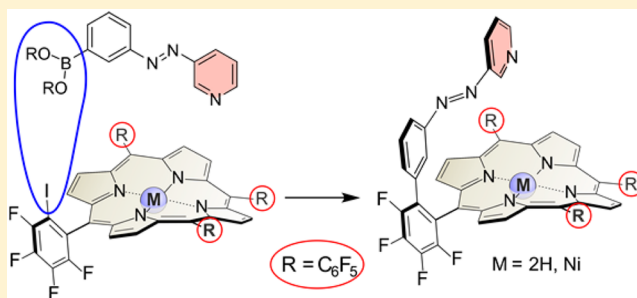


Synthesis of Functionalized Perfluorinated Porphyrins for Improved Spin Switching

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Supporting Information

ABSTRACT: We have established a method to synthesize perfluorinated *meso*-phenylporphyrins with one phenyl group bearing a substituent in the *ortho* position. These novel electron-deficient porphyrins are interesting for model enzymes, catalysis, photodynamic therapy, and electron transfer. The key step is the synthesis of an iodine-substituted porphyrin and its Suzuki cross coupling with boronic acid derivatives. We applied the novel strategy to synthesize a highly electron-deficient, azopyridine-substituted Ni-porphyrin that undergoes an improved ligand-driven coordination-induced spin-state switch.



Nickel-porphyrins are known to change their spin state upon coordination of axial ligands, which is also known as a coordination-induced spin-state switch (CISSS).^{1,2} Ni-porphyrins without axial ligands and square planar geometry are always diamagnetic (low spin, LS, $S = 0$). Upon axial coordination of ligands, square-pyramidal and octahedral complexes are formed which are paramagnetic (high spin, HS, $S = 1$). The process is fully reversible and can be controlled by light (LD-CISSS) using photochromic azopyridines as free ligands (photo-dissociable ligands, PDL)³ or azopyridines covalently attached to the Ni-porphyrin (record player, RP concept) (Figure 1).⁴ The systems are designed in such a way

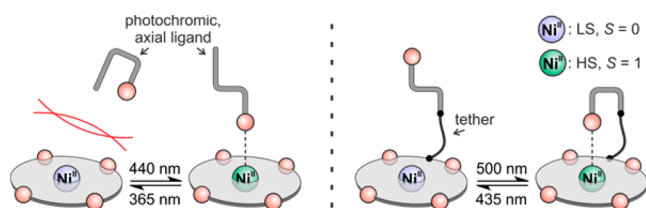


Figure 1. Spin-state switching using PDLs (left) and the RP concept (right).

that only one of the two azopyridine configurations coordinates to the Ni ion (*trans* isomer for PDL, *cis* isomer for RP), whereas the other isomer does not. Consequently, isomerization of the azo group changes the coordination number and thereby switches the spin state of the nickel.

The switching efficiency (diamagnetic to paramagnetic) depends on the association constants of the axial ligands to the porphyrin. Generally, a strong coordination of the binding isomer is advantageous to achieve a high conversion to the high spin state. It is known that electron-deficient porphyrins exhibit

a higher association constant to axial ligands.² For the realization of the PDL concept, therefore, *meso*-tetrakis-(pentafluorophenyl)nickel(II)porphyrin (Ni-TPPF₂₀, **1**) was used as the square-planar Ni complex. Ni-TPPF₂₀ is one of the most electron-deficient porphyrins.³ The RP concept is also based on *meso*-tetraarylporphyrins; however, one of the *ortho* positions of the aryl groups is equipped with an azopyridine unit as the switching ligand (Figure 2). So far, the synthesis of

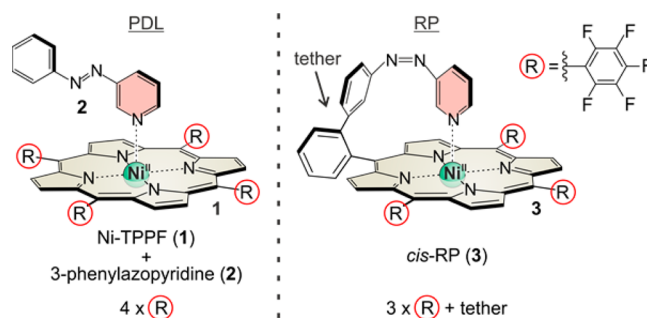


Figure 2. Association of the axial ligand to the Ni-porphyrin by untethered free 3-phenylazopyridine (**2**) (PDL concept, left) and by intramolecular coordination (RP concept, right).

RP systems has been performed via the “mixed aldehyde synthesis”. Consequently, in previous designs, only three of the four *meso* positions are substituted with electron-withdrawing pentafluorophenyl groups (Figure 2), which give rise to an incomplete intramolecular coordination. Only 74% of *cis*-RP **3**

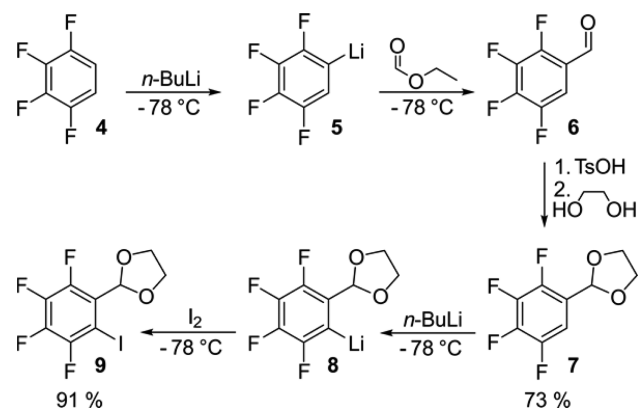
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is in the paramagnetic, coordinated form (300 K, acetone- d_6), and 26% remain noncoordinating and diamagnetic.

Perfluorination of the fourth *meso* position, to which the tether is attached, should enhance the intramolecular association. Thus, we developed a novel strategy to prepare porphyrins with three pentafluorophenyl substituents and one *ortho*-substituted tetrafluorophenyl substituent. With an iodine at this position, aryl substituents such as azopyridines can be introduced using cross-coupling reactions. A further advantage of this strategy compared to the mixed aldehyde approach is the fact that the yields are considerably higher with respect to the functional unit, which should be introduced.

The starting material is the commercially available 1,2,3,4-tetrafluorobenzene (4). It is known that metalation of 4 is possible with *n*-butyllithium (*n*-BuLi).⁵ The metalated species 5 is well characterized.⁶ At temperatures higher than -40°C , lithium fluoride is eliminated and an aryne is formed. At lower temperatures, 5 is stable and can react with electrophiles. We were able to obtain the formylated product 6 by addition of ethyl formate (Scheme 1) in analogy to the reaction of the

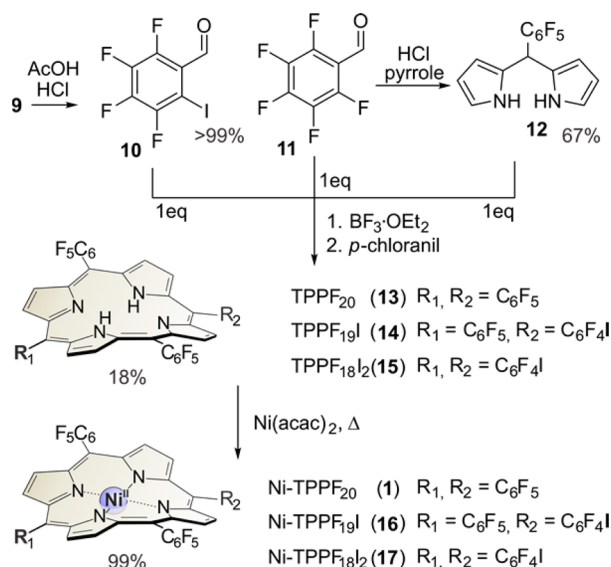
Scheme 1. Synthesis of 9



regioisomer 1,2,4,5-tetrafluorobenzene.⁷ Formylation with dimethylformamide (DMF) failed because the aryne formation is faster than the reaction with DMF. The lithiation/formylation sequence is the first one-pot preparation of 2,3,4,5-tetrafluorobenzaldehyde (6) from commercially available 1,2,3,4-tetrafluorobenzene (4). Thus far, it has been obtained by Grignard reaction from the less accessible 1-bromo-2,3,4,5-tetrafluorobenzene⁸ or by Swern oxidation of the corresponding benzylic alcohol.⁹ 2,3,4,5-Tetrafluorobenzaldehyde (6) rapidly oxidizes under air to the corresponding carboxylic acid. To prevent oxidation and to allow metalation, the crude aldehyde was immediately protected with ethylene glycol yielding 2-(2,3,4,5-tetrafluorophenyl)-1,3-dioxolane (7) with an overall yield of 73% over three steps from 1,2,3,4-tetrafluorobenzene (Scheme 1). Compound 7 was metalated with *n*-BuLi in analogy to the corresponding carboxylic acid.¹⁰ Addition of iodine gave the 2-(2-iodo-3,4,5,6-tetrafluorophenyl)-1,3-dioxolane (9) with a yield of 91% (Scheme 1). A structural analysis of 9 is available in the Supporting Information.

Deprotection of dioxolane 9 to the corresponding aldehyde was achieved quantitatively with AcOH/HCl. The (iodo, tetrafluorophenyl) tris(pentafluorophenyl) porphyrin 14 was prepared by the mixed aldehyde synthesis also known as the Lindsey method (Scheme 2).¹¹ To reduce the number of

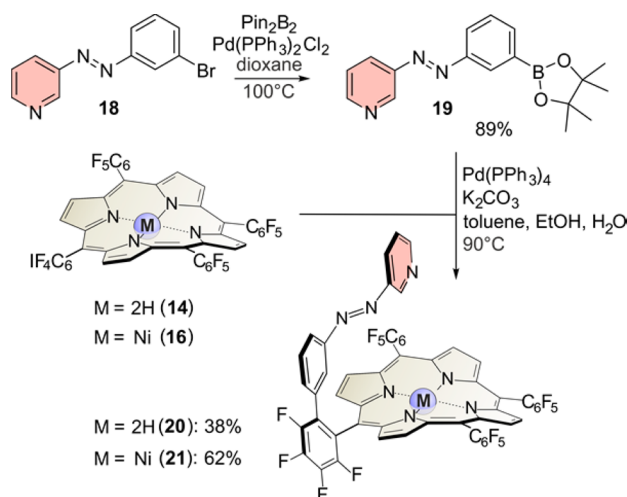
Scheme 2. Synthesis of the Porphyrin Mixtures 13–15 and the Corresponding Nickel Derivatives 1, 16, and 17



possible products from 6 to 3, prefabricated *meso*-(pentafluorophenyl)dipyrromethane (12) (synthesized from pentafluorobenzaldehyde (11) and pyrrole) was used instead of pyrrole as one of the three components.¹² The resulting porphyrins TPPF₂₀ (13), TPPF₁₉I (14), and TPPF₁₈I₂ (15) cannot be separated and therefore are used as a mixture. The yields correspond to the statistical product distribution of 1:2:1. The porphyrin mixture was metalated quantitatively with nickel(II) acetylacetonate (Ni(acac)₂) yielding a Ni-porphyrin mixture of Ni-TPPF₂₀ (1), Ni-TPPF₁₉I (16), and Ni-TPPF₁₈I₂ (17).

The porphyrin mixtures 13–15 and the corresponding Ni compounds 1, 16, and 17 were used for Suzuki cross-coupling reactions¹³ with pinacol boronic ester 19 to prepare record player molecules 20 and 21 (Scheme 3). Compound 19 was synthesized by a Miyaura borylation reaction¹⁴ with the brominated phenylazopyridine 18 as starting material.⁴ Note

Scheme 3. Miyaura Borylation of Phenylazopyridine 18 Yields Pinacol Boronic Ester 19, Which Is Utilized for Suzuki Cross-Coupling Reaction with Porphyrins 14 and 16 To Prepare the Record Players 20 and 21



that separation of the porphyrins is not possible before the cross-coupling reaction.

The improved coordination of perfluorinated RP **21** (compared to the parent system **3**) can be observed by NMR spectroscopy. The intramolecular association was quantified by the ^1H NMR shift of the pyrrole protons. The maximum shift (100% paramagnetic complex) for **3** and **21** is identical (~ 53 ppm). The latter was measured by addition of an excess of an axial ligand (pyridine- d_5). The diamagnetic shift (~ 9 ppm) is known from the *trans* isomer and the corresponding Zn-porphyrin.⁴ The equilibrium between the paramagnetic and diamagnetic conformer is faster than the ^1H NMR time scale. Hence, an average shift is observed that is directly proportional to the amount of the paramagnetic complex. By irradiation with light of 500 nm 61% of the *cis*-isomer was obtained, which is the same percentage as for the parent system **3**. Hence, the perfluorination does not influence the photochromism. As expected, the pyrrole protons of the perfluorinated RP **21** ($X = \text{F}$) resonate at lower fields as those of the parent system **3** ($X = \text{H}$) (Figure 3). The average shift rises from 41.7 to 48.2 ppm

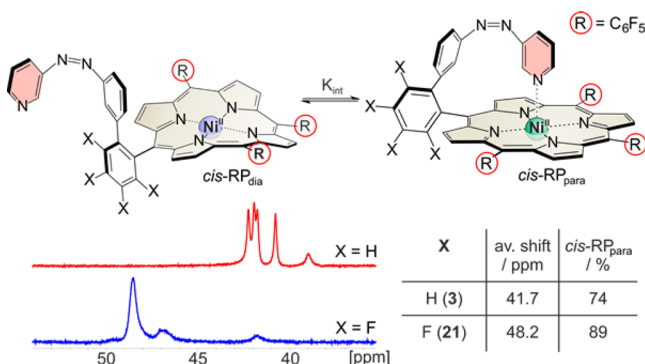


Figure 3. Equilibrium between the dia- (*cis*-RP_{dia}) and paramagnetic (*cis*-RP_{para}) conformations of the perfluorinated RP **21** ($X = \text{F}$) and of the parent system **3** ($X = \text{H}$). Average shift is the average chemical shift of the four pyrrole protons; *cis*-RP_{para} is the percentage of the paramagnetic *cis* isomer relative to the total amount of *cis* isomer.

(acetone- d_6), which corresponds to 15% higher percentage of the paramagnetic *cis* isomer (*cis*-RP_{para}). The overall switching efficiency (diamagnetic to paramagnetic) has increased from 45% to 54%.

In summary, we present a novel, modular approach to prepare highly electron-deficient functionalized porphyrins. Key intermediates are the porphyrins TPPF₁₉I (**14**) and Ni-TPPF₁₉I (**16**). Cross-coupling reactions were used to functionalize these porphyrins as demonstrated by the synthesis of perfluorinated RP **21**, a Ni-porphyrin that exhibits an improved LD-CISSS. Our approach provides access to a number of perfluorinated mono *meso-o*-phenyl-functionalized porphyrins which have not been described so far and which are difficult to prepare by the established mixed aldehyde synthesis. TPPF₁₉I (**14**) is a suitable building block to tether various functional groups, particularly axial ligands. Besides spin switching, metalated derivatives of such porphyrins are of broad interest as model enzymes¹⁵ and for catalysis,¹⁶ photodynamic therapy (PDT),¹⁷ and electron-transfer processes.¹⁸

EXPERIMENTAL SECTION

General Experimental Methods. Tetrahydrofuran was dried and distilled from sodium/benzophenone. All compounds were characterized using ^1H , ^{13}C and, if possible, ^{19}F NMR spectroscopy. The signals were assigned using 2D spectroscopy. For ^1H and ^{13}C NMR signal assignment we performed HSQC and HMBC. For ^{19}F signal assignment we applied ^{19}F COSY.

Synthesis of 2-(2,3,4,5-Tetrafluorophenyl)-1,3-dioxolane (7). 1,2,3,4-Tetrafluorobenzene (**4**) (10.0 g, 7.09 mL, 66.6 mmol) was mixed with tetrahydrofuran (200 mL) and cooled to -78°C . *n*-Butyllithium (30 mL, 75.0 mmol, 2.5 M in hexane) was slowly added, and the reaction mixture was stirred for another 1 h at -78°C . Ethyl formate (27 mL, 333 mmol) was slowly added, and the mixture was allowed to warm to room temperature overnight. Diethyl ether (500 mL) was added. The organic layer was washed with water three times and dried over magnesium sulfate, and the solvent was removed under reduced pressure. Crude product of 2,3,4,5-tetrafluorobenzaldehyde (**3**) (12.4 g) was obtained as a pale yellow liquid. The crude product was mixed with benzene (500 mL) and ethylene glycol (12.4 g, 200 mmol). *p*-Toluenesulfonic acid monohydrate (111 mg, 0.583 mmol) was added, and the benzene water mixture was removed by azeotropic distillation. The residue was treated with triethylamine (2 mL) and diethyl ether (200 mL). The organic layer was successively washed with saturated sodium carbonate, diluted sodium carbonate solution, and water. The organic phase was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product (11.8 g yellow liquid) was purified by vacuum distillation (bp 105°C , 0.7 mbar) to obtain 2-(2,3,4,5-tetrafluorophenyl)-1,3-dioxolane (**7**) (10.8 g, 48.6 mmol, 73%) as a colorless liquid. $n_D^{20} = 1.4561$. FT-IR: $\nu = 2892$ (m), 1635 (w), 1524 (s), 1488 (vs), 1406 (m), 1371 (m), 1265 (w), 1194 (w), 1134 (s), 1103 (w), 1030 (s), 973 (s), 946 (vs), 868 (m), 757 (m), 708 (m), 616 (m), 560 (w), 499 (w) cm^{-1} . ^1H NMR (500 MHz, 300 K, CDCl_3): $\delta = 7.04$ (m, 1H, Ar-H), 5.90 (s, 1H, CHO_2), 4.02–3.91 (m, 4H, CH_2) ppm. ^{13}C NMR (125 MHz, 300 K, CDCl_3): $\delta = 147.1$ (dddd, $^1J = 247$ Hz, $^2J = 10.2$ Hz, $^3J = 3.7$ Hz, $^4J = 1.9$ Hz, C5), 146.1 (dddd, $^1J = 250$ Hz, $^2J = 10.9$ Hz, $^3J = 3.8$ Hz, $^4J = 1.7$ Hz, C2), 141.0 (dddd, $^1J = 255$ Hz, $^2J = 16.8$, 12.2 Hz, $^3J = 3.3$ Hz, C4), 140.7 (dddd, $^1J = 254$ Hz, $^2J = 16.5$, 12.3 Hz, $^3J = 3.6$ Hz, C3), 122.3 (dddd, $^2J = 11.6$ Hz, $^3J = 5.9$, 3.9 Hz, $^4J = 0.7$ Hz, C1), 109.0 (dt, $^2J = 20.5$ Hz, $^3J = 3.7$ Hz, C6), 97.7 (m, CHO_2), 65.6 (s, CH_2) ppm. ^{19}F NMR (470 MHz, 300 K, CDCl_3): $\delta = -139.14$ (ddd, $^3J = 20.9$ Hz, $^5J = 13.1$ Hz, $^4J = 2.4$ Hz, 1F, F-5), -145.00 (ddd, $^3J = 20.3$ Hz, $^5J = 13.1$ Hz, $^4J = 3.9$ Hz, 1F, F-2), -154.92 (td, $^3J = 20.1$ Hz, $^4J = 3.9$ Hz, 1F, F-4), -153.73 (td, $^3J = 19.9$ Hz, $^4J = 2.4$ Hz, 1F, F3) ppm. MS (EI, TOF): $m/z = 222$ (67) $[\text{M}]^+$, 203 (45) $[\text{M} - \text{F}]^+$, 178 (100) $[\text{M} - \text{C}_2\text{H}_4\text{O}]^+$. HRMS (EI, TOF-Q) m/z : $[\text{M}]^+$ calcd for $\text{C}_9\text{H}_6\text{F}_4\text{O}_2$ 222.0304, found 222.0305.

Synthesis of 2-(2-Iodo-3,4,5,6-tetrafluorophenyl)-1,3-dioxolane (9). 2-(2,3,4,5-Tetrafluorophenyl)-1,3-dioxolane (**7**) (9.29 g, 41.8 mmol) was mixed with tetrahydrofuran (150 mL) and cooled to -78°C . *n*-Butyllithium (18.4 mL, 46.0 mmol, 2.5 M in hexane) was added within 1 h whereby the solution became pale red. The mixture was stirred for another 1 h at -78°C . Iodine (11.7 g, 46.0 mmol) was dissolved in tetrahydrofuran (50 mL) and slowly added with a syringe pump within 1.5 h. Finally, the color of iodine did not disappear upon addition. The reaction mixture was allowed to warm to room temperature and added to diethyl ether (300 mL). The organic layer was washed with diluted sodium carbonate and saturated sodium thiosulfate and once again with diluted sodium carbonate solution. Then it was dried over magnesium sulfate, and the solvent was removed under reduced pressure. A pale yellow solid was obtained which was dissolved in a minimum amount of dichloromethane. By addition of pentane the product **9** precipitated as a fluffy, colorless solid (13.2 g, 37.9 mmol, 91%). Crystals for structure analysis were obtained by vapor diffusion of pentane in a saturated solution of **9** in dichloromethane. Mp: 128.3°C . FT-IR: $\nu = 2909$ (m), 1627 (w), 1506 (s), 1470 (m), 1395 (m), 1353 (w), 1337 (m), 1270 (w), 1170 (w), 1148 (s), 1094 (m), 1070 (m), 1017 (w), 994 (m), 964 (s), 950 (vs), 925 (s), 809 (s), 753 (m), 724 (m), 652 (w), 624 (s), 617 (m),

519 (w) cm^{-1} . ^1H NMR (500 MHz, 300 K, CDCl_3): δ = 6.06 (s, 1H, CHO_2), 4.18–3.96 (m, 4H, CH_2) ppm. ^{13}C NMR (125 MHz, 300 K, CDCl_3): δ = 147.2 (dddd, 1J = 242 Hz, 2J = 11.0 Hz, 3J = 4.3 Hz, 4J = 2.0 Hz, C3), 146.8 (dddd, 1J = 257 Hz, 2J = 11.1 Hz, 3J = 3.9 Hz, 4J = 2.0 Hz, C6), 141.0 (dddd, 1J = 255 Hz, 2J = 17.3, 12.3 Hz, 3J = 3.7 Hz, C5), 140.3 (dddd, 1J = 259 Hz, 2J = 19.7, 12.8 Hz, 3J = 3.9 Hz, C4), 122.9 (dm, 2J = 9.6 Hz, C1), 105.1 (dd, 3J = 4.6 Hz, 4J = 2.3 Hz, CH), 78.5 (dt, 2J = 24.9 Hz, 3J = 3.3 Hz, C2), 66.2 (d, 5J = 1.2 Hz, CH_2) ppm. ^{19}F NMR (470 MHz, 300 K, CDCl_3): δ = –113.04 (ddd, 3J = 23.3 Hz, 5J = 9.8 Hz, 4J = 3.9 Hz, 1F, F-3), –140.52 (ddd, 3J = 20.3 Hz, 5J = 9.8 Hz, 4J = 5.2 Hz, 1F, F-6), –151.29 (td, 3J = 21.5 Hz, 4J = 5.2 Hz, 1F, F-4), –153.73 (td, 3J = 19.9 Hz, 4J = 3.9 Hz, 1F, F-5) ppm. MS (EI, TOF): m/z = 348 (100) $[\text{M}]^+$, 303 (31) $[\text{M} - \text{C}_2\text{H}_4\text{O}]^+$, 275 (6) $[\text{M} - \text{C}_3\text{H}_5\text{O}_2]^+$, 221 (20) $[\text{M} - \text{I}]^+$. Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_4\text{O}_2\text{I}$: C, 31.06; H, 1.45. Found: C, 31.21; H, 1.47.

Synthesis of 2-Iodo-3,4,5,6-tetrafluorophenylbenzaldehyde (10). 2-(2-Iodo-3,4,5,6-tetrafluorophenyl)-1,3-dioxolane (9) (1.01 g, 2.90 mmol) was dissolved in acetic acid (25 mL). After dropwise addition of concentrated hydrochloric acid (6 mL), the mixture was stirred for 3 h. Ethyl acetate (200 mL) was added. The organic layer was washed with water and saturated sodium carbonate solution and dried over magnesium sulfate. The solvent was removed under reduced pressure. The obtained aldehyde (883 mg, 2.90 mmol, >99%) is sensitive to oxidation and therefore was directly used for the porphyrin synthesis. ^1H NMR (500 MHz, 300 K, CDCl_3): δ = 10.05 (s, 1H, CH) ppm. ^{13}C NMR (125 MHz, 300 K, CDCl_3): δ = 188.1 (m, CH), 149.2 (dddd, 1J = 267 Hz, 2J = 11.1 Hz, 3J = 3.7 Hz, 4J = 2.4 Hz, C3), 147.9 (dddd, 1J = 245 Hz, 2J = 11.1 Hz, 3J = 4.4 Hz, 4J = 1.5 Hz, C6), 144.0 (dddd, 1J = 267 Hz, 2J = 19.7, 12.7 Hz, 3J = 3.9 Hz, C5), 140.9 (dddd, 1J = 259 Hz, 2J = 16.2, 12.5 Hz, 3J = 3.3 Hz, C4), 119.9 (dd, 2J = 7.2 Hz, 3J = 3.8 Hz, C1), 78.4 (dd, 2J = 25.5 Hz, 3J = 4.7 Hz, C2) ppm. ^{19}F NMR (470 MHz, 300 K, CDCl_3): δ = –113.29 (ddd, 3J = 23.1 Hz, 5J = 10.6 Hz, 4J = 4.8 Hz, 1F, F-3), –142.84 (ddd, 3J = 19.8 Hz, 5J = 10.6 Hz, 4J = 8.7 Hz, 1F, F-6), –143.89 (ddd, 3J = 23.1, 19.1 Hz, 4J = 8.7 Hz, 1F, F-4), –152.45 (td, 3J = 19.5 Hz, 4J = 4.8 Hz, 1F, F-5) ppm.

Synthesis of 3-(3-(Pinacol boronic ester)phenylazo)pyridine (19). A solution of 3-(3-bromophenylazo)pyridine (18) (1.00 g, 3.82 mmol) and potassium acetate (748 mg, 7.62 mmol) in dioxane (40 mL) was dried over molecular sieves (3 Å) by heating to 120 °C for 4 h. Bis(pinacolato)diboron (1.07 g, 4.20 mmol) and bis-(triphenylphosphine)palladium(II) dichloride (140 mg, 0.20 FT-IRded and the solution was kept at 100 °C overnight without stirring. After cooling the molecular sieve and all solid components were filtered off. The volume of the filtrate was doubled with water and extracted twice with dichloromethane. The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane/ethyl acetate = 6:4, R_f = 0.15). The product was obtained as an orange solid (1.05 g, 3.40 mmol, 89%). Mp: 86.6 °C. FT-IR (layer): ν = 2975 (m), 1422 (m), 1356 (s), 1333 (s), 1273 (w), 1213 (w), 1139 (s), 1064 (m), 967 (w), 918 (w), 851 (m), 817 (s), 698 (vs), 676 (m), 618 (w), 566 (w), 538 (m), 512 (w) cm^{-1} . ^1H NMR (500 MHz, 300 K, CDCl_3): δ = 9.21 (dd, 4J = 2.3, 5J = 0.5 Hz, 1H, H-2), 8.70 (dd, 3J = 4.7 Hz, 4J = 1.6 Hz 1H, H-6), 8.37 (m, 1H, H-8), 8.14 (ddd, 3J = 8.2 Hz, 4J = 2.3, 1.6 Hz, 1H, H-4), 8.02 (ddd, 3J = 7.9 Hz, 4J = 2.3, 1.2 Hz, 1H, H-12), 7.95 (dt, 3J = 7.3 Hz, 4J = 1.2 Hz, 1H, H-10), 7.54 (t, 3J = 7.6 Hz, 1H, H-11), 7.45 (ddd, 3J = 8.2, 4.7 Hz, 5J = 0.5 Hz, 1H, H-5), 1.38 (s, 12H, CH_3) ppm. ^{13}C NMR (125 MHz, 300 K, CDCl_3): δ = 152.1 (C7), 151.7 (C6), 148.1 (C3), 147.5 (C2), 138.2 (C10), 130.7 (C9), 129.7 (C8), 128.8 (C11), 127.1 (C4), 125.6 (C12), 124.1 (C5), 25.1 (CH_3) ppm. MS (EI, TOF): m/z = 319 (29) $[\text{M}]^+$, 203 (100) $[\text{PhBPIn}]^+$. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{BN}_3\text{O}_2$: C, 66.04; H, 6.52; N, 13.59. Found: C, 65.71; H, 6.80; N, 13.52.

Synthesis of Metal-Free Record Player 20. 2-Iodo-3,4,5,6-tetrafluorophenylbenzaldehyde (10) (883 mg, 2.90 mmol) and pentafluorophenylbenzaldehyde (11) (568 mg, 2.90 mmol) were dissolved in dichloromethane (700 mL) under nitrogen atmosphere. Boron trifluoride diethyl etherate (280 μL , 0.50 mmol) was added dropwise. Pentafluorophenyl dipyrromethane (12) (1.81 g, 5.81

mmol) dissolved in dichloromethane (100 mL) was added, and the mixture was stirred for 14 h. *p*-Chloranil (1.50 g, 6.09 mmol) was added, and the mixture was stirred under reflux for 4 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (cyclohexane/chloroform = 1:1, R_f = 0.45). The mixture of three porphyrins (13–15) was obtained as a purple solid (555 mg, 513 μmol , 18% assuming a 1:2:1 porphyrin mixture). HRMS (EI, TOF-Q) m/z : $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_{10}\text{F}_{20}\text{N}_4$ 974.059, found 974.055; $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_{10}\text{F}_{19}\text{IN}_4$ 1081.964, found 1081.961; $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_{10}\text{F}_{18}\text{I}_2\text{N}_4$ 1189.871, found 1189.866. The metal-free porphyrin mixture (13–15) (229 mg, 212 μmol), pinacol boronic ester 19 (157 mg, 0.51 mmol), and tetrakis-(triphenylphosphine)palladium(0) (~10 mg) were dissolved in a toluene (6.5 mL)/ethanol (2 mL) mixture under nitrogen atmosphere. Potassium carbonate (232 mg, 1.68 mmol) dissolved in 1.5 mL of water was added, and the mixture was stirred overnight at 80 °C. Water (50 mL) was added, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane/ethyl acetate = 7:3, R_f = 0.15). The product was obtained as a purple solid (46 mg, 40.4 μmol , 38% assuming a 1:2:1 porphyrin mixture as starting material). Mp: 216.2 °C. FT-IR (layer): ν = 3316 (w), 1651 (w), 1516 (s), 1495 (s), 1391 (m), 1080 (w), 1066 (m), 1043 (m), 1026 (w), 987 (vs), 917 (vs), 801 (s), 768 (m), 754 (s), 722 (m), 700 (s), 645 (w) cm^{-1} . ^1H NMR (500 MHz, 300 K, acetone- d_6): δ = 9.51 (s, br, 2H, *H*-Por), 9.36 (s, br, 2H, *H*-Por), 9.32–9.27 (m, 4H, *H*-Por), 8.64 (s, 1H, NCH), 8.60 (d, 3J = 4.5 Hz, 1H, NCH), 7.78 (t, 4J = 1.7 Hz, 1H, N_2CCH), 7.50 (d, 3J = 8.1 Hz, 1H, NCHCHCH), 7.44 (dm, 3J = 7.9 Hz, 1H, N_2CCH), 7.30 (dd, 3J = 8.1, 4.5 Hz, 1H, NCHCH), 7.01 (ddd, 3J = 7.9 Hz, 4J = 2.0, 1.1 Hz, 1H, $\text{N}_2\text{CCHCHCH}$), 7.54 (t, 3J = 7.9 Hz, 1H, N_2CCHCH), –3.01 (s, 2H, *H*-N) ppm. ^{13}C NMR (125 MHz, 300 K, acetone- d_6): δ = 152.8 (NCH), 151.0 ($\text{N}_2\text{C}(\text{CH})_2$), 148.0 (NCHCN $_2$), 147.2 (NCH), 133.9 (N_2CCHCH), 133.6 (N_2CHC), 129.4 (N_2CCHCH), 127.0 (NCHCHCH), 124.8 (NCHCH), 124.5 (N_2CCHC), 123.9 ($\text{N}_2\text{CCHCHCH}$) ppm, C atoms of the porphyrin and of the perfluorinated *meso* phenyl substituents cannot be assigned. ^{19}F NMR (470 MHz, 300 K, acetone- d_6): δ = –137.19 (ddd, 3J = 23.2 Hz, 5J = 11.9 Hz, 4J = 3.5 Hz, 1F, F-*o'*-C), –139.72 (dd, 3J = 23.8 Hz, 5J = 7.9 Hz, 2F, F-*o'*-A), –139.82 to –139.94 (m, 4F, F-*o*-A, F-*o*-B, F-*o'*-B), –142.78 (ddd, 3J = 22.2 Hz, 5J = 11.9 Hz, 4J = 3.1 Hz, 1F, F-*m*-C), –155.44 (t, 3J = 20.5 Hz, 2F, F-*p*-A), –155.49 (t, 3J = 20.2 Hz, 1F, F-*p*-B), –156.80 (td, 3J = 21.0 Hz, 4J = 3.5 Hz, 1F, F-*p*-C), –159.23 (td, 3J = 21.8 Hz, 4J = 3.1 Hz, 1F, F-*m'*-C), –164.18 (td, 3J = 22.2 Hz, 5J = 8.0 Hz, 2F, F-*m'*-A), –164.46 to –164.61 (m, 4F, F-*m*-A, F-*m*-B, F-*m'*-B) ppm. HRMS (EI, TOF-Q) m/z : $[\text{M}]^+$ calcd for $\text{C}_{55}\text{H}_{18}\text{F}_{19}\text{N}_7$ 1137.1320, found 1137.1350.

Synthesis of Record Player 21. The metal-free porphyrin mixture (150 mg, 139 μmol) and nickel(II) acetylacetonate (360 mg, 1.40 mmol) were dissolved in toluene (30 mL) and stirred under reflux for 4 d. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (cyclohexane/ethyl acetate = 3:1, R_f = 0.30). The mixture of three Ni-porphyrins (1, 16, and 17) was obtained as a purple solid (156 mg, 137 μmol , 99% assuming a 1:2:1 Ni-porphyrin mixture). HRMS (EI, TOF-Q) m/z : $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_8\text{F}_{20}\text{N}_4\text{Ni}$ 1029.978, found 1029.974; $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_8\text{F}_{19}\text{IN}_4\text{Ni}$ 1137.884, found 1137.880; $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_8\text{F}_{18}\text{I}_2\text{N}_4\text{Ni}$ 1245.790, found 1245.785. The Ni-porphyrin mixture (1, 16, 17) (156 mg, 137 μmol), pinacol boronic ester 19 (103 mg, 333 μmol), and tetrakis(triphenylphosphine)-palladium(0) (~10 mg) were dissolved in a toluene (6.5 mL)/ethanol (2 mL) mixture under nitrogen atmosphere. Potassium carbonate (151 mg, 1.09 mmol) dissolved in 1.5 mL of water was added, and the mixture was stirred overnight at 80 °C. Water (50 mL) was added, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane/ethyl acetate = 2:1, R_f = 0.20). The product was obtained as a purple solid (49.2 mg, 41.9

μmol , 62% assuming a 1:2:1 Ni–porphyrin mixture as starting material). Mp: 209.0 °C. FT-IR (layer): $\nu = 2980$ (w), 1652 (w), 1518 (s), 1486 (s), 1346 (m), 1079 (m), 1061 (m), 1025 (w), 985 (vs), 937 (vs), 800 (m), 760 (s), 732 (w), 701 (s), 644 (m) cm^{-1} . ^1H NMR (500 MHz, 300 K, acetone- d_6): $\delta = 9.60$ (s, br, 2H, *H*-Por), 9.41 (s, br, 6H, *H*-Por), 9.28 (s, br, 1H, NCH), 9.21 (s, br, NCH), 9.15 (s, br, NCHCHCH), 7.53 (s, 1H, N_2CCH), 7.44 (d, $^3J = 7.9$ Hz, 1H, NCHCH), 7.27 (d, $^3J = 7.9$ Hz, 1H, N_2CCH), 7.06 (d, $^3J = 7.9$ Hz, 1H, $\text{N}_2\text{CCHCHCH}$), 6.81 (t, $^3J = 7.9$ Hz, 1H, N_2CCHCH) ppm. ^{13}C NMR (125 MHz, 300 K, acetone- d_6): $\delta = 152.0$ (N_2C), 134.0 (N_2CCH), 133.1 (N_2CCHC), 129.9 (N_2CCHCH), 124.2 (N_2CCH), 124.0 ($\text{N}_2\text{CCHCHCH}$) ppm, C atoms of the pyridine, porphyrin, and the perfluorinated *meso* aryl substituents are not detectable because of the low concentration and slight paramagnetism due to intermolecular coordination. ^{19}F NMR (470 MHz, 300 K, acetone- d_6): $\delta = -136.97$ (dd, $^3J = 21.2$ Hz, $^5J = 10.8$ Hz, 1F, *F*-*o'*-C), -139.59 to -139.69 (m, 3F, *F*-*o'*-A, *F*-*o'*-B), -139.96 to -140.06 (m, 3F, *F*-*o*-A, *F*-*o*-B), -142.76 (dd, $^3J = 21.6$ Hz, $^5J = 10.8$ Hz, 1F, *F*-*m*-C), -155.60 (t, $^3J = 20.4$ Hz, 2F, *F*-*p*-A), -155.63 (t, $^3J = 20.4$ Hz, 1F, *F*-*p*-B), -156.92 (t, $^3J = 21.5$ Hz, 1F, *F*-*p*-C), -159.07 (t, $^3J = 21.3$ Hz, 1F, *F*-*m'*-C), -164.13 (td, $^3J = 21.6$ Hz, $^5J = 7.5$ Hz, 2F, *F*-*m'*-A), -164.42 (td, $^3J = 22.3$ Hz, $^5J = 7.8$ Hz, 1F, *F*-*m'*-B), -164.46 to -164.59 (m, 3F, *F*-*m*-A, *F*-*m*-B) ppm. UV–vis (MeCN): λ_{max} ($\lg \epsilon$) = 311 (4.547), 403 (5.390), 523 (4.234), 556 (4.125) nm. HRMS (EI, TOF-Q) m/z : $[\text{M}]^+$ calcd for $\text{C}_{55}\text{H}_{16}\text{F}_{19}\text{N}_7\text{Ni}$ 1193.0517, found 1193.0528.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01524. CCDC-1409964 contains the supplementary crystallographic data for compound 9. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

^1H , ^{13}C , ^{19}F , and 2D NMR spectra of new compounds and crystal structure data for 2-(2-iodo-3,4,5,6-tetraphenyl)-1,3-dioxolane (9) (PDF)

X-ray crystallographic data for compound 9 (CIF)

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Notes

The authors declare no competing financial interest.

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