantly higher than the $\Delta E_p$ at the {100} facet. At the slowest scan rate recorded, 5 mV/s, the peak separation was 195 mV which was larger than the expected Nernstian value of 57 mV for a one-electron process indicating a semi-reversible process at the electrode surface.

Between the two crystallographic orientations, the {100} facet maintained smaller peak separations for the transformation of [Fe(CN)\textsubscript{6}]\textsuperscript{3−/4−} across the range of scan rates (5–1000 mV/s), consistent with a faster electron transfer rate. The $k^0$ for these materials with the surface-sensitive probe K\textsubscript{3}Fe(CN)\textsubscript{6} were measured to be $8.4 \times 10^{-5}$ cm/s at the {001} facet, and $2.2 \times 10^{-3}$ cm/s at the {100} facet. The observed HETR constant was 26 times higher on the {100} facet than the basal plane {001} facet indicating both a faster transformation and a catalyzed transformation of the surface-sensitive analyte. We hypothesized that the significantly different properties were a result of differences in surface chemistry caused by changes in the crystallographic orientation of the material ({100} versus {001}). These properties were attributed to changes in the ability of the surface to catalyze the electron transfer reaction.
**K₄IrCl₆ on Ni₃(HHTP)₂ {001} and {100} Interfaces**

![Figure S34](image-url)  
Figure S34. Cyclic voltammograms of the Ni₃(HHTP)₂ materials against the inorganic probe K₄IrCl₆. Randles–Ševčík plots are shown to the right of their corresponding voltammograms.

**The electrochemical response of K₄IrCl₆ on Ni₃(HHTP)₂.** K₄IrCl₆ served as another surface-insensitive probe. The CVs using both the {100} and the {001} interfaces of Ni₃(HHTP)₂ showed small peak separations across a range of scan rates (5–1000 mV/s). We attributed the observed oxidation and reduction waves to the [IrCl₆³⁻/⁴⁻] redox couple. Further analysis of the voltammograms revealed that the inorganic probe was diffusion-limited at the electrodes which allowed characterization of the HETR k⁰ values. On the {100} interface we measured a k⁰ of 5.1×10⁻² cm/s and on the {001} interface we measured a k⁰ of 2.2×10⁻² cm/s.
XII. Electrochemical performance of organic probes on Ni₃(HHTP)₂ \{001\} and \{100\} Interfaces

Ascorbic Acid on Ni₃(HHTP)₂ \{001\} and \{100\} Interfaces

Figure S35. Cyclic voltammograms of the Ni₃(HHTP)₂ materials against the organic probe ascorbic acid (AA). Randles–Ševčík plots are shown to the right of their corresponding CVs.

Electrochemical performance of AA on Ni₃(HHTP)₂. CV experiments showed that both \{100\} and \{001\} Ni₃(HHTP)₂ could participate in the redox transformation of AA (presumably \(2e^-/H^+\)) at the working electrode. However, neither material showed a linear diffusion-controlled process (Figure S35).
**Dopamine on Ni$_3$(HHTP)$_2$ {001} and {100} Interfaces**

**Figure S36.** Cyclic voltammograms of the Ni$_3$(HHTP)$_2$ materials against the organic probe dopamine (DA). Randles–Ševčík plots are shown to the right of their corresponding CVs.

**Cyclic voltammograms of DA on Ni$_3$(HHTP)$_2$ materials.** The electrochemical reaction of 10 µM DA on Ni$_3$(HHTP)$_2$ surfaces was explored using cyclic voltammetry. On the {100} facet, the CV of DA at 50 mV/s showed one oxidation peak at +161 mV with a peak current of 1.9 µA (Figure S27a). Two reduction peaks were observed at -33 mV and -569 mV (Figure S27a). The single oxidation peak corresponded to the 2e$^-$/2H$^+$ oxidation of the catechol group of DA to a quinone oxidation state. We assigned the second reduction peak to the transformation from leuco-dopaminequinone to leuco-dopaminechrome. The overall reaction was assigned to be ECE in nature.$^{85}$ On the {001} facets, the CV of DA at 50 mV/s showed one oxidation peak at +241 mV with a peak current of 6.1 µA (Figure S27b). Two reduction peaks were observed at -26 mV and -635 mV (Figure S27b). Similar to the process on the {100} facets, the single oxidation peak
corresponded to the $2e^\text{/}2H^+$ oxidation of the catechol group of DA. The two reduction peaks at high and low reduction potentials were assigned to the $2e^\text{/}2H^+$ reduction of dopaminequinone and leuco-dopaminechrome, respectively.

Both the \{100\} and \{001\} facets of Ni$_3$(HHTP)$_2$ demonstrated the ability to electrochemically transform DA to DA-quinone via $2e^\text{/}2H^+$ oxidation of the catechol group (Figure S36). CV revealed that DA on \{100\} and \{001\} facets exhibited two distinct differences. First, the maximum current of the oxidation peak of DA was higher on the \{001\} facet over the \{100\} facet (6.1 μA versus 1.9 μA). Second, the potential of the peak was shifted to lower potentials on the \{100\} facet compared to the \{001\} facet by almost 80 mV. The trend in the potential shift was consistent with the trend observed for inorganic probes. The large difference in peak current between the two materials under similar experimental conditions in the detection of DA was attributed to differential adsorption on the \{001\} facet compared to the \{100\} facet. We anticipated that the large difference in peak current would also manifest as a large difference in detection properties between the two distinct orientations, with the \{001\} facet presumably being able to convey larger signals at similar concentrations.
Uric Acid on Ni$_3$(HHTP)$_2$ {001} and {100} Interfaces

**Figure S37.** Cyclic voltammograms of the Ni$_3$(HHTP)$_2$ materials against the organic probe uric acid (UA). Randles–Ševčík plots are shown to the right of their corresponding CVs.

**UA at Ni$_3$(HHTP)$_2$.** We tested UA at a concentration of 0.1 mM. The response at the {001} was higher than the response at the {100} interface. Both materials exhibited similar R-Š curves across a range of scan rates. We assumed there were different regimes of adsorption and diffusion control that were at play and were more pronounced at different scan rates.
**DOPAC on Ni₃(HHTP)₂ {001} and {100} Interfaces**

**Figure S38.** Cyclic voltammograms of the Ni₃(HHTP)₂ materials against the organic probe 3,4-dihydroxyphenylacetic acid (DOPAC). Randles–Ševčík plots are shown to the right of their corresponding CVs.

**DOPAC on Ni₃(HHTP)₂.** The response of DOPAC was determined at the surface of the {100} and {001} facets at a concentration of 100 µM in PBS. The pH of the solution was 7.4. At the {100} facet, the response of DOPAC was observed as $2e^-/2H^+$ oxidation and reduction of the catechol group. At a scan rate of 50 mV/s, an oxidation peak was observed at +301 mV and a reduction peak was observed at -77 mV (Figure S29). The reduction peak was significantly sharper and the oxidation peak more diffuse, indicating an inverse value for $\alpha$ compared to DA. The large peak separation indicated a quasi-reversible process changing to an irreversible process at higher scan rates. At the {001} facet, the electrochemical reaction of DOPAC experienced a significantly higher overpotential. At a scan rate of 50 mV/s, oxidation on the {001} facet was observed at...
+661 mV and the reduction peak was observed at +254 mV. The reduction peak was significantly weaker in intensity compared to the oxidation peak. At sufficiently slow scan rates <5 mV/s, the reduction peak of DOPAC on the {001} facet was not observed, whereas the reduction peak of DOPAC on the {100} was observed even at scan rates as slow as 1 mV/s (Figure S29b).

**Serotonin on Ni$_3$(HHTP)$_2$ {001} and {100} Interfaces**

![Cyclic voltammograms of the Ni$_3$(HHTP)$_2$ materials against the organic probe 5-hydroxytryptamine (5-HT). Randles–Ševčík plots are shown to the right of their corresponding CVs.](image)

**Figure S39.** Cyclic voltammograms of the Ni$_3$(HHTP)$_2$ materials against the organic probe 5-hydroxytryptamine (5-HT). Randles–Ševčík plots are shown to the right of their corresponding CVs.

5-HT on Ni$_3$(HHTP)$_2$. Serotonin produced a weak signal on the MOFs and the response did not appear to be a diffusion-controlled process at the electrode interface. Both the {100} and {001} interfaces produced similar responses with neither material showing dramatic sensitivity. The R-Š plots were reminiscent of those of UA on {001} Ni$_3$(HHTP)$_2$. 

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Figure S40. Summary of M₃(HHTP)₂ electrodes with inorganic probes. Cyclic voltammograms of the \{100\} and \{001\} facets of (a–c) Ni₃(HHTP)₂ and (d–f) Co₃(HHTP)₂ with the inorganic analytes (left to right) Ru(NH₃)₆Cl₃, K₃Fe(CN)₆, and K₄IrCl₆. The concentration of all the inorganic analytes was 1 mM. All voltammograms were recorded in 0.1 M KCl. A scan rate of 50 mV/s was used to obtain all traces.
XIII. Analysis of Electrochemically Active Surface Area (ECSA)

ECSA values are unitless ratios that describe the actual surface area involved in an electrochemical system. The values obtained are unique to each analyte-electrode pairing and higher values indicate more surface area is accessible for electrode-analyte interactions.

Analysis of the non-Faradaic current in the presence of a specific analyte across a range of scan rates (1000 mV/s to 5 mV/s) allows the capacitive double layer (Cdl) to be extracted from the slope of a current-scan rate plot (Figure S31). Since the scan rate is in units of volts/second, and the current density obtained from CV data is defined as A/cm², the slope of the current/scan rate plot describes a capacitance value in F/cm² when multiplied by the electrode geometric area. The Cdl of nanorods, {001} films, and GCE were normalized against the Cdl of GCE which provided a reference of surface area for a smooth non-porous surface.
Figure S41: Scan rate studies of A) GCE, B) films of \{001\} oriented Ni₃(HHTP)₂, and C) nanorods in the presence of 10 μM and the respective current-scan rate plots. Black arrows indicate the potential at which the non-Faradaic current was monitored to produce the current-scan rate plots. The ECSA values we found indicated that nanorods have nearly twice the active surface area of the \{001\} interface. CAT: catechol
Figure S42. Electrochemical surface area study of Ni$_3$(HHTP)$_2$ materials. The values from this study are shown in Table S1 and were used in the Langmuir isotherm studies. The error bars in plots represent standard deviation of current densities from the mean. 3–4 replicates of each experiment were performed.

| Electrode Material | Ni$_3$(HHTP)$_2$ (100) | Ni$_3$(HHTP)$_2$ (001) | Glassy Carbon |
|--------------------|-------------------------|-------------------------|---------------|
| Normalized ECSA    | 1.54 ± 0.07             | 0.71 ± 0.12             | 1.00 ± 0.08   |
| Electrode Surface Area (mm$^2$) | 10.9 ± 0.50 | 4.99 ± 0.54 | 7.07 ± 0.40 |

Table S1. Summary of ECSA values used in the Langmuir isotherm studies.
XIV. Differential Pulse Adsorption Stripping Voltammetry (DPASV) of DA on Ni₃(HHTP)₂

Differential pulse techniques are a powerful analytical electrochemical method because they mitigate capacitive interference of electrolyte double-layers at the electrode surfaces before measurement. The technique is quantitative and is the method we chose to determine limits of detection (LOD) for MOFs towards analytes. DPASV was used to take advantage of and enhance the favorable Coulombic interactions we inferred between DA and the nanomaterials. The DPASV waveform was composed of a typical DPV waveform (scan rate: 50 mV/s, pulse width: 20 mV) preceded by a low and continuous ‘cell-on’ potential (-0.1 V) for 2 min. The Ni₃(HHTP)₂ materials showed the best sensitivity towards DA in CV experiments, and we focused our efforts on that material–analyte pair.

**Figure S43.** Three iterations of the detection of DA on Ni₃(HHTP)₂ {001} interface using the DPASV method. Over the three repetitions used in this study, the LOD was found to be 9.9±2 nM.
XV. Differential Pulse Adsorption Stripping Voltammetry (DPASV) of DA in the Presence of DOPAC on the \{001\} Interface of Ni$_3$(HHTP)$_2$

Figure S44. DPASV experiments were used to determine the LOD towards DA in the presence of (left) 5 μM DOPAC and (right) 50 μM DOPAC. The calibration curves at lower [DA] show good linearity, at higher [DA] the curves show a saturation response.
XVI. Detection of Dopamine in Simulated Cerebrospinal Fluid.

To determine the efficacy of the nanostructured nanomaterial Ni$_3$(HHTP)$_2$ {001} towards the detection of DA in biological media, we performed DPASV experiments in simulated cerebrospinal fluid (CSF). The simulated CSF was based on a 1X PBS buffer augmented with 7 μM uric acid, 5 mM glucose, and 0.5 % (500 mg/L) of bovine serum albumin (BSA). This mixture constituted a challenging media for the detection of dopamine due to the presence of redox active UA, and the high concentration of the protein BSA. The LOD we determined for DA using DPASV in simulated CSF was 214 ± 48 nM (n = 3, Figure S45).

![Figure S45](image_url)  

**Figure S45.** Three DPASV experiments for the detection of DA in simulated cerebrospinal fluid CSF). The working electrode was Ni$_3$(HHTP)$_2$ {001}.
XVII. Langmuir Isotherm Studies of the Adsorption of DA and DOPAC on Ni₃(HHTP)₂ Interfaces.

Isotherms are plots of the amount of analyte adsorbed on a surface versus the analyte concentration or pressure. The information from these plots can be used to better understand analyte adsorption mechanisms and analyte–surface interactions. Langmuir adsorption isotherms, based off the isotherm model by Irving Langmuir, were originally designed to model gas–solid adsorption, but can be used to determine the surface coverage and adsorption strength of liquid-phase analytes to an electrode surface. Previous work has utilized Langmuir isotherms to compare the efficacy of different electrode materials in detecting biological analytes such as DA. Ross and coworkers studied isotherms to identify the binding parameters of purine NTs to plasma-treated carbon fiber microelectrodes. We used Langmuir adsorption isotherms to quantify MOF–analyte interactions. This model assumes that a fixed number of heterogeneous host sites are available for adsorption, and that only a monolayer of analyte adsorbs. While these assumptions limit our ability to differentiate between unique adsorptions that may be occurring at the anisotropic MOF surface, the Langmuir model can still provide information about the ensemble-level interactions occurring at the morphologically tuned surfaces of Ni₃(HHTP)₂{100} and Ni₃(HHTP)₂{001}.

**Figure S46.** Schematic of experimental approach. An electrochemical cell is used to collect cyclic voltammograms at varying analyte concentrations. A Langmuir isotherm is created by converting the peak current \( i_p \) from the voltammogram to surface coverage \( \Gamma_A \) and plotting \( \Gamma_A \) versus analyte concentration. From this plot, key binding parameters such as saturation surface coverage \( \Gamma_S \), and Gibbs free energy of adsorption \( \Delta G^o \) are derived.

Oxidative peak currents derived from cyclic voltammograms can be used to calculate electrode surface coverage using **Equation S1**, in which \( i_p \) is the maximum oxidative peak current (A), \( n \) is the number of electrons transferred in the redox reaction, \( F \) is the Faraday constant (C

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mol\(^{-1}\)), \(v\) is the scan rate (V s\(^{-1}\)), \(A\) is the electrode surface area (m\(^2\)), \(\Gamma_A\) is the surface coverage (pmol cm\(^{-2}\)), \(R\) is the ideal gas constant (J mol\(^{-1}\) K\(^{-1}\)), and \(T\) is the temperature (K).\(^{11}\)

\[
i_p = \frac{n^2 F^2 v A \Gamma_A}{4RT} \quad \text{eq. S1}
\]

The analyte concentration \([A]\) (μmol L\(^{-1}\)) can then be plotted versus \(\Gamma_A\), and a best fit curve for this relationship is calculated using the Langmuir adsorption equation (Equation S2).\(^{11}\) The saturation surface coverage \(\Gamma_S\) (pmol cm\(^{-2}\)) and thermodynamic equilibrium constant of adsorption \(\beta\) (cm\(^3\) pmol\(^{-1}\)) can be determined by computationally adjusting the two parameters until the weighted least-squares curve is found.

\[
\Gamma_A = \frac{\Gamma_S \beta [A]}{1 + \beta [A]} \quad \text{eq. S2}
\]

Lastly, \(\beta\) can be used to calculate the Gibbs free energy of adsorption \(\Delta G^\circ\) (KJ mol\(^{-1}\)) using Equation S3.\(^{13}\)

\[
\Delta G^\circ = -RT \ln(\beta) \quad \text{eq. S3}
\]

Isotherm experiments were used to determine parameters related to the adsorption of DA and DOPAC on the electrode materials GCE, Ni\(_3\)(HHTP)\(_2\) \{100\}, and Ni\(_3\)(HHTP)\(_2\) \{001\}. Isotherm experiments consisted of a series of CVs wherein analyte (DA or DOPAC) was added to three electrode cell with a working electrode of the desired type, in a series of additions each followed by one CV scan. After each analyte addition, the electrochemical cell was briefly swirled then left undisturbed for two minutes to allow the analyte to diffuse throughout the electrolyte. Then, a CV scan across the -0.7–0.7 V potential window at 50 mV/s was taken. Experiments included analyte concentrations of 10, 20, 40, 60, 80, 100, 200, 400, 600, 800, 1000, 2000, and 3000 μM. The oxidative peak for each CV was then measured, plotted against concentration, and fit to the Langmuir model.

We chose to focus our Langmuir isotherm studies on the analytes DA and DOPAC with working electrodes based on the Ni\(_3\)(HHTP)\(_2\) system. This system represented both the most analytically promising set of materials from a sensitivity perspective, but also the most promising set of materials considering the ability to differentiate between analytes (DA versus UA) and suppress the analytical response towards undesired interferents (DOPAC) by voltammetry. We also chose to study the adsorption parameters of GCE towards DA and DOPAC as a benchmark.
material and to provide context due to the inherently weak sensitivity and selectivity we and others observed for DA in this study.

| Electrode Material | Ni$_3$(HHTP)$_2$ {100} | Ni$_3$(HHTP)$_2$ {001} | Glassy Carbon |
|--------------------|------------------------|------------------------|---------------|
| Analyte            | DA                     | DOPAC                  | DOPAC         |
| $\Gamma_S$ (pmol/cm$^2$) | 3946 ± 86              | 2614 ± 501             | 2714 ± 62     |
| $\beta$ (cm$^3$/pmol) | 3.43×10$^{-3}$ ± 0.31×10$^{-3}$ | 2.55×10$^{-4}$ ± 0.72×10$^{-4}$ | 1.38×10$^{-2}$ ± 0.14×10$^{-2}$ |
| $\Delta G$ (kJ/mol)  | - 20.2 ± 0.2           | - 13.7 ± 0.7           | - 23.6 ± 0.3 |
| $\Gamma_S$ (pmol/cm$^2$) | 5155 ± 1118             | 22951 ± 9049            |               |
| $\beta$ (cm$^3$/pmol) | 2.69×10$^{-4}$ ± 0.91×10$^{-4}$ | 3.14×10$^{-5}$ ± 1.16×10$^{-5}$ |               |
| $\Delta G$ (kJ/mol)  | - 13.9 ± 0.8           | - 8.5 ± 0.9            |               |

**Table S2.** Adsorption parameters obtained from Langmuir isotherm experiments.
Figure S47. Cyclic voltammograms of Ni$_3$(HHTP)$_2$ (100) and Ni$_3$(HHTP)$_2$ (001), and GCE against DA and DOPAC. Analytes were measured at 100 μM and voltammograms were measured at 50 mV/s in 0.1 M PBS.
XVIII. Computational Methods, Process, and Results

The models used for our simulations of the Co$_3$(HHTP)$_2$ and Ni$_3$(HHTP)$_2$ MOFs were based on the crystal structures reported by Hmadeh et al.\textsuperscript{1} In the preparation of the systems for our simulations, the MOF structures were created by alternatively stacking three layers of the extended structures formed by the coordination of metal ions and HHTP linkers and two layers formed by trinuclear complexes of type M$_3$(HHTP)(H$_2$O)$_{12}$ (where M = Co or Ni).\textsuperscript{1} Each system was created by placing one type of MOF (Co$_3$(HHTP)$_2$ or Ni$_3$(HHTP)$_2$) at the center of the simulation box, then adding 27 molecules of a given analyte of interest (Dopamine or DOPAC) around the MOF (Figure S49). Each system was then solvated with TIP3P water and equilibrated for 100 ps at 293 K and 1 atm. Following equilibration, molecular dynamics (MD) simulations were performed in the NPT ensemble on each system for 20 ns with a time step of 2 fs using the DL_POLY_4 package.\textsuperscript{2} Restraints were added to the oxygen atoms in the HHTP fragments to ensure the stability of the layered structure of the MOF was kept in place throughout the simulations.

Figure S48. Optimized structures from MD simulations of the MOFs showing the a) {001} interface of Ni$_3$(HHTP)$_2$, b) {001} interface of Co$_3$(HHTP)$_2$, c) the {100} interface of Ni$_3$(HHTP)$_2$, and d) {100} interface of Co$_3$(HHTP)$_2$. These structures were used as the starting point for all-atom simulations with analytes. Water molecules not directly bound to the MOF structure are not shown for clarity.
Force field parameters

The force field parameters to model the interactions of dopamine, DOPAC, and organic linker (HHTP) molecules were obtained from the General Amber Force Field (GAFF).\(^3\) To describe the interactions involving Co\(^{2+}\) in the extended Co\(\text{III}(\text{HHTP})_2\) structures, we used the force field parameters reported by Shi et al.\(^4\) The Lennard-Jones (LJ) parameters for Co were also obtained from the work performed by Shi et al.,\(^4\) while the LJ parameters for Ni were obtained from the Universal Force Field (UFF).\(^5\)

![Figure S49](image)

**Figure S49.** The initial structure of a model system for Co\(\text{III}(\text{HHTP})_2\) with 27 dopamine molecules. (a) Basal facet view. (b) Edge facet view.

We developed the force field parameters for the interactions involving Co\(^{2+}\) in the trinuclear complex (Co\(\text{III}(\text{HHTP})(\text{H}_2\text{O})_{12}\)), as well as for the interactions involving Ni\(^{2+}\) in both the extended structure (Ni\(\text{III}(\text{HHTP})_2\)) and the trinuclear complex (Ni\(\text{III}(\text{HHTP})(\text{H}_2\text{O})_{12}\)). To develop the parameters, we first identified subunits in the Ni\(\text{III}(\text{HHTP})_2\), Ni\(\text{III}(\text{HHTP})(\text{H}_2\text{O})_{12}\), and Co\(\text{III}(\text{HHTP})(\text{H}_2\text{O})_{12}\) structures (**Figure S35**), then we performed molecular optimization and vibrational frequency calculations on these subunits with the B3LYP/6-31G basis set using the GAMESS-US software.\(^6\) Based on the vibrational frequency data for the subunit of each structure, the Seminario method was implemented using the VFFDT software\(^7\) to generate the bond and angle parameters for the force field.
Figure S50. Subunits structures used in force-field development. (a) Ni₃(HHTP)₂, (b) Ni₃(HHTP)(H₂O)₁₂, and (c) Co₃(HHTP)(H₂O)₁₂.
Summary of simulations

At the endpoint of the simulations, the interactions between the adsorbed analyte and MOF sites were tabulated (Table S1–S4). Analytes that did not interact with the MOF were not included.

Figure S51. Types of interactions observed between different analytes and MOFs. Structures of the MOFs are represented by spheres (blue = Ni, gold = Co, red = O, gray = C, protons and aqua ligands were removed for clarity), and analytes are represented by stick structures. (a) Hydrogen bonding between both the catechol and ammonium termini of dopamine (DA) and heteroatoms of the organic ligand on {100} Ni$_3$(HHTP)$_2$. (b) Hydrogen bonding between the ammonium end of DA and the organic ligand of {001} Ni$_3$(HHTP)$_2$. (c) DA adsorbed to {100} Co$_3$(HHTP)$_2$ via both the catechol and the ammonium termini and the heteroatoms of the HHTP ligands. (d) DA adsorbed to {001} Co$_3$(HHTP)$_2$ via H-bonding between the ammonium termini and the heteroatoms of the MOF. (e) DOPAC adsorbed to {100} Ni$_3$(HHTP)$_2$ via hydrogen bonding between the catechol and the heteroatoms of the HHTP ligands. (f) Acetate end of DOPAC interacting directly with the Ni$^{2+}$ on {001} Ni$_3$(HHTP)$_2$. (g) Hydrogen bonding between the acetate end of DOPAC and aqua ligands on Co$^{2+}$ of {100} Co$_3$(HHTP)$_2$. (h) Acetate end on DOPAC directly coordinating with Co$^{2+}$ of {001} Co$_3$(HHTP)$_2$. When analytes are adsorbed on the basal face of the MOF, they also interact with the MOF via π-π stacking, observed in panels (b), (d), and (f).
Table S3. Observed interactions between dopamine and Ni$_3$(HHTP)$_2$ in simulations.

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Ammonium         |              |
| 0                  | 0                | 0            |

{1 0 0}

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Ammonium         | Both         |
| 0                  | 0                | 2            |

{0 0 1}

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Ammonium         | Both         |
| 0                  | 0                | 0            |

{0 0 1}

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Table S4. Observed interactions between DOPAC and Ni$_3$(HHTP)$_2$ in simulation.

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Acetate          |              |
| 0                  | 2                |              |

{1 0 0}

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Acetate          | Both         |
| 0                  | 2                | 2            |

{0 0 1}

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Acetate          | Both         |
| 0                  | 0                | 0            |

{0 0 1}

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Table S5. Observed interactions between dopamine and Co$_3$(HHTP)$_2$ in simulations.

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Ammonium         |              |
| 0                  | 0                | 1            |

{1 0 0}

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Ammonium         | Both         |
| 0                  | 0                | 9            |

{0 0 1}

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol           | Ammonium         | Both         |
| 0                  | 0                | 1            |

{0 0 1}

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Table S6. Observed interactions between DOPAC and Co₃(HHTP)₂ in simulations.

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol          | Acetate          | Both         |
| 0                  | 1                | 0            |

Co₃(HHTP)₂ + DOPAC

| Metal Coordination | Hydrogen Bonding | π-π Stacking |
|--------------------|------------------|--------------|
| Catechol          | Acetate          | Both         |
| 0                  | 3                | 0            |
XIX. References

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