Host-Guest Interactions on Electrode Surfaces for Immobilization of Molecular Catalysts

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Host-guest interactions on electrode surfaces for immobilization of molecular catalysts

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Abstract

The strategy of anchoring molecular catalysts on electrode surfaces combines the high selectivity and activity of molecular systems with the practicality of heterogeneous systems. The stability of molecular catalysts is, however, far less than that of traditional heterogeneous electrocatalysts, and therefore a method to easily replace anchored molecular catalysts that have degraded could make such electrosynthetic systems more attractive. Here, we apply a non-covalent “click” chemistry approach to reversibly bind molecular electrocatalysts to electrode surfaces via host-guest complexation with surface-anchored cyclodextrins. The host-guest interaction is remarkably strong and allows the flow of electrons between the electrode and the guest catalyst. Electrosynthesis in both organic and aqueous media was demonstrated on metal oxide electrodes, with stability on the order of hours. The catalytic surfaces can be recycled by controlled release of the guest from the host cavities and readsoption of fresh guest. This strategy represents a new approach to practical molecular-based catalytic systems.
Molecular electrocatalysts can exhibit surprisingly high activities and selectivities that are unmatched by most heterogeneous catalysts.\textsuperscript{1,2} Therefore, the development of robust immobilization strategies for these molecular species on electrode surfaces is of great interest if these molecular catalytic activities and selectivities are to be transferred to more practical heterogeneous electrosynthetic systems,\textsuperscript{3} which have already shown promising results for CO\textsubscript{2} reduction, water reduction and water oxidation in the context of storage of renewable energy.\textsuperscript{4-6} Over the past decades, many immobilization strategies have been developed,\textsuperscript{7} which can be categorized into covalent binding (achieved by adding anchoring groups such as carboxylate to the catalysts),\textsuperscript{8} non-covalent binding (pi-stacking on carbon-based electrodes)\textsuperscript{9,10} and polymerization-based binding.\textsuperscript{11-13} Here, we report a new strategy for surface immobilization of molecular electrocatalysts, which relies on a non-covalent “click” chemistry approach to bind molecular species in well-defined sites on electrode surfaces.\textsuperscript{14}

The binding of electroactive molecular guests into molecular pockets by means of host-guest complex (HGC) formation has previously been studied by several groups, including those of Stoddart and Kaifer,\textsuperscript{15} Reinhoudt\textsuperscript{16,17} and Huskens.\textsuperscript{18} Liu \textit{et al.} reported the HGC-formation on gold surfaces with the C\textsubscript{60} monoanion as guest, which was found to be electrochemically stable over prolonged durations.\textsuperscript{19} Light-induced electron transfer to and from dye molecules bound via the HGC approach was also demonstrated by Freitag and Galoppini.\textsuperscript{20,21} The group of Sun demonstrated the use of HGC to improve electron transfer between a molecular catalyst and a dye molecule bound onto TiO\textsubscript{2}.\textsuperscript{22}

Among the diverse class of host molecules, cyclodextrins, cucurbiturils and calixarenes are the most studied for HGC formation on different surfaces.\textsuperscript{23,24} For cyclodextrins, the electron transfer rates between the electrode and guest molecules situated inside the surface-bound hosts have been reported to be on the order of 100 s\textsuperscript{-1}, indicating the potential applicability of these systems for molecular electrocatalysis.\textsuperscript{25} It was found that the binding of the guest was not affected by redox processes if the binding units do not undergo oxidation themselves.
Although rapid electron transfer to HGC-bound molecules has been demonstrated, to the best of our knowledge there have been no reports on using this approach to bind molecular catalysts to electrode surfaces, likely because the dynamic HGC formation in solution phase suggests that rapid desorption would occur. We demonstrate, however, that molecular guests bind with surprisingly high stability and show that these are catalytically active. We also show that the binding of the guests is reversible under controlled conditions and exchange of these guests can be induced. We further demonstrate regeneration of the catalytic activity of the electrodes after re-adsorption of fresh electrocatalytic guests, implying the high stability of the host under operational conditions of the bound catalysts.

**Results and Discussion**

We designed the immobilization system to be as compact as possible, using short tethers to attach the hosts to the electrode surface, ensuring close contact between the electroactive guest and the electrode surface. An aromatic binding unit was chosen as guest binding unit to facilitate electron transfer to the catalytically active site of the guest. With the compact design, displacement of the guests by water or solvent from the opposite face of the host should be inhibited. Higher binding constants of guests in surface-bound hosts compared to the binding in solution have been reported, and the increased binding strength was proposed to be related to further interactions between guest and surface. For hosts with long, flexible chains connecting them to the surface, studies with multi-valent guests showed that HGCs could be stable on a multi-hour time-scale.

**Analysis of host-guest complex formation on electrode surfaces**

Following our design criteria, we chose to study the per-thiolated derivate of β-cyclodextrin, on gold as a model for host binding close to the surface (Figure 1 a), as this molecule has been thoroughly studied for its surface-functionalization and surface HGC formation behaviour on gold. As guests, we chose to investigate ruthenium-based electrocatalyst, inspired by the class of molecular catalysts that has very
recently been shown to be active for ammonia oxidation in organic electrolytes (ammonia being a promising candidate as storage medium for hydrogen).\textsuperscript{31–34} We also investigated structurally similar ruthenium-based electrocatalyst 3, a derivate of which we have reported to be active for water oxidation.\textsuperscript{35} As a control, fluorescent platinum complex 4 was synthesized, which served as a non-electroactive guest. The complexes used in this study and their crystal structures are given in Figure 1 b-d. The common design feature in the guest metal complexes is the naphthyl substitution on the terpyridine ligand, which was employed as the binding unit of the guests inside the cyclodextrin cavity.

\textbf{Figure 1. Structures of the main compounds used in this paper:} a) host 1 (thiolated cyclodextrin) and host 5 (bisphosphonated cyclodextrin), along with a depiction of the host cavity; b) guest 2 c) guest 3 d) guest 4. The crystal structures of guests are displayed showing the 50 \% thermal ellipsoids. Solvent and counterions (PF\textsubscript{6}– for guests 2 and 3; ClO\textsubscript{4}– for guest 4) are omitted for clarity.

To confirm that binding between the guests and cyclodextrin takes place in solution, fluorescence titrations and NMR experiments were performed (see Figures S1 and S2 in Supporting Info). A 1:1 stoichiometry binding constant for fluorescent guest 4 with β-CD was determined and a binding constant of $K_{11} = 6.5 \cdot 10^3 \text{ M}^{-1}$ was obtained, which is 2-4 times higher than for other naphthyl-based guests with β-CD.\textsuperscript{36,37}
The attachment of $\textbf{1}$ on gold substrate was investigated by X-ray photoelectron spectroscopy (XPS) (Figure S3) and tip-enhanced Raman spectroscopy (TERS) (*vide infra*). The spectra indicated the expected attachment of the cyclodextrin host via the thiol groups, as was evidenced by the loss of the $\nu$(S-H) Raman band upon adsorption. The surface density of $\textbf{1}$ on Au(111) determined by XPS was found to be up to 0.46 nm$^{-2}$, corresponding to a relatively compact layer of host molecules on the substrate. We note that the maximum coverage of the surface was achieved with dipping times of 3 minutes, with no further increase in the surface coverage of $\textbf{1}$ at longer exposure of the gold substrate (Figure S4).

The formation of HGCs with the gold-bound $\textbf{1}$ was investigated using TERS, and DFT calculations were performed to gain a better understanding of this system. The optimization of $\textbf{1}$ on an Au(111) slab (more details in Methods and SI) revealed the expected binding of the host via all seven thiol groups, despite the mismatch in symmetry with the gold substrate (Figure 2a), and is consistent with the complete loss of the $\nu$(S-H) band in the TER spectra of $\textbf{1}$ on Au (see Figure 3a).
Figure 2. DFT optimized binding structure of 1 on gold in a) plan view and b) side view, showing each thiol group bound to gold in a unique binding geometry. c), d) and e) The optimized structures of HGC bound metal guests 2, 3 and 4, respectively, on gold show the guests bound tightly into the host cavity very close to the surface of the electrode, with the catalytically active site (for guests 2 and 3) above the top face of the host.

Formation of the HGCs was first computed at the DFT level of theory for all guests in the gas phase (more details in SI and Figures S5, S6 and S7), which gave binding energies between 1 host and the guests of -2.03 eV (guest 4) and -2.17 eV (guests 2 and 3). On the Au(111) surface, the binding energies between guests and surface-bound 1 were found to be between -4.31 eV and -4.89 eV, which reveals a dramatic increase in adsorption energy into the cyclodextrin cavity. This large increase in the adsorption energy is related to delocalization of electronic states of the guest molecules and the gold substrate (see Figure S8 and S9), which
is evidenced by significant mixing of gold and guest orbitals. The strong interactions and delocalization of electronic states indicate that oxidation or reduction of electroactive guests (2 and 3) can be easily achieved. However, strong coupling also implies that the diagnostic redox peaks of the guest in cyclic voltammetry (CV) experiments would be absent, similar to the case with graphite-conjugated molecules that lack clear redox peaks in CV experiments.39 Indeed, we did not observe redox peaks for the ruthenium-based guests bound to 1 on gold at the respective redox potentials found in solution (Figure S10), even as a low catalytic current was observed from the HGC of guest 2 with host 1 on dodecanethiol-poisoned gold substrates (Figure S11).

The large binding energies obtained from the DFT calculations provide an understanding of the experimentally observed greater stability of the guests bound to the host-functionalized surface versus HGC binding in solution. Thus, conditions need to be developed to actively remove the guests from the surface-bound hosts for recycling purposes. The desorption of guests under competitive HGC formation in solution has been reported,28,40 and this strategy was also employed to show that guest binding to the 1 modified gold substrates could be controlled under specific conditions.

Using TERS (Figure 3a), we were able to track the presence of guest 3 on gold functionalized with host 1. Formation of the HGC on the Au surfaces was visualized by the appearance of an intense Raman fingerprint of the guest between 1000 and 1600 cm⁻¹ compared to the moderately strong ν(C-H) band of 1 at 2900 cm⁻¹ (cyclodextrins are very weak Raman scatterers). Desorption of the majority of guest was achieved by soaking and sonication of the sample in a concentrated β-CD solution (indicated by the strong decrease in the guest/host Raman band intensity ratio). Re-adsorption of the guest was observed after re-soaking the desorbed sample in a solution of 3. In a separate experiment, we also showed that guest 4 (Pt complex) can be exchanged for a second guest 2 by initial desorption of 4 using concentrated β-CD solution and subsequent incubation in a solution of guest 2 (Figure 3b). The exchange was enabled by the release of guest 4 from the surface-bound host cavities during the desorption step and cannot be explained with stronger binding of guest 2 compared to guest 4, as the reverse exchange (2 for 4) is also feasible (Figure S12). Interestingly,
complete loss of guest signal after the desorption treatment was never observed, which again hints towards
the unexpectedly strong interaction between the guest and the 1-functionalized gold. Raman and TERS
measurements of guest 2 revealed a red-shift of the guest’s optical absorption maximum upon host-guest
binding on the gold surface, which illustrates the shrinking of the HOMO-LUMO gap predicted by the DFT
calculations, providing further evidence for the strong coupling between the gold substrate and the guest
(Figure S13). Direct observation of 1 and the HGCs on Au(111) was attempted by STM, however a clear image
could not be obtained despite significant efforts (Figure S14).

Studying the electrochemical properties of the HGCs on gold alone was not sufficient to obtain a clear picture
of our catalytic system. Gold electrodes are known to undergo surface oxidation,\textsuperscript{41} which leads to the
desorption of thiol-based adsorbates.\textsuperscript{42,43} Furthermore, the relatively low surface area and high background
activities of gold for many catalytic processes make the analysis of catalytically active adsorbates very
difficult.\textsuperscript{44}

To address these issues and to compliment the array of available analytical techniques to study the surface-
bound HGCs, metal oxide (MO) substrates were used, specifically indium tin oxide (ITO), zirconium dioxide
(ZrO\textsubscript{2}), and titanium dioxide (TiO\textsubscript{2}). As these materials have similar properties in terms of surface-adsorption
chemistry,\textsuperscript{45} the choice of substrate can be tailored to the application of analytical technique (ITO for
electrochemical measurements, ZrO\textsubscript{2} for fluorescence and IR, and TiO\textsubscript{2} for solid state NMR). Furthermore, by
preparing mesoporous layers of the MOs, higher surface areas are easily accessible, allowing for the use of
further spectroscopic methods and simplifying the analysis of electrochemical data.
Figure 3. Regeneration and exchange of the catalysts on the host-functionalized Au surface. a) The binding of 1 to Au via all seven thiolate groups is confirmed by the complete absence of the S-H stretching vibration in the TERS spectrum I of 1-functionalized gold. Reversible adsorption and desorption of 3 on host-functionalized gold is reflected in the varying intensity of the peaks at 1000-1600 cm\(^{-1}\) in spectra II-IV. The spectra are normalized with respect to the C-H stretching band of 1 at 2900 cm\(^{-1}\) (highlighted in green). b) Desorption and subsequent exchange of 4 by 2 on host-functionalized gold is confirmed by the shift of the ring breathing modes (RBM) of the metal-coordinated pyridyl rings from 1050 cm\(^{-1}\) for Pt toward 1030 cm\(^{-1}\) for Ru (highlighted in blue). The incomplete desorption of 4 is reflected in the residual intensity of 4 in spectrum II and in the mixed signals of 4 and 2 in spectrum III.

To transfer the HGC chemistry from the gold to the MO substrates, two strategies were employed: direct introduction of multiple suitable binding groups, geminal bisphosphonates (BP),\(^{46}\) to the host scaffold (host 5, see Figure 1) or pre-functionalization of the MO substrates with propiolic acid and subsequent thiol-yne click chemistry on the surface.\(^{47}\) Both strategies are schematically shown in Figure S15. The host molecules on MO substrates are slightly further away from the surface, and electrons are more localized and tightly bound in MOs.\(^{48, 49}\) These factors may lead to decreased electronic coupling of the guests with the surface.
Surface binding of the CD hosts was analysed by IR spectroscopy, XPS and solid state NMR (Figures S16, S17 and S18 in SI). Furthermore, impedance spectroscopy revealed the increased charge-transfer resistance after binding of host 5 to an ITO electrode, which is in accordance with previous observations on gold electrodes (Figure S19). Submersion of the host-functionalized electrodes into guest solutions led to the formation of surface-bound HGCs accompanied by physisorbed guest species. The presence of the guests on the surface could be clearly determined by various spectroscopic methods and by electrochemical measurements (Figures S20, S21, S22 and S23). Removal of physisorbed species was achieved by treatment of the samples with 100 mM acetic acid in methanol, as was determined by the loss of guest fluorescence signal from a physisorbed sample on ZrO₂ (Figure S24). Formation of the host-guest complexes could also be seen during cyclic voltammetry experiments: whereas physisorbed guests rapidly desorb after a few cycles, redox-features of the HGCs could be observed even after extended cycling (Figure S25). A binding constant for HGC formation of guest 3 with host 5 on ZrO₂ of \( K_{11}^{\text{surf}} = 3.3 \times 10^5 \text{ M}^{-1} \) was calculated based on a Langmuir-type model (Figure S26).

Exposing mesoporous ZrO₂ substrates with HGC-bound guests to the desorption conditions used for the gold (with heating of the solution instead of sonication, to preserve the mesoporous substrate), the removal of guests from the surface could be tracked by fluorescence spectroscopy. The same reversible desorption and re-adsorption of different guests (as was shown for the gold electrode using TERS) indicates that the surface can be modified without degrading the surface-bound hosts (Figure S27).

**Catalysis using host-guest complex bound molecular electrocatalysts**

Catalyst 2 –designed as a molecular ammonia oxidation catalyst and equipped with a naphthyl binding group– shows the expected homogeneous phase catalytic activity for NH₃ oxidation in THF solution around its first oxidation potential (Figure 4a). A sample with HGC-bound 2 was then tested under the same conditions and also showed a clear onset of catalysis at the same potential as in solution (around -0.1 V vs. Fc/Fc⁺, Figure 4b). The control samples with non-active guest 4 showed a much later onset of NH₃ oxidation (taking place...
directly on the electrode surface), and physisorbed catalyst led to lower current with a rapid loss of activity during operation (Figure S28).

**Figure 4. Electrocatalytic oxidation of NH₃ in THF solution.** a) CV scan under homogeneous reaction conditions using an ITO working electrode in NH₃ saturated THF solution (0.2 M TBAPF₆ and 0.1 M NH₄PF₆ as conducting salt and proton source; 10 mV/s scan rate). Without catalyst (black) shows low activity. For a 0.1 mM solution of guest 2 in the absence of NH₃, the Ru(II)/Ru(III) redox peak is observed (green). Upon addition of ammonia, a catalytic onset for ammonia oxidation is observed at the Ru(II)/Ru(III) oxidation potential (magenta). b) CV scans of HGC-bound guests 2 (magenta) and 4 (black) with host 5 on mesoporous ITO show the same catalytic behaviour in the presence of the ruthenium catalyst, with onset at the Ru(II)/Ru(III) oxidation potential measured for HGC-bound 2 without NH₃ (green). The conditions are the same as for (a). c) Chronoamperometry at 0.08 V vs Fc/Fc⁺ using host 5-bound catalyst guests 2 and 4
(the latter as a non-catalytically active reference). Readsortion of guest 2 after 30 minutes of catalysis into the host-functionalized electrodes leads to complete regeneration of catalytic activity.

The stability of the HGC-bound electrocatalyst 2 under operation was analysed by chronoamperometry, revealing a slow decrease in current to roughly 70 % of the initial value over 30 minutes (Figure 4c), with significantly higher currents observed than for physisorbed 2 without host present (Figure S29). Readsortion of fresh 2 regenerated the catalytic activity of the electrode, which clearly indicates that the host molecules on the electrode surface are intact and can be used to bind fresh catalyst guests. The decrease of current could either be due to slow desorption of the guests or degradation of the HGC-bound catalyst. Nevertheless, these results show that our immobilization strategy of molecular electrocatalysts using HGCs can be employed to bind active catalysts to electrodes. Moreover, this strategy was effectively used in organic electrolyte, which is notable considering the general competition for occupying the host cavity between guests and solvent molecules.50,51 This observation underlines the strong adsorption interaction between the guest molecules and the surface bound hosts. Additional soaking experiments of the HGC in organic solvents used in electrochemical catalysis revealed hours of HGC stability in methanol, acetonitrile, dichloromethane and toluene, indicating that a wide range of electrocatalytic conditions are compatible with this approach (Figures S30 and S31).

Electrochemical water oxidation was also attempted using guest 3, which was shown to be active (though sluggish) for this reaction in solution (Figure S32a). Unfortunately, we could not observe an unambiguous catalytic response for water oxidation versus the background. To nevertheless confirm the activity of HGC-bound guests, we were able to demonstrate catalytic oxidation of a water-soluble phosphine to the corresponding phosphine oxide with HGC-bound 3 on ITO as a model reaction (Figure S33). This system also showed similar stability as the case for NH₃ oxidation in organic media. Regeneration of catalytic activity upon readsortion of 3 indicates the robustness of the host on the surface (Figure S34).
To confirm that the host is stable during electrocatalysis, we analysed host 5-functionalized ITO substrates before and after electrochemical measurements (with HGC-bound guest 2). We observed no peak shifts or decreased intensities for the carbon, phosphorus or sulfur signals pertaining to host 5 between the two measurements (Figure 5) indicating that there is no oxidation on any part of the host structure. To demonstrate the stability also under challenging conditions for most classically anchored catalysts, CV cycling at pH 10 under strong oxidative bias was performed (Figure S35), showing only a slow decrease of the guest redox features. Analysis of the sample surface by XPS showed a modest decrease of carbon, sulfur and phosphorus related to surface-bound 5 (Fig S36), indicating that the majority of the surface binding sites remained stable under such harsh conditions on the order of hours. The stability of host 5 under catalytic conditions implies the potential use of this immobilization strategy for different molecular electrocatalysts, with the option of electrode recycling. This also implies that the stability of the anchoring group for surface binding can be decoupled from catalyst design and separately optimized on the host, which presents a promising new approach to developing and improving new ways of coupling molecular electrocatalysts with different electrode surfaces.
Figure 5. XP spectra of ITO electrodes functionalized with host 5 and HGC-bound guest 2 before and after electrocatalytic measurements (NH₃ oxidation in THF solution). a) C1s spectra. b) P2p spectra. c) S2p spectra. For S2p and P2p, no difference between the sample before and after electrocatalysis is observed, showing no change in oxidation state or decrease in surface coverage for either of the elements. In the case of C1s, a decrease in signal intensity is only observed for the peak at 285 eV which is attributed to adventitious carbon, with the signal from host C-O carbon species remains unchanged. Overall the data indicate that no degradation of the host takes place under operating conditions.

Conclusion

Host-guest complex formation on electrode surfaces can be used to immobilize molecular electrocatalysts. A detailed study on the formation of such HGCs on gold, along with DFT calculations, shows a strong binding of the guests to the surface-bound cyclodextrin hosts. By demonstrating the catalytic activity of HGC-bound guests in both organic and aqueous electrolyte, our experiments show the versatility of using this approach to immobilize different electrocatalytic guests for operation in different chemical environments. The high stability of the host structures on the electrode surface allows for regeneration of the electrodes by
re-adsorption of fresh catalyst guests, which overcomes one of the largest challenges in immobilized molecular electrocatalysis: the electrodes can be reused even when the catalyst molecules have degraded.

Our work sets the basis for the use of HGC chemistry for catalyst immobilization. Future research efforts focusing on the preparation of new host structures and families, expanding the scope of the catalytic reactions and understanding and improving the control over the interactions between guest, host and surface will allow for this immobilization strategy to be used for many different applications.

**Methods**

**Host-functionalization of gold substrates:** Gold substrates were used either as prepared (directly after deposition of the gold layer) or cleaned in an O₂ plasma before functionalization. Compound 1 was attached to the gold by soaking the substrates in a solution of 1 (0.1 mM) prepared with either DMSO or DMF. Although adsorption was found to take place in less than 5 minutes, the substrates were soaked for 1 h. The substrates were then soaked in pure solvent (5 minutes), MeOH (5 min) and dried under a stream of N₂. The host-functionalized gold was used immediately or dipped in guest solutions very soon after preparation.

**Host-functionalization of metal oxide substrates**

**Two-step procedure for binding of host 1:** The metal oxide substrate was dipped in a solution of propiolic acid (10 μl in 10 ml MeCN) for 30 min. After this, the substrates were dipped in pure MeCN for 5 min to remove excess propiolic acid, then dried under a stream of N₂. The samples were subsequently immersed in a solution of 1 (0.7 mM) in DMF (10 ml) containing NEt₃ (20 μl) for 1 h. The substrates were then soaked in pure DMF (15 ml, 5 min), pure MeOH (10 ml, 5 min) and finally dried under a stream of N₂.

**Direct binding procedure for host 5:** The salt form of 5 was dissolved in H₂O to give a 0.1 mM solution, to which was added 1 v% of 1 M H₂SO₄, resulting in a pH 2 solution. The metal oxide substrate was then
immersed in this solution for 1 h, after which it was placed in pure H₂O (15 ml, 5 min) and MeOH (10 ml, 5
min). The samples were then dried under a stream of N₂.

**Guest functionalization of substrates:** The appropriate substrates were immersed in a solution of the guest in
MeOH (0.05 – 0.1 mM) for 1 h, after which they were soaked in pure MeOH twice (5 minutes each). The
substrates were then dried under a stream of N₂. HGC formation was easily observed by eye on mesoporous
substrates due to coloration of the films.

**Tip-enhanced Raman spectroscopy:** TERS measurements were performed on the host-functionalized gold
samples using electrochemically etched silver tips and a 632.8 nm He-Ne laser. The samples were placed into
a scanning tunneling microscope equipped with a 0.7 NA top-illumination objective. The laser beam was
focused on the tip-sample junction, and plasmon-enhanced Raman spectra were collected from the
molecules residing in the plasmonic hot spot under the tip. The spectra in Figures 3, S12 and S13 are average
spectra collected over grids of 100-225 locations. This approach, along with the low laser power applied (1.4-
21.2 kW/cm²), allowed the minimization of photoinduced sample damage.

**DFT calculations:** Optimized structures, energies and electronic properties were obtained by DFT simulations
using the Gaussian and plane waves method as implemented in the CP2K program package. The HGCs on
gold were simulated using an Au(111) slab model with four 9x9 layers and periodic boundary conditions were
applied. The adsorption energies of the host-guest complexes in the gas phase were computed by comparing
the energy of the optimized complex and the energies of the individually optimized CD and catalyst

\[ E_{\text{Ads}} = E_{\text{HGC, gas}} - (E_{\text{host, gas}} + E_{\text{guest, gas}}) \]

The adsorption energy of the guest into the anchored CD on
Au(111) were computer as

\[ E_{\text{Ads}} = E_{\text{HGC, Au}} - (E_{\text{host, Au}} + E_{\text{guest, gas}}) \]
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Author Contributions

L.S. and S.D.T conceived and the project. L.S. performed synthesis, electrochemical and catalytic experiments. I.T. assisted with synthesis and electrochemical experiments. J.S. and R.Z. conducted and evaluated TERS experiments. M.T. and J.O. conducted and evaluated XPS and STM experiments. O.B. measured and refined crystal structures. G.T., C.C., F.B.N and M.I. designed, conducted and evaluated calculations. L.S. and S.D.T wrote the manuscript. All authors contributed to discuss the results and revise the manuscript.

Competing Interests

The authors declare no competing interest.
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Supplementary Information

Host-guest interactions on electrode surfaces for immobilization of molecular catalysts

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1. Experimental Procedures

1.1. General experimental details

All reagents used were purchased from Sigma-Aldrich (Switzerland), TCI Europe or Fluorochem (UK), with the exception of 1 (6-per-thio-β-cyclodextrin) (≥97% purity, Cyclolab, Hungary or Cyclodextrin-shop, the Netherlands) and 4,4′-bis(dimethy lamino)-2,2′-bipyridine (99%, Hetcat, Switzerland), and were purchased as their purest grade. All solvents used were of at least analytical grade. Water used in any experiment was ultraclean (MilliQ grade). Nanoparticles (20 nm ZrO₂, 5 nm anatase TiO₂, 18 nm ITO) were purchased from US-nano. FTO and ITO on glass was obtained from Pilkington (Tokyo, Japan). Dry solvents were purchased and handled under inert atmosphere (Schlenk line or glovebox, N₂) to ensure their dryness. Reactions were carried out by standard Schlenk line techniques when inert conditions were required. NMR spectra were recorded with Bruker 400 or 500 MHz spectrometers and chemical shifts were calibrated using the residual solvent signals. IR spectra of reagents and products in powder form were obtained using a Perkin Elmer Spectrum Two FT-IR spectrometer in ATR sample detection geometry, using solid samples. High-resolution mass spectra were acquired on a QExactive instrument (ThermoFisher Scientific, Bremen, Germany) equipped with a heated electrospray (ESI) ionization source and connected to a Dionex Ultimate 3000 UHPLC system (ThermoFisher Scientifics, Germering, Germany). The samples were dissolved in appropriate organic solvents and detected using a positive detection mode.

1.2. Synthesis

Tetraethyl ethenyl-1,1-bisphosphonate was synthesized according to literature methods and purified by vacuum distillation at 0.3 mbar.¹ Pt(dms)₂Cl₂ was prepared following the procedure described by Wayland and coworkers.²

4′-(2-naphthyl)-2,2′:6′,2″-terpyridine – tpy-np

0.55 g of naphthaldehyde (3.5 mmol, 1.0 equiv.) was dissolved in 80 mL MeOH, then 0.2 g of KOH (3.5 mmol, 1.0 equiv.) and 3 ml concentrated NH₄OH solution (25%) were added. Next, 0.79 ml of 2-acetylpyridine (7.05 mmol, 2.0 equiv.) was added and the solution was refluxed for 2 h. A white, fluorescent precipitate formed and was filtered off after cooling the reaction mixture to room temperature. The precipitate was washed with
cold MeOH (2 x 30 mL) and Et2O (20 mL), then air dried. Yield: 0.441 g, 1.23 mmol, 35%.

$^1$H-NMR (400 MHz, chloroform-d): $\delta$ 8.88 (s, 2H), 8.79 – 8.75 (m, 2H), 8.71 (d, $J = 8.0$ Hz, 2H), 8.42 (s, 1H), 8.06 – 8.02 (m, 1H), 8.01 – 7.96 (m, 2H), 7.94 – 7.87 (m, 3H), 7.57 – 7.53 (m, 2H), 7.38 (dd, $J = 7.5$, 4.8, 1.2 Hz, 2H).

$^{13}$C-NMR (101 MHz, CDCl3): $\delta$ 156.43, 156.13, 150.42, 149.29, 137.10, 135.89, 133.70, 128.85, 128.75, 127.86, 126.89, 126.83, 126.66, 125.16, 124.03, 121.61, 119.25.

Spectroscopic data conform to literature values.3

$$[\text{Ru(tpy-np)}(\text{bpy-NMe}_2\text{Cl})\text{PF}_6] - 2$$

Intermediate Ru(tpy-np)Cl3:

0.224 g of tpy-np (0.62 mmol, 1.0 equiv.) and 0.150 g of RuCl3 (42 wt% Ru, 0.62 mmol, 1.0 equiv.) were refluxed in methanol for 3 h under N2. The resulting red–brown powder was filtered off and washed with EtOH (20 ml), acetone (20 ml) and Et2O (20 ml). Yield: 0.24 g, 0.42mmol, 68 %.

60 mg of Ru(tpy-np)Cl3 (106 μmol, 1 equiv.), 25.8 mg of bpy-NMe2 (106 μmol, 1.0 equiv.) and 32 mg of LiCl (0.78 mmol, 7.4 equiv.) were suspended in 14 ml of a water-methanol mixture (1:5) and degassed by N2 bubbling. 0.06 ml of NEt3 (0.43 mmol, 4.1 equiv.) was added and the solution refluxed for 3 h. After cooling to room temperature, 1.2 ml of sat. aq. NH4PF6 solution was added and a precipitate formed. The crude product was filtered off, washed with Et2O (20 ml) and dried in air at 60 °C. The product was purified by column chromatography over silica gel using CH2Cl2:MeOH 20:1 as eluent. Yield: 0.052 g, 0.059 mmol, 56 %.

$^1$H-NMR (400 MHz, acetone-d6): $\delta$ 9.80 (d, $J = 6.7$ Hz, 1H), 9.10 (s, 2H), 8.79 (s, 1H), 8.73 (d, $J = 8.1$ Hz, 2H), 8.33 (dd, $J = 8.7$ Hz, 1H), 8.18 (d, $J = 8.6$ Hz, 1H), 8.09 – 8.02 (m, 2H), 7.99 – 7.95 (m, 3H), 7.89 (dd, $J = 7.1$ Hz, 2H), 7.69 – 7.61 (m, 3H), 7.45 (dd, $J = 6.0$ Hz, 2H), 7.33 (dd, $J = 6.7$, 2.8 Hz, 1H), 6.72 (d, $J = 6.9$ Hz, 1H), 6.24 (dd, $J = 6.9$, 2.8 Hz, 1H), 3.39 (s, 6H), 2.99 (s, 6H).

$^{13}$C-NMR (126 MHz, Acetone) $\delta$ 160.64, 160.53, 158.86, 156.91, 155.83, 154.72, 152.87, 151.93, 150.37, 144.07, 136.73, 135.68, 134.82, 134.78, 130.07, 129.64, 128.81, 128.16, 128.01, 127.99, 127.92, 125.74, 124.22, 120.69, 110.18, 109.91, 106.33, 106.06, 39.97, 39.57.

$^{31}$P-NMR (162 MHz, acetone-d6): $\delta$ -135.52, -139.88, -144.25, -148.62, -152.98.
$^{19}$F-NMR (376 MHz, acetone-d6): $\delta$ -71.71, -73.59.

HR-MS: [M]$^+$ 738.16905 (calc. 738.16805).

$$[\text{Ru(tpy-np)(bpy)}\text{Cl}][\text{PF}_6] - 3$$

0.15 g of Ru(tpy-np)Cl$_3$ (0.26 mmol, 1 equiv.), 0.043 g of 2,2'-bipyridyl (0.27 mmol, 1.03 equiv.) and 0.056 g of LiCl (1.37 mmol, 5.2 equiv.) were suspended in 25 ml of a water-methanol mixture (1:4) and degassed by N$_2$ bubbling. 0.12 ml of NEt$_3$ (0.86 mmol, 3.2 equiv.) was added and the solution refluxed for 3 h. After cooling to room temperature, 2 mL of sat. aq. NH$_4$PF$_6$ solution was added and a precipitate formed. The crude product was filtered off and purified by column chromatography over silica gel using CH$_2$Cl$_2$:MeOH 10:1 as eluent. Yield: 0.1 g, 0.13 mmol, 47 %.

$^1$H-NMR (500 MHz, acetone-d6): $\delta$ 10.44 (d, J = 5.5 Hz, 1H), 9.12 (s, 2H), 8.89 (d, J = 8.2 Hz, 1H), 8.80 (s, 1H), 8.68 (d, J = 8.1 Hz, 2H), 8.60 (d, J = 8.2 Hz, 1H), 8.41 (td, J = 7.9, 1.5 Hz, 1H), 8.32 (dd, J = 8.6, 1.9 Hz, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.15 – 8.11 (m, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.90 – 7.82 (m, 4H), 7.81 – 7.77 (m, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.40 – 7.34 (m, 2H), 7.08 (td, J = 5.9, 2.8 Hz, 1H).

$^{13}$C-NMR (126 MHz, acetone-d6): $\delta$ 159.00, 158.90, 158.23, 156.35, 152.65, 152.16, 151.94, 145.27, 136.73, 136.59, 134.50, 133.94, 133.75, 133.67, 129.06, 128.75, 127.74, 127.34, 127.20, 126.92, 126.83, 126.29, 124.55, 123.72, 123.49, 123.29, 119.95.

$^{31}$P-NMR (203 MHz, acetone-d6): $\delta$ -133.76, -137.26, -140.75, -144.25, -147.74, -147.75, -151.23, -154.73.

$^{19}$F-NMR (471 MHz, acetone-d6): $\delta$ -71.86, -73.36.

HRMS: [M]$^+$ 652.08417 (calc. 652.08365).

$$[\text{Pt(tpy-np)}][\text{C=C-Ph(CF}_3)_2]\text{ClO}_4 - 4$$
Intermediate [Pt(tpy-np)Cl]Cl:
0.340 g of tpy-np (0.95 mmol, 1.0 equiv.) and 0.4 g of Pt(dmsø)2Cl2 (0.95 mmol, 1.0 equiv.) were refluxed in methanol for 1 h under N2. After cooling and stirring at room temperature overnight, an orange suspension formed, which was filtered off and washed with methanol (30 ml), acetone (3 x 40 ml) and Et2O (20 ml). Yield: 0.435 g, 0.70 mmol, 73 %.

1H-NMR (400 MHz, DMSO-d6) δ 9.15 (s, 2H), 8.98 (d, J = 5.3 Hz, 2H), 8.92 (d, J = 8.0 Hz, 2H), 8.85 (s, 1H), 8.58 (dd, J = 7.6 Hz, 2H), 8.32 (d, J = 8.3 Hz, 1H), 8.22 (d, J = 8.9 Hz, 1H), 8.13 – 8.05 (m, 2H), 7.99 (dd, J = 6.6 Hz, 2H), 7.74 – 7.66 (m, 2H).

0.2 g of [Pt(tpy-np)Cl]Cl (0.32 mmol, 1 equiv.) was dissolved in 15 ml of DMF and 2.3 ml NEt3 (16.5 mmol, 52 equiv.) followed by the addition of 130 μl 3,5-bis(trifluoromethyl)-ethynylbenzene (0.74 mmol, 2.3 equiv.). The solution was degassed by 2 freeze-pump-thaw cycles then 0.015 g of CuI (0.08 mmol, 0.25 equiv.) was added. The solution was refluxed under N2 overnight then cooled to room temperature. The precipitate was filtered off and washed with Et2O (20 ml). The filtrate was suspended in acetonitrile (50 ml) and 0.082 mg of AgClO4 (0.4 mmol, 1.2 equiv.) was added [Caution: perchlorates may exhibit explosive properties]. After refluxing overnight under N2 and cooling to room temperature, the product was filtered off and washed with MeCN (20 ml) and Et2O (40 ml). The product was obtained as thin crystals that changed from yellow to red depending on their dryness relative to the solvent used for washing. Two further batches were obtained after partial evaporation of the filtrate solutions and cooling. Yield: 102 mg, 0.11 mmol, 36 %.

1H-NMR (400 MHz, DMSO-d6) δ 9.22 (d, J = 5.6 Hz, 2H), 9.18 (s, 2H), 8.90 (d, J = 8.2 Hz, 2H), 8.79 (s, 1H), 8.55 (dd, J = 7.8 Hz, 2H), 8.27 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.15 (s, 2H), 8.10 – 8.03 (m, 2H), 7.96 – 7.90 (m, 3H), 7.72 – 7.65 (m, 2H).

13C-NMR (126 MHz, DMSO-d6) δ 159.10, 155.15, 154.61, 153.47, 142.59, 134.40, 133.26, 132.89, 132.52, 130.97, 130.71, 130.31, 129.58, 129.29, 128.70, 128.26, 127.78, 126.52, 124.89, 124.79, 122.62, 121.94, 105.50, 101.28.

19F-NMR (376 MHz, DMSO-d6) δ -61.27.

HRMS: [M]+ 791.12046 (calc. 791.12037).
0.249 g of freshly distilled tetraethyl vinylbisphosphonate (0.83 mmol, 5.2 equiv.) was dissolved in dry DMF (15 ml) and the solution degassed by sparging with N₂. 0.202 g of 6-per-thio-β-cyclodextrin (1, 0.16 mmol, 1 equiv.) was added, followed by addition of NEt₃ (0.27 ml, 12 equiv.). The reaction mixture was heated to 80 °C for 72 h, then the volatiles were removed under reduced pressure (80 °C, 20 mbar, 15 min). MeOH (30 ml) was added to the crude and the mixture was sonicated for 15 minutes forming a white precipitate, which was removed by filtration. The pure product was precipitated from the filtrate solution by addition of Et₂O (250 ml) under stirring, then filtered off, washed with Et₂O (30 ml) and dried under vacuum. The product was obtained as an off-white powder that was very soluble in MeOH. Yield: 205 mg, 0.06 mmol, 40 %.

**1H-NMR (500 MHz, Methanol-d₄)**
δ 5.05 – 4.97, 4.62 – 4.54, 4.30 – 4.10 (m, 56H, P(=O)OC₂H₃), 4.04 – 3.92, 3.92 – 3.75, 3.70 – 3.63, 3.59 – 3.41, 3.25 – 3.03, 1.56 – 1.26 (m, 84H, P(=O)OCH₂C₂H₅). Very broad peaks were observed for all protons connected directly to the glucose units making up the CD ring, we believe that this is due to slowed down tumbling of the large molecules.

**13C-NMR (126 MHz, MeOD)**
δ 102.42, 84.15, 72.88, 72.26, 65.50, 63.17, 63.12, 63.04, 34.58, 29.03, 15.72, 15.68, 15.61, 15.26, 15.21.

**31P-NMR (162 MHz, MeOD)**
δ 22.22, 21.95.

**HRMS:** [M]²⁺ 1696.40599 (calc. 1696.40621).

### 6-BP-S-cyclodextrin-potassium salt - 5

116 mg of 6 (0.035 mmol, 1 equiv.) was suspended in dry DCM under N₂ and 0.8 ml of trimethylsilyl bromide (6.06 mmol, 175 equiv.) was added. The reaction mixture was stirred at RT for 22 h and the volatiles were then removed. MeOH (25 ml) was added to the residue, followed by 1 ml KOH (1 M in H₂O), and the reaction
was stirred for 20 min during which a white precipitate formed. The product was then filtered off, washed with MeOH (2 x 10 ml) and Et₂O (20 ml), yielding the product as potassium salt of the phosphonic acid groups. Yield: 0.114 g, 0.031 mmol, 91 %.

¹H-NMR (500 MHz, Deuterium Oxide, DCl (pD= 2)) δ 5.07 (d, 1H), 4.11 – 3.96 (m, 1H), 3.94 – 3.74 (m, 2H), 3.72 – 3.55 (m, 2H), 3.24 – 3.05 (m, 2H), 3.04 – 2.87 (m, 1H), 2.71 – 2.39 (m, 1H). Very broad peaks were observed for all protons, presumably due to the large hydrodynamic radius of the highly charged molecules including solvation.

¹³C-NMR (126 MHz, D₂O) δ 101.82, 83.38, 71.89, 39.40, 38.48, 33.96, 28.89, 27.18.

³¹P-NMR (203 MHz, MeOD) δ 19.36 (broad).
2. **Instrumentation**

2.1. **Electrochemical measurements**

The details for electrochemical measurements are noted in the captions of each Figure containing electrochemical data. For the measurements, BioLogic sp-50, sp-200 or sp-300 instruments were used.

Experiments performed in water were measured against an aqueous Ag/AgCl electrode in saturated KCl. For measurements in organic electrolyte, an organic Ag/AgCl reference electrode was fabricated in a custom-made cell using an etched silver wire (1 M HCl, 2 min, 1.0 V vs Ag/AgCl) and a 0.2 M solution of tetrabutylammonium chloride in dry acetonitrile. This electrode was referenced against ferrocene before and after electrochemical measurements, with \( E_{\text{Fc/Fc}^+} = 0.98 \text{ V vs Ag/AgCl}_{\text{org}} \). Measurements in organic electrolytes were performed under exclusion of oxygen and water. Aqueous electrochemical experiments were performed under nitrogen with N\(_2\)-sparged solutions, with the exception of impedance measurements and stability measurements at pH 10 that were performed under ambient conditions.

For measurements in solution, a 1 cm x 2.5 cm piece of FTO on glass (cleaned by sonication in acetone, Deconex solution, water and EtOH for 10 minutes each) was used as the working electrode, submersed by ca. 1 cm (giving a rough geometric electrode surface area of 1 cm\(^2\)).

Scan rates of 20, 50, 100 or 500 mV/s were typically used. Voltages reported versus the reversible hydrogen electrode (RHE) were obtained by converting the potentials measured with the Ag/AgCl electrode using the Nernst equation, according to equation 1:

\[
E_{\text{RHE}} = E_{\text{Ag}}^{\text{AgCl}} + 0.059 \cdot pH + E_{\text{Ag}}^{0} \text{AgCl}
\]  

2.2. **Electrochemical Impedance Measurements**

Flat ITO samples (without host, with host or with host + guest) were used as the working electrodes for the impedance measurements. The electrolyte was 0.1 M Na\(_2\)SO\(_4\) (pH 2.4) with a 1:1 mixture of K\(_4\)[Fe(CN)\(_6\)] and K\(_3\)[Fe(CN)\(_6\)] (25 mM each) as redox couple in solution. Before and after each EIS measurement a CV was recorded with a scan rate or 100 mV/s to check whether the sample had degraded during the EIS measurement.

The electrochemical impedance measurements were performed using a BioLogic SP-200 in 3 electrode configuration. The DC potential applied was from 100 mV to -100 mV vs \( V_{\text{OC}} \) in 50 mV steps. At each desired DC potential, the device was stabilized for 25s before the start of the actual impedance measurement. The AC voltage perturbation was 25 mV applied in a frequency range from 7 MHz to 0.1 Hz.
The EIS data were fitted with a reduced Randles circuit. A constant phase element (CPE_if) was used to model the interface capacitance (Cif). The EIS data were fitted with ZView software from Scribner. The CPE was converted to C using equation 2:

\[ C_{if} = \frac{(R_{ct} \times Q)^{1/n}}{R_{ct}} \]  

with \( R_{ct} \) being the charge transfer resistance, \( Q \) the charge from CPE and \( n \) as the CPE exponent.

2.3. UV/Vis spectroscopy
UV/Vis spectra were recorded on a Shimadzu UV-3600 spectrometer using a quartz cell (\( L = 1 \) cm) for liquid samples. Solid samples (mesoporous ZrO\(_2\) on glass substrates) were placed in a custom-made holder with a pinhole of ca. 3 mm. Background spectra were measured using pure solvent (liquid samples) or an unfunctionalized substrate (solid samples).

2.4. Fourier-transform infrared spectroscopy
FTIR spectra were measured in transmission mode on a Bruker IR spectrometer. Substrates used for FTIR analysis were CaF\(_2\) windows (Thorlabs, USA) coated with 10 nm or ALD-ZrO\(_2\) and a doctor-bladed layer of mesoporous ZrO\(_2\), annealed at 550 °C (1 h). The preparation of the mesoporous films is analogous to the procedure described below (sample preparation for mesoporous ZrO\(_2\) on glass). Background spectra were measured using pristine substrate.

2.5. X-ray photoelectron spectroscopy
XPS measurements were conducted in a modified VG ESCALAB 220 UHV system with a base pressure of 2.10\(^{-10}\) mbar. The sample was irradiated with non-monochromatized Mg-K\(_{\alpha}\) X-rays with a photon energy of \( h\nu = 1253.6 \) eV and photoelectrons were measured at normal emission. The energy scale was calibrated as described by Seah.\(^4\)

Coverage Analysis
In order to estimate the coverage of host 1 on Au surfaces, the photoemission intensity of S2p (\( I_{S2p} \)) was measured and referenced against the intensity of Ag3p\(_{3/2}\) (\( I_{Ag} \)) emission from a polycrystalline silver sample measured with the same photon flux and sampling area. This method reduces the model dependence of XPS
quantitative analysis and was used successfully by Zabka et al. Since sulphur atoms bridge the Au surface or phosphonated metal oxide and cyclodextrin molecules, the sulfur signal $I_S$ is attenuated by a factor $e^{-d_{CD}/(\lambda_{CD}(E_{Kin}^{S^{2p}}) \cos \theta)}$, where $d_{CD} \sim 7.8 \text{ Å}$ is the thickness of cyclodextrin, $\theta$ is the electron emission angle with respect to surface normal and $\lambda_{CD}(E_{Kin}^{S^{2p}})$ is the inelastic mean free path of S2p photoelectrons in cyclodextrin at the measured kinetic energy as calculated with the Tanuma-Powell-Penn (TPP-2M) equation. Following Zabka et al., the number of sulfur atoms per unit area $N_S^{surf}$ can be obtained as

$$N_S^{surf} = \frac{I_S}{\sigma_S e^{-d_{CD}/(\lambda_{CD}(E_{Kin}^{S^{2p}}) \cos \theta)} \sigma_{Ag} n_{Ag} \lambda_{Ag}(E_{Kin}^{Ag^{3p3/2}}) \cos \theta}$$

where $\sigma_S$, $\sigma_{Ag}$ are photoionization cross sections for S2p and Ag3p3/2 core levels, respectively. $n_{Ag} = 58.7 \text{ n m}^{-3}$ is the density of silver atoms, and $\lambda_{Ag}(E_{Kin}^{Ag^{3p3/2}})$ is the inelastic mean-free path of Ag3p3/2 photoelectrons in Ag. In order to give a fractional monolayer coverage, a hexagonal close packed structure is assumed for the surface unit cell of a complete monolayer of 6S-B-CD molecules. According to this model, a full coverage (i.e. 7 sulfur atoms in the molecular surface unit cell) yields $N_S^{surf, full} = \frac{7}{A} = 2.8 \text{ nm}^{-2}$. Finally, the fractional coverage can be calculated by $\phi = N_S^{surf} / N_S^{surf, full}$.

### 2.6. Tip-enhanced Raman spectroscopy

Top–illumination TERS was performed with Ag tips and Au substrates, forming a gap plasmon between the substrate and the tip. We used a scanning tunneling microscope (STM; Ntegra Spectra Upright, NT-MDT), equipped with a 0.7 NA 100× objective (Mitutoyo), coupled to a Raman spectrometer (Solar T-II, NT-MDT) with a CCD (Newton 971 UVB, Andor) thermoelectrically cooled to -85 °C. The STM was operated in constant current mode. Low bias voltage (0.1 V applied to the sample) was used to avoid injection of tunneling electrons into the investigated molecules.

TERS tips were obtained by electrochemical etching of Ag wire (0.25 mm diameter, 99.9995%, Alfa Aesar) in a hot solution (20 vol%) of perchloric acid (70%, VWR) in ethanol (absolute, Fluka). A Pt ring counter electrode (0.5 mm wire, 1 cm ring diameter, 99.997%, Alfa Aesar) was dipped below the surface of the etching solution. The Ag wire was dipped 2 mm into the solution, at the center of the Pt counter electrode. In order to ensure the sharpness of the tips, the etching voltage of 10 V was cut off shortly before the end of the process by an automated circuit detecting a high gradient of the current. Following the etching, the tips were rinsed with MilliQ water and ethanol.
TER spectra were acquired on square grids with 100-225 pixels (from 10 × 10 to 15 × 15 pixels), with laser illumination at 632.8 nm (HeNe laser) and laser power between 1.4 and 21.2 kW/cm². The integration time was 1–3 s. The TER spectra presented in Figures 3 and SI-10 are average spectra accumulated over grids of pixels.

**2.7. Fluorescence spectroscopy**

A Fluorolog-3 instrument (Horiba) was used for fluorescence measurements of liquid and solid samples, using a 450 W Xe arc lamp as broadband excitation source. Liquid measurements were performed using a quartz cuvette with 1.00 cm path lengths in both directions and detection in a 90° angle configuration. For strongly emissive samples, the bandpass width was adjusted to 1 nm for both excitation and detection. For measurement of the fluorescent guest molecules on mesoporous ZrO₂ on glass films, the samples were placed in a sample holder at a 30° angle to the excitation beam and detected at a 90° angle. Bandpass widths were 2 nm, 6 nm and 8 nm for the spectra obtained at excitation wavelengths of 435 nm, 510 nm and 580 nm, respectively.

**2.8. Single crystal X-ray diffraction**

Single crystal X-ray diffraction data were collected at 160K on a Rigaku OD Synergy (Pilatus 200K detector) diffractometer equipped with an Oxford liquid-nitrogen Cryostream cooler and using a single wavelength X-ray source from a micro-focus sealed X-ray tube (Cu K_{α} radiation, λ = 1.54184 Å). Suitable single crystals were manipulated into polybutene oil, mounted on a flexible loop fixed on a goniometer head and transferred to the diffractometer. Pre-experiments, data collections, data reductions and analytical absorption corrections were performed with the program suite CrysAlisPro (RigakuOxford). Using Olex2, the structures were solved with the SHELXT small molecule structure solution program and refined with the SHELXL program package by full-matrix least-squares minimization on F². The crystal data collections and structure refinement parameters are summarized in Tables S1. CCDC 1996726 (for 2), 1996727 (for 3), 1996728 (for 4) contain the supplementary crystallographic data for these compounds, and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The molecular structures obtained for 2, 3 and 4 are shown in section 6 below.

In the crystal structure of 2, the cationic species cocrystallized with PF₆⁻ counterions and solvent molecules of acetone in a ratio 4/4/3. The structure was refined as a merohedral twin with a 0.612(6):0.388(6) domain ratio. The twin law used was (-1 0 0 0 1 0 0 0 -1). In the crystal structure of 3, there are two independent C_{35}H_{25}ClN_{5}Ru⁺ cations in the asymmetric unit, two PF₆⁻ counterions (one showing disorder), one isolated water molecule and solvent molecule(s) of acetone. It appeared to be more convenient to use the PLATON
SQUEEZE\textsuperscript{6} tool to calculate the number of electrons attributed to solvent molecules in the primitive cell and to take this solvent contribution into account in the calculated structure factors (25 electrons were found in the \textit{P1} unit cell which were considered as one molecule of acetone). In the crystal structure of 4, the ClO\textsubscript{4}\textsuperscript{−} counterion is partially disordered over two sets of positions. The F atoms of one CF\textsubscript{3} group are also disordered over two sets of positions. The solvent molecules of DMSO are distinguishable but it was not possible to get a reasonable modelling due to disorders. The \textit{PLATON SQUEEZE} \textsuperscript{12} tool was used to calculate the number of electrons attributed to solvent molecules in the primitive cell and to take this solvent contribution into account in the calculated structure factors. Based on the results, two solvent molecules were considered in the primitive cell.

2.9. Solid state NMR spectroscopy

5 nm TiO\textsubscript{2} nanoparticles were used as substrate for the measurement of solid state NMR to analyse the surface binding of the cyclodextrin hosts in the two-step procedure. 1 g of TiO\textsubscript{2} was added to a solution of propiolic acid in acetonitrile (0.8 ml in 50 ml) and left in the dark for 45 min. The particles were centrifuged, the liquid was decanted and pure MeCN (40 ml) was added to the particles. After 5 min of sonication, the suspension was again centrifuged. After repeating the washing procedure 3 times the powder was dried in air. 50 mg of this sample (TiO2-A) was used for measurement of ssNMR.

0.4 g of TiO\textsubscript{2}-A were added to a solution of 6S-B-CD in DMF with NEt\textsubscript{3} (0.7 mM 6S-B-CD) and left in the dark for 1 h. The particles were centrifuged, the liquid was decanted and pure DMF (40 ml) was added to the particles. After 5 min of sonication, the suspension was again centrifuged. The washing procedure was then repeated with methanol 2 times and the powder then dried in air. 50 mg of this sample was used for measurement of ssNMR.

The solid state \textsuperscript{13}C-NMR (125.78 MHz) was run at room temperature under cp-MAS conditions (1H,13C cross polarization, 25 kHz magic angle spinning).

2.10. STM measurements

For ex-situ prepared H\textsubscript{2} flame annealed Au samples, STM measurements were performed in commercially available ultra-high vacuum system (Omicron VT-STM) with base pressure of 1.10\textsuperscript{10} mbar. The STM measurements were carried out with electrochemically etched W tips. Positive bias voltage indicates electrons tunnel from the tip to the sample.
2.11. Solvent stability measurements of HGCs

Solvent stability of HGC-bound guest was monitored by UV/Vis absorption spectroscopy. Mesoporous ZrO$_2$ functionalized with host 5 and guest 3 were soaked in pure solvent for a period of 4 h and 20 h. UV/Vis spectra were acquired after initial guest binding and after removal of physisorbed species, before the solvent soaking experiment. Due to limited mechanical stability of the mesoporous substrate, measurements performed in acidic and basic aqueous solutions were unsuccessful.

2.12. Adsorption isotherm measurement

Adsorption isotherm measurements were carried out on mesoporous ZrO$_2$ substrates using UV/Vis spectroscopy. These were first functionalized with the host molecules, and blank spectra were measured for each individual sample. The samples were dipped for 24 h in methanolic solutions of guest 3 with varying concentrations. They were then dipped in pure methanol for 5 minutes and subjected to the acetic acid desorption protocol (see 3.5.1) before collection of the spectra.

A simple Langmuir-type absorption model was chosen to estimate a binding constant between the guests and the host on the surface.$^{13}$ Some limitations of this model include the assumption of a flat surface and a single type of non-interacting binding sites. We argue that the single type of binding site is given in our case, as only one guest can fit into one host, and any physisorbed species is removed by the acetic acid treatment prior to spectral acquisition. The long immersion time in the guest solutions should also mitigate effects of having a mesoporous surface on transport limitations into the pores.

The fractional occupancy $\theta_A = \frac{[S_{Ads}]}{[S_{tot}]}$ is the fraction of surfaces sites occupied by the adsorbed guest over the total number of surface sites. For a full coverage, this value tends to 1. We determine the amount of guest on the surface using the absorption spectra at the absorption maximum (at 500 nm), where no other part of the sample absorbs. The normalized absorptions can be used as a measure for the fractional occupancy of the guest in the Langmuir equation:

$$\theta_A = \frac{A_{Ads}}{A_{Ads}^{max}} = \frac{K_{eq}[G]}{1+K_{eq}[G]}$$

(4)

where $A_{Ads}$ is the absorbance of the sample at a given concentration of guest, [G], and $A_{Ads}^{max}$ is the absorbance of a sample with full guest coverage. The host-guest complex formation constant $K_{eq}$ can be obtained from a fit of the measured data using equation 4.

To reduce measurement errors from sample variation, the experiments were performed twice, and the datasets were averaged before fitting.
3. **Substrate preparation**

3.1. **Preparation of metal oxide pastes**

Metal oxide nanoparticles (2 g, 20 nm ZrO₂ or 18 nm ITO) were ball-milled for 3 h at 500 rpm using ZrO₂ beads (1 mm, 20 g) in the presence of EtOH (1.5 ml), acetic acid (1.5 ml) and H₂O (0.3 ml). Afterwards, the beads were sieved off and washed with 100 ml of EtOH. To the particle suspension was added ethyl cellulose (0.5 g), α-terpineol (5 g) and EtOH (100 ml). The suspension was then sonicated for 30 minutes and afterwards the volatiles were removed on a rotary evaporator (40 °C, 20 mbar, 30 minutes).

3.2. **Preparation of mesoporous substrates**

3.2.1. **Meso-ZrO₂ substrates**

A glass microscope slide (7.5 cm x 2.5 cm, Thermo Fisher Scientific, Braunschweig, Germany) was scored at 1.2 cm intervals and cleaned by sonicating in acetone, Deconex solution in water (5%), distilled water and then EtOH for 10 min each. After drying in a stream of N₂, the pieces were partially covered with scotch tape, covering 2 mm along both long edges of the slide. A few drops of freshly sonicated ZrO₂ paste were applied to the sample and the film was spread evenly using a glass Pasteur pipette. After the doctor blading, the tape was removed and the slide annealed in air at 550 °C for one hour. After cooling to room temperature, the coated glass slide was broken into the desired sample size along the score marks, yielding 1.2 cm x 2.5 cm samples.

3.2.2. **Meso-ITO substrates**

FTO slides (10 cm x 2.5 cm) were scored at 1.2 cm intervals and cleaned by sonicating in acetone, Deconex solution in water (5%), distilled water and then EtOH for 10 min each. After drying in a stream of N₂, the pieces were partially covered with scotch tape, covering 10 mm and 2 mm along the long edges of the slide. A few drops of freshly sonicated ITO paste were applied to the sample and the film was spread evenly using a glass Pasteur pipette. After the doctor blading, the tape was removed and the slide annealed in air at 450 °C for 30 min. After cooling to room temperature, the coated FTO slide was broken into the desired sample size along the score marks, yielding 1.2 cm x 2.5 cm samples.

Alternatively, for measurements performed under basic aqueous conditions, meso-ITO films were prepared by repeated spin-coating as described previously,¹⁴ due to better mechanical stability. For these
measurements, an additional annealing for 90 minutes at 120 °C under N₂ atmosphere was performed after functionalizing the surface with host 5.

3.3. Preparation of gold substrates

3.3.1. Electron beam evaporation
Cleaned ITO pieces (1.2 cm x 2.5 cm) were placed into a mask exposing 1.0 cm diameter holes on the ITO face of the glass pieces. 10 nm of Ti and 500 nm Au were then deposited sequentially by e-beam evaporation (UNIVEX 300, Leybold, Germany). Before the deposition, the chamber vacuum was evacuated to a pressure below 2·10⁻⁶ mbar. The working current for Ti was 20 mA and 200 mA for Au.

3.3.2. Sputtering
Cleaned ITO pieces (1.0 cm x 2.5 cm) were covered by Teflon tape or glass slides to expose an area of 1.0 cm x 1.5 cm. A Safematic CCU-010 sputter coater was used to deposit gold to a thickness of 200 nm. A working current of 60 mA and a working pressure of 1·10⁻² mbar were used.

3.3.3. H₂-annealed gold substrates
Gold was sputtered in the same manner as stated above on clean silicon pieces (0.7 cm x 0.7 cm) to a thickness of 200 nm. After deposition of the gold, the samples were individually heated in an H₂ flame for 45 s until very slight delamination on the edges of the Si substrate were observed. The samples were then immediately removed from the flame, cooled to RT in air and subsequently functionalized or taken into a UHV system to prevent adsorption of impurities to the surface.

3.4. Flat metal oxide electrodes
Flat metal oxide electrodes were prepared from FTO or ITO by cutting the appropriate window into 1.0 cm x 2.5 cm pieces. The pieces were cleaned by sonicating in acetone, Deconex solution in water (5%), distilled water and then ethanol for 10 min each. The electrodes were functionalized or used in a short delay after cleaning them.

3.5. Desorption treatments for host-guest functionalized surfaces

3.5.1. Acetic acid treatment (removal of physisorbed species)
Guest-functionalized substrates were immersed in a solution of acetic acid in MeOH (0.1 M) for 10 min, then soaked in MeOH (5 min) and dried under a stream of N₂.
3.5.2. **Cyclodextrin desorption treatment**

Guest-functionalized substrates were immersed in a solution of B-cyclodextrin in H$_2$O (15 mM) at 80 °C for 30 min. After that, they were soaked in pure H$_2$O (5 min) and MeOH (5 min), and dried under a stream of N$_2$. For TERS sample desorption studies, the substrates were sonicated in a solution of B-cyclodextrin in H$_2$O (10 mM), then rinsed with H$_2$O, ethanol and dried under a stream of N$_2$.

4. **DFT calculations**

All simulations were carried out using the CP2K program package$^{15}$ and electronic structure method based on the Kohn-Sham DFT approach. Valence electrons were treated explicitly, while norm-conserving Goedecker-Teter-Hutter (GTH) pseudo potentials$^{16}$ were used to describe the interactions between the valence electrons and the atomic cores. The Gaussian and plane wave formalism is applied by expanding the molecular orbitals in double-zeta valence plus polarization (DZVP) basis sets,$^{17}$ which were optimized on molecular geometries (Mol-Opt method). A cutoff of 600 Ry was used for the auxiliary plane wave basis set. The geometry optimizations were performed using the Perdew-Burke-Enzerhof (PBE) exchange-correlation functional.$^{18}$ Dispersion interactions were included via the nonlocal electron correlation scheme conceived by Vydrov and Van Voorhis, in the revised form (rVV10) proposed by Sabatini et al.$^{19}$ The electronic densities of states were refined at the hybrid functional level of theory, specifically the HSE06.$^{20}$

All calculations were carried out without the solvent. This holds for the interface systems, i.e. the host-guest complexes on Au, for the host-guest complexes in the gas phase, as well for the host and guests taken alone. Hence, no solvation energy is taken into account, which means that the absolute values of the adsorption energies are overestimated. However, we discuss the interaction energy of the guest inserted into the host on the Au surface, in comparison to when it is binding to the free-standing CD. Since the reference state for the guest is the same, the observed stabilization due to the coupling with the metal is sound. Taking into account the solvent explicitly and running molecular dynamics to estimate solvation free energies seems not to be needed at this stage to draw conclusions on the stabilizing role of the substrate.
5. Supplementary Figures

Figure S1. a) Fluorescence spectra of guest 4 in a MeCN/H₂O 1:1 solution, showing a decrease in fluorescence intensity with increasing concentration of B-CD. An excitation wavelength of 425 nm was used; the guest concentration was 10 μM. b) Non-linear fitting model used to determine the 1:1 binding constant between the guest and the host. The fitting model was adapted from ²¹. The origin for the quenching effect upon HGC formation was not investigated in detail, but has been observed before for a number different fluorescent guest molecules. ²²

Figure S 2 a) Job's plot of selected protons of guest 3 and β-CD in a mixed solution of DMSO-d₆ and D₂O (3:1). b) Assignment of the protons of guest 3 that are shown in the Job's plot. The cyclodextrin host is schematically depicted with dashed lines forming a HGC with the guest. Protons H₆ and H₉ show the largest extent in change of concentration-weighted change in chemical shift due to their stronger interaction with the host. Proton H₁, which is relatively far away from the host cavity shows a negative change in chemical shift. The maximum (or minimum) for all curves is situated at a normalized guest concentration of 0.5 (equal to the concentration of host), indicating a 1:1 binding stoichiometry.
Figure S 3. XP spectra of host 1 binding to Au(111). a) C1s spectra, b) O1s spectra, c) S2p spectra of Au(111) after immobilization of host 1 achieved by immersion of the freshly cleaned single-crystal gold film into a DMSO solution of 1 for 3 minutes and rinsing by clean DMSO for 10 minutes. d) The sulfur spectra were fitted with the constraints of 1.16 eV splitting between the spin-orbit doublet of S2p and gave a single broad signal for the sulfur which is attributed to gold-bound thiols. The broadness is due to the different binding geometries experienced by the individual sulfur atoms in this system. The lack of features at higher binding energies (>164 eV) indicate that no or only very small amounts of free thiol remain on the surface.
Figure S 4 Dependence of the surface coverage and atomic ratios on the duration of self-assembly and rinsing. 
a) C1s XP spectra. b) O1s XP spectra. c) S2p XP spectra. d) The modeled slab of gold used to calculate the surface coverage is shown with the repeating unit represented by a blue lozenge. e) Table summarizing the fractional surface coverage for different dipping times of the Au(111) substrate into the solution of 1 and subsequent dipping into the solvent to remove physisorbed species from the surface. These coverages were obtained by comparison of actual surface density of 1 with the expected density according to the model.
Figure S 5. Optimized gas phase structures of host guest complexes with host 1. a) Guest 2 (ruthenium complex). b) Guest 3 (ruthenium complex). c) Guest 4 (platinum complex).

Figure S 6. Calculated density of states of guests 2 (a), 3 (b) and 4 (c) in vacuum (top panel), and corresponding HOMOs taken at 0.03 el./bohr$^3$ (bottom panel). We note that the HOMO is mainly on the Ru and C for guests 2 and 3, and on C and Pt for guest 4.
Figure S 7. Densities of states (DOS) computed at the HSE06 level of theory for the host-guest complex as optimized in the gas-phase for guests 2 (a), 3 (b) and 4 (c). The bottom panels show the projected DOS (PDOS) on all the atoms of the guest (black), on all the atoms of the CD (brown), and on the CD’s oxygen atoms (red) and sulfur atoms (yellow) separately. The top panels show the total guest’s PDOS together with the separated Ru (orange), Cl (green), N (blue), Pt (grey), and F (pink) contributions. a), b) and c) label guest 2, guest 3 and guest 4, respectively. We note that the complex’s HOMO is on the guest for guest 2, mainly on Ru and Cl; it is distributed also on the sulfur atoms in the case of guest 3; and it is only on the CD’s sulfur atoms for guest 4. The LUMO is in all three cases on the guest.
Figure S 8 Total electron density corresponding to the energy levels between -1 and 0 V vs $E_F$ in HGC-bound 2 on Au(111). Iso-surface taken at the electron density value of 0.005 el./bohr$^3$. The Iso-surface extending also all over the Au(111) surface and within the metal bulk is hidden by the VdW spheres representing the Au atoms. The distribution of these electrons over the entire guest molecule as well as within the gold layer (not visible) indicates strong coupling between the guest and the gold substrate as well as delocalization of the states close to $E_F$. 
Figure S 9. PDOS of HGC-bound guests on Au(111) with host 1. The top panels show the PDOS projected on all guests’ atoms (black) and specifically on some of its elements, i.e., Ru, Cl, N. The bottom panels show the PDOS on the guest (black), on the atoms of the CD (brown), also distinguishing the S (yellow) and O (red) contributions, and on the Au atoms (dark green). a) Guest 2. b) Guest 3. c) Guest 4. The overlap of guest states close to the Fermi energy $E_F$ with the states of the metal show the strong interaction and mixing of these states. From the PDOS of the host-guest complex (for guests 2 and 3) anchored to the Au(111) surface, one observes a partial hybridization of the highest occupied states of the guest with the metal’s d-band (green curve in bottom panels). These are states just below the Fermi energy (set at zero in these plots), presumably favoring charge transfer. This interaction induces an upwards shift of these states with respect to the unoccupied states, which are at about 1.5 eV above $E_{\text{Fermi}}$, thus resulting in a reduction of the molecular gap. Such rearrangement of the PDOS is not observed for the free-standing host-guest complexes.
Figure S 10. CVs of HGC-bound guests 2 (Ru, magenta) and 4 (Pt, green) with host 1 on gold electrodes, measured in THF solution (0.2 M TBAPF₆, 500 mV/s scan rate). An increased current for both guests compared to the purely host-functionalized electrode (black), however no redox peaks can be observed with respect to the redox-active guest 2 versus the non-redox-active guest 4 (compare with Figure S 23 for molecular redox peaks in THF solution).

Figure S 11. CVs of electrodes of gold substrates that were non-functionalized (black), dodecanethiol-functionalized (green), functionalized with host 1 and then dodecanethiol (blue), and functionalized with host 1, then guest 2 and finally dodecanethiol (magenta), measured in NH₃ saturated THF solution (0.2 M TBAPF₆ + 0.1 M NH₄PF₆, 100 mV/s scan rate). The large background catalytic current of the gold substrate could be effectively suppressed by functionalizing it with a dodecanethiol blocking layer. The reproducibility of the measurement was tested over 3 batches and the current for the guest-modified sample was always higher than the sample without guest, although differences in absolute currents were observed between the batches. The earlier onset of catalytic current for the guest functionalized sample correlates with the onset of catalysis from guest 2 in solution (shown in Figure S 23).
Figure S 12. Desorption and subsequent exchange of 2 by 4 on host-functionalized gold is confirmed by the shift of the ring breathing modes (RBM) of the metal-coordinated pyridyl rings from 1030 toward 1050 cm⁻¹ (highlighted in blue). The incomplete desorption of 2 is reflected in the residual intensity of 2 in spectrum II and in the mixed signals of 2 and 4 in spectrum III.
Figure S 13. Red-shift of the resonance Raman effect upon formation of a HGC on the Au surface. The Raman spectra of guest 2 show intense scattering at 532 nm excitation (a), compared to 633 nm excitation (b), thanks to efficient absorption of the 532 nm light by the guest. Conversely, the TERS spectra of the HGC on Au show a weak signal of guest 2 at 532 nm excitation (c), compared to the 633 nm excitation (d). The red-shift of resonance Raman scattering reflects the red-shift of optical absorption, which is a landmark of strong interaction between guest 2 in the HGC and the Au surface. The spectrum in panel b was baseline-corrected, because of high fluorescence background.

Figure S 14. a) and b) STM images of HGC-bound guest 4 in host 1 on an H2-annelaed Au(111) substrate. Images were obtained under a positive bias of 1 V. The features observed are in a similar size domain as expected from the computed host-guest structures but cannot be unambiguously identified as such.
Figure S 15. a) Schematic depiction of the two-step for functionalization of a metal oxide substrate with host 1, where the substrate is first reacted with propiolic acid in MeCN solution, then exposed to a DMF solution of 1 in the presence of triethylamine as catalyst. b) Functionalization of a metal oxide substrate with host 5, achieved by immersion of the substrate into an aqueous solution of 5 in water (pH 2, adjusted by addition of H₂SO₄). The in situ formation of the free acid form of 5 as well as the positive surfacecharge of the metal oxide allow for fast and highly stable binding of the host to the surface (stable even over 24 h at pH 10).

Figure S 16. FTIR spectra showing the binding of hosts onto ZrO₂ films. For the two-step binding procedure of host 1, the substrate is first dipped in propiolic acid, leading to the appearance of terminal alkyne bands on
the surface at 3320 cm^{-1} and 2120 cm^{-1} (black). After reaction with 1, these alkyne bands disappear and additional bands in the C-H stretching region as well as in the fingerprint region between 1700 cm^{-1} and 900 cm^{-1} appear (red), which are attributed to the bound CD structure. Functionalization of ZrO_2 with host 5 results in the appearance of C-H stretching features around 2900 cm^{-1} which is clearly attributed to the CD-based molecules along with features between 1600 cm^{-1} and 900 cm^{-1} (blue). Although clear attributions of the bands between 1250 cm^{-1} and 1000 cm^{-1} is not possible, the comparison with the IR spectrum of 5 as a powder (green) suggests that these bands are due to the presence of the phosphonate groups on the surface.

Figure S 17. XP spectra of host 5 on ITO. a) C1s spectra, b) P2p spectra and c) S2p spectra of 5 bound to ITO via the bisphosphonate anchoring groups. The signals for S2p and P2p are a combination of the respective spin-orbit components. The peak in b) designated by * is associated to In4s from the ITO substrate. Although a precise determination of the surface coverage was not possible, the estimated value was found to be in the same range as for the gold substrate, between 0.41 nm^{-1} and 0.33 nm^{-1}, depending on the model used.

Figure S 18. Solid state ^13C-NMR analysis of the two-step binding procedure to immobilize host 1 on TiO_2 nanoparticles. The binding of propiolic acid (PPA, brown) is evidenced by a single peak around 69 ppm, which
is attributed to the alkyne carbon binding to the only proton of PPA. After reaction of PPA-functionalized TiO$_2$ with 1, the appearance of several peaks attributed to the C-H of the host, which strongly resembles the solution $^{13}$C-NMR spectrum of host 5. Specifically, the band at 103 ppm is attributed to the C1 atom of the glucose units making up the CD hosts, with the remaining sugar carbons and the alkene protons obtained during the thiol-yne click reaction resulting in the bands between 90 and 65 ppm. The remaining signals between 50 and 20 ppm are attributed to the other carbon atoms in the surface-bound molecules.

Figure S 19. Charge transfer (CT) resistances of ITO electrodes with different surface modifications in solutions of equimolar K$_3$[Fe(CN)$_6$] and K$_4$[Fe(CN)$_6$] (25 mM in Na$_2$SO$_4$ 0.1 M solution). The charge transfer from the electrode to the redox couple at open circuit potential ($V_{OC}$) is hindered when host 5 is bound to the surface (blue), as the cavity is too small for the ferrocyanate molecules to enter. With HGC formation with guest 4 (red), the additional barrier for electron transfer leads to the observed increase in CT resistance. Desorption of the guest with B-CD solution regenerates the 5-functionalized surface with the same CT resistance as before (green). Unfunctionalized ITO shows the lowest CT resistance as expected (black).
Figure S 20. a) Normalized absorption spectra of guests 2, 3 and 4 in acetone. b) Normalized absorption spectra of guests 2, 3 and 4 as HGCs with host 5 on mesoporous ZrO$_2$ films. The absorption features of the guests is observed on the metal oxide surfaces, with slight shifts of the absorption maxima for 2 and 3 in the solid state samples. Wave-like signals at high wavelengths for b) are due to interference effects of the thin films.

Figure S 21. a) Normalized emission spectra of guests 2, 3 and 4 in acetone. b) Normalized emission spectra of guests 2, 3 and 4 as HGCs with host 5 on mesoporous ZrO$_2$ films. Spectra were collected by exciting at the maximum of absorption for each of the respective guests. The shoulder observed for 4 is attributed to emission from aggregates of 4.
Figure S 22. FTIR spectra of HGC-bound guests. a) Guest 2. b) Guest 3. c) Guest 4. The spectra of host 5-functionalized ZrO2 before (black) and after (red) HGC formation with the respective guests are shown. Difference spectra calculated from these two measured spectra are shown (green) and clearly show the guest bands when compared to the respective guest powder spectra (blue).

Figure S 23. a) CVs of guests 2, 3 and 4 in THF solution (0.2 M TBAPF₆, 10 mV/s scan rate) showing the reversible Ru(II)/Ru(III) redox waves for the two electroactive guests. b) CVs of HGC-bound guests 2, 3 and 4 with host 5 on mesoporous ITO electrodes in THF solution (0.2 M TBAPF₆, 10 mV/s scan rate). The Ru(II)/Ru(III) redox features are clearly visible and show a oxidation-reduction peak separation < 59 mV, indicating that the redox reaction is taking place on species attached to the surface of the electrode.
Figure S 24. Fluorescence spectra of guest 2 on mesoporous ZrO$_2$, with and without the presence of host 5 (with and without HGC-formation). Treatment of the freshly prepared samples (black) with acetic acid (0.1 M in MeOH, 10 min) leads to near complete loss of signal for the physisorbed species (which are not HGC-bound).

Figure S 25. CV scans in aqueous solution (0.1 M Na$_2$SO$_4$, pH 2.4, 100 mV/s scan rate) of mesoporous ITO electrodes with guest 3 physisorbed (green curves) and HGC-bound with host 5 (pink curves). a) The respective 3$^{rd}$ and 7$^{th}$ scans of freshly prepared samples show a clear oxidation peak for the HGC-bound guest (the peak shift is due to exchange of the chloride ligand with water during the electrochemical measurement). For the physisorbed guest, a small oxidation peak is observed. b) The respective 3$^{rd}$ and 7$^{th}$ scans of acetic acid washed samples show stable redox peaks for the HGC-bound guest, but no oxidation peak for the physisorbed species is observed after the 7$^{th}$ scan.
Figure S 26. Langmuir adsorption model for the formation of HGCs on mesoporous ZrO$_2$ films functionalized with host 5 as binding sites and guest 3 as adsorbent. The normalized absorption of the sample is used as a direct measure for the fractional occupancy of the guest on the surface. The measurements were performed after treatment of the samples with acetic acid to remove any contributions from physisorbed guests. A control experiment without host 5 on the surface showed no signal of the guest after the same treatment.

Figure S 27. Exchange of HGC-bound guests on mesoporous ZrO$_2$ films with host 5, using 510 nm excitation. a) Freshly prepared HGC-bound guest 4 (black) shows a large band (two peaks, molecular fluorescence and aggregate fluorescence) which decreases after treatment of the sample with acetic acid (purple), indicating removal of a large portion of mainly physisorbed 4. Further treatment with B-CD solution removes most of 4 from the surface (blue). After immersion of the desorbed sample into a solution of guest 2, the expected fluorescence signal for 2 is observed. b) The same procedure and observations as for a) are made, with the difference that the initial guest is 2 and it is exchanged by guest 4. The relatively intense signal of remaining 2 after BCD treatment hints towards incomplete removal; this is also indicated by the fact that the emission spectrum after dipping in a solution of 4 leads to a mixed response from both guests. Overall, the exchange experiments on metal oxide substrates match the ones obtained by TERS on gold substrates relatively well, with the difference that full replacement of guest 4 is achievable to a greater extent on ZrO$_2$. 
Figure S 28. a) CVs of mesoporous ITO electrodes functionalized with different guests measured in NH₃ saturated THF solution (0.2 M TBAPF₆ + 0.1 M NH₄PF₆; 10 mV/s scan rate) before chronoamperometry (at 0.08 V for 30 min) was performed. A clear catalytic onset is observed for HGC-bound and physisorbed guest 2 (with and without washing by acetic acid treatment), with the HGC-bound non-washed sample showing the highest activity. Furthermore, the initial catalytic activity is restored after resoaking the host-functionalized electrode in a solution of fresh guest 2. b) CVs after chronoamperometry under the same conditions, with the HGC-bound samples still showing the same onset (although lower current) while the physisorbed samples essentially lose catalytic activity (presumably due to desorption of the guest from the surface).

Figure S 29. Chronoamperometry at 0.08 V vs Fc/Fc⁺ using host 5-bound catalyst guests 2 and 4 (NH₃ saturated THF solution, 0.2 M TBAPF₆ and 0.1 M NH₄PF₆). HGC-bound 4 (Pt, black) shows nearly no activity, as is expected from this non-catalytic guest. Physisorbed guest 2 (turquoise) shows some activity, with initial current decreasing by about 50 % over the 30 minute measurement. HGC-bound 2 (magenta) shows significantly higher current than the physisorbed 2, and also a smaller decrease in activity over the measurement.
Figure S 30. Soaking of HGC-bound guest 3 on meso-ZrO$_2$ (green curve) after removal of physisorbed species (red curve) in different solvent over 4 hours (blue curve) and 20 hours (purple curve) measured via UV/Vis absorption spectroscopy. A significant decrease in absorption of the guest was observed in DMF and DMSO, and moderate desorption in acetone and THF. In the other cases, the guest remains bound to the surface, despite being soluble in the solvents (with the exception of toluene; see Figure S 31). A resoaking of the DMSO-soaked sample in fresh solution of the guest, followed by removal of physisorbed species, regenerated the initial absorption spectrum (orange curve in figure d), indicating that the hosts are not affected by the solvent soaking.
Figure S 31. UV/Vis spectra of guest 3 in various solvents used to determine HGC stability on a ZrO$_2$ surface. The significant absorption peak shift in water (purple) is likely due to ligand exchange on the guest. 3 is insoluble in toluene. Solutions were prepared to have a concentration of 25 μM or to be saturated where applicable.

Figure S 32. a) CV of guest 3 in aqueous solution (10% MeCN, 0.1 M Na$_2$SO$_4$, pH 2.4, 10 mV/s scan rate), showing a redox feature corresponding to Ru(II)/Ru(III) oxidation at 1.15 V vs RHE and an irreversible oxidation peak (Ru(III)/Ru(IV)) around 1.55 V, along with a slow onset of water oxidation at 1.75 V. b) CV of guest 3 under the same conditions, with addition of TPPSNa (2mM), showing a catalytic onset around 1.4 V for the oxidation of TPPSNa.
Figure S 33. a) CVs of mesoporous ITO electrodes functionalized with guests 3 and 4 in aqueous solution (0.1 M Na₂SO₄, pH 2.4, 10 mV/s scan rate). The HGC-bound electroactive 3 (host 5, green and yellow) shows the expected redox peaks also observed in solution. b) CVs of the same electrodes after addition of TPPSNa (2mM) show a clear catalytic onset around 1.4 V similar to the case in solution, corresponding to the oxidation of TPPSNa catalyzed by guest 3. Chronoamperometry at 1.4 V vs RHE decreases the current response, presumably due to loss or decomposition of the catalytic guest. Readsoption of fresh 3 on a sample after chronoamperometric measurements leads to complete regeneration of catalytic current, which shows the high stability of hosts on the metal oxide surface.

Figure S 34. Chronoamperometry at 1.4 V vs RHE with mesoporous ITO electrodes functionalized with guests 3 and 4 in aqueous solution containing TPPSNa (2 mM TPPSNa, 0.1 M Na₂SO₄, pH 2.4). Host 5 HGC-bound guest 3 shows catalytic current in freshly adsorbed (green) or acetic acid washed (orange) electrodes. Physisorbed 3 (acetic acid washed, blue) does not show any catalytic activity. Readsoption of fresh 3 into the host sites of the HGC-bound and washed sample (magenta) fully regenerates the catalytic activity for TPPSNa oxidation.
Figure S5. Repeated CVs of meso-ITO functionalized with host 5 and HGC-bound guest 3 in pH 10 solution (0.1 M carbonate buffer, 500 mV/s scan rate). After preparation, the sample was cycled between 1 and 1.85 V vs RHE for a total of 230 cycles, at scan rates of 100 mV/s (except for periodic fast scans shown here, which better show the redox peaks). The initial oxidation peak of 3 (between 1.3 and 1.6 V vs RHE) decreases over cycling time (black to blue to green curve). Resoaking the sample after the initial 230 cycle-CV into a fresh solution of 3 led to the reemergence of the redox peak (red curve). The redox peak of guest 3 is very broad, presumably due to surface heterogeneity.
Figure S 36. XP spectra of ITO electrodes functionalized with host 5 and HGC-bound guest 3 before and after oxidative CV cycling in pH 10 carbonate solution. a) C1s spectra, b) P2p spectra and c) XP spectra of the freshly HGC functionalized electrodes (black) and the HGC functionalized electrodes after 230 cycles (or 2 hours of cycling) between 0.8 and 1.85 V vs RHE. A decrease of the intensity of all three elements suggests partial desorption from the surface (around 25-30 %). In the sulfur spectrum, the appearance of a weak signal at 169 eV may indicate oxidation of a subset of sulfur atoms, which would be reasonable under the extremely oxidizing conditions the system was subjected to. Despite this, it is clear that the majority of host molecules remains intact on the electrode surface after the cycling experiment.
### 6. Crystal Structures

**Table S 1. Crystal data and structure refinement parameters for compounds 2.PF₆⁻, 3.PF₆⁻ and 4.ClO₄⁻.**

|                      | 2.PF₆⁻ | 3.PF₆⁻ | 4.ClO₄⁻ |
|----------------------|---------|---------|---------|
| CCDC number          | 1996726 | 1996727 | 1976728 |
| Empirical formula    | C₁₆₅H₁₅₈Cl₄F₂₄N₂₈O₃P₄Ru₄ | C₁₄₃H₁₁₀Cl₄F₂₄N₂₀O₃P₄Ru₄ | C₃₇H₂₆ClF₆N₃O₅PtS |
| Formula moiety       | 4(C₃₉H₃₅ClN₇Ru⁺), 4(F₆P⁻), 3(C₃H₆O) | 4(C₃₉H₃₅ClN₇Ru⁺), 4(F₆P⁻), 2(H₂O), C₃H₆O | 4(C₃₅H₂₅ClN₅Ru⁺), 4(F₆P⁻), C₂H₆OS |
| Formula weight       | 3707.14 | 3282.46 | 969.21  |
| Temperature/K        | 160(1)  | 160(1)  | 160(1)  |
| Crystal colour       | red     | red     | orange  |
| Crystal system       | monoclinic | triclinic | triclinic |
| Space group          | Cc      | P-1     | P-1     |
| a/Å                  | 14.45507(6) | 12.1576(4) | 7.19780(10) |
| b/Å                  | 26.84350(11) | 14.4722(4) | 13.14680(10) |
| c/Å                  | 23.21800(9)  | 20.8984(5)  | 20.1868(3)  |
| α/°                  | 90       | 72.382(2)   | 98.3470(10) |
| β/°                  | 99.5968(4) | 73.819(2)   | 91.8760(10) |
| γ/°                  | 90       | 81.164(2)   | 101.4120(10) |
| Volume/Å³            | 8883.08(6) | 3356.06(16) | 1848.91(4) |
| Z                    | 2        | 1        | 2       |
| ρ<sub>cak</sub>/cm³  | 1.386    | 1.624    | 1.741   |
| μ/mm⁻¹               | 4.303    | 5.594    | 8.976   |
| F(000)               | 3776.0   | 1652.0   | 948.0   |
| Crystal size/mm³     | 0.13 × 0.06 × 0.04 | 0.16 × 0.08 × 0.02 | 0.14 × 0.02 × 0.02 |
| Radiation            | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) |
| 2θ range for data collection/" | 7.5 to 149.006 | 7.594 to 136.5 | 6.942 to 149.002 |
| Index ranges         | -18 ≤ h ≤ 18, -33 ≤ k ≤ 33, -29 ≤ l ≤ 28 | -9 ≤ h ≤ 14, -17 ≤ k ≤ 17, -24 ≤ l ≤ 25 | -8 ≤ h ≤ 8, -16 ≤ k ≤ 13, -24 ≤ l ≤ 25 |
The molecular structure of 2. PF₆⁻ with displacement ellipsoids drawn at the 30% probability level (hydrogen atoms, counterions and solvent molecules are omitted for clarity).
The molecular structure of 3.PF₆⁻ with displacement ellipsoids drawn at the 30% probability level (hydrogen atoms and counterions are omitted for clarity).

The molecular structure of 4.CLO₄⁻ with displacement ellipsoids drawn at the 30% probability level (hydrogen atoms, counterions and disorders are omitted for clarity).
7. NMR Spectra

tpy-np – $^1$H-NMR

\[ \begin{align*}
&\text{tpy-np – } ^1\text{H-NMR} \\
&\text{2 – } ^1\text{H-NMR}
\end{align*} \]
$2 - ^{13}$C(NH)-NMR

$2 - ^{19}$F(NH)-NMR
2 – $^{31}$P{$^{1}$H}-NMR

3 – $^{1}$H-NMR (acetone) – ligand exchange with water causes apparition of extra peaks
3 – $^1$H-NMR (CDCl$_3$/CD$_2$CN 15:1) – no ligand exchange observed

3 – $^{13}$C($^1$H)-NMR
4 - $^1$H-NMR

4 - $^{13}$C($^1$H)-NMR
6 - $^{13}\text{C}^1\text{H}$-NMR

6 - $^{31}\text{P}^1\text{H}$-NMR
5. $^1$H-NMR (D$_2$O/DCl pD = 2) * = residual solvent possibly trapped in host cavity

5. $^{13}$C($^1$H)-NMR
$\text{5} - ^{31}\text{P}^{1\text{H}}\text{-NMR}$

\[
\begin{array}{c}
\text{H}_2\text{PO}_4\text{P} \\
\text{PO}_4\text{H}_2 \\
\text{S} \\
\text{O} \\
\text{HO} \\
\text{HO} \\
\end{array}
\]
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