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Aromatic Nucleophilic Substitution (S_NAr) of *meso*-Nitroporphyrin with Azide and Amines as an Alternative Metal Catalyst Free Synthetic Approach To Obtain *meso*-*N*-Substituted Porphyrins

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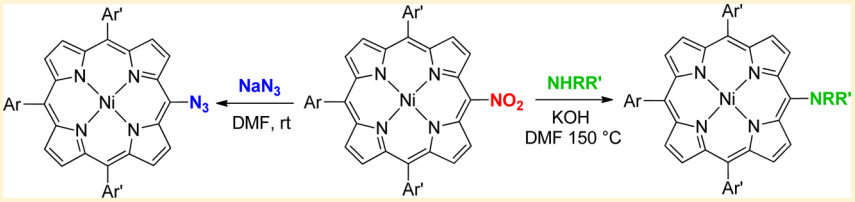
Supporting Information



ABSTRACT: Aromatic nucleophilic substitution reaction of the nitro group of *meso*-nitroporphyrins with azide and various amines was achieved and represents an alternative procedure to C−N coupling reactions usually needed to obtain such *meso*-*N*-substituted porphyrins in good yields.

INTRODUCTION

Porphyrin functionalization is unavoidable to produce original materials with specific optical, biological, chemical, and/or electronic properties.[1] For such a purpose, several synthetic reactions are known: aromatic nucleophilic substitution (S_NAr) reactions with organometallic reagents[2] or organic nucleophiles,[3] nucleophilic reactions on porphyrin π-cation radicals,[4] electrophilic substitutions,[5] and transition-metal-catalyzed reactions.[6] These latter reactions generally make possible the introduction of a wide range of functional groups starting from brominated/iodinated porphyrin precursors. In particular, the grafting of a nitrogen atom at the periphery of the porphyrin core is a relatively well explored field, since the conjugation of nitrogen induces new electronic properties to exploit. Synthetic routes leading to nitrogen-substituted porphyrins consist of the chemical transformation of amino porphyrins[7] or transition-metal-catalyzed C−N (amine or amide) bond formation from haloporphyrins.[8] However, transition-metal catalysts are sometimes expensive or are not easily available.

C−N bond formation at the *meso* positions of porphyrins with nitrogen-based groups, through S_NAr reactions, was first described by Balaban and co-workers with free base *meso*-bromoporphyrins as electrophiles and primary/secondary amines used in large excess (>100 equiv) as nucleophiles.[3b,c] More recently, Yamashita et al. reported the efficient and mild *meso* functionalization of nickel(II) *meso*-bromoporphyrins with sodium azide.[3d] Usually, S_NAr reactions are favored with electron-deficient aromatics. That is why easily available *meso*- and β-nitroporphyrins should be better candidates than brominated/iodinated ones. Although several examples of S_NAr reactions are reported with *meso*- and β-nitroporphyrins with a few nucleophiles (Cl^-, Br^-, MeO^-, $PhCH{=}NO^-$, PhS^-, EtS^-, MeMgI, and $PhCH_2O^-$),[9] only one example involved an uncatalyzed C−N coupling reaction between a nitroporphyrin (substituted at the β position) and aniline derivatives.[3a] In this last case, the yield was rather low ($\leq$32%) and the palladium-catalyzed route was finally preferred. Surprisingly, to the best of our knowledge, no example of a S_NAr reaction between a *meso*-nitroporphyrin and a nitrogen-based nucleophile is known. Given the relevance of azido-[3d,10] and aminoporphyrins[7] in numerous potential applications, we report herein the S_NAr reaction of the nitro group of [5-nitro-10,20-di-*p*-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NO_2**; Scheme 1) with azide and amines. This easy to set up synthetic procedure represents an alternative efficient and cost-effective synthetic approach avoiding the use of expensive metal-based catalysts to obtain various *meso*-*N*-substituted porphyrins.

RESULTS AND DISCUSSION

The Ni complex **NiP-NO_2** was synthesized in five steps starting from pyrrole according to known methods (Scheme 1).[11] Thus, dipyrromethane, **DTP**, **DTPhP**, **H_2P-NO_2**, and **NiP-NO_2** were synthesized according to the Lindsey,[12] Habermeyer,[11c] Senge,[2a,c] Kuvshinova,[13] and Adler[11a] procedures, respectively.

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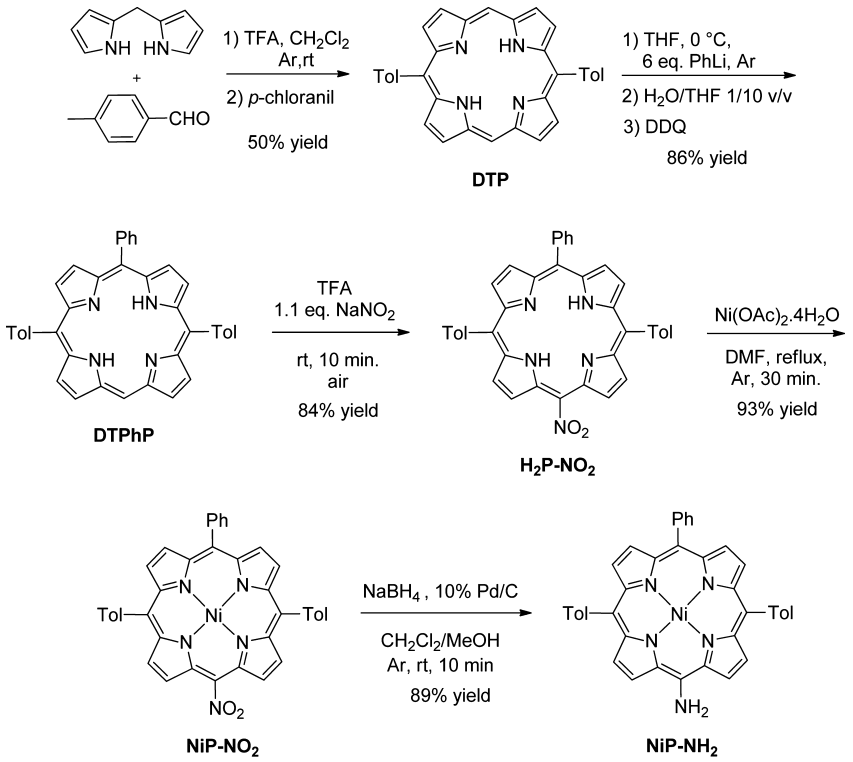
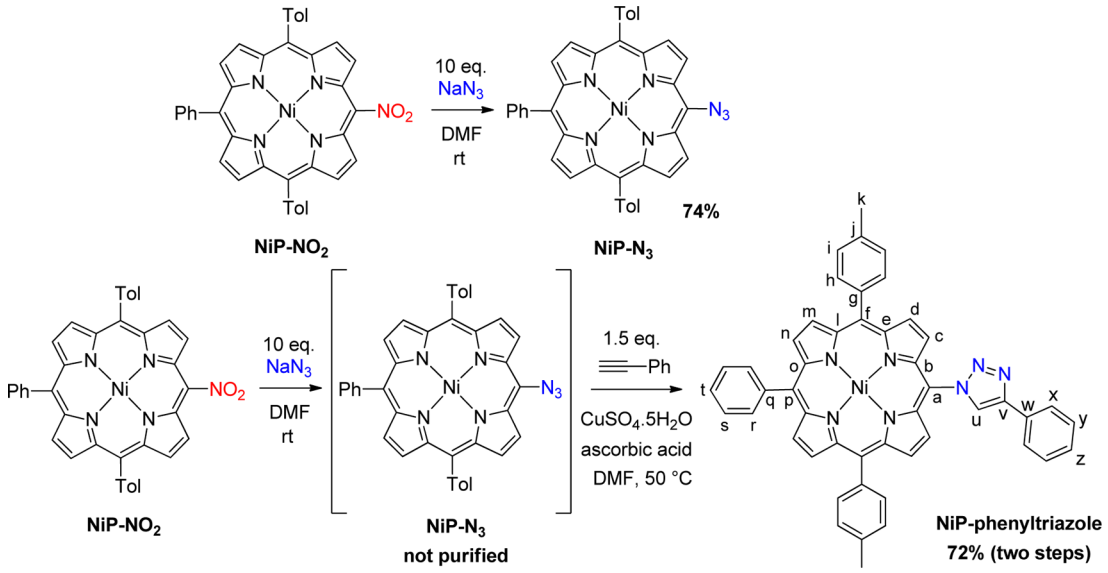
Scheme 1. Synthesis of MP-NO_2 (M = H_2, Ni) and NiP-NH_2



Scheme 2. S_NAr Reaction of the Nitro Group of the *meso*-Nitroporphyrin NiP-NO_2 with NaN_3 and Subsequent Transformation of the Azide NiP-N_3 Compound into the 1,2,3-Triazole Derivative NiP-phenyltriazole[a]



[a]H atoms are labeled according to NMR data. See the Experimental Section and Figure S31 in the Supporting Information.

S_NAr Reaction with Azide Anion. In the first attempt, the reactivity of **NiP-NO_2** toward nitrogenated nucleophiles was tested with azide anion using the optimized conditions described by Yamashita et al.[3d] i.e., 10 equiv of NaN_3 in DMF at 40 °C under an inert atmosphere in the absence of light (Scheme 2).

NiP-NO_2 was fully consumed in 3.5 h, showing the higher reactivity of *meso*-nitroporphyrins in comparison to *meso*-bromoporphyrins, for which extended reaction times were required[3d] (between 7 and 16.5 h). The *meso*-azidoporphyrin **NiP-N_3** was thus formed in more than 95% yield according to ^{1}H NMR spectroscopy (yield estimated by ^{1}H NMR spectroscopy; see Figure S22 in the Supporting Information for an example of the ^{1}H NMR spectrum of the crude solution). At room temperature (19 ± 2 °C), **NiP-N_3** was also formed in very high yield (ca. 95% yield estimated by ^{1}H NMR spectroscopy), but a longer reaction time (24 h) was needed, as expected. Under these latter conditions, after purification by flash column chromatography with protection from light and further crystallization in CH_2Cl_2/MeOH, **NiP-N_3** was isolated

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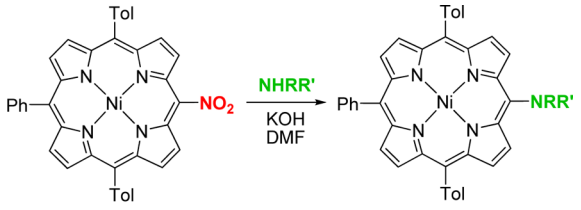
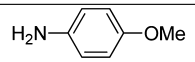
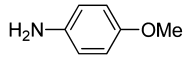
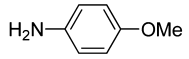
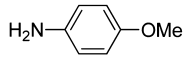
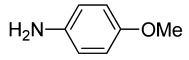
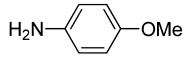
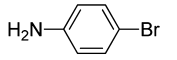
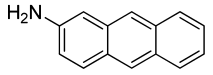
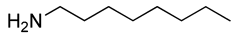
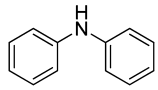
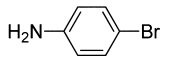
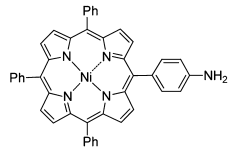
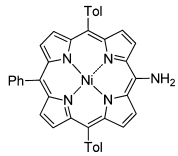
Table 1. S_NAr Reaction of the Nitro Group of NiP-NO_2 with Various Amines in the Presence of KOH



NiP-NO_2 **NiP-NRR'**

entry	amine	equiv. amine *vs* **NiP-NO_2**	base	*T* (°C)	time (h)	**NiP-NRR'** yield (%)
1		10	no base	40	24	0[a]
2		10	no base	150	1	0[a]
3		10	KOH	40	24	0[a]
4		10	KOH	150	1	66[b]
5		3	KOH	150	1	60[b]
6		3	KOH	150	1	19[b,c]
7		3	KOH	150	1	55[b]
8		3	KOH	150	1	60[b]
9		3	KOH	150	1	50[b]
10		3	KOH	150	1	59[b]
11		4	KOH	150	1	49[b]
12		3[d]	KOH	150	1	6[b,e]
13		1.5	KOH	150	1	61[b]
14		1	KOH	150	0.33	76[b]

[a]Estimated by ^{1}H NMR. [b]Obtained for isolated compounds. [c]Performed in DMSO. [d]**ZnP-NO_2** used as starting material. [e]Corresponding *N*-substituted porphyrin obtained: **ZnP-NH(Ph-(4-Br))**.

in a good yield of 74%, which is intermediate in comparison to those obtained by Yamashita and co-workers (between 68 and 93%).[3d] The characteristic stretching vibration of the azide group of **NiP-N_3** was observed at 2098 cm^{-1} by IR spectroscopy (see Figure S29 in the Supporting Information). It should be noted that full decomposition of **NiP-N_3** occurred upon drying the solid for 1 h under reduced pressure at only 60 °C. In addition, when **NiP-N_3** was stocked in a brown glass vial at room temperature, decomposition was also observed, but in a few days. This poor stability was previously mentioned for other similar azidoporphyrins.[3d,10] Consequently, we recommend to keep **NiP-N_3** in a brown glass vial at −18 °C as much

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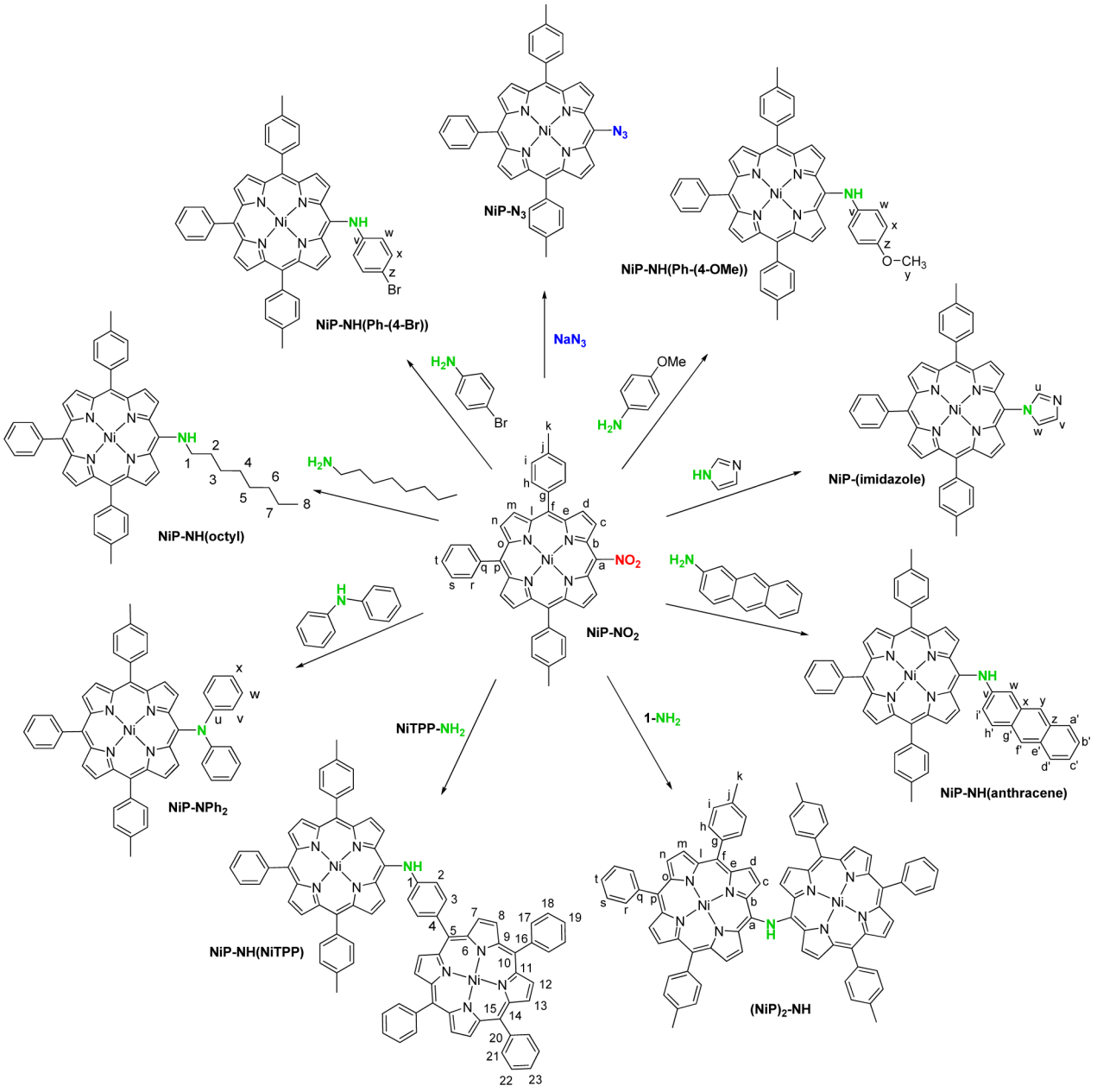
Scheme 3. S_NAr Reaction of the Nitro Group of NiP-NO_2 with Nitrogenated Nucleophiles[a]



[a]H atoms are labeled according to 1D/2D ^{1}H NMR data. KOH was used as a base except when NaN_3 was used as a nucleophile. See the Experimental Section and the Supporting Information.

as possible. Under these conditions, it was possible to perform full characterization of this azide without significant degradation for at least 24 h. Finally, definitive proof of its molecular structure was obtained from X-ray diffraction analysis of single monocrystals of **NiP-N_3** grown at −18 °C (see below).

To test the azide function reactivity, crude **NiP-N_3** obtained through the S_NAr reaction was directly engaged under common Huisgen cycloaddition reaction conditions ($CuSO_4$, ascorbic acid, DMF) with phenylacetylene, adapting the protocol reported by Chen and co-workers for *β*-substituted azidoporphyrin (bottom of Scheme 2).[10b] **NiP-phenyltriazole** (Scheme 2) was thus obtained in 72% global yield. It is worth noting that a very similar compound was synthesized by Odobel and co-workers in 2007 under different reaction conditions (copper carbene complex, THF/water mixture).[10a]

S_NAr Reactions with Amines in the Presence of Potassium Hydroxide. To extend the scope of the S_NAr reactions with *meso*-nitroporphyrin **NiP-NO_2**, several amines (primary and secondary amines, aryl- or alkylamines bearing electron-withdrawing or electron-donating groups) were tested under different experimental conditions (Table 1). **NiP-NO_2** was first treated with 10 equiv of 4-methoxyaniline in DMF under argon. At 40 and 150 °C, no reaction occurs at all (entries 1 and 2). Addition of KOH (one pellet, i.e. 20−40 equiv vs **NiP-NO_2**) and high temperature were both needed to perform the S_NAr reaction (entries 3 and 4). Lowering the molar amount of amine to 3 equiv did not significantly lower the yield of C−N coupling product (entries 4 and 5, 66 and 60% yields, respectively). Keeping the same conditions as entry 5 but switching from DMF to another aprotic polar solvent

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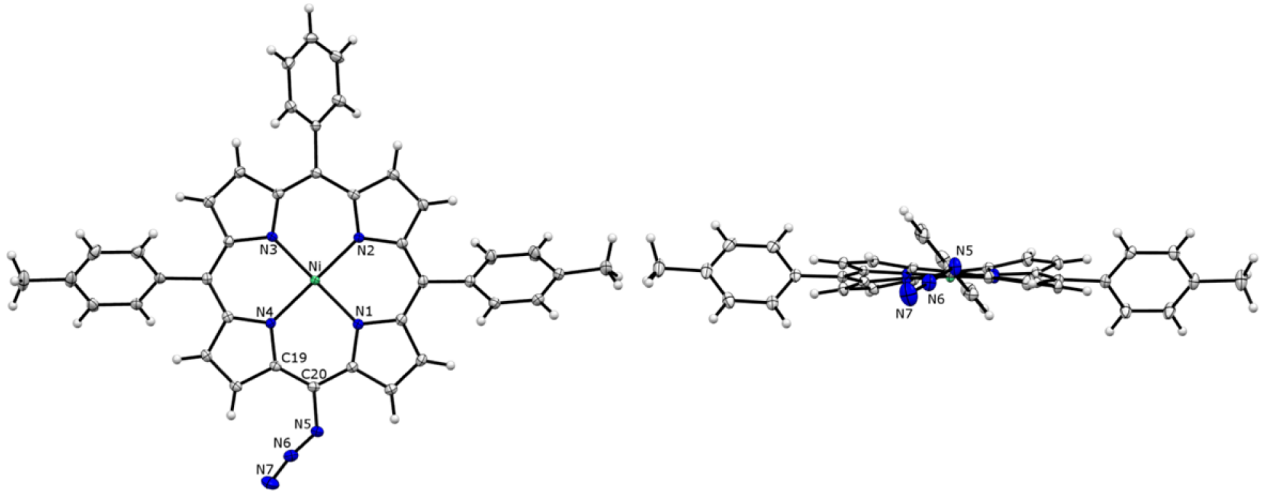

Figure 1. Front and side Ortep views of **NiP-N$_3$**. Thermal ellipsoids are scaled to the 50% probability level.

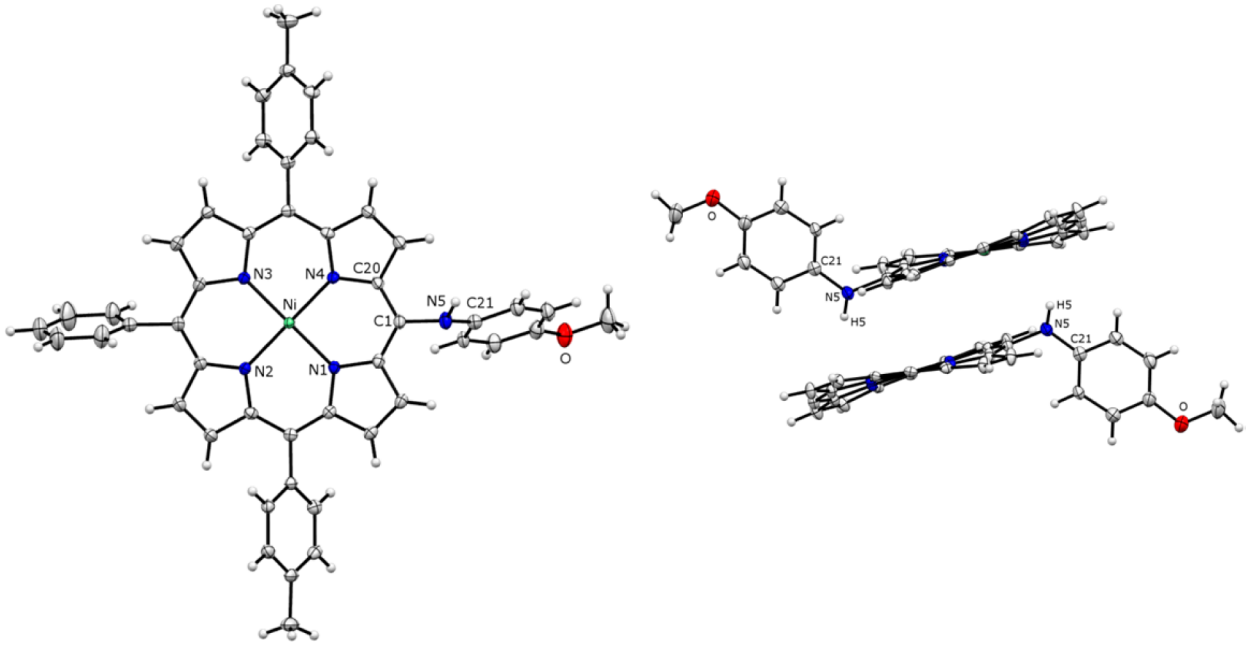

Figure 2. Front and π-stacked dimer Ortep views of NiP-NH(Ph-(4-OMe)). Disordered toluene solvent molecules have been omitted for clarity. For the π-stacked dimer structure, phenyl and *p*-tolyl groups have been omitted for clarity. Thermal ellipsoids are scaled to the 50% probability level.

such as DMSO drastically decreased the yield to 19% (entry 6). In this case, the starting material **NiP-NO$_2$** was fully consumed and the only identified product was the [5-hydroxy-10,20-di-*p*-tolyl-15-phenylporphyrinato]nickel(II) species, **NiP-OH**,[14] which was isolated in a very low amount (<2% yield). The major fraction consists of a mixture of polar byproducts that have not yet been properly isolated and characterized. According to MALDI-TOF mass spectrometry and UV−visible absorption spectroscopy, they do not correspond to a denitration reaction or a demetalation of the porphyrin core.

Thus, the reaction conditions of entry 5 were kept to extend the scope of the S_NAr reaction to other amines. The nitro function was successfully substituted with *p*-bromoaniline, 2-aminoanthracene, octylamine, imidazole, and diphenylamine (Table 1, entries 7−11), with yields ranging from 49 to 60% (Scheme 3). It is worth noting that, although these yields are not quantitative, our synthetic procedure presents several advantages over the metal-catalyzed procedure to get porphyrins with C(*meso*)-N bonds: (i) amines are used in lower molar amounts,[8a−c,g,i] (ii) the completion of the reaction is achieved in only 1 h in comparison to several hours or even days with catalysis,[8] and (iii) the reaction efficiency does not seem to be sensitive to the type of amine, in contrast, for instance, to what was reported for C−N coupling mediated by nickel(II) catalysts.[8b] To explain this last point, it should be noted that strong basic conditions are needed to perform this S_NAr reaction and that no reaction occurred in the absence of KOH. The pK_a value reported for H_2O in a polar aprotic solvent such as DMSO is reported to be 31.4[15] and is higher in comparison to the pK_a values in DMSO reported for the common primary and secondary amines used in this study. For example, in this solvent, pK_a values of 4-bromoaniline, diphenylamine, and imidazole are 29.1,[16] 25.0,[17] and 18.6,[18] respectively. Therefore, it is reasonnable to consider that the nucleophilic species in these S_NAr reactions are the amides issued from deprotonation of the corresponding amines with

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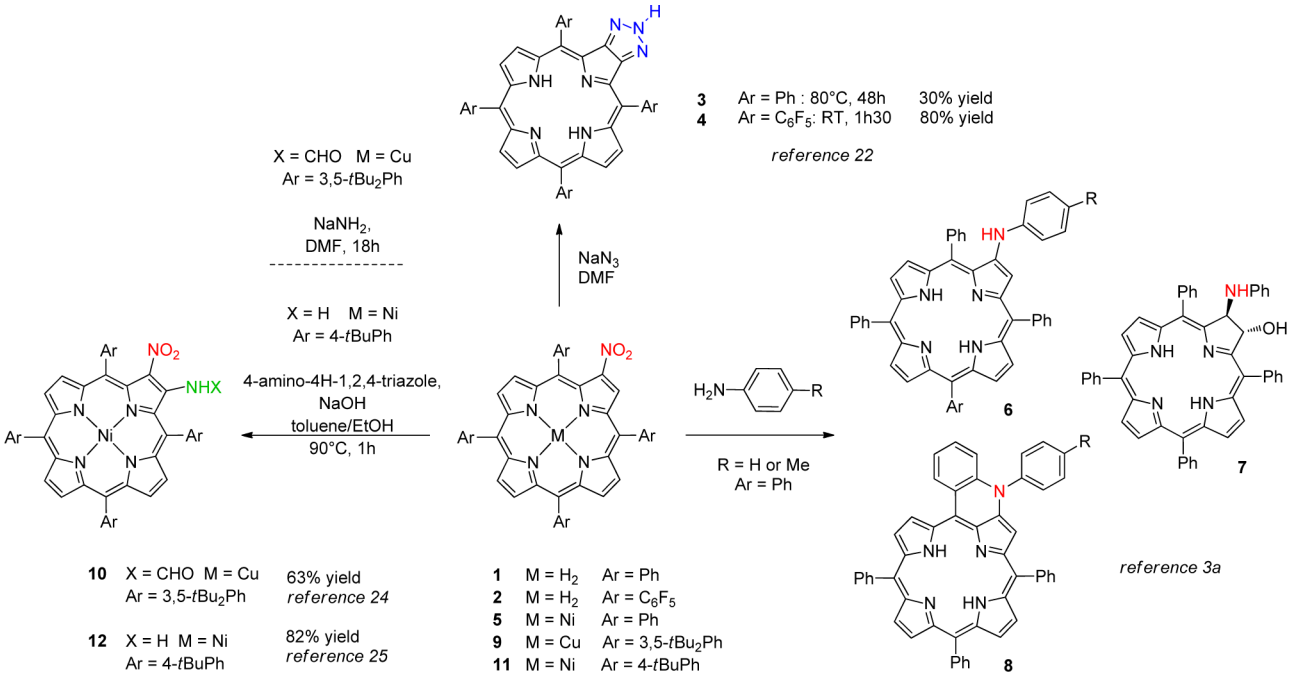
Scheme 4. Overview of the Reactivity of β-Nitroporphyrins with Nitrogen-Based Nucleophiles



KOH in refluxing DMF. The similar yields in isolated *N*-substituted porphyrins observed for these S_NAr reactions are also in agreement with this hypothesis, because a good nucleophile such as an alkylamine should have given a much better yield than a poor nucleophile such as diphenylamine.

X-ray Diffraction Analyses. Single crystals of **NiP-N$_3$** (Figure 1) and **NiP-NH(Ph-(4-OMe))** (Figure 2) suitable for X-ray crystallography analyses were grown from slow diffusion of MeOH into a concentrated CH_2Cl_2 or toluene solution of the respective porphyrins. **NiP-N$_3$** and **NiP-NH(Ph-(4-OMe))** porphyrin cores adopt a slightly ruffled conformation, and the Ni−N(porphyrin) average distances are similar (1.9509(15) and 1.9523(17) Å, respectively). The azido moiety of **NiP-N$_3$** is slightly tilted out of the porphyrin plane with a C19−C20−N5−N6 dihedral angle of 41.7(3)°, whereas the amine group of **NiP-NH(Ph-(4-OMe))** is nearly orthogonal to the porphyrin plane (C20−C1−N5−C21 = −84.9(3)°) because of the steric repulsion between the amino group and the contiguous β-hydrogen atoms of the porphyrin. C_{meso}−N5 distances are similar for **NiP-N$_3$** (1.430(3) Å) and **NiP-NH(Ph-(4-OMe))** (1.428(3) Å). In the particular case of **NiP-N$_3$**, the N5−N6 and the N6−N7 bond lengths are respectively 1.237(2) and 1.137(3) Å, while the N5−N6−N7 angle is 169.3(2)°, in agreement with typical values found for aryl azides.[3d] Interestingly, **NiP-NH(Ph-(4-OMe))** forms a π-stacked dimer with a slipped cofacial orientation. The interplanar and the centroid-to-centroid distances, both calculated from the 24 porphyrin atoms, are 3.454 and 5.009 Å, respectively. The difference between these two distances indicates that the porphyrin rings are significantly slipped. The slip angle (angle between the normal to the planes and the centroid−centroid vector) is 46.4°, corresponding to a slippage distance of 3.63 Å.

Synthesis of Diporphyrinylamines. Two aminoporphyrins, i.e. the [5-(*p*-aminophenyl)-10,15,20-triphenylporphyrinato]nickel(II) complex (**NiTPP-NH$_2$**), obtained by reducing the nitro group of the [5-(*p*-nitrophenyl)-10,15,20-triphenylporphyrinato]nickel(II) complex with $NaBH_4$−Pd/C,[9a] and [5-amino-10,20-di-*p*-tolyl-15-phenylporphyrinato]nickel(II) complex (**NiP-NH$_2$**), obtained by reducing the nitro group of **NiP-NO$_2$** with $NaBH_4$−Pd/C,[9a] as described in Scheme 1 were also tested under the aforementioned conditions but with only 1−1.5 equiv vs **NiP-NO$_2$** (Table 1, entries 12 and 13). Gratifyingly, the corresponding diporphyrinylamines **NiP-NH(NiTPP)** and **(NiP)$_2$-NH** were obtained in fair to good yields (61 and 76%, respectively; see their corresponding structures in Scheme 3). Moreover, the resulting symmetric diporphyrinylamine **(NiP)$_2$-NH** was isolated by crystallization without any column chromatography. It is worth noting that a very similar diporphyrinylamine (phenyl groups instead of *p*-tolyl) was first synthesized in 25% yield by Arnold and co-workers by a palladium-catalyzed amination reaction starting with a *meso*-bromoporphyrin and a *meso*-aminoporphyrin.[19] More recently, Ruppert and co-workers synthesized the same diporphyrinylamine in 56% yield using Buchwald catalytic conditions in the reaction between a *meso*-iodoporphyrin and [5-amino-10,15,20-triphenylporphyrinato]nickel(II).[8f] Indeed, the easy to set up synthetic procedure presented here is also efficient to obtain such diporphyrinylamines with significant yield improvement. **(NiP)$_2$-NH** exhibits an interesting Davydov splitting[20] of the Soret band (see Figure S95 in the Supporting Information), in agreement with a significant electronic communication between both macrocycles through the C_{meso}−NH−C_{meso} bonds.

Effect of the Central Metal Ion. All of the results presented so far were obtained with nickel(II) as the inner metal in the porphyrin. Knowing that the central metal is of great importance in the modulation of the porphyrin electronic properties and, therefore, the reactivity of the *meso*- and β-pyrrolic positions, we also investigated its influence on the S_NAr reaction. Zinc(II) cation is an electropositive ion, and the corresponding zinc(II) porphyrin complexes are usually π-electron-rich species, as illustrated by their cathodically shifted redox potentials.[21] This feature was verified by comparison of

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the first oxidation potentials of **ZnP-NO$_2$**, **H$_2$P-NO$_2$**, and **NiP-NO$_2$**. These monoelectronic and reversible redox systems are located at $E_{1/2}$ = 1.00, 1.25, and 1.25 V vs SCE, respectively (see Figure S97 and Table S1 in the Supporting Information for full cyclic voltammograms). As expected, the electronic density is more important with **ZnP-NO$_2$** than with **H$_2$P-NO$_2$** and **NiP-NO$_2$**, which exhibit identical first oxidation potentials. In the present work, the question remains whether this S_NAr reaction is applicable to more electron rich porphyrins such as the zinc(II) complex **ZnP-NO$_2$** (Table 1, entry 12). After 1 h in refluxing DMF in the presence of KOH and 4-bromoaniline, the corresponding *N*-substituted porphyrin **ZnP-NH(Ph-(4-Br))** was obtained in only 6% yield. The remaining starting material **ZnP-NO$_2$** was recovered in ∼58% yield after purification by column chromatography. This result confirms that the zinc(II) cation dramatically decreases the electrophilicity of the *meso* carbon bearing the NO_2 group in comparison to nickel(II) (Table 1, entry 7). The same S_NAr reaction with the corresponding free base *meso* nitroporphyrin **H$_2$P-NO$_2$** as electrophile proved to be unsuccessful. In this case, a green color developed in the reaction mixture immediately after the addition of KOH, which is attributed to the deprotonation of the inner NH of the porphyrin. The resulting anionic charges were expected to dramatically deactivate the porphyrin ring system and the *meso* carbon bearing the NO_2 group toward nucleophilic attack.[22] Washing the reaction mixture with water afforded quantitatively the starting material **H$_2$P-NO$_2$**. Thus, a moderately electronegative ion such as nickel(II) is probably one of the most suitable inner metals for this S_NAr reaction because (i) it protects the inner nitrogen atoms of the porphyrin and prevents the formation of anionic unreactive species and (ii) it allows the *meso* position bearing the nitro group to react as an electrophile (this is not the case with zinc(II)).

About the S_NAr Reaction with β-Nitroporphyrins. It is well-known that the β-nitro group is also able to act as a leaving group and can be displaced by a nucleophile through a S_NAr reaction.[23] As previously shown in this paper, *meso*-azidoporphyrins could be obtained in good yields by reacting NaN_3 with *meso*-nitroporphyrins. Cavaleiro and co-workers performed very similar reactions with β-nitroporphyrins (except that free base derivatives **1** and **2** were used) and surprisingly isolated [1,2,3]triazolo[4,5-*b*]porphyrins **3** and **4** in moderate to good yields (30−80%; Scheme 4, top).[24] Therefore, the localization of the nitro group is an important structural feature that affects the way in which *meso*- and β-nitroporphyrins react. Knowing that, the S_NAr reaction was tested under the conditions of Table 1, entry 7, with [2-nitro-5,10,15,20-tetraphenylporphyrinato]nickel(II) complex **5** as the starting material instead of **NiP-NO$_2$**. After 1 h, TLC analyses showed that **5** was fully converted into several compounds (∼10) which have not yet been properly isolated and characterized. The question remains: why were so many compounds obtained? One can argue that the versatile reactivity of β-nitroporphyrins illustrated by the following examples extracted from the literature may be the reason.

Cavaleiro and co-workers reported that β-arylaminoporphyrin **6** could be obtained through a S_NAr reaction between free base β-nitroporphyrin **1** and aniline derivatives (Scheme 4, right).[3a] They also observed the formation of chlorin **7** and *N*-arylquinolino[2,3,4-*at*]porphyrin **8** issued from an intramolecular oxidative cyclization reaction. Indeed, the formation of **8** illustrates that the close proximity between β-pyrrolic groups and the neighboring *meso* aryl groups allows them to react together, leading in some cases to the formation of unexpected compounds.[3a] β-Nitroporphyrins can also react in a very different way and undergo Michael additions with a wide range of nucleophiles, including nitrogen-based nucleophiles. For example, reaction of the copper(II) β-nitroporphyrin **9** with $NaNH_2$ in DMF afforded 2-formamido-3-nitroporphyrins **10** in 63% yield (Scheme 4, left).[25] More recently, a similar reaction performed between the nickel(II) β-nitroporphyrin **11** and 4-amino-4*H*-1,2,4-triazole and NaOH in a refluxing toluene/EtOH mixture allowed us to obtain the corresponding 2-amino-3-nitroporphyin **12** in 82% yield (Scheme 4, left).[5d,26]

These selected examples highlight the versatile reactivity of β-nitroporphyrins and show that many compounds can be obtained by using β-nitroporphyrins as starting materials. All in all, it is clear that C−N coupling reactions previously described by others and making use of β-haloporphyrins and transition-metal catalysts are more efficient synthetic procedures in comparison to S_NAr reactions to obtain the corresponding β-*N*-substituted porphyrins and to avoid the formation of nondesired compounds such as cyclized species, chlorins, or 2-amino-3-nitroporphyrin derivatives.

CONCLUSION

To summarize, a very simple S_NAr reaction of the nitro group of *meso*-nitroporphyrins by azide and amines has been developed to obtain the corresponding *meso*-*N*-functionalized porphyrin derivatives. Azide anion is sufficiently nucleophilic to react at ambient temperature without any additive, affording the corresponding *meso*-azidoporphyrin in 74% yield. The versatile reactivity of the azide group[27] opens the door to numerous subsequent transformation of *meso*-azidoporphyrins. Amines are not nucleophilic enough to react with the *meso*-mononitroporphyrin **NiP-NO$_2$**. Addition of a strong base such as KOH in refluxing DMF is necessary to generate in situ the more nucleophilic corresponding amides. The corresponding *meso*-aminoporphyrins were obtained in fair to good yields, provided that KOH is added in excess and the reaction mixture is heated to 150 °C. Interestingly, the S_NAr reaction yields remain practically unchanged, whatever the nature of the amines that have been used so far (primary or secondary amines, aryl- or alkylamines, bearing electron-withdrawing or electron-donating groups). Of particular interest is the possibility to synthesize very easily diporphyrinylamines using a stoichiometric amount or slight excess of aminoporphyrins. This S_NAr reaction does not occur with the free base **H$_2$P-NO$_2$** due to deprotonation of the inner NH of the porphyrin core and gives a very poor yield with the less electrophilic zinc(II) complex **ZnP-NO$_2$**. We are now extending the scope of this method to other original nucleophiles and to multinitrated porphyrins.

EXPERIMENTAL SECTION

General Comments. Unless otherwise noted, all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. THF was distilled under argon over Na/benzophenone. DMF was distilled over CaH_2 under reduced pressure and then kept under argon. For UV−vis absorption measurements, CH_2Cl_2 was distilled over P_2O_5. Chemicals were obtained from commercial suppliers and used as received. 5,15-Di-*p*-tolylporphyrin (**DTP**)[11c,12] and [5-nitro-10,20-di-*p*-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NO$_2$**)[2a,11a,d,13] were synthesized according to known procedures. NMR spectra were recorded with 500, 400, and 300 MHz NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated to TMS

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on the basis of the relative chemical shift of the solvent as an internal standard. See Scheme 3 for attribution of the NMR signals reported below. UV−visible absorption spectra were recorded with UV−vis spectrophotometers in quartz cells. High-resolution mass spectra (HRMS) were recorded on ESI-TOF Q instruments in positive mode with the sample in solution in CH_2Cl_2 or on a MALDI-TOF spectrometer in positive mode using dithranol as a matrix and PEG as internal reference. IR spectra were studied with an FT-IR spectrophotometer equipped with an ATR system. All electrochemical manipulations were performed using Schlenk techniques under an atmosphere of dry, oxygen-free argon at room temperature (20 ± 2 °C). The supporting electrolyte was a 0.1 mol L^{-1} $TBAPF_6$ (tetra-*n*-butylammonium hexafluorophosphate)/CH_2Cl_2 solution, which was degassed under vacuum before use. Voltammetric analyses were carried out in a conventional three-electrode cell. A double-junction saturated calomel electrode (SCE), with background electrolyte between the two frits, was used as reference electrode. The auxiliary electrode was a platinum slab in an independent compartment filled with the background electrolyte and separated from the analyzed solution by a sintered glass disk. For all voltammetric measurements, the working electrode was a platinum-disk electrode (diameter 2 mm). Before each experiment, the Pt electrode was polished with a diamond suspension, followed by several ultrasonic cleanings in distilled water and dichloromethane solvent. Under these conditions, the Fc^+/Fc redox potential is found to be 0.40 V vs SCE.

Synthesis. *[5-Nitro-10,20-di-p-tolyl-15-phenylporphyrinato]-nickel(II) (**NiP-NO$_2$**).* 5,15-Di-*p*-tolylporphyrin (**DTP**; 513 mg, 1.045 mmol) was placed in a Schlenk tube, and three vacuum/argon cycles were carried out. Under argon, freshly distilled THF (150 mL) was added and the solution was cooled to 0 °C (ice bath). Then, phenyllithium (3.5 mL of a solution at 1.9 M in di-*n*-butyl ether, 6.4 equiv) was added dropwise and the solution was stirred for 15 min at 0 °C. After removal of the ice bath, the reaction mixture was stirred for another 15 min, followed by addition of a predegassed (argon) H_2O/THF mixture (5 mL/50 mL). After the mixture was stirred for 10 min, 4.2 equiv of DDQ (989 mg) was added and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated, and the residue was purified by column chromatography (Al_2O_3, CH_2Cl_2) followed by recrystallization from CH_2Cl_2/MeOH to give 5,15-di-*p*-tolyl-10-phenylporphyrin (**DTPhP**) in 86% yield (510 mg, 0.900 mmol). Analytical data (NMR, MS, UV−vis) were in agreement with those published in ref 11d. 5-Nitro-10,20-di-*p*-tolyl-15-phenylporphyrin (**H$_2$P-NO$_2$**) was synthesized following an adaptation of the protocol described by Kuvshinova et al.[13] The porphyrin **DTPhP** (510 mg, 0.899 mmol) was dissolved in trifluoroacetic acid (10 mL). Then, $NaNO_2$ (68 mg, 0.990 mmol) was added in one portion. This mixture was then stirred at room temperature under air for 10 min. This crude solution was then slowly and carefully poured (projections!) into a concentrated aqueous solution of NH_3 (100 mL, 25% in water). Dichloromethane (100 mL) was then added, and the organic phase was washed three times with water. Solvent was evaporated, and the residue was purified by column chromatography (Al_2O_3, CH_2Cl_2). The first red fraction was evaporated and recrystallized from a CH_2Cl_2/MeOH mixture to give **H$_2$P-NO$_2$** in 84% yield (466 mg, 0.762 mmol), as a pure purple microcrystalline solid. ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ (ppm) 9.33 (d, $^3J_{H-H}$ = 4.9 Hz, *Hc*, 2H), 9.01 (d, $^3J_{H-H}$ = 4.9 Hz, *Hd*, 2H), 8.85 (d, $^3J_{H-H}$ = 4.8 Hz, *Hm*, 2H). 8.83 (d, $^3J_{H-H}$ = 4.8 Hz, *Hn*, 2H), 8.20 (m, *Hr*, 2H), 8.08 (d, $^3J_{H-H}$ = 7.9 Hz, *Hh*, 4H), 7.78 (m, *Hs,t*, 3H), 7.58 (d, $^3J_{H-H}$ = 7.7 Hz, *Hi*, 4H), 2.72 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 300 K): δ (ppm) 141.6, 138.3, 134.6, 134.5, 133.7, 132.3, 131.5, 128.6, 128.3, ∼128.0, 127.8, 126.9, 124.7, 123.1, 21.6. R_f 0.85 (SiO_2, CH_2Cl_2/*n*-pentane, 50/50, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 244 (4.16), 420 (5.30), 519 (4.11), 560 (3.89), 589 (3.81), 648 (3.65). HRMS (MALDI-TOF): *m*/*z* calcd for $C_{40}H_{30}N_5O_2$ $[M + H]^+$ 612.2399, found 612.2408.

The porphyrin **NiP-NO$_2$** was synthesized by metalating **H$_2$P-NO$_2$** with $Ni(OAc)_2{\cdot}4H_2O$ according to the procedure of Adler et al.[11a] The porphyrin **H$_2$P-NO$_2$** (350 mg, 0.573 mmol) was dissolved in DMF (20 mL), and $Ni(OAc)_2{\cdot}4H_2O$ (717 mg, 2.882 mmol) was added in one portion. The reaction mixture was then degassed with argon for 10 min and heated at reflux in a preheated oil bath (170 °C) over 15 min under argon. After the mixture was cooled to room temperature, deionized water (30 mL) was added and the resulting solid was isolated by filtration and washed with water. This residue was finally purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from a CH_2Cl_2/MeOH mixture to give **NiP-NO$_2$** in 93% yield (357 mg, 0.534 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ (ppm) 9.22 (d, $^3J_{H-H}$ = 5.1 Hz, *Hc*, 2H), 8.87 (d, $^3J_{H-H}$ = 5.1 Hz, *Hd*, 2H), 8.69 (*ca.* s, *Hm,n*, 4H), 7.97 (m, *Hr*, 2H), 7.85 (d, $^3J_{H-H}$ = 8.0 Hz, *Hh*, 4H), 7.68 (m, *Hs,t*, 3H), 7.50 (d, $^3J_{H-H}$ = 8.0 Hz, *Hi*, 4H), 2.65 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 300 K): δ (ppm) 144.5, 143.1, 142.9, 140.3, 138.1, 137.9, 137.1, 134.9, 133.7 (two peaks), 133.4, 132.8, 129.3, 128.3, 128.0, 127.7, 127.1, 122.7, 121.5, 21.6; R_f 0.80 (SiO_2, CH_2Cl_2/*n*-pentane, 50/50, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 318 (4.15), 416 (5.14), 532 (4.07), 570 (3.88). HRMS (ESI-MS): *m*/*z* calcd for $C_{40}H_{27}O_2N_5NaNi$ $[M + Na]^+$ 690.1410, found 690.1422.

*[5-Amino-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NH$_2$**).* The porphyrin **NiP-NH$_2$** was synthesized following known procedures.[28] Thus, the porphyrin **NiP-NO$_2$** (201 mg, 0.300 mmol) was dissolved in CH_2Cl_2 (50 mL), and MeOH (50 mL) and 10% Pd/C (155 mg) was added. The mixture was degassed with argon for 10 min, and $NaBH_4$ (178 mg, 4.700 mmol) was added. The mixture was stirred for 10 min under argon and then filtered on Celite. The solvents were removed, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/Et_3N 99.9/0.1). The green-blue fraction was evaporated, and the obtained solid was recrystallized from CH_2Cl_2/MeOH and dried under vacuum at 120 °C. The porphyrin **NiP-NH$_2$** was obtained in 89% yield (172 mg, 0.270 mmol). ^{1}H NMR (CD_3COCD_3, 300 MHz, 300 K): δ (ppm) 9.26 (d, $^3J_{H-H}$ = 4.8 Hz, *Hc*, 2H), 8.37 (d, $^3J_{H-H}$ = 5.0 Hz, *Hm*, 2H), 8.33 (d, $^3J_{H-H}$ = 4.8 Hz, *Hd*, 2H), 8.26 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 7.89 (m, *Hr*, 2H), 7.79 (d, $^3J_{H-H}$ = 7.9 Hz, *Hh*, 4H), 7.66 (m, *Hs,t*, 3H), ∼7.51 (br s, NH_2, 2H), 7.50 (d, $^3J_{H-H}$ = 7.9 Hz, *Hi*, 4H), 2.60 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 125 MHz, 300 K): δ (ppm) 144.5, 143.1, 142.9, 140.3, 138.1, 137.9, 137.1, 134.9, 133.7 (two peaks), 133.4, 132.8, 129.3, 128.3, 128.0, 127.7, 127.1, 122.7, 121.5, 21.6. R_f 0.48 (SiO_2, CH_2Cl_2/*n*-pentane, 50/50, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 291 (4.24), 359 (3.94), 425 (5.30), 542 (3.92), 599 (4.13). HRMS (ESI-MS): *m*/*z* calcd for $C_{40}H_{29}N_5Ni$ $[M]^+$ 637.1771, found 637.1765.

*[5-Azido-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-N$_3$**).* The porphyrin **NiP-NO$_2$** (41 mg, 0.061 mmol) was dissolved in dry DMF (6 mL). This solution was purged with argon for 10 min. Then, NaN_3 (39 mg, 0.600 mmol) was added and the resulting mixture was stirred at room temperature (19 ± 2 °C) for 24 h with protection from light, under argon. All subsequent manipulations were performed in the absence of light as much as possible. Dichloromethane (20 mL) was added, the organic phase was washed with deionized water (5 × 50 mL), and the organic solvent was evaporated (bath temperature ≤30 °C). The crude residue was purified by flash column chromatography (SiO_2, *n*-heptane/CH_2Cl_2 60/40). The first red fraction was evaporated (bath temperature ≤30 °C) and recrystallized from CH_2Cl_2/MeOH to give **NiP-N$_3$** as a red-brown solid in 74% yield (30 mg, 0.045 mmol). As reported by Yamashita et al.,[3d] we also observed a rapid decomposition of **NiP-N$_3$** in solution under ambient light and room temperature ($T_{1/2}$ ≈ 1 h under these conditions). Moreover, even in a brown glass vial in the solid state at room temperature, decomposition of **NiP-N$_3$** also occurred, but more slowly ($T_{1/2}$ ≈ 1 week). Thus, full characterization of **NiP-N$_3$** was performed in a few hours, with the solid kept in the dark (brown glass vial) at −18 °C as much as possible. ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ (ppm) 9.38 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.80 (d, $^3J_{H-H}$ = 5.0 Hz, *Hd*, 2H), 8.69 (d, $^3J_{H-H}$ = 5.0 Hz, *Hm*, 2H), 8.65 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 7.96 (m, *Hr*, 2H), 7.85 (d, $^3J_{H-H}$ = 7.9 Hz, *Hh*, 4H), 7.66 (m, *Hs,t*, 3H), 7.48 (d, $^3J_{H-H}$ = 7.9 Hz, *Hi*, 4H), 2.65 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 300 K): δ (ppm) 143.4, 142.9, 142.4, 140.8, 137.8, 137.7, 137.6, 133.8, 133.7, 132.9, 132.8, 132.3, 127.9, 127.8, 127.4, 127.1, 119.6, 118.9, 116.7, 21.6. R_f 0.83 (SiO_2, CH_2Cl_2/*n*-pentane, 30/70, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 299 (4.19), 421 (5.34), 536 (4.18). HRMS (ESI-MS): *m*/*z* calcd for $C_{40}H_{27}N_5Ni$ [M

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$-N_2]^+$ 635.1615, found 635.1607. IR (ATR) ν (cm^{-1}) 3028, 2918, 2098 (s, ν_{N3}), 1506, 1352, 1180, 1003, 793, 756, 702, 559, 503.

[5-[4-Phenyltriazole]-10,20-di-p-tolyl-15-phenylporphyrinato]-nickel(II) (**NiP-phenyltriazole**). The same protocol for the synthesis of **NiP-N_3** (50 mg, 0.075 mmol) was used, but without the last purification steps (column chromatography and recrystallization from CH_2Cl_2/MeOH). The crude **NiP-N_3** was dissolved in DMF (6 mL) in the presence of phenylacetylene (1.5 equiv, 12 μL, 0.109 mmol), and this solution was purged with argon for 15 min, with protection from light. $CuSO_4{\cdot}5H_2O$ (0.17 equiv, 3.2 mg, 0.013 mmol) and ascorbic acid (0.6 equiv, 8.0 mg, 0.045 mmol) were then added, and the resulting solution was stirred at 50 °C, under argon, for 17 h. After the solution was cooled to room temperature, dichloromethane (25 mL) was added and the organic phase was washed with water (3 × 50 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2). The major red fraction was evaporated, recrystallized from CH_2Cl_2/MeOH, and dried overnight under vacuum at 120 °C, affording **NiP-phenyltriazole** in 72% global yield (42 mg, 0.055 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K): δ (ppm) 8.85 (d, $^3J_{H-H}$ = 5.0 Hz, *Hd*, 2H), 8.79 (d, $^3J_{H-H}$ = 4.9 Hz, *Hm*, 2H), 8.76 (d, $^3J_{H-H}$ = 4.9 Hz, *Hn*, 2H), 8.70 (s, *Hu*, 1H), 8.61 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.16 (d, $^3J_{H-H}$ = 7.2 Hz, *Hx*, 2H), 8.02 (d, $^3J_{H-H}$ = 6.7 Hz, *Hr*, 2H), 7.89 (d, $^3J_{H-H}$ = 7.8 Hz, *Hh*, 4H), 7.75−7.67 (m, *Hs,t*, 3H), 7.56 (t, $^3J_{H-H}$ = 7.6 Hz, *Hy*, 2H), 7.49 (d, $^3J_{H-H}$ = 7.8 Hz, *Hi*, 4H), 7.46 (t, $^3J_{H-H}$ = 7.6 Hz, *Hz*, 1H), 2.65 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 300 K): δ (ppm) 147.0, 144.1, 143.7, 143.1, 141.2, 140.7, 138.0, 137.5, 134.1, 133.8, 132.9, 132.8, 130.5, 129.3, 128.7, 128.5, 128.1, 127.9, 127.1, 126.3, 121.3, 120.7, 111.6, 21.6. R_f 0.58 (SiO_2, CH_2Cl_2). λ_{max} (CH_2Cl_2)/nm (log ε): 293 (4.20), 413 (5.40), 526 (4.26), 557 (3.82). HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{34}N_7Ni$ $[M + H]^+$ 766.2229, found 766.2240.

[5-[[4-Methoxyphenyl]amino]-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NH(Ph-(4-OMe))**). The porphyrin **NiP-NO_2** (40 mg, 0.060 mmol) was dissolved in dry DMF (3 mL) in the presence of *p*-methoxyaniline (23 mg, 0.186 mmol) and one KOH pellet (105 mg, 1.872 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic phase was washed with water (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-heptane 50/50). The second red fraction was evaporated, recrystallized from CH_2Cl_2/*n*-pentane, and dried overnight under vacuum at 120 °C, affording **NiP-NH(Ph-(4-OMe))** in 60% yield (27 mg, 0.036 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ (ppm) 9.07 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.64 (m, *Hm,d,n*, 6H), 7.98 (m, *Hr*, 2H), 7.84 (d, $^3J_{H-H}$ = 7.9 Hz, *Hh*, 4H), 7.67 (m, *Hs,t*, 3H), 7.46 (d, $^3J_{H-H}$ = 7.8 Hz, *Hi*, 4H), 7.15 (br s, *NH*, 1H), 6.70 (m, *Hx,w*, 4H), 3.71 (s, *Hy*, 3H), 2.63 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 300 K): δ (ppm) 153.7, 145.0, 143.3, 142.7, 142.5, 141.9, 141.1, 137.9, 137.5, 133.8, 133.7, 132.5, 132.1, 131.9, 128.7, 127.8, 127.1, 119.6, 119.2, 117.1, 114.8, 55.8, 21.6. R_f 0.48 (Al_2O_3, CH_2Cl_2/*n*-pentane, 20/80, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 296 (4.27), 425 (5.06), 535 (4.14), 592 (3.82). HRMS (ESI-MS): *m/z* calcd for $C_{47}H_{35}ON_5Ni$ $[M]^+$ 743.2190, found 743.2194.

[5-[[4-Bromophenyl]amino]-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NH(Ph-(4-Br))**). The porphyrin **NiP-NO_2** (50 mg, 0.075 mmol) was dissolved in dry DMF (4 mL) in the presence of *p*-bromoaniline (41 mg, 0.238 mmol) and one KOH pellet (92 mg, 1.640 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic phase was washed with water (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-heptane 50/50). The major red fraction was collected, evaporated, recrystallized from CH_2Cl_2/MeOH, and dried overnight under vacuum at 120 °C, affording **NiP-NH(Ph-(4-Br))** in 55% yield (33.0 mg, 0.041 mmol). ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ (ppm) 10.06 (s, N*H*u, 1H), 9.28 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.63 (d, $^3J_{H-H}$ = 5.0 Hz, *Hd*, 2H), 8.61 (d, $^3J_{H-H}$ = 5.0 Hz, *Hm*, 2H), 8.57 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 7.98−7.91 (m, *Hr*, 2H), 7.83 (d, $^3J_{H-H}$ = 7.3 Hz, *Hh*, 4H), 7.76−7.67 (m, *Hs,t*, 3H), 7.50 (d, $^3J_{H-H}$ = 7.3 Hz, *Hi*, 4H), 7.18 (d, $^3J_{H-H}$ = 8.8 Hz, *Hx*, 2H), 6.63 (d, $^3J_{H-H}$ = 8.8 Hz, *Hw*, 2H), 2.57 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 300 K): δ (ppm) 150.6, 142.2, 141.8, 141.6, 139.9, 137.3, 136.9, 133.2, 132.5, 131.9, 131.6, 129.9, 128.0, 127.8, 127.2, 118.8, 118.7, 116.3, 109.1, 21.0. R_f 0.30 (Al_2O_3, CH_2Cl_2/*n*-pentane, 20/80, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 422 (5.15), 532 (4.20), 590 sh (3.66). HRMS (ESI-MS): *m/z* calcd for $C_{46}H_{32}N_5BrNi$ $[M]^+$ 791.1190, found 791.1195.

[5-[2-Aminoanthracene]-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NH(anthracene)**). The porphyrin **NiP-NO_2** (49 mg, 0.074 mmol) was dissolved in dry DMF (4 mL) in the presence of 2-aminoanthracene (44 mg, 0.226 mmol) and one KOH pellet (97 mg, 1.729 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic phase was washed with brine (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (Al_2O_3, CH_2Cl_2/*n*-heptane 20/80 → 60/40). The major brownish fraction was collected, evaporated, recrystallized from CH_2Cl_2/*n*-heptane, and dried overnight under vacuum at 120 °C, affording **NiP-NH(anthracene)** in 60% yield (36 mg, 0.044 mmol). ^{1}H NMR (CD_2Cl_2, 300 MHz, 300 K): δ (ppm) 8.96 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.72 (t, $^3J_{H-H}$ = 5.1 Hz, *Hm,n*, 4H), 8.57 (d, $^3J_{H-H}$ = 5.0 Hz, *Hd*, 2H), 8.22 (s, *Hf′*, 1H), 8.01 (m, *Hr*, 2H), 7.86−7.81 (m, *Hd′,h′,h*, 6H, the doublet of Hh is clearly visible at 7.82 ppm, $^3J_{H-H}$ = 8.0 Hz,), 7.73−7.57 (m, *Hs,t,y,a′*, 5H), 7.45 (d, $^3J_{H-H}$ = 7.8 Hz, *Hi*, 4H), 7.26 (m, *Hb′,c′*, 2H), 7.09 (dd, $^3J_{H-H}$ = 9.1 Hz, $^4J_{H-H}$ = 2.2 Hz, *Hi′*, 1H), 7.02 (br s, *NH*, 1H), 6.64 (d, $^4J_{H-H}$ = 1.9 Hz, *Hw*, 1H), 2.61 (s, *Hk*, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 300 K): δ (ppm) 149.2, 143.49, 143.44, 143.41, 143.3, 141.3, 138.10, 138.08, 134.1, 134.0, 133.5, 132.8, 132.6, 132.3, 130.3, 129.9, 129.3, 128.5, 128.3, 128.2, 128.0, 127.7, 127.4, 126.4, 125.7, 124.3, 123.4, 120.0, 119.8, 119.6, 117.2, 106.9, 21.6. R_f 0.58 (Al_2O_3, CH_2Cl_2/*n*-pentane, 20/80, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 270 (4.87), 412 (5.15), 534 (4.17). HRMS (ESI-MS): *m/z* calcd for $C_{54}H_{37}N_5Ni$ $[M]^+$ 813.2397, found 813.2392.

[5-Aminooctyl-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-NH(octyl)**). The porphyrin **NiP-NO_2** (50 mg, 0.075 mmol) was dissolved in dry DMF (4 mL) in the presence of *n*-octylamine (30 mg, 0.234 mmol) and one KOH pellet (86 mg, 1.533 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic phase was washed with water (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-pentane 50/50). The first greenish fraction was collected, evaporated, recrystallized from CH_2Cl_2/MeOH, and dried overnight under vacuum at 120 °C affording **NiP-NH(octyl)** in 50% yield (28 mg, 0.037 mmol). ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ (ppm) 8.94 (d, $^3J_{H-H}$ = 4.8 Hz, *Hc*, 2H), 8.43 (2d, $^3J_{H-H}$ = 4.8 and 5.0 Hz, *Hd,m*, 4H), 8.37 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 7.93−7.87 (m, *Hr*, 2H), 7.78 (d, $^3J_{H-H}$ = 7.8 Hz, *Hh*, 4H), 7.65−7.59 (m, *Hs,t*, 3H), 7.45 (d, $^3J_{H-H}$ = 7.8 Hz, *Hi*, 4H), 5.49 (br s, *NH*, 1H), 3.90 (t, $^3J_{H-H}$ = 7.1 Hz, *H1*, 2H), 2.61 (s, *Hk*, 6H), 1.71 (qu, $^3J_{H-H}$ = 7.1 Hz, *H2*, 2H), 1.40−1.10 (m, *H3*,4,5,6,7, 10H), 0.81 (t, 7.0 Hz, *H8*, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400 MHz, 298 K): δ (ppm) 144.8, 141.4, 141.2, 138.2, 138.0, 135.7, 134.2, 133.9, 133.0, 132.7, 131.1, 129.7, 128.2, 127.9, 127.6, 126.5, 119.5, 115.1, 32.3, 31.9, 29.8, 29.7, 27.5, 23.1, 21.7, 14.4. R_f 0.44 (Al_2O_3, CH_2Cl_2/*n*-pentane, 20/80, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 432 (5.22), 544 (3.86), 592 sh (3.94), 622 (4.02). HRMS (ESI-MS): *m/z* calcd for $C_{48}H_{46}N_5Ni$ $[MH]^+$ 750.3109, found 750.3107.

[5-Imidazole-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) (**NiP-(imidazole)**). The porphyrin **NiP-NO_2** (51 mg, 0.076 mmol) was dissolved in dry DMF (4 mL) in the presence of imidazole (16 mg, 0.236 mmol) and one KOH pellet (106 mg, 1.889 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic

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phase was washed with water (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH 98/2 → CH_2Cl_2/MeOH 95/5). The polar red fraction was collected, evaporated, recrystallized from CH_2Cl_2/MeOH, and dried overnight under vacuum at 120 °C, affording **NiP-(imidazole)** in 59% yield (31 mg, 0.045 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ (ppm) 8.85 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.80 (d, $^3J_{H-H}$ = 5.0 Hz, *Hm*, 2H), 8.77 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 8.64 (d, $^3J_{H-H}$ = 5.0 Hz, *Hd*, 2H), 8.41 (br s, *Hu*, 1H), 8.00 (br s + m, *Hw,r*, 3H), 7.88 (d, $^3J_{H-H}$ = 7.9 Hz, *Hh*, 4H), 7.67 (m, *Hs,t*, 3H), 7.58 (br s, *Hv*, 1H), 7.50 (d, $^3J_{H-H}$ = 7.9 Hz, *Hi*, 4H), 2.66 (s, *Hk*, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 300 K): δ (ppm) 144.0, 143.8, 143.4, 141.9, 140.7, 137.9, 137.5, 134.1, 133.82, 133.79, 133.1, 128.8, 128.1, 127.9, 127.1, 120.7, 120.4, 21.6. R_f 0.60 (Al_2O_3, CH_2Cl_2/*n*-pentane, 50/50, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 294 (4.15), 413 (5.35), 527 (4.23). HRMS (ESI-MS): *m/z* calcd for $C_{43}H_{31}N_6Ni$ $[M + H]^+$ 689.1958, found 689.1972.

[5-Diphenylamino-10,20-di-p-tolyl-15-phenylporphyrinato]-nickel(II) ***(NiP-NPh$_2$)***. The porphyrin **NiP-NO$_2$** (50 mg, 0.075 mmol) was dissolved in dry DMF (4 mL) in the presence of diphenylamine (51 mg, 0.301 mmol) and one KOH pellet (93 mg, 1.658 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic phase was washed with water (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-pentane 50/50). The major red fraction was collected, evaporated, recrystallized from CH_2Cl_2/MeOH, and dried overnight under vacuum at 120 °C, affording **NiP-NPh$_2$** in 49% yield (29 mg, 0.037 mmol). ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ (ppm) 9.11 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 2H), 8.72 (d, $^3J_{H-H}$ = 5.0 Hz, *Hm*, 2H), 8.70 (d, $^3J_{H-H}$ = 5.0 Hz, *Hd*, 2H), 8.69 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 8.00 (dd, $^3J_{H-H}$ = 7.4 Hz and $^4J_{H-H}$ = 1.8 Hz, *Hr*, 2H), 7.86 (d, $^3J_{H-H}$ = 7.8 Hz, *Hh*, 4H), 7.75−7.64 (m, *Hs,t*, 3H), 7.47 (d, $^3J_{H-H}$ = 7.8 Hz, *Hi*, 4H), 7.26−7.13 (m, *Hv,w*, 8H), 6.88 (t, $^3J_{H-H}$ = 7.0 Hz, *Hx*, 2H), 2.62(s, *Hk*, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz, 298 K): δ (ppm) 152.2, 145.7, 144.0, 143.6, 143.0, 141.4, 138.3, 138.2, 134.2, 134.1, 133.7, 132.7, 132.6, 131.0, 129.8, 129.7, 128.4, 128.1, 127.5, 122.4, 121.8, 121.6, 121.4, 120.4, 120.0, 118.2, 21.7. R_f 0.81 (Al_2O_3, CH_2Cl_2/*n*-pentane, 20/80, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 408 (5.00), 446 sh (4.73), 538 (4.20), 586 sh (3.62). HRMS (ESI-MS): *m/z* calcd for $C_{52}H_{37}N_5Ni$ $[M]^+$ 789.2404, found 789.2402.

[5-[[5-(4-Aminophenyl)-10,15,20-triphenylporphyrinato]nickel-(II)]-10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) ***(NiP-NH-(NiTPP))***. The porphyrin **NiP-NO$_2$** (40 mg, 0.060 mmol) was dissolved in dry DMF (4 mL) in the presence of [5-(4-amino-phenyl)-10,15,20-triphenylporphyrinato]nickel(II) (**NiTPP-NH$_2$**) (60 mg, 0.088 mmol) and one KOH pellet (98.0 mg, 1.747 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 1 h. After the solution was cooled to room temperature, dichloromethane (50 mL) was added and the organic phase was washed with water (5 × 100 mL). After evaporation of the solvent, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-pentane 50/50). The major red fraction was collected, evaporated, recrystallized from CH_2Cl_2/MeOH, and dried overnight under vacuum at 120 °C, affording **NiP-NH(NiTPP)** in 61% yield (48 mg, 0.037 mmol). ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ (ppm) 9.03 (d, $^3J_{H-H}$ = 4.4 Hz, *Hc*, 2H), 8.80 (d, $^3J_{H-H}$ = 4.6 Hz, *Hn*, 2H), 8.75−8.64 (m, *H7*,8,12,13, 8H), 8.68 (d, $^3J_{H-H}$ = 4.6 Hz, *Hm*, 2H), 8.62 (d, $^3J_{H-H}$ = 4.4 Hz, *Hd*, 2H), 8.06−7.87 (m, *Hr*,17,21, 8H), 7.82 (d, $^3J_{H-H}$ = 7.3 Hz, *Hh*, 4H), 7.74−7.50 (m, *Hs,t*,3,18,19,22,23, 14H), 7.43 (d, $^3J_{H-H}$ = 7.3 Hz, *Hi*, 4H), 6.90 (br s, *NH*, 1H), 6.65 (d, $^3J_{H-H}$ = 7.8 Hz, *H2*, 2H), 2.61 (s, *Hk*, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz, 298 K): δ (ppm) 151.4, 143.8, 143.6, 143.5, 143.3, 143.3, 143.3, 143.2, 141.4, 141.4, 138.2, 138.2, 135.2, 134.3, 134.2, 132.8, 132.8, 132.5, 132.4, 132.3, 131.6, 129.4, 128.2, 128.1, 127.4, 127.4, 120.2, 119.9, 119.7, 119.6, 119.4, 117.3, 113.2, 21.7. R_f 0.71 (Al_2O_3, CH_2Cl_2/*n*-pentane, 40/60, v/v). λ_{max} (CH_2Cl_2)/nm (log ε): 416 (5.37), 532 (4.50), 584 sh (3.86). HRMS (MALDI-TOF): *m/z* calcd for $C_{84}H_{55}N_9Ni_2$ $[M]^+$ 1305.3287, found 1305.3279.

5,5′-Bis[10,20-di-p-tolyl-15-phenylporphyrinato]nickel(II) amine ***((NiP)$_2$-NH)***. The porphyrin **NiP-NO$_2$** (31.0 mg, 0.046 mmol) was dissolved in dry DMF (3 mL) in the presence of **NiP-NH$_2$** (29.2 mg, 0.046 mmol, 1.0 equiv) and one KOH pellet (105 mg, 1.872 mmol). This solution was purged with argon for 10 min and then heated to 150 °C (preheated oil bath) over 20 min. After the solution was cooled to room temperature, water (25 mL) was added and the green precipitate was isolated by filtration and washed with water. The solid was dissolved in THF (5 mL) and placed in a glass tube. Methanol (20 mL) was then gently added on top of the THF solution. The tube was sealed with a silicon septum and placed in the dark at room temperature for 1 month to allow the slow full diffusion of methanol into the THF solution. The resulting green needle-shaped crystals were then filtered, washed with MeOH, and dried overnight under vacuum at 120 °C, giving **(NiP)$_2$-NH** in 76% yield (44 mg, 0.045 mmol). ^{1}H NMR (THF-d_8, 300 MHz, 300 K): δ (ppm) 11.32 (br s, NH, 1H), 8.95 (d, $^3J_{H-H}$ = 5.0 Hz, *Hc*, 4H), 8.46 (s, *Hm,n*, 8H), 8.27 (d, $^3J_{H-H}$ = 5.0 Hz, *Hn*, 2H), 7.93 (m, *Hr*, 4H), 7.66 (m, *Hh,s,t*, 14H), 7.33 (d, $^3J_{H-H}$ = 7.9 Hz, *Hi*, 8H), 2.44 (s, *Hk*, 6H). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz, 300 K): δ (ppm) 144.5, 143.0, 142.2, 142.0, 140.9, 138.8, 138.1, 134.4, 134.2, 133.0, 131.9, 131.8, 129.5, 128.8, 128.4, 128.3, 127.8, 119.7, 117.7, 21.3. R_f 0.63 (Al_2O_3, CH_2Cl_2/*n*-pentane, 20/80, v/v). λ_{max} (THF)/nm (log ε): 294 (4.52), 408 (5.23), 446 (5.12), 527 (4.37), 629 (4.49). HRMS (MALDI-TOF): *m/z* calcd for $C_{80}H_{55}N_9Ni_2$ $[M]^+$ 1257.3287, found 1257.3284.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving ^{1}H, ^{13}C, and 2D NMR spectra for all new compounds, HR-ESI and MALDI-TOF mass spectra, IR spectrum of **NiP-N$_3$**, cyclic voltammograms of **ZnP-NO$_2$**, **H$_2$P-NO$_2$**, and **NiP-NO$_2$**, and X-ray crystallographic data for **NiP-N$_3$** and **NiP-NH(Ph-(4-OMe))**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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