Chemisorption of Exchange-Coupled [Ni₂L(dppba)]⁺ Complexes on Gold by Using Ambidentate 4-(Diphenylphosphino)benzoate Co-Ligands**

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Abstract: A new strategy for the fixation of redox-active dinickel(II) complexes with high-spin ground states to gold surfaces was developed. The dinickel(II) complex [Ni₂L(Cl)]ClO₄ (1ClO₄), in which L^{2-} represents a 24membered macrocyclic hexaaza-dithiophenolate ligand, reacts with ambidentate 4-(diphenylphosphino)benzoate (dppba) to form the carboxylato-bridged complex $[Ni_2L(dppba)]^+$, which can be isolated as an air-stable perchlorate [Ni₂L(dppba)]ClO₄ (2ClO₄) or tetraphenylborate [Ni₂L(dppba)]BPh₄ $(2BPh_4)$ salt. The auration of $2ClO_4$ was probed on a molecular level, by reaction with AuCl, which leads to the monoaurated Ni^{II}₂Au^I complex [Ni^{II}₂L- (dppba)Au¹Cl]ClO₄ (**3**ClO₄). Metathesis of **3**ClO₄ with NaBPh₄ produces $[Ni^{II}_{2}L(dppba)Au^{I}Ph]BPh_4$ (**4**BPh₄), in which the Cl⁻ is replaced by a Ph⁻ group. The complexes were fully characterized by ESI mass spectrometry, IR and UV/Vis spectroscopy, X-ray crystallography (**2**BPh₄ and **4**BPh₄), cyclic voltammetry, SQUID magnetometry and HF-ESR spectroscopy. Temperature-dependent magnetic susceptibility measurements reveal a ferromagnetic coupling J = +15.9 and +17.9 cm⁻¹ be-

Keywords: chemisorption • gold • ligands • macrocyclic ligands • nickel • phosphorus heterocycles tween the two Ni^{II} ions in 2ClO₄ and 4BPh₄ (H= $-2JS_1S_2$). HF-ESR measurements yield a negative axial magnetic anisotropy (D < 0), which implies a bistable (easy axis) magnetic ground state. The binding of the [Ni₂L-(dppba)]ClO₄ complex to gold was ascertained by four complementary surface analytical methods: contact angle measurements, atomic-force microscopy, X-ray photoelectron spectroscopy, and spectroscopic ellipsometry. The results indicate that the complexes are attached to the Au surface through coordinative Au–P bonds in a monolayer.

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- [**] dppba=4-(diphenylphosphino)benzoate.
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Introduction

The deposition of magnetically or electronically bistable transition-metal complexes on planar surfaces in which the spatially addressable functional units are assembled at the molecular level is an attractive research field,^[1,2] and has perspectives for the storage of information at the molecular level^[3,4] and in molecular electronics.^[5-10] Most research to date has focused on the physisorption or chemisorption of phthalocyanines,^[11] porphyrines,^[12] spin-crossover compounds, and more recently also single molecule magnets,^[13,23] and several strategies have been developed to obtain these materials as rows,^[14] thin films,^[15,16] or multilayers.^[17] The thermal evaporation of polynuclear transition-metal complexes, however, has found limited applicability in surface deposition due to their limited thermal and kinetic stability,^[18] and so new solution-based methods for surface functionalization had to be devised. Due to the high affinity of thiolates for gold,^[19,20] the ease of Au-S bond formation (i.e., deposition of thiols from solution) and the possibility of surface patterning by soft-lithography,^[21] the surface fixation of open-shell transition-metal complexes bearing thiol functions have therefore become the focus of intense investigations.

Two major strategies have evolved in the field of molecular magnetism that allow the deposition of polynuclear transition-metal carboxylato complexes with single molecule magnetism (SMM) behavior on gold. In the first approach, a self-assembled monolayer of a bifunctional thiol HS-X-L is prepared (L is usually a carboxylate function, whereas X is a spacer), which is then reacted with the carboxylato cluster by using a ligand exchange reaction.^[22] In the second approach, a SMM molecule with a properly functionalized ligand shell is directly deposited.^[23,24] Both strategies have their advantages and disadvantages. In the latter method, for example, the thiol has to be protected as it reacts with the cluster core. The solution methods have the advantage that they can be applied to more relevant substrates, like silicon, silicon oxides, or ferromagnetic metal oxides (such as $La_{0.7}Sr_{0.3}MnO_3$).

Our team is interested in the synthesis and characterization of exchange-coupled transition-metal complexes stabilized by macrocyclic polyaza-polythiophenolate ligands. Particularly well-investigated are dinuclear complexes of the N₆S₂ macrocycle H₂L (Figure 1).^[25,26] The N₆S₂ macrocycle supports mixed-ligand complexes of the type $[M_2L(L')]^{n+1}$ with a doubly thiolato-bridged $N_3M(\mu-SR)_2(\mu-L')MN_3$ core structure. The complexes are distinguished by the fact that the co-ligand L' is readily exchanged. Thus, a large number of closely related $[Ni^{II}_{2}L(\mu-L')]^{+}$ complexes (e.g., $L' = Cl^{-}$, OH^- , SH^- , NO_2^- , NO_3^- , N_3^- , N_2H_4 , $CH_3CO_2^-$, HCO_3^- , H₂PO₄⁻, ClO₄⁻, ReO₄⁻, CrO₄²⁻, MoO₄²⁻, WO₄²⁻, alkyl carbonates (ROCO₂⁻), alkyl carbamates (RNCO₂⁻), pyrazolate, tetrazolate, and tetrahydridoborate (BH₄⁻)) were prepared and their stability,^[27,28] reactivity,^[29,30] and electronic structures^[31,32] were studied as a function of the type of co-ligand and oxidation state.



Figure 1. Left: Structure of dinuclear complexes $[M_2L(L')]^+$ of the macrocyclic ligand H_2L . Right: Sketch of a chemisorbed $[Ni_2L(O_2CC_6H_4PPh_2)]ClO_4$ complex on a gold surface.

Since the magnetic properties of the $[Ni_2L(L')]^+$ complexes can be switched by using chemical^[33,34] or electrochemical methods,^[35] we became interested in the immobilization of such complexes on surfaces. We designed a strategy that is based on the direct deposition of SMMs on surfaces. We anticipated that the [LNi₂]²⁺ fragment would react with the hard donor function (H) of an ambidentate coligand H-Y-S to form a well-defined and isolable [LNi2(H-Y-S)]⁺ complex as shown in Figure 1. The macrocyclic supporting ligand L was expected to impose thermodynamic and kinetic stability on the complex, thus preventing a backbiting of the soft donor function (S) with the cluster core. The soft phosphine donor in the precursor [LNi₂(H-Y-S)]⁺ would then bind to the gold surface.^[36,37] Notice the salt-like composition of the adsorbate, containing monocations and anions. Thus, the anion is deposited along with the cation, but is only physisorbed.

The present study focuses on the ambidentate 4-(diphenylphosphino)benzoate ligand (Hdppba)^[38] with a soft diphenylphosphine and a hard carboxylate function. We report the preparation and isolation of the complex salts [Ni₂L(dppba)]ClO₄ and [Ni₂L(dppba)]BPh₄, their successful auration with AuCl, and their chemisorption on gold. The crystal structures, electrochemistry, reactivity features, magnetic and electrochemical properties of the complexes are described, as are the results of four complementary surface analytical methods: contact angle measurements, atomicforce microscopy, X-ray photoelectron spectroscopy, and ellipsometry. The coordination chemistry of transition-metal complexes with phosphine complexes is well-established. Phosphine-protected gold nanoparticles were reported.^[39-44] Little work has been performed in the field of phosphines adsorbed on gold surfaces;^[36,37,45] to the best of our knowledge, this is the first approach for the chemisorption of exchange coupled metal clusters through ambidentate phosphine-carboxylate ligands.

Results and Discussion

Synthesis and characterization of metal complexes: The synthetic procedures are summarized in Scheme 1. Treatment



Scheme 1. Preparation of complexes 2-4.

of $[Ni_2L(\mu-Cl)]ClO_4$ (1ClO₄)^[46] with 4-(diphenylphosphino)benzoic acid in MeOH in the presence of NEt₃ under Ar provides a green solution from which upon addition of LiClO₄ the green, air-sensitive target compound, $[Ni_2L(\mu$ dppba)]ClO₄ (2ClO₄) precipitates in 86% yield. The electrospray ionization mass spectrum (ESI-MS) of a dilute methanol solution of 2ClO₄ exhibited a molecular ion peak for $[Ni_2L(\mu-dppba)]^+$ (m/z = 1089.4), and the combustion analysis agreed well with the formula 2ClO₄. The presence of two IR absorption bands at 1550 cm⁻¹ ($\nu_{as}(RCO_2^{-})$) and 1408 cm⁻¹ ($\nu_{s}(RCO_{2}^{-})$) are indicative of a bridging carboxylate function as anticipated. Electronic absorption bands at 650 and 1122 nm attributable to spin-allowed v_2 and v_1 transitions of a six-coordinated NiN₃S₂O^{carboxylate} chromophore suggest that this structure is maintained in the solution state as well.^[28]

Efforts to obtain single crystals of 2CIO_4 suitable for Xray diffraction analysis were unsuccessful.^[47] However, such crystals could be obtained in the case of the tetraphenylborate salt 2BPh_4 which was synthesized by metathesis of 2CIO_4 with NaBPh₄. Figure 2 shows that the dppba ligand bridges the two Ni^{II} ions through its carboxylate function, in a symmetrical fashion leading to a Ni···Ni distance of 3.481(2) Å. The benzoate group of the dppba ligand is long enough so that the P atom is exposed out of the binding pocket of the [Ni₂L]²⁺ fragment. In addition, the C-P-C angles in 2CIO_4 (101.1, 101.7, and 106.5°) are very similar to



Figure 2. ORTEP (left) and van der Waals plot (right) of the molecular structure of the $[Ni_2L(O_2CC_6H_4PPh_2)]^+$ cation in crystals of 2BPh₄. Thermal ellipsoids are at 50% probability. Selected bond lengths [Å] and angles [°]: Ni1-O1 1.984(3), Ni1-N1 2.265(4), Ni1-N2 2.138(4), Ni1-N3 2.301(4), Ni1-S1 2.4742(13), Ni1-S2 2.4434(14), Ni2-O2 2.039(3), Ni2-N4 2.266(4), Ni2-N5 2.135(3), Ni2-N6 2.273(4), Ni2-S1 2.4713(16), Ni2-S2 2.4757(14); Ni2-S1-Ni1 89.47(5), Ni1-S2-Ni2 90.08(5).

those in PPh₃ (103.3, 103.3, and 101.7°)^[48] indicating that the structure of the dppba ligand is not markedly perturbed by the $[Ni_2L]^{2+}$ fragment. To our knowledge, there are not many paramagnetic 3d metal complexes of the dppba ligand. However, the Walton group reported a number of multiply bonded dimolybdenum and dirhenium complexes with this ligand.^[49] Overall, the $[Ni_2L]^{2+}$ complex binds the dppba selectively through the carboxylate function in a chelating manner leaving an uncoordinated P atom for anchoring to metal surfaces.

We decided to examine the aurophilicity^[50] of the [Ni₂L-(dppba)]ClO₄ salt prior to surface deposition studies, by treating it with suitable gold(I) compounds. An aurated species was also sought for as a reference compound in the XPS studies. [Ni₂L(dppba)]⁺ has three potential gold binding sites, the two thiolate sulfur atoms from the macrocycle L^{2-} and the exposed P atom from the dppba ligand. No apparent color changes took place when 2ClO₄ was allowed to react with AuCl in a 1:1 ratio in CH₂Cl₂ for 24 h (Scheme 1), however, an ESI-MS spectrum of the green reaction mixture showed the presence of a new species, formulated as the monogold(I) adduct $[Ni_2L(dppba)AuCl]^+$ (3, m/z = 1321.4), which can be isolated as a perchlorate salt $3ClO_4$ in 91% yield. The addition of further equivalents of AuCl to $2ClO_4$ or $3ClO_4$ did not result in a polyaurated species,^[51] which shows that there is indeed only one gold binding site in 2.

Unfortunately, we were not successful in growing single crystals of $3ClO_4$. However, crystals of the tetraphenylborate salt of the related complex [Ni₂L(dppba)AuPh]BPh₄ (4BPh₄), which is accessible by metathesis of $3ClO_4$ with NaBPh₄ (Scheme 1), can be obtained by recrystallization from a mixed CHCl₃/CH₂Cl₂/hexanes solution. Notice that the gold-bound chlorido ligand is replaced by a phenyl group in this reaction. The ability of the [BPh₄]⁻ ion to transfer a phenyl group is not unusual^[52,53] and some of these reactions occur even in aqueous solution.^[54] The phenyl compound is formed in high yield and is air stable.

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The crystal structure determination of $4BPh_4 \cdot 3CH_2Cl_2 \cdot CHCl_3 \cdot H_2O$ revealed the presence of two crystallographically independent but chemically identical molecules A and B of the trinuclear $[Ni_2L(dppba)AuPh]^+$ complex 4. A perspective drawing of one of them is shown in Figure 3, whereas selected bond lengths and angles are



Figure 3. ORTEP (left) and van der Waals plot (right) of the molecular structure of the $[Ni_2L(dppba)AuPh]]^+$ cation (molecule A) in crystals of 4BPh₄·3CH₂Cl₂·CHCl₃·H₂O. Thermal ellipsoids are at 50% probability. Selected bond lengths [Å] and angles [°] for molecule a [molecule b]: Au-C58 2.048(7) [2.041(5)], Au-P 2.3013(13) [2.294(1)], Ni1-O1 2.004(3) [2.002(3)], Ni1-N1 2.259(4) [2.215(4)], Ni1-N2 2.144(4) [2.127(4)], Ni1-N3 2.276(5) [2.335(4)], Ni1-S1 2.482(2) [2.465(1)], Ni1-S2 2.469(1) [2.474(2)], Ni2-O2 2.019(3) [2.031(3)], Ni2-N4 2.232(4) [2.223(4)], Ni2-N5 2.138(4) [2.165(4)], Ni2-N6 2.329(4) [2.298(4)], Ni2-S1 2.459(1) [2.444(2)], Ni2-S2 2.478(2) [2.496(1)]; C58-Au-P 177.82(18) [175.73(14)], Ni2-S1-Ni1 89.16(4) [89.54(5)], Ni1-S2-Ni2 88.99(5) [88.16(4)].

given in the Figure caption. The complexes are well separated from each other. The Au^I-Ph fragment is attached to the terminal phosphorus atom of the dppba co-ligand.^[55] The coordination geometry of the gold atom is almost perfectly linear, with the C-Au-P angle being 177.8(2)°. The Au-C and Au-P bond lengths are 2.048(7) and 2.3013(12) Å, respectively. The bond lengths and angles in 4 are very similar to those in [Au(Ph)(PPh₃)] (Au-C 2.045(6), Au-P 2.296(2) Å, P-Au-C 175.5(2)°).^[56] Notice that the binding of the [AuPh]⁺ fragment does not significantly alter the structure of the $[Ni_2L(dppba)]^+$ complex. The main difference is the smaller twist angle (14°) between the planes through the aromatic ring of the benzoate moiety and the carboxylato group. The orientation of the PPh₂ group with respect to the tert-butyl substituents is also different in 4, indicating that the Ph_2P group can freely rotate around the $Ph_2P-C_6H_4CO_2$ bond. The cleft-like structure of the complex cations appears to be of importance in the binding to the gold surface. In fact, the cleft, which holds the ambidentate co-ligand, directs the complexes to bind to the surface in an "upside-down" fashion. In summary, the diphenylphosphino group in 2ClO₄ is the only potential binding site for gold atoms, and the binding does not alter the overall structure of the [Ni₂L]²⁺ fragment.

Cyclic voltammetry: Cyclic voltammetry (CV) experiments

were carried out to investigate the redox behavior of $[Ni_2L(dppba)]ClO_4$ (2ClO₄), $[Ni_2L(pdbba)AuCl]ClO_4$ (3ClO₄), and $[Ni_2L(pdbba)AuPh]BPh_4$ (4BPh₄). Figure 4 shows the cyclic voltammograms of solutions of these compounds in CH₂Cl₂. The CV of the acetato-bridged complex $[Ni_2L(OAc)]ClO_4$ was reported previously,^[57] and is included for comparison.



Figure 4. Cyclic voltammogram of 2ClO_4 - 4ClO_4 (in CH₂Cl₂) and [Ni₂L-(OAc)]ClO₄ (in CH₃CN) at 298 K. Experimental conditions: 0.1 M [*n*-Bu₄N]PF₆, sample concentration of approximately 1×10^{-3} M, Pt disk working electrode, Ag wire reference electrode, scan rate = 100 mVs⁻¹, [Co(Cp₂)]PF₆ internal reference.

The CV of **2**ClO₄ shows two redox waves, one at $E_{1/2}^{1}$ = + 0.52 V (vs. a saturated calomel electrode (SCE)) with a peak-to-peak separation $\Delta E_{\rm p}$ of 0.07 V and one at $E_{1/2}^{2}$ = + 1.31 V with $\Delta E_{\rm p}$ = 0.10 V. The first oxidation is a one-electron process as confirmed by controlled potential coulometry at 273 K. Thus, the oxidation of [Ni₂L(dppba)]ClO₄ at an applied potential of +1.0 V versus SCE in CH₃CN solution consumed n=0.95 e⁻ per complex, whereas re-reduction at 0.0 V versus SCE caused transfer of 96% of the charge

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passed in oxidation. In addition, the CV of the electrogenerated $[Ni_2L(dppba)]^{2+}$ dication is identical to that of the parent $[Ni_2L(dppba)]^+$ monocation.

The electrochemical behavior of $[Ni_2L(dppba)]^+$ is similar to that of the acetato-bridged complex $[Ni_2L(OAc)]ClO_4$, which shows two redox waves at $E^{1}_{1/2}=0.56$ V and $E^{2}_{1/2}=1.36$ V.^[56] The redox waves can be assigned to metal-centered (Ni^{II}Ni^{II} \rightarrow Ni^{II}Ni^{III}) and ligand-based oxidations (RS⁻(thiolate) \rightarrow RS⁻ (thiyl radical)) within the $[Ni_2L]^{2+}$ unit as represented in Equations (1) and (2).^[58]

Similarly, for **3**ClO₄ two redox waves are observed at $E_{1/2}^{1}=0.59$ V ($\Delta E_{\rm p}=0.14$ V) and $E_{1/2}^{2}=1.38$ V ($\Delta E_{\rm p}=0.13$ V) indicative of the same redox behavior. The first oxidation yields a mixed-valent Ni^{II}Ni^{III}Au^I complex **3**²⁺ as indicated in Equation (3)^[59] and the second oxidation is ligand centered. The small shift to more anodic potentials is presumably a consequence of an electron-withdrawing effect of the AuCl unit. This decreases the electron density of the carboxylate function, which increases the stability of the Ni^{II}Ni^{II} form to some extent. For **4**BPh₄, the same is evident, with the $E_{1/2}^{1}$ and $E_{1/2}^{2}$ values of 0.59 V ($\Delta E_{\rm p}=0.10$ V) and 1.4 V ($\Delta E_{\rm p}=0.16$ V). The irreversible redox wave at 0.91 V is attributed to an oxidation of the tetraphenylborate anion.

The dication 3^{2+} can also be prepared by chemical oxidation. Green solutions of 3ClO4 turn dark red upon addition of one equivalent of $Cu(ClO_4)_2$. The UV/Vis spectra of such solutions reveal several strong absorption bands ($\lambda_{max} = 782$ (4945), 517 (2735), 397 (2998), 330 (9864), and 304 nm $(13560 \,\mathrm{M}^{-1} \mathrm{cm}^{-1})$ attributable to ligand-to-metal (RS⁻ \rightarrow Ni^{III}) charge-transfer transitions. The same absorption features are observed for electrochemically generated solutions of 3^{2+} , showing that both processes produce the same species. Interestingly, there is also a feature at 1590 nm $(2538 \,\mathrm{M}^{-1} \mathrm{cm}^{-1})$ attributable to an intervalence transition. Electrospray ionization mass spectrometry provided final conformation for the identity of the dication 3^{2+} , with a peak at m/z = 1420.29 for a mixed-valent [Ni^{II}Ni^{III}L-(dppba)AuCl](ClO₄)⁺ monocation and a peak at m/z =661.61 for the mixed-valent [Ni^{II}Ni^{III}L(dppba)AuCl]²⁺ dication.

$$[NillNillL(dpbba)]^{+} \xrightarrow{-e^{-}} [NillNillL(dpbba)]^{2+}$$
(1)

$$2^{+} 2^{2+}$$

$$[Ni||Ni|||L(dpbba)]^{2+} \stackrel{\bullet}{\longleftarrow} [Ni||Ni|||L^{\bullet}(dpbba)]^{3+}$$
(2)
$$2^{2+} 2^{3+}$$

The redox chemistry of the two-coordinate Au^I complexes was investigated by other research groups. Au^I complexes with mixed Cl⁻ and PPh₃ donor ligands generally undergo an irreversible reduction to Au⁰ at cathodic potentials of less than $-2 \text{ V}^{[60,61]}$ The form and position of the reduction peaks also depend on the Au coverage of the electrode. For the present Ni₂Au complexes there are no redox waves in a potential window ranging from -2 to +2.5 V versus SCE that can be attributed to reduction of the dppba-Au^IPh group, which is in good agreement with the reported trend.^[60] It can be concluded that this unit is redox inactive in this potential range. The +III oxidation level is common in nickel thiolate chemistry, and several other mixed-valent nickel thiolate complexes have been reported in the past two decades.^[62-66] However, to our knowledge, trinuclear Ni^{II}Ni^{III}Au^I species are not described nor reported in the literature yet.

Magnetic properties of 2ClO₄ and 4BPh₄: *Static magnetization measurements*: Static magnetization measurements for the paramagnetic Ni^{II}_2 and $Ni^{II}_2Au^I$ complexes **2**ClO₄ and **4**BPh₄ were performed with a commercial SQUID (superconducting quantum interference device) magnetometer from Quantum Design in the temperature range from 2 to 300 K in magnetic fields from 0 to 5 T. Figure 5 shows the



Figure 5. Magnetic field dependence of the static magnetization of $2CIO_4$ (\triangle) and $4BPh_4$ (\bigcirc) measured at T=1.8 K.

field dependence of the magnetization of 2ClO_4 and 4BPh_4 measured at T=1.8 K. The saturation magnetization is similar for the two complexes and is around 4.2 μ_{B} . This value corresponds to a total spin $S_{\text{tot}}=2$ in the ground state and indicates a ferromagnetic coupling between Ni²⁺ ions (3d⁸, $S_{\text{Ni}}=1$) in both complexes.

Figure 6 shows the temperature dependence of the magnetic susceptibility $\chi(T) = M(T)/B$ and the inverse susceptibility $\chi^{-1}(T)$ of both complexes in an applied magnetic field

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Figure 6. Temperature dependence of the static magnetic susceptibility, $\chi = M/B$ and the inverse susceptibility χ^{-1} of a) **2**ClO₄ and b) **4**BPh₄ measured at B = 1 T. Black lines correspond to the result of the fitting using the Hamiltonian [Eq. (5)] and \odot = data.

of 1 T. The data were analyzed using the Hamiltonian in Equation (5):

$$H = -2J\vec{S}_1 \bullet \vec{S}_2 + \mu_B \sum_{i=1}^2 g\vec{S}_i \bullet \vec{B} + \sum_{i=1}^2 D_i \left[S_{z,i}^2 - \frac{1}{3} S_i (S_i + 1) \right]$$
(5)

in which the first term describes the isotropic magnetic coupling between the two Ni ions. Here, J is the Heisenberg exchange constant and S_1 and S_2 are the spin operators. The second term describes the Zeeman interaction with the magnetic field B and the last term describes the single ion anisotropy of the Ni ions. Here, g denotes the isotropic g-factor of the ion, μ_B is the Bohr magneton, B is the external magnetic field and D_i is the axial single-ion anisotropy constant. Based on those parameters, the susceptibility $\chi(T)$ and the inverse susceptibility $\chi^{-1}(T)$ were simulated by using the julX simulation program.^[67] The values of the g-factor and of the magnetic anisotropy parameter D were taken from the ESR measurements (see below). We have found, however, that taking into account the D parameter does not change the result of the fit of the susceptibility data, which is most likely related to the smallness of the D value.^[68] The modeling reveals a ferromagnetic coupling of 23 (16 cm⁻¹) and 26 K (18 cm⁻¹) between the two Ni ions for **2**ClO₄ and for **4**BPh₄, respectively. These values agree well with those of other carboxylato-bridged Ni^{II}₂ complexes bridged by the hexaaza-dithiophenolate macrocycle.^[33]

High-field electron spin resonance (HF-ESR) measurements: High-field ESR (HF-ESR) measurements were performed on 2ClO₄ and 4BPh₄ with a homemade spectrometer on the basis of a Millimeterwave Vector Network Analyzer from AB Milimetre.^[69] The samples were measured as oriented powders in magnetic fields up to 15 T for excitation frequencies $\nu = 80-350$ GHz. The typical ESR spectra of 2ClO₄ and 4BPh₄ at different temperatures and a frequency of 332 GHz are plotted in Figure 7. The spectra of both com-



Figure 7. The temperature dependence of the ESR spectra of a) $2CIO_4$ and b) $4BPh_4$ at $\nu = 332$ GHz.

pounds look very similar. At T=4 K we observe a single resonance line in the ESR spectrum, however, at higher T the number of lines increases. Above T=20 K we observe four resonance lines corresponding to the transitions within the ground state multiplet S=2. Such a transfer of the spectral weight to lower magnetic field with decreasing the temperature is the first indication for an axial magnetic anisotropy of the molecules (D < 0).

Figure 8 shows the frequency versus resonance field dependencies for 2ClO_4 and 4BPh_4 together with representative ESR spectra. The slopes of the four resonance branches in both cases reveal a *g*-factor of 2.17. By the extrapolation of the first resonance branch (line 1) to the zero field, the magnetic anisotropy of both compounds was estimated. We



Figure 8. The frequency dependence of the ESR spectrum of a) 2ClO_4 at T=20 K ($\Delta=40 \text{ GHz}$) and b) 4BPh_4 at T=25 K ($\Delta=35 \text{ GHz}$; g=2.17 for both). $\blacksquare=\text{Line 1}; \bullet=\text{line 2}; \bullet=\text{line 3}; \text{and } \blacktriangledown=\text{line 4}.$

find anisotropy gaps of 40 and 35 GHz for $2CIO_4$ and $4BPh_4$, respectively.

For the analysis of the ESR spectra we introduced a model that describes only the ground state of the molecule. The effective spin Hamiltonian in this case can be written as Equation (6):

$$H = g\mu_B \vec{S} \bullet \vec{B} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]$$
(6)

in which the first term describes the Zeeman interaction of the total spin of the molecule with the magnetic field *B* and the second term describes the magnetic anisotropy of the molecule. We assume that each molecule has a single total spin S=2, a g-factor of 2.17, and a magnetic anisotropy parameter $D = \Delta/(S^2 - (S-1)^2)$, which amounts to -13.3 GHz (-0.063 K) for 2ClO₄ and -11.6 GHz (-0.056 K) for 4BPh₄.

The simulation of the ESR spectra was performed for $\nu =$ 332 GHz, T = 20 K and parallel orientation of the magnetic

anisotropy axis to the applied magnetic field. The experimental and modeled ESR spectra are plotted in Figure 9 with the calculated energy-level diagram. As can be seen,



Figure 9. Experimental and modeled ESR spectra at $\nu = 332$ GHz, T = 20 K and corresponding energy-level diagrams for a) **2**ClO₄ and b) **4**BPh₄.

the simulation reproduces the experimental ESR spectra very well. The modeling confirms the negative sign of the axial magnetic anisotropy parameter (D < 0) and the Dvalues of -13.3 GHz (-0.063 K) and -11.6 GHz (-0.056 K) for 2ClO₄ and 4BPh₄, respectively. Overall, the magnetization and ESR measurements show no significant difference between compounds 2ClO₄ and 4BPh₄. The magnetic properties of 2 are not significantly changed upon attachment of the Au to the phosphorus atom. On the other hand, it is also clear that the magnetic anisotropy barrier is too small for getting sufficient retention of magnetization at finite temperature.

Chemisorption of 2\text{ClO}_4 on gold: To test whether 2ClO_4 can be immobilized on surfaces, it was brought in contact with a planar gold substrate. The deposition of the [Ni₂L-(dppba)]ClO₄ complex salt with its pendant PPh₂ group was performed in analogy to the preparation of self-assembled

thiol monolayers on gold as described in the literature.^[70] A clean gold-coated Si wafer was immersed in a 1×10^{-3} M solution of **2**ClO₄ in EtOH for 24 h followed by washing with EtOH and drying. To analyze the so modified Au surfaces we used four complementary surface sensitive analytical techniques (contact angle measurements, atomic-force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and spectroscopic ellipsometry).^[71]

Contact angles and atomic-force microscopy: The immobilization of 2ClO_4 to gold was expected to change the wettability and roughness of the surface. Therefore, the immobilization of the complexes was probed by static water contact angle measurements and AFM topography analysis. Table 1 lists the results.

Table 1. Water contact angles and rms roughness data obtained for gold films modified with various dinickel(II) complexes.

Entry	Compound	Contact angle [°] ^[a]	rms roughness [nm]
1	bare gold (EtOH)	75.8 (1.5)	0.6 (1)
2	$PPh_2(C_6H_4-4-CO_2H)$	74.9 (1.4)	n.d. ^[b]
3	$[Ni_{2}L(dppba)]ClO_{4}$ $(2ClO_{4})$	71.5 (1.6)	1.7 (5)
4	$[Ni_2L(dppba)]BPh_4$ (2 BPh ₄)	76.7 (1.9)	1.6 (2)
5	$[Ni_2L(dppba)]ClO_4$ (2ClO ₄) (after washing with NaBPh ₄)	76.5 (2.1)	n.d. ^[b]
6	[Ni ₂ L(O ₂ CPh)]ClO ₄	75.9 (2.0)	0.6
7	[Ni ₂ L(OAc)]BPh ₄	75.8 (1.5)	0.6

[a] The values represent the average of ten 4 μ L drops of destilled, deionized water. Standard deviations are given in parentheses. The "bare" gold surfaces were identically treated to the modified surfaces except with omission of any adsorbate in the solvent. [b] n.d. = not determined.

The contact angle measurements showed small but significant variations, indicating that the complexes bind indeed to the gold surface. For the unmodified gold-containing adventitious, nonpolar material a contact angle of 75.8° was obtained, which agrees with the value reported in the literature.^[72] Very little is known about water contact angle of tertiary phosphines on the coinage metals.^[35,36,73,74] The contact angle of the free Hdppba ligand has not been reported previously.^[75] The value of 74.9° is relatively high for a carboxylate terminated monolayer, suggesting that the CO₂H groups are involved in intermolecular H-bonding interactions. Indeed, such an effect is known to increase the hydrophobicity of rather polar molecules.^[76] Upon immobilization of the $[Ni_2L(dppba)]ClO_4$ complex salt, the contact angle reduces slightly relative to the unmodified gold, indicating a surface transition to a more hydrophilic state. This is not surprising given the salt-like character of the adsorbates. The contact angle for immobilized 2ClO₄ on gold (Table 1, entry 3) is comparable with those of alkane thiol monolayers terminated with ester, alkoxy, or thioester groups.^[77] The angle seems to be quite high for an ionic compound, but given that the charges are well-shielded by the apolar groups of the macrocyclic ligands, this is not surprising. A thin film of the more lipophilic tetraphenylborate salt 2BPh₄ on gold increases the contact angle by 5.2° (Table 1, entry 4), which could be expected since the BPh₄⁻ group is more hydrophobic than the ClO_4^{-} ion. The contact angle measurements also revealed that complexes such as [Ni₂L-(O₂CPh)]BPh₄ and [Ni₂L(OAc)]ClO₄, which lack end groups for surface fixation, are not chemisorbed on the gold surfaces (Table 1, entries 6 and 7). It is also interesting to note that the physisorbed anions of the immobilized salts can be exchanged for one another by surface metathesis reactions. The chemisorbed cationic complexes remain attached on the surfaces. Thus [Ni₂L(dppba)]ClO₄ on gold when treated with NaBPh₄ undergoes an anion exchange reaction to produce $[Ni_2L(dppba)]BPh_4$ (Table 1, entry 5). Such anion exchange reactions were observed by others, for example, for polycations attached to solid surfaces.^[78]

The trend observed with the contact angle measurements is also reflected in the values of the root mean squared (rms) roughness determined by using AFM. Figure 10 shows



Figure 10. AFM topography characteristics considering a $1 \times 1 \ \mu m^2$ area, a) Au substrate as grown with a roughness of 0.6(1) nm (rms), b) Au substrate after deposition of $[Ni_2L(dppba)]CIO_4$ with a roughness of 1.7(5) nm (rms), c) AFM profile following the white-dotted lines in (a) and (b).

a comparison between the topography of $[Ni_2L(dppba)]ClO_4$ (2ClO₄) and of the uncovered Au substrate along with the comparison of two line profiles. As can be seen, the rms roughness of $[Ni_2L(dppba)]ClO_4$ on gold is by 10 Å larger than that of the pure gold substrate. In addition, the rms roughnesses of the $[Ni_2L(O_2CMe)]ClO_4$ and $[Ni_2L-(O_2CPh)]ClO_4$ compounds (Table 1, entries 6 and 7) had similar rms values as the substrate.

XPS studies: The attachment of $[Ni_2L(dppba)]ClO_4$ (**2**ClO₄) to the gold surface was further analyzed by X-ray photoelec-

tron spectroscopy (XPS).^[69] XPS spectra were recorded for bulk **2**ClO₄ and for a freshly prepared sample of **2**ClO₄ chemisorbed on gold. Photoelectron peaks of Ni, P, S, Cl, C, and O were observed. However, the long exposure time led to significant X-ray-induced damage, which particularly affected the ClO₄⁻ groups, the bridging thiolate sulfur atoms of the N₆S₂ macrocycle, and the P atoms as further detailed below.^[79] Table 2 lists the selected peak positions and their assignments.

Table 2. XPS binding energies (eV) for ${\rm 2ClO_4}$ and for ${\rm 2ClO_4}$ chemisorbed on gold. $^{[a]}$

Element	Bulk $2ClO_4^{[b]}$	2ClO ₄ on Au(111) ^[c]	Assignment
P(2p _{3/2})	132.2	131.1	R ₃ P
P(2p _{1/2})	133.2	132.1	
Relative intensity [%]	33	39	
P(2p _{3/2})	134.1	133.4	R_3PO , (or $P(OR)_3$)
P(2p _{1/2})	135.1	134.4	
Relative intensity [%]	49	61	
P(2p _{3/2})	139.9	n.o. ^[d]	PO_{4}^{3-}
$P(2p_{1/2})$	140.9	n.o. ^[d]	
Relative intensity [%]	18		
Ni(2p _{3/2})	856.5	856.8	Ni ²⁺
	861.7	862.1	"satellite"
	865.6	866.0	"satellite"
Ni(2p _{1/2}) (main peak)	873.4	874.0	Ni ²⁺
	878.2	878.6	"satellite"
	882.7	883.0	"satellite"
S(2p _{3/2})	163.7	162.3	Ni–µSR–Ni
$S(2p_{1/2})$	164.7	163.3	
Total intensity [%]	100	50	
S(2p _{3/2})	169.8 ^[b]	169.7	Ni–µSO3R–Ni
$S(2p_{1/2})$	170.8 ^[b]	170.7	
Total intensity [%]	traces	50	
Cl(2p _{3/2})	209	209	ClO ₄ ⁻
$Cl(2p_{1/2})$	211	211	
Total intensity [%]	60	traces	
$Cl(2p_{3/2})$	200	199.5	Cl-
$Cl(2p_{1/2})$	202	201.5	
Total intensity [%]	40	100	
N(1s)	403	399	NR ₃
O(1s)	533.5	533	RCO ₂ , RSO ₃
C(1s)	287	284.9	CH (aliph. + arom.)
		286.1	C-S, C-P
		288.2	RCO ₂ ⁻

[a] The binding energies are referenced to Au $4f_{7/2}$ (84.0 eV). [b] Data acquisition time: 58 h (165 cycles). [c] Data acquisition time: 44 h (106 cycles), [d] n.o. = not observed.

Of particular evidence for surface Au–P single bonds are the oxygenation reactions that 2ClO_4 undergoes in the bulk and on the gold surface. These oxidations are induced by O atoms, which stem from the decomposition of the $\text{ClO}_4^$ ions by the incident X-ray beams.^[80] The XPS spectrum of bulk 2ClO_4 shows two $P(2p_{3/2})$ and $P(2p_{1/2})$ photo peaks at binding energies typical for a phosphine group (Figure 11).^[81,82] The feature at higher energies (134.1 eV) is assumed to be due to a phosphine oxide (R₃PO), which arises from X-ray-induced damage. The oxidation of physisorbed PR₃ ligands to R₃PO ligands was observed previously.^[83] For chemisorbed 2ClO_4 on gold, again two $P(2p_{3/2})$ and

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Figure 11. XPS $P(2p_{3/2})$ and $P(2p_{1/2})$ peaks for bulk $2CIO_4$ and for a monolayer of $2CIO_4$ on gold.

 $P(2p_{1/2})$ photo peaks are observed. Upon binding to Au the peak for the phosphine group is shifted to 131.1 eV, clearly showing the chemisorption of the [Ni₂L(dppba)]⁺ complexes to the Au surface. The peak at 133.4 is attributed to X-ray induced-damage. Notice that this value is different from that of bulk 2ClO₄. This suggests the formation of a different oxygenated species, perhaps a phosphite group $(P(OR)_3)$. The incorporation of O atoms into the P-C bonds (rather than the Au-P) would be consistent with the presence of the Au-P bonds. This finding is also in excellent agreement with the previous knowledge that the P donor in the [Ni₂L-(dppba)AuPh]⁺ complex is much more resistant towards oxidation than in the parent [Ni₂L(dppba)]⁺ complex with the free -PPh₂ group (see above). Notice that binding of the phosphine to the gold surface shifts the $P(2p_{1/2})$ peaks only slightly. This specific behavior has been observed by others for R₃P ligands.^[84]

The photoelectron peaks in the $Ni(2p_{3/2})$ region for bulk $2CIO_4$ and for chemisorbed $2CIO_4$ on gold with the wellknown satellites at 862.5 and 863 eV are characteristic of divalent, six-coordinate nickel complexes (Figure 12). These data imply that complex 2ClO₄ undergoes no redox changes upon surface fixation.^[85-88] However, the Cl(2p) regions show, besides the presence of ClO_4^- ions (209 eV), additional spectral features corresponding to chloride ions (see the Supporting Information). The observed behavior is the result of photoinduced decomposition of ClO₄⁻ ion into Cl⁻ and was reported previously.^[76] A similar photoinduced conversion of the Ni-bound RS⁻ to RSO₃⁻ moieties can be observed for chemisorbed 2ClO₄. The O atoms most likely stem again from the decomposition of the ClO₄⁻ ions. It is interesting that these O atoms oxidize the P atoms in bulk $2ClO_4$ and the RS⁻ groups in chemisorbed $2ClO_4$. This can be taken as additional evidence for the formation of an Au-P bond between molecules of 2 and the gold surface. As mentioned before, the coordination of a PR₃ ligand to a gold atom increases its stability towards oxidation, and the



Figure 12. XPS $Ni(2p_{3/2})$ peaks for bulk $2ClO_4$ and for a monolayer of $2ClO_4$ on gold.

same applies here as well. The absence of signals for free phosphine groups also rules out the presence of overlayers.

Photoelectron peaks of C, O, and Cl are also observed (the Supporting Information). The C(1 s) spectrum can be deconvoluted to three signals. The strong C(1s) signal at 284.9 eV can be attributed to the aliphatic and aromatic (CH) carbon atoms of the dppba ligand and the N₆S₂ macrocycle. The shoulder at 286.1 eV is attributed to the five electron-deficient carbon atoms bonded to electronegative sulfur and phosphorus atoms.^[89] There is also a weak peak at 288.2 eV which can be attributed to the carboxylate function.^[90] Taken together, the XPS spectrum provides strong evidence for a covalent Au-P linkage between **2** and the Au surface in a monolayer.

Optical thicknesses: To probe the thickness of the films spectroscopic ellipsometry measurements were carried out for a monolayer of complex $2ClO_4$ on gold, the tetraphenylborate salt $2BPh_4$, and the free phosphine Hdppba. The ellipsometry data were analyzed by using the Cauchy formula [Eq. (7)] for thin monolayers,^[91] in which three parameters define the wavelength-dependent refractive index.

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(7)

The parameter A strongly correlates with the film thickness d, which means that fitting both A and d at the same time is not reasonable. Therefore A was kept constant at the value of 1.45, which is commonly used for the refractive index of monolayers described as transparent media.^[92,93] By using this model, reasonable fits were produced resulting in average thicknesses of (4.8 ± 4) Å for Hdppba, (16.3 ± 7) Å for 2ClO₄, and (15.1 ± 8) Å for 2BPh₄. The observed layer thickness of the Hdppba ligand is somewhat smaller than the calculated molecule size of approximately 7 Å assuming that the molecules are oriented with their pseudo-threefold axis perpendicular to the surface and that the average C-P-

C angle is 105°. This deviation from the expected thickness value of one monolayer most likely arises from the relatively high film roughness of the gold substrates used rather than from an ordering by intermolecular hydrogen-bonding interactions between the adsorbate molecules. The strong dependence of film thicknesses on the film roughness was also observed by others.^[94]

Nevertheless, the observed film thicknesses observed for the perchlorate and tetraphenylborate salts are in good agreement with the molecule size of ≈ 15 Å for the $[Ni_2L(O_2CC_6H_4PPh_2)]^+$ cation in $2ClO_4$ and $2BPh_4$ (on the basis of the corresponding atomic distances in the crystal structure of $2ClO_4$). Interestingly, the thicknesses of the layers of the perchlorate and tetraphenylborate salts are almost identical suggesting that the ClO_4^- and BPh_4^- ions are located beneath the $[Ni_2L(dppba)]^+$ moieties rather than above them in a second layer. Therefore, the ellipsometric data further support the assumption that both $2ClO_4$ and $2BPh_4$ form monolayers rather than multilayer films, with the cationic $[Ni_2L(dppba)]^+$ molecules oriented perpendicular to the Au surface.

Surface-binding model: If it can be assumed that the observed Au–P bonding interactions in $4BPh_4$ are maintained in chemisorbed [Ni₂L(dppba)]ClO₄ on gold, one can propose a hypothetical surface structure. Figure 13 shows a likely ori-



Figure 13. Proposed binding mode of 2CIO_4 to gold (left: van der Waals representation of the cation 2; right: representation with a Lewis formula. The macrocycle is shown as an ellipse encircling the two Ni²⁺ ions for clarity).

entation of **2**ClO₄ on the gold surface. The height of the $[Ni_2 L(dppba)]^+$ complex on the surface in this case is given by the distance between two opposing NMe substituents, which amounts to approximately 12.3 Å. In an alternate orientation (not shown in Figure 12) the $[Ni_2L]^{2+}$ fragment is rotated by 90° around the O₂CC₆H₄–PPh₂ bond. In this case, the height is given by two opposing *tert*-butyl CH₃ groups, which amounts to 15.5 Å (H32a···H37b).^[95] This value is in reasonable agreement with the thickness determined by ellipsometry. Irrespective of the actual orientation of the $[LNi_2]^{2+}$ fragment, the surface complex presumably is also stabilized by van der Waals interactions between the Au surface and the methylene or methyl groups of the supporting macrocycle. The thiolate sulfur atoms, however, are out of range of bonding interactions with the Au surface.

Conclusion

The main findings of the present work can be summarized 1) The dinuclear Ni^{II} as follows: complex $[Ni_{2}L(O_{2}CC_{6}H_{4}PPh_{2})]^{+}$ supported by a macrocyclic hexazadithiophenolate ligand is readily prepared and can be isolated as the air-sensitive perchlorate [Ni₂L(dppba)]ClO₄ $(2ClO_4)$ or tetraphenylborate $[Ni_2L(dppba)]BPh_4$ $(2BPh_4)$ salt. 2) The X-ray structure determination showed that the ambidentate 4-(diphenylphosphino)benzoate co-ligand binds specifically, through its carboxylate function, to the $[Ni_2L]^{2+}$ fragment such that the soft phosphorus atom is positioned in the periphery of the complex. 3) The mode of auration of $2ClO_4$ with AuCl demonstrates that $2ClO_4$ exhibits only one gold binding site. Only the phosphine group in $2CIO_4$ is aurated. The two thiolate sulfur atoms in 2ClO₄ exhibit no aurophilicity. 4) The $[Ni_{2}^{II}L(dppba)]^{+}$ complexes exhibit an S=2 ground state that is attained by ferromagnetic coupling of the two Ni^{II} ($S_i = 1$) ions. HF-ESR measurements yield a negative axial magnetic anisotropy (D < 0), which implies a bistable (easy axis) magnetic ground state. 5) The [Ni₂L-(dppba)]⁺ complex is redox-active and is also accessible in a mixed-valent Ni^{II}Ni^{III} form of a different S = 3/2 ground spin state. 6) Complexes of 2ClO₄ can be chemisorbed on gold surfaces through the formation of Au-P surface bonds as clearly established by contact angle measurements, AFM spectroscopy, XPS spectroscopy, and spectroscopic ellipsometry. Finally, 7) the complexes do not change their oxidation state upon surface fixation. It would be interesting to see whether the oxidation state of $2ClO_4$ (and hence the spin state) can be switched by the tip of a scanning tunneling microscope. Such studies are underway.

Experimental Section

Materials and methods: All reagents were purchased from commercial sources unless otherwise specified. Compound [Ni₂L(Cl)]ClO₄ (1ClO₄) was prepared as described in the literature.^[45] 4-(diphenylphosphane)benzoic acid was prepared by using a fluoride-catalyzed reaction from 4fluoroethylbenzoate and diphenyl(trimethylsilyl)phosphine.[96] Ethanol was deoxygenated with nitrogen before use. Acetonitrile was distilled from calcium hydride. The syntheses of the metal complexes were carried out under a protective atmosphere of argon. Melting points were determined in open glass capillaries and are uncorrected. The infrared spectra were recorded as KBr discs by using a Bruker Tensor 27 FT-IR spectrophotometer. Electronic absorption spectra were recorded on a Jasco V-670 UV/Vis/near-IR spectrophotometer. Elemental analysis was carried out on a VARIO EL-elemental analyzer. ESI mass spectra were recorded on a Bruker Daltronics ESQUIRE3000 PLUS spectrometer. Cyclic voltammetry measurements were carried out at 25°C with an EG&G Princeton Applied Research potentiostat/galvanostat model 263 A. Cobaltocenium hexafluorophosphate (Cp₂CoPF₆) was used as an internal standard. All potentials are given versus SCE but are standardized against the ferrocenium/ferrocene couple.[97] Temperature-dependent magnetic susceptibility measurements on powdered solid samples were carried out by using a MPMS 7XL SQUID magnetometer (Quantum Design) over a temperature range 2-330 K at an applied magnetic field of 0.5 Tesla. The observed susceptibility data were corrected for underlying diamagnetism. CAUTION! Perchlorate salts of transition-metal complexes are hazardous and may explode. Only small quantities should be prepared and great care should be taken.

[Ni₂L(dppba)]ClO₄ (2ClO₄): A solution of Hdppba (50 mg, 0.163 mmol) in MeOH was added to a solution of [Ni₂L(µ-Cl)]ClO₄ (100 mg, 0.108 mmol) in MeOH (25 mL). Triethylamine (16.2 mg, 0.16 mmol) was then added and the ocher-colored suspension turned into a clear-green solution, which was stirred for 48 h at RT. A solution of LiClO₄·3H₂O (87.1 mg. 0.54 mmol) in EtOH (20 mL) was added, and stirring was continued for 30 min. The mixture was concentrated (rotary evaporator) to \approx 25 mL. The green, microcrystalline precipitate was filtered, washed with EtOH and Et₂O. Yield: 111 mg (86%). M.p. 320-324°C (decomp.); IR (KBr pellet): $\tilde{v} = 3443$ (w), 2961 (m), 2867 (m), 1599 (s), 1550 (m, v_{as} (RCO2^-)), 1461 (s), 1408 (s, $\nu_{\rm s}$ (RCO2^-)), 1363 (m), 1309 (w), 1265 (w), 1233 (w), 1201 (w), 1152 (w), 1092 (vs, ClO₄⁻), 1040 (m), 931 (w), 913 (m), 881 (w), 825 (m), 817 (m), 768 (m), 746 (w), 719 (w), 699 (m), 623 (m, ClO₄⁻), 495 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 227 (48400), 272 (15000), 334 (11800), 385 (2100), 650 (34), 1122 nm ($68 \text{ m}^{-1} \text{ cm}^{-1}$); MS (ESI): m/z (CH₃CN) = 1089.4 [M-ClO₄]⁺; elemental analysis calcd (%) for C₅₇H₇₈ClN₆Ni₂O₆PS₂ (1191.21): C 57.47, H 6.60, N 7.06, S 5.38; found: C 57.25, H 6.39, N 6.97, S 5.27. The tetraphenylborate salt 2BPh₄ was prepared by adding a solution of NaBPh₄ (14.4 mg, 42.0 µmol) in EtOH (10 mL) to a solution of $2 ClO_4$ (10.0 mg, 8.39 $\mu mol)$ in $CH_2 Cl_2$ (10 mL). Yield: 11.5 mg (97%). IR (KBr pellet): $\tilde{v} = 3424$ (vw), 3052 (m), 3033 (m), 2961 (m), 2925 (m), 2839 (m), 1589 (s), 1548 (w), 1479 (m), 1458 (s), 1420 (vs), 1394 (m), 1363 (m), 1308 (w), 1264 (m), 1231 (w), 1199 (vw), 1181 (vw), 1150 (w), 1133 (w), 1075 (m), 1058 (m), 1039 (m), 1001 (w), 929 (w), 912 (m), 879 (m), 844 (m), 823 (m), 777 (vw), 748 (m), 733 (m), 703 (vs), 629 (w), 611 (m), 562 (w), 536 (w), 486 cm⁻¹ (m).

 $[Ni_2L(dppba)AuCl]ClO_4$ (3ClO₄): A green-colored solution of $[Ni_2L-$ (dppba)]ClO₄ (100 mg, 83.4 µmol) in CH₂Cl₂ (15 mL) was added through a dropping funnel over a 30 min period to an ocher-colored suspension of AuCl (19.5 mg, 80.0 µmol) in CH₂Cl₂ (15 mL). The resulting green solution was stirred for an additional 24 h at ambient temperature, filtered, and the filtrate combined with a solution of LiClO₄·3H₂O (67.3 mg, 0.42 mmol) in EtOH. After stirring for a further 30 min, the CH₂Cl₂ was removed by rotary evaporation to give the product as a green solid, which was filtered and washed with cold EtOH and Et2O. Yield: 108 mg (91% based on [Ni₂L(dppba)]ClO₄). M.p. 268–270°C (decomposes without melting.); IR (KBr pellet): $\tilde{\nu}$ = 3447 (w), 2953 (m), 2864 (m), 1602 (s), 1553 (m, v_{as} (RCO₂⁻)), 1461 (s), 1438 (m, v_s (RCO₂⁻)), 1398 (s), 1363 (m), 1308 (w), 1265 (w), 1233 (w), 1200 (vw), 1153 (w), 1097 (vs, ClO₄⁻), 1039 (m), 999 (w), 930 (w), 912 (w), 881 (w), 825 (m), 768 (w), 752 (w), 726 (m), 694 (m), 623 (m, CIO_4^-), 564 (w), 534 (w), 490 (w), 415 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ϵ)=231 (47700), 304 (13400), 334 (9900), 381 (1900), 652 (35), 1119 nm (70 m^{-1} cm⁻¹); MS (ESI): m/z (CH₃CN)= 1321.4 $[M-ClO_4]^+;$ elemental analysis calcd (%) for C₅₇H₇₈AuCl₂N₆Ni₂O₆PS₂ (1423.63): C 48.09; H 5.52, N 5.90, S 4.50; found: C 48.09, H 5.64, N 5.59, S 4.63.

[Ni₂L(dppba)AuPh]BPh₄ (4BPh₄): A solution of NaBPh₄ (120 mg, 350 µmol) in EtOH (10 mL) was added to a solution of [Ni2L-(dppba)AuCl]ClO₄ (100 mg, 70.24 µmol) in CH₂Cl₂ (15 mL). The mixture was stirred for 1 h, when CH2Cl2 was removed under reduced pressure. The resulting green solid was isolated by filtration, washed with cold EtOH and Et2O. Yield: 93% (based on [Ni2L(dppba)AuCl]ClO4). The crude product was purified by recrystallization from a mixed CH2Cl2/ CHCl₃/n-hexanes solvent system. M.p. 263-265°C (decomposes without melting.); IR (KBr pellet): v=3444 (w), 3052 (m), 3049 (w), 2962 (m), 2857 (m), 1600 (s), 1552 (m, v_{as} (RCO₂⁻)), 1460 (vs), 1437 (m, v_s (RCO2-)), 1395 (s), 1263 (m), 1307 (w), 1265 (w), 1232 (w), 1151 (w), 1099 (w), 1076 (m), 1057 (m), 1041 (m), 999 (w), 930 (w), 912 (w), 881 (w), 825 (m), 768 (w), 728 (s), 703 (vs, BPh_4^-), 631 (m), 612 (m), 525 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ϵ)=229 (68100), 306 (11300), 334 (8000), 387 (1300), 651 (33), 1119 nm (68 M^{-1} cm⁻¹); MS (ESI): m/z $(CH_3CN) = 1363.3 [M-BPh_4]^+$; elemental analysis calcd (%) for C₈₇H₁₀₃AuBN₆Ni₂O₂PS₂ (1685.06): C 62.01; H 6.16; N 4.99; S 3.81; found: C 61.95; H 6.08; N 4.98; S 3.82.

Preparation of gold substrates: Substrates were prepared by magnetron sputtering of 100 nm Au onto polished silicon wafers Si(111), pre-coated

with a 20 nm thick adhesion layer of titanium. The root mean square roughness of the gold substrates was ≤ 0.6 nm (by using AFM). The substrates were cut into pieces (1 cm×1 cm), cleaned by ultrasonic treatment in piranha solution (H₂SO₄/H₂O₂, 3:1; CAUTION! piranha solution reacts violently with organic materials),^[19,98] followed by washing with dichloromethane, ethanol, and deionized water.

Contact angles: Surface hydrophobicity was examined by performing water contact angle measurements (Sessile Drop Method) with a DSA II (Krüss, Hamburg, Germany) contact angle analyzer. The contact angle measurements were collected by using a 4 μ L drop size of deionized, distilled water. At least 10 contact angles per five different locations were averaged. The spectra were analyzed according to Owens-Wendt-Rabel-Kaelble.

Atomic-force microscopy: Topography data were acquired with an Agilent 5600 LS AFM system, under Argon (Ar)-controlled environmental conditions to maintain the integrity of the organic system. Measurements were performed in tapping mode to minimize the contact between the AFM probe and the sample surface and avoid damage or modification of the topographic characteristics. Special ultra-sharp (4–10 nm tip radius) Olympus cantilevers were employed allowing high sensitivity measurements. Data shown in the respective Figure 10 correspond to an area of $1 \times 1 \, \mu m^2$, although a mapping of the topographic characteristics was performed on different points of the samples to verify the uniformity of the organic system over the Au substrate.

Ellipsometry: A M-2000 T-Solar ellipsometer (J. A. Woollam Co., Inc.) operating with a Xe lamp was employed for ellipsometric measurements in the spectral range from 0.7 to 5 eV. The cleaned gold substrates were immersed in a 1×10^{-3} M solution of the complexes in dichloromethane for at least 12 h, after which they were rinsed with absolute ethanol, blown dry with ultrahigh purity nitrogen, and immediately measured under ambient conditions. The reported thickness values represent the average of at least nine measurements at different locations on the surface of the sample at three different incident angles (65, 70, and 75°). Every samples series evaluated by spectroscopic ellipsometry consists of 3 to 5 samples of the same molecular complex produced under the same experimental conditions. The error bars represent the standard deviation from the mean thickness value within one sample series. The scatter observed in the data was typically ±0.6 nm, arising most likely from a film roughness of the gold substrates of about 0.8 nm (measured by AFM).

The data analysis was performed with the CompleteEASE software from the J. A. Woollam Company.^[99] The model used for the thickness determination consists of two layers, whereby the first one is the gold substrate and the second one is a Cauchy layer. As the theory describing this layer is applicable only for non-absorbing films, one usually has to restrict the evaluated energy range to an appropriate spectral region. Because of the small layer thickness the absorption was small enough to use the data of the entire energy range from 0.7 to 5.0 eV.

X-ray photoelectron spectroscopy: XPS spectra were obtained on a commercial PHI 5600 spectrometer equipped with two light sources. A monochromatized Al_{Ka} source provided photons with an energy of 1486.6 eV, which was used for the core level studies. The total energy resolution was 350 meV. The gold foils (Au, purity 99.59%) were cleaned in a ultrasonic bath. The substrate was immersed in a $1\times10^{-3}\,\mathrm{m}$ solution of 2ClO_4 in dichloromethane for at least 12 h, washed with dichloromethane, then ethanol, and immediately transferred into the spectrometer. Energy referencing was based on the Au $4f_{7/2}$ peak at 84.0 eV. All samples were studied at room temperature at a pressure of approximately $2\times10^{-10}\,\mathrm{mbar}$. Spectra were analyzed using CasaXPS.^[100]

Crystallography: Single crystals of **2**BPh₄ suitable for X-ray crystallography were obtained by recrystallization from MeCN/EtOH. Single crystals of **4**BPh₄•1.5CH₂Cl₂•0.5CHCl₃•0.5H₂O were obtained by slow evaporation of a mixed CHCl₃, CH₂Cl₂, hexanes (1:1:1, v/v/v) solution. The diffraction experiments were carried out at 203 K on a STOE IPDS-2T X-ray diffractometer. The intensity data were processed with the program STOE X-AREA.^[101] Structures were solved by direct methods^[102] and refined by full-matrix least-squares on the basis of all data against F^2 by using SHELXL-97.^[103] PLATON was used to search for higher symmetry.^[104] H atoms were placed in calculated positions and treated isotropically by

using the 1.2-fold $U_{\rm iso}$ value of the parent atom except methyl protons, which were assigned the 1.5-fold $U_{\rm iso}$ value of the parent C atoms. Unless otherwise noted, all non-hydrogen atoms were refined anisotropically. ORTEP-3 was used for the artwork of the structures.^[105]

In the crystal structure of 4BPh₄·1.5CH₂Cl₂·0.5CHCl₃·0.5H₂O, one *t*Bu group of one of the two crystallographically independent molecules was found to be disordered over two positions. A split atom model with restrained C–C and C···C distances was applied by using SADI instructions implemented in SHELXTL. The site occupancies of the respective orientations were refined as follows: C(32a)C(33a)C(34a)/C(32b)C(33b)C(34b) = 0.60:0.40. The C and Cl atoms of one CH₂Cl₂ solvate molecule were refined isotropically.

Crystallographic data for [Ni₂L(dppba)]BPh₄: $C_{s1}H_{98}BN_6Ni_2O_2PS_2$, $M_w = 1410.97$, triclinic, space group $P\bar{1}$, a=11.033(2), b=17.813(4), c=19.616(4) Å, $\alpha = 100.48(3)$, $\beta = 104.44(3)$, $\gamma = 98.58(3)$ °, V = 3593.6(12) Å³, Z=2, $\rho_{calcd} = 1.304$ g cm⁻³, $\mu(Mo_{Ka}) = 0.656$ mm⁻¹, crystal size $0.30 \times 0.25 \times 0.20$ mm, θ limits: 1.42-27.39°. T=183 K. Of 29738 measured reflections ($R_{int} = 0.094$), 15471 were unique and 8558 observed ($I > 2\sigma(I)$). Refinement converged to $R_1 = 0.0649$, $wR_2 = 0.1507$ (for observed data), $R_1 = 0.1236$, $wR_2 = 0.1537$ for all data. Max, min peaks: 0.990, -0.879 e Å³.

Crystallographic data for [Ni₂L(dppba)AuPh)]BPh₄·1.5 CH₂Cl₂ •0.5 CHCl₃·0.5 H₂O: C₈₉H_{107.50}AuBCl_{4.50}N₆Ni₂O_{2.50}PS₂, M_w = 1881.12, monoclinic, space group P_2 ₁/n, a = 14.159(3), b = 37.431(8), c = 32.374(7) Å, β = 93.17(3)°, V=17131(6) Å³, Z=8, ρ_{calcd} = 1.459 g cm⁻³, μ (Mo_{Kα}) = 2.403 mm⁻¹, crystal size 0.25×0.20×0.20 mm, θ limits: 1.42–27.39°. T = 181(2) K. Of 166354 measured reflections (R_{int} =0.11), 43106 were unique and 24877 observed ($I > 2\sigma(I)$). Refinement converged to R_1 =0.0522, wR_2 =0.1283 (for observed data), R_1 =0.0993, wR_2 =0.1428 for all data. Max, min peaks: 1.937, -1.878 e Å³.

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