# A Facile and Potent Synthesis of *meso*,*meso*-Linked Porphyrin Arrays Using Iodine(III) Reagents

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The synthesis of *meso*,*meso*-linked fluoroalkylporphyrin arrays has been accomplished, in excellent yields, by the simple treatment of a $CHCl_3$ solution of zincated 5-fluoroalkyl-10,20-diarylporphyrins (where fluoroalkyl = $CF_3$, $ClC_2F_4$, *n*-$ClC_4F_8$, *n*-$C_6F_{13}$, etc.) with iodine(III) reagents such as PhI(O–CO–$CF_3$)$_2$ (PIFA, also named as bis(trifluoroacetoxy)iodo]-benzene) or PhI(OAc)$_2$ (PIDA). For nonfluorinated zincated 5-substituted-10–20-diarylporphyrins (where substituent = phenyl, 4-methoxyphenyl, 4-methylphenyl, etc.) the similar coupling reactions also proceed fast and quantitatively. Moreover, various 15-unsubstituted metalloporphyrins can also be coupled in high yields.


## Introduction

Covalent multiporphyrin arrays are attracting interest as multichromophoric model systems for the study of electron transfer in natural photosynthetic systems, as well as in the development of novel functional materials.[1] Among them, direct *meso*,*meso*-linked fully conjugated porphyrin rods are exceptionally promising scaffolds for nanotechnology and optoelectronic applications as they demonstrate highly efficient energy transfer along the arrays.[2]

No method to form a direct link at the *meso* position was known until the first rational synthesis by Susumu et al. in 1996.[3] Since then, several approaches have been reported to prepare such *meso*,*meso*-linked porphyrin arrays, such as Smith's condensation of a dipyrromethane derivative with tetrakis(5-formyl-2-pyrrolyl)ethane,[4] Osuka's oxidative dimerisation of monomeric porphyrins, either chemically with silver salts or electrochemically,[5] Senge's oxidative dimerisation of anionic adducts induced by 2,3-dichloro-5,6-dicyanoquinone (DDQ)[6] and Liebeskind's solvent-dependent DDQ-induced oxidative dimerisation of zincated substituted porphyrins.[7]

In connection with our successful synthesis of β-fluoroalkylporphyrins from tetraarylporphyrins and commercially available perfluoroalkyl iodides under sulfinatohalogenation conditions[8] and the regioselective preparation of mono *meso*- or β-fluoroalkylporphyrins,[9] we were interested in this oxidative dimerisation of fluorinated porphyrins and found a facile and potent method for coupling fluorinated or non-fluorinated porphyrins. The results are presented here.

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## Results and Discussion

Recently, when we iodinated the zinc(II) 5-perfluorohexyl-10,20-diphenylporphyrin (**Zn-1d**)[9] by Dolphin's method (PIFA/$I_2$),[10,11] we surprisingly found that neither the *meso*- nor the β-iodinated porphyrin was formed, but rather the *meso*,*meso*-linked porphyrin **Zn-2d**.

The structure of the dimeric zincated porphyrin was determined by $^{1}H$ and $^{19}F$ NMR spectroscopy, MALDI-MS and UV/Vis spectroscopy. During the reaction, the *meso* proton signal of **Zn-1d** ($\delta$ = 10.10 ppm) disappeared and one of the four β-proton signals of **Zn-1d** was shifted upfield by 0.7 ppm (from $\delta$ = 8.95 to 8.23 ppm), the latter observation suggesting that these protons are located in the shielding region of the adjacent porphyrin ring.[5a] This is typical for structures of type **2** due to the orthogonal relationship of the two porphyrin rings. The MALDI mass spectrum of **Zn-2d** gave $M^+$ = 1682.1 (calculated: 1682.1); in addition, a cluster of peaks with the same pattern as one calculated based upon the isotopic distribution of the formula was observed.

Additional evidence for the structure of the dimer **Zn-2d** was obtained from its UV/Vis spectrum,[3–7] which shows split Soret absorption bands at 414 and 449 nm of nearly equal intensity. This pattern of the B-band absorption is also very typical for porphyrin dimers.[3,7,12]

These results initiated our interest in expanding the coupling reactions promoted by PIFA. We found that PIFA was indeed a very good coupling reagent. For example, treatment of other zinc(II) 5-fluoroalkyl-10,20-diphenylporphyrins (**1**)[9] with 0.6 equivalents of PIFA in $CHCl_3$ at room temperature afforded the *meso,meso*-linked bisporphyrins **2** in greater than 90% isolated yield after only one minute (Scheme 1). The results are listed in Table 1.

Table 1. Synthesis of dimeric porphyrins with PIFA or PIDA at room temperature.

| Entry | Compd. | Iodine(III) reagent | Solvent | Product | Yield [%] (time)[a] |
|---|---|---|---|---|---|
| 1 | **Zn-1a** | PIFA | $CHCl_3$ | **Zn-2a** | 95 (≈1 min) |
| 2 | **Zn-1b** | PIFA | $CHCl_3$ | **Zn-2b** | 93 (≈1 min) |
| 3 | **Zn-1c** | PIFA | $CHCl_3$ | **Zn-2c** | 95 (≈1 min) |
| 4 | **Zn-1d** | PIFA | $CHCl_3$ | **Zn-2d** | 92 (≈1 min) |
| 5 | **Zn-1e** | PIFA | $CHCl_3$ | **Zn-2e** | 95 (≈1 min) |
| 6 | **Zn-3aa** | PIFA | $CHCl_3$ | **Zn-4aa** | 98 (≈1 min) |
| 7 | **Zn-3ac** | PIFA | $CHCl_3$ | **Zn-4ac** | 95 (≈1 min) |
| 8 | **Zn-3ad** | PIFA | $CHCl_3$ | **Zn-4ad** | 95 (≈1 min) |
| 9 | **Zn-3ae** | PIFA | $CHCl_3$ | **Zn-4ae** | 98 (≈1 min) |
| 10 | **Zn-3af** | PIFA | $CHCl_3$ | **Zn-4af** | 95 (≈1 min) |
| 11 | **Zn-3bb** | PIFA | $CHCl_3$ | **Zn-4bb** | 95 (≈1 min) |
| 12 | **Zn-3aa** | PIFA | THF | **Zn-4aa** | 30[b] (48 h) |
| 13 | **Pd-3aa** | PIFA | $CHCl_3$ | **Pd-4aa** | 90 (10 min) |
| 14 | **Pd-3aa** | PIFA | THF | – | – (48 h)[c] |
| 15 | **Cu-3aa** | PIFA | $CHCl_3$ | **Cu-4aa** | 90 (5 min) |
| 16 | **Cu-3aa** | PIFA | THF | – | – (48 h)[c] |
| 17 | **Ni-3aa** | PIFA | $CHCl_3$ | **Ni-4aa** | >90 (5 min) |
| 18 | **Ni-3aa** | PIFA | THF | – | – (48 h)[c] |
| 19 | **Zn-3aa** | PIDA | $CHCl_3$ | **Zn-4aa** | 98 (2.5 h) |
| 20 | **Zn-3aa** | PIDA | THF | **Zn-4aa** | 30[b] (48 h) |
| 21 | **Ni-3aa** | PIDA | $CHCl_3$ | **Ni-4aa** | trace (48 h) |
| 22 | **Ni-3aa** | PIDA | THF | – | –[c] (48 h) |
| 23 | **Cu-3aa** | PIDA | $CHCl_3$ | **Cu-4aa** | trace (48 h) |

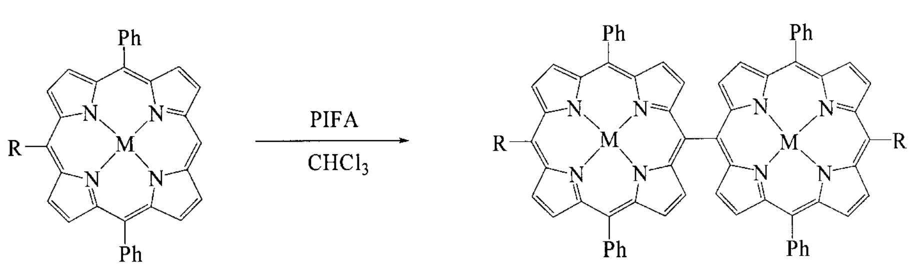
[a] Isolated yields. [b] Together with recovery of 70% of the starting porphyrin. [c] No reaction.

Interestingly, this PIFA treatment can be applied to other metallated non-fluorinated 5,10,20-triarylporphyrins. The coupling procedure is also very simple: just treating metalloporphyrins **3** with 0.6 equivalents of PIFA in $CHCl_3$ at room temperature for one to several minutes affords the *meso,meso*-linked porphyrins in excellent yields (Scheme 2 and Table 1). All the bisporphyrins were fully characterised by their $^1$H NMR, mass and UV/Vis spectra. Notably, the zincated bisporphyrin, such as **Zn-4aa**, can be demetallated smoothly with concentrated HCl, while **Cu-4aa** and **Ni-4aa** can be demetallated with neat $H_2SO_4$ quantitatively. The spectroscopic data of the resulting free-base bisporphyrins agree very well with the reported values.[6]

It is worth noting that the solvent plays an important role in the reaction. When THF was used as the solvent instead of $CHCl_3$, for example with **Zn-3aa**, the reaction was not complete even after 48 h (Table 1, entry 12), whereas for other metalloporphyrins the coupling reaction did not even occur in the same period (Table 1, entries 14, 16 and 18). This might be due to the coordination of THF rather than PIFA to the central metal, thus resulting in low or no coupling.[7]

In order to compare our coupling method with PIFA with that promoted by $Ag^I$ (Osuka's method),[5] the same reactions were also performed in the presence of $AgPF_6$ under otherwise identical reaction conditions. As shown in Table 2, when using $AgPF_6$ as the sole coupling reagent only trace amounts of coupling products were detected for zincated porphyrins, even after 24 h (entries 1–5), while for other metallated porphyrins, such as **Cu-3aa**, **Ni-3aa** and **Pd-3aa**, no products were detected after 24 h (entries 6–8). The addition of $I_2$ accelerated the reaction markedly;[5] thus, for zincated porphyrins such as **Zn-3aa**, **Zn-3ac**, **Zn-3ad**, **Zn-3ae** and **Zn-3af**, the coupling products were obtained within 15 min in 60–80% yields (entries 1–5, last column), whereas for **Cu-3aa**, **Ni-3aa** and **Pd-3aa**, under the same conditions, the coupling products were isolated in only low yields, even after 24 h (entries 6–8, last column). These results show that PIFA is better than $Ag^I$ in the porphyrin-coupling reactions.

Other iodine(III) reagents such as $PhI(OAc)_2$ (PIDA)[13] have a similar effect in this coupling reaction with zincated porphyrin. Thus, mixing **Zn-3aa** with one equivalent of PIDA in $CHCl_3$ at room temperature for 2.5 h afforded the coupling product **Zn-4aa** quantitatively, whereas for other metalloporphyrins, such as **Cu-3aa** and **Ni-3aa**, only trace



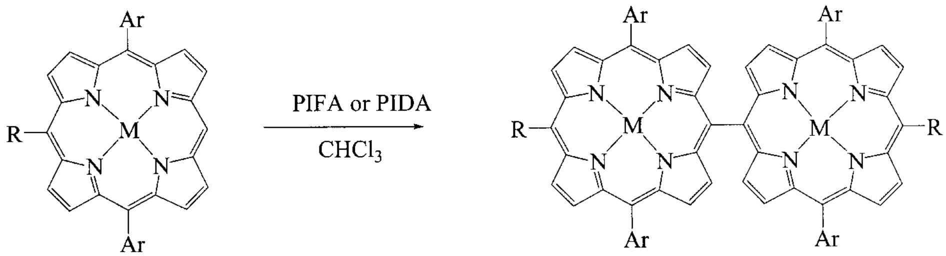

**1** M = Zn

R = $CF_3$ (**a**)
= $ClC_2F_4$- (**b**)
= $ClC_4F_8$- (**c**)
= $C_6F_{13}$- (**d**)
= $C_2F_4OC_2F_4SO_2F$ (**e**)

**2** M = Zn

Scheme 1.



**3** M = Zn, Cu, Ni, Pd

**4** M = Zn, Cu, Ni, Pd

Ar = $C_6H_5$- **(a)**
= *p*-Cl-$C_6H_4$- **(b)**

R = $C_6H_5$- **(a)**
= *p*-Cl-$C_6H_4$- **(b)**
= *p*-$CF_3$-$C_6H_4$- **(c)**
= *p*-$CH_3O$-$C_6H_4$- **(d)**
= *p*-$CH_3$-$C_6H_4$- **(e)**
= Br **(f)**

Scheme 2.

Table 2. Comparison of the reaction time and yield with PIFA and Ag[I].

| Entry | Compd. | Yield [%] (time)[a] | Yield [%] (time)[b] | Yield [%] (time)[c] |
|---|---|---|---|---|
| 1 | **Zn-3aa** | 98 (≈1 min) | trace (24 h) | 70 (≈5 min) |
| 2 | **Zn-3ac** | 95 (≈1 min) | trace (24 h) | 80 (≈15 min) |
| 3 | **Zn-3ad** | 95 (≈1 min) | trace (24 h) | 75 (≈5 min) |
| 4 | **Zn-3ae** | 98 (≈1 min) | trace (24 h) | 70 (≈5 min) |
| 5 | **Zn-3af** | 95 (≈1 min) | trace (24 h) | 60 (≈5 min) |
| 6 | **Pd-3aa** | 90 (10 min) | –[d] (24 h) | –[e] (24 h) |
| 7 | **Cu-3aa** | 90 (5 min) | –[d] (24 h) | –[e] (24 h) |
| 8 | **Ni-3aa** | >90 (5 min) | –[d] (24 h) | –[e] (24 h) |

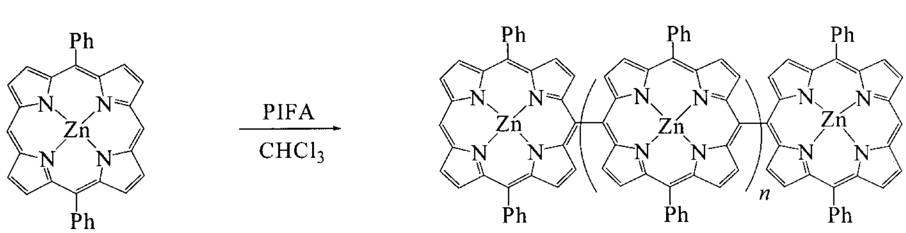
[a] With 0.6 equiv. PIFA as the oxidative reagent. [b] With 2 equiv. $AgPF_6$ as the oxidative reagent under otherwise identical reaction conditions (same scale, temperature and solvent). [c] With 2 equiv. of $I_2$ under otherwise identical conditions to b. [d] No reaction. [e] The reaction mixture was too complex to be separated and characterised.

amounts of coupling products were detected even after 48 h (Table 1, entries 19, 21 and 23). As expected, the reaction did not take place in THF (Table 1, entry 22).

When zincated 5,15-diphenylporphyrin, which has two free *meso* positions, was treated with PIFA, several porphyrin oligomers were obtained. For example, treatment of **5**[14] with PIFA (0.3 equiv.) in chloroform for 30 min, followed by standard chromatographic purification, gave **6a** (17%), **6b** (16%), **6c** (11%) and **6d** (7%) along with recovery of the starting porphyrin (41%; Scheme 3). The oligomeric porphyrin arrays were easily separated by standard chromatography. All the oligomers were fully characterised by MS and UV/Vis and $^1$H NMR spectroscopy. Additionally, to confirm the structure, a direct observation of **6a**, **6c** and **6d** was performed by atomic force microscopy (AFM). As exemplified for **6c**, the depth of the substrate is 3.5 nm, which is consistent with the molecular size of **6c** estimated by a semi-empirical molecular orbital optimisation (3.3 nm).[5d] The product distributions depend on the amount of PIFA used: the use of one or more equivalents of PIFA led to decomposition of the porphyrins and lower yields of the oligomeric porphyrin arrays under otherwise identical reaction conditions. Employing less than 0.3 equiv. of PIFA increased the yield of **6a**, but lowered the conversion of **5**.

Significantly, treatment of **7**,[9] with 0.6 equivalents of PIFA in chloroform for 1 min gave the porphyrin dimer **8** quantitatively without any oligomers (Scheme 4), probably due to the severe steric congestion of the neighbouring β-fluoroalkyl substituent in porphyrin **7**.

The most probable reaction mechanism, similar to that prompted by Ag[I],[5] is through the radical cation generated from the oxidation of porphyrin by PIFA.[10b] In $CHCl_3$, the porphyrin radical cation is prone to couple to itself to

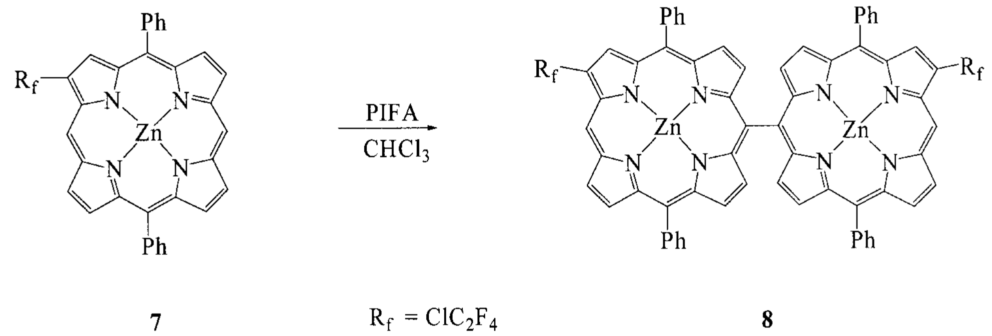


**5**

**6** *n* = 0 **(a)** (17%)
= 1 **(b)** (16%)
= 2 **(c)** (11%)
= 3 **(d)** (7%)

Scheme 3.



Scheme 4.

form the dimer product rather than react with a neutral porphyrin, as in the DDQ-induced coupling reaction.[7] This explanation was supported by the following experiment: a solution of equivalent amounts of **Zn-3aa** and **Ni-3aa** in $CHCl_3$ was treated with PIFA, **Zn-4aa** was formed immediately but **Ni-3aa** was unchanged. As the reaction progressed further, **Ni-4aa** then formed.

In summary, we have presented a very facile and efficient entry to *meso,meso*-linked porphyrin arrays including fluoroalkyl ($CF_3$, $ClC_2F_4$, $ClC_4F_8$, $C_6F_{13}$, etc.) and aryl substituents promoted by iodine(III) reagents. Compared to $Ag^I$, the iodine(III) reagents have a wider range of applications: good results were obtained not only for zincated porphyrins but also for copper(II), nickel(II) and palladium(II) porphyrins.

## Experimental Section

**Starting Materials:** The iodine(III) reagents PIFA[10] and $PhI(OAc)_2$[13] were prepared by literature methods. 5,10,20-Triphenylporphyrin (**3aa**) and the corresponding zinc(II) and nickel(II) complexes were synthesised by the previous methods.[15] Zinc(II) 5-(4-methoxyphenyl)-10,20-diphenylporphyrin (**Zn-3ad**)[7] and zinc(II) 5-bromo-10,20-diphenylporphyrin (**Zn-3af**)[16] were also prepared according to the literature methods.

**Compound Zn-1a:** Following the general trifluoromethylation procedure,[17] a sample of zinc(II) 5-iodo-10,20-diphenylporphyrin (65 mg, 0.1 mmol), $FSO_2CF_2CO_2Me$ (58 µL, 1 mmol) and CuI (190 mg, 1 mmol) in DMF (3 mL) and HMPA (3 mL) was stirred at 100 °C for 2 h. After the mixture had cooled down to room temperature, $CH_2Cl_2$ (50 mL) was added and the mixture was washed with water. The organic phase was separated and dried ($Na_2SO_4$). The solvent was removed under reduced pressure to afford a purple solid. The crude product was then purified by column chromatography [200–300 mesh silica gel, $CH_2Cl_2$/hexanes (1:1)] to give **Zn-1a** (90%, 53 mg). $^1H$ NMR ($CDCl_3$): $\delta$ = 10.18 (s, 1 H, *meso*), 9.78 (dd, $J$ = 3.1, 2.8 Hz, 2 H, β), 9.31 (d, $J$ = 4.8 Hz, 2 H, β), 9.09 (d, $J$ = 4.6 Hz, 2 H, β), 8.98 (d, $J$ = 4.6 Hz, 2 H, β), 8.20 (m, 4 H, Ph), 7.82 (m, 6 H, Ph) ppm. $^{19}F$ NMR ($CDCl_3$): $\delta$ = –34.48 (t, $J$ = 3 Hz, 3F). MS (ESI): $m/z$ = 592.0 [$M^+$]. MS (MALDI): $m/z$ = 592.6 [$M^+$]. UV/Vis: $\lambda_{max}$ = 410 nm, 541, 575. HRMS (MALDI): calcd. for $C_{33}H_{19}F_3N_4Zn$ 592.0848; found 592.0855.

**5,10,20-Triphenylporphyrinatocopper(II) (Cu-3aa):** A suspension of $Cu(OAc)_2$ (2.5 mmol) in methanol (20 mL) was added to a solution of **3aa** (0.25 mmol) in $CH_2Cl_2$ (100 mL). Then, the mixture was stirred at room temperature for 1 h. After washing with water, the organic layer was dried with $Na_2SO_4$ and then on a rotary evaporator to give **Cu-3aa** (135 mg, 90%). UV/Vis: $\lambda_{max}$ = 409 nm, 532. MS (MALDI): $m/z$ = 599.1 (calcd. for $C_{38}H_{24}CuN_4$: 599.1). HRMS (MALDI): calcd. for $C_{38}H_{24}CuN_4$ 599.1292; found 599.1318.

**5,10,20-Triphenylporphyrinatopalladium(II) (Pd-3aa):** A suspension of $Pd(OAc)_2$ (2.5 mmol) in methanol (20 mL) was added to a solution of **3aa** (0.25 mmol) in $CH_2Cl_2$ (100 mL). Then, the mixture was stirred at room temperature for 24 h. The resulting red solution was washed with water and the organic layer was dried with $Na_2SO_4$ and then on a rotary evaporator to give **Pd-3aa** (128 mg, 80%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 10.20 (s, 1 H, *meso*), 9.25 (d, $J$ = 4.7 Hz, 2 H, β), 8.97 (d, $J$ = 5.1 Hz, 2 H, β), 8.86 (dd, $J$ = 5.2, 4.5 Hz, 4 H, β), 8.19 (m, 6 H, Ph), 7.75 (m, 9 H, Ph). UV/Vis: $\lambda_{max}$ = 409 nm, 517, 548. MS (MALDI): $m/z$ = 642.1 (calcd. for $C_{38}H_{24}N_4Pd$: 642.1). HRMS (MALDI): calcd. for $C_{38}H_{24}N_4Pd$ 642.1030; found 642.1057.

**10,20-Diphenyl-5-[4-(trifluoromethyl)phenyl]porphyrinatozinc(II) (Zn-3ac):** According to Lindsey's general method for the synthesis of asymmetric porphyrins,[18] a solution of EtMgBr (125 mL, 125 mmol) in THF was added slowly to a stirred solution of 5-[4-(trifluoromethyl)phenyl]dipyrromethane (7.25 g, 25 mmol)[19] in toluene (500 mL) under $N_2$. The resulting brown solution was stirred for 30 min at room temperature, then a solution of acid chloride (8.75 g, 62.5 mmol) in toluene (62.5 mL) was added over 10 min. The mixture was stirred for an additional 10 min. The reaction was quenched by adding satd. aq. $NH_4Cl$ (400 mL). Ethyl acetate (500 mL) was then added. The organic phase was washed successively with water and brine and then dried ($Na_2SO_4$). The solvent was removed and the crude product was then purified by column chromatography and the main fractions combined to give the diacyldipyrromethane 1,9-dibenzoyl-5-[4-(trifluoromethyl)phenyl]-dipyrromethane (6.2 g, 50%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 11.81 (br. s, 2 H), 7.76–7.38 (m, 14 H), 6.57 (s, 2 H), 5.97 (s, 2 H), 5.79 (s, 1 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 184.7, 144.5, 140.1, 138.0, 131.8, 131.3, 129.6, 129.3, 128.1, 125.8 (m, $CF_3$), 120.9, 111.4, 44.9 ppm. A sample of the diacyldipyrromethane (3.6 mmol) was then dissolved in dry THF/methanol (10:1, 160 mL) at room temperature and $NaBH_4$ (72 mmol, 20 mol equiv.) was added in small portions (ca. 0.5 g every 2 min) with rapid stirring. The progress of the reduction was monitored by TLC analysis. After the reaction was complete, the reaction mixture was poured into a stirred mixture of satd. aq. $NH_4Cl$ (200 mL) and $CH_2Cl_2$ (400 mL). The organic phase was separated then washed with water and dried ($Na_2SO_4$), and removal of the solvent yielded the dicarbinol as a foam-like solid. The dicarbinol was then dissolved in acetonitrile (1.44 L) and dipyrromethane[20] (3.6 mmol) was added. The mixture was stirred for 5 min, and trifluoroacetic acid (43.2 mmol) was added. After 10 min, DDQ (10.8 mmol) was added and the mixture was stirred at room temperature for 1 h. Then, triethylamine was added and the solvent was removed. The residue was dissolved in $CH_2Cl_2$ (200 mL) and filtered though a pad of $SiO_2$. The mainly purple band was collected to give 10,20-diphenyl-5-[4-(trifluoromethyl)phenyl]porphyrin (**3ac**; 610 mg, 28%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.24 (s, 1 H, *meso*), 9.35 (d, $J$ = 5 Hz, 2 H, β), 9.04 (d, $J$ = 5 Hz, 2 H, β), 8.95 (d, $J$ = 4.9 Hz, 2 H, β), 8.81 (d, $J$ = 4.9 Hz, 2 H, β), 8.35 (d, $J$ = 8.2 Hz, 2 H, $p$-$CF_3$-$C_6H_4$), 8.26 (m, 4 H, Ph), 8.03 (d, $J$ = 8.1 Hz, 2 H, $p$-$CF_3$-$C_6H_4$), 7.81 (m, 6 H, Ph), –2.98 (s, 1 H, NH) ppm. UV/Vis: $\lambda_{max}$ = 411 nm, 508, 541, 581, 636. MS (MALDI): $m/z$ = 606.2. $C_{39}H_{25}F_3N_4{\cdot}H_2O$: calcd. C 74.99, H 4.36, N 8.97; found 75.04, H 4.46, N 8.87. Treatment of **3ac** (100 mg, 0.165 mmol) with $Zn(OAc)_2$ (363 mg, 1.65 mmol) in $CH_2Cl_2$ (100 mL) and $CH_3OH$ (10 mL) at room temperature afforded **Zn-3ac** (105 mg, 95%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.17 (s, 1 H, *meso*), 9.34 (m, 2 H, β), 9.07 (d, $J$ = 3.6 Hz, 2 H, β), 9.02 (d, $J$ = 4.5 Hz, 2 H, β), 8.90 (d, $J$ = 4.9 Hz, 2 H, β), 8.35 (d, $J$ = 7.8 Hz, 2 H, $p$-$CF_3$-$C_6H_4$), 8.24 (m, 4 H, Ph), 8.04 (d, $J$ = 7.9 Hz, 2 H, $p$-$CF_3$-$C_6H_4$), 7.79 (m, 6 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 412 nm, 541. MS (MALDI): $m/z$ = 668.1. $C_{39}H_{23}F_3N_4Zn$: calcd. C 69.91, H 3.46, N 8.36; found C 69.95, H 4.13, N 8.12.

**5-(4-Methylphenyl)-10,20-diphenylporphyrinatozinc(II) (Zn-3ae):** A sample of 1,9-dibenzoyl-5-(4-methylphenyl)dipyrromethane[21] (3.6 mmol) was dissolved in dry THF/methanol (10:1, 160 mL) at room temperature. Then, $NaBH_4$ (72 mmol, 20 mol equiv.) was added in small portions (ca. 0.5 g every 2 min) with rapid stirring. The progress of the reduction was monitored by TLC analysis. After the reaction was complete, the reaction mixture was poured into a stirred mixture of satd. aq. $NH_4Cl$ (200 mL) and $CH_2Cl_2$ (400 mL). The organic phase was separated then washed with water and dried ($Na_2SO_4$), and removal of the solvent yielded the dicarbinol as a foam-like solid. The dicarbinol was then dissolved in acetonitrile (1.44 L) and dipyrromethane (3.6 mmol) was added. The mixture was stirred for 5 min, and trifluoroacetic acid (43.2 mmol) was added. After 10 min, DDQ (10.8 mmol) was added and the mixture was stirred at room temperature for 1 h. Then, triethylamine was added and the solvent was removed. The residue was dissolved in $CH_2Cl_2$ (200 mL) and filtered through a pad of $SiO_2$ and the mainly purple band was collected to give 5-(4-methylphenyl)-10,20-diphenylporphyrin (**3ae**; 496 mg, 25%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.23 (s, 1 H, *meso*), 9.35 (d, $J$ = 4.8 Hz, 2 H, β), 9.04 (d, $J$ = 4.6 Hz, 2 H, β), 8.92 (s, 4 H, β), 8.27 (m, 4 H, Ph), 8.12 (d, 8.4 Hz, 2 H, $p$-$CH_3$-$C_6H_4$), 7.80 (m, 6 H, Ph), 7.57 (d, $J$ = 7.6 Hz, 2 H, $p$-$CH_3$-$C_6H_4$), 2.73 (s, 3 H, $CH_3$), –2.99 (s, 2 H, NH). UV/Vis: $\lambda_{max}$ = 411 nm, 509, 542, 582, 639. MS (MALDI): $m/z$ = 552.2 (calcd. for $C_{39}H_{28}N_4$: 552.2). $C_{39}H_{28}N_4$: calcd. C 84.76, H 5.11, N 10.14; found C 84.36, H 5.42, N 10.24. Accordingly, reaction of **3ae** (100 mg, 0.181 mmol) with $Zn(OAc)_2$ (398 mg, 1.81 mmol) in $CH_2Cl_2$ (100 mL) and $CH_3OH$ (10 mL) at room temperature produced the title compound **Zn-3ae** (111 mg, 100%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.85 (s, 1 H, *meso*), 9.12 (d, $J$ = 4.9 Hz, 2 H, β), 9.03 (dd, $J$ = 5.0, 4.9 Hz, 4 H, β), 8.95 (d, $J$ = 4.7 Hz, 2 H, β), 8.22 (m, 4 H, Ph), 8.13 (d, $J$ = 7.6 Hz, 2 H, $p$-$CH_3$-$C_6H_4$), 7.80 (m, 6 H, Ph), 7.59 (d, $J$ = 7.6 Hz, 2 H, $p$-$CH_3$-$C_6H_4$), 2.76 (s, 3 H, $CH_3$) ppm. UV/Vis: $\lambda_{max}$ = 413 nm, 542. MS (MALDI): $m/z$ = 614.1 (calcd. for $C_{39}H_{26}N_4Zn$: 614.1). $C_{39}H_{26}N_4Zn$: calcd. C 76.04, H 4.25, N 9.09; found C 75.83, H 4.80, N 8.92. HRMS (MALDI): calcd. for $C_{39}H_{26}N_4Zn$ 614.1443; found 614.1428.

**5,10,20-Tris(4-chlorophenyl)porphyrinatozinc(II) (Zn-3bb):** In a similar manner, 1,9-bis(4-chlorobenzoyl)-5-(4-chlorophenyl)dipyrromethane was obtained from 5-(4-chlorophenyl)dipyrromethane (6.4 g, 25 mmol),[22] EtMgBr (125 ml, 125 mmol) and the acid chloride (8.75 g, 62.5 mmol) in 50% yield (6.6 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 12.44 (s, 2 H), 7.67 (d, $J$ = 8.0 Hz, 4 H), 7.58 (d, $J$ = 8.0 Hz, 2 H), 7.39 (d, $J$ = 7.6 Hz, 6 H), 6.47 (m, 2 H), 5.96 (m, 2 H), 5.70 (s, 1 H) ppm. MS (MALDI): $m/z$ = 532.1 (calcd. for $C_{29}H_{19}Cl_3N_2O_2$: 532.05). Then, a sample of the diacyldipyrromethane (3.6 mmol) was dissolved in dry THF/methanol (10:1, 160 mL) at room temperature and $NaBH_4$ (72 mmol, 20 mol equiv.) was added in small portions (ca. 0.5 g every 2 min) with rapid stirring. The progress of the reduction was monitored by TLC analysis. After the reaction was complete, the reaction mixture was poured into a stirred mixture of satd. aq. $NH_4Cl$ (200 mL) and $CH_2Cl_2$ (400 mL). The organic phase was separated then washed with water, dried ($Na_2SO_4$), and removal of the solvent gave the dicarbinol as a foam-like solid. This was then dissolved in acetonitrile (1.44 L) and dipyrromethane (3.6 mmol) was added. The mixture was stirred for 5 min, and trifluoroacetic acid (43.2 mmol) was added. After 10 min, DDQ (10.8 mmol) was added and the mixture was stirred at room temperature for 1 h. Then, triethylamine was added and the solvent was removed. The residue was dissolved in $CH_2Cl_2$ (200 mL) and filtered though a pad of $SiO_2$ and the mainly purple band was collected to give 5,10,20-tris(4-chlorophenyl)porphyrin (**3bb**) (460 mg, 20%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.24 (s, 1 H, *meso*), 9.35 (d, $J$ = 5.1 Hz, 2 H, β), 8.99 (d, $J$ = 4.8 Hz, 2 H, β), 8.89 (d, $J$ = 4.8 Hz, 2 H, β), 8.86 (d, $J$ = 4.8 Hz, 2 H, β), 8.15 (m, 6 H, $p$-Cl-$C_6H_4$), 7.76 (m, 6 H, $p$-Cl-$C_6H_4$), –3.06 (s, 2 H, NH) ppm. UV/Vis: $\lambda_{max}$ = 412 nm, 508, 542, 582, 636. MS (MALDI): $m/z$ = 640.1. (calcd. for $C_{38}H_{23}Cl_3N_4$: 640.1). HRMS (MALDI): calcd. for $C_{38}H_{23}Cl_3N_4{\cdot}H^+$ 641.1061; found 641.1088. Treatment of **3bb** (100 mg, 0.156 mmol) with $Zn(OAc)_2$ (343 mg, 1.56 mmol) in $CH_2Cl_2$ (100 mL) and $CH_3OH$ (10 mL) at room temperature afforded **Zn-3bb** (98 mg, 90%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.17 (s, 1 H, *meso*), 9.34 (d, $J$ = 4.0 Hz, 2 H, β), 9.03 (d, $J$ = 4.6 Hz, 2 H, β), 8.97 (dd, $J$ = 4.8, 4.6 Hz, 4 H, β), 8.15 (m, 6 H, $p$-Cl-$C_6H_4$), 7.76 (m, 6 H, $p$-Cl-$C_6H_4$) ppm. UV/Vis: $\lambda_{max}$ = 413 nm, 541. MS (MALDI): $m/z$ = 702.0 (calcd. for $C_{38}H_{21}Cl_3N_4Zn$: 702.0). HRMS (MALDI): calcd. for $C_{38}H_{21}Cl_3N_4Zn$ 702.0118; found 702.0145.

**Synthesis of Porphyrin Dimers**

**Compound Zn-2a:** A sample of zinc(II) 10,20-diphenyl-5-(trifluoromethyl)porphyrin (30 mg, 0.05 mmol) and PIFA (13 mg, 0.03 mmol) in 30 mL of $CHCl_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, $CH_2Cl_2$/hexanes = 1:1) to give **Zn-2a** (28 mg, 95%). $^1$H NMR ($CDCl_3$): $\delta$ = 9.82 (dd, $J$ = 2.7 Hz, 3 Hz, 4 H, β), 9.10 (d, $J$ = 5.0 Hz, 4 H, β), 8.60 (d, $J$ = 4.7 Hz, 4 H, β), 8.18 (m, 8 H, Ph), 8.10 (d, $J$ = 4.7 Hz, 4 H, β), 7.67 (m, 12 H, Ph) ppm. $^{19}$F NMR ($CDCl_3$): $\delta$ = –35.11 (s) ppm. MS (MALDI): $m/z$ = 1182.1 [$M^+$]. UV/Vis: $\lambda_{max}$ = 416 nm, 449, 558, 585. HRMS (MALDI): calcd. for $C_{66}H_{36}N_8F_6Zn_2$ 1182.1545; found 1182.1582.

**Compound Zn-2b:** A sample of zinc(II) 5-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (66 mg, 0.1 mmol) and PIFA (26 mg, 0.06 mmol) in 30 mL of $CHCl_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, $CH_2Cl_2$/hexanes = 1:1) to give **Zn-2b** (61 mg, 93%). $^1$H NMR (300 MHz,$CDCl_3$, TMS): $\delta$ = 9.74 (d, $J$ = 2.7 Hz, 4 H, β), 9.10 (d,

$J$ = 5.4 Hz, 4 H, β), 8.60 (d, $J$ = 4.2 Hz, 4 H, β), 8.20 (d, $J$ = 6.6 Hz, 8 H, Ph), 8.10 (d, $J$ = 5.1 Hz, 4 H, β), 7.68 (m, 12 H, Ph) ppm. $^{19}$F NMR (282 MHz,CDCl$_3$, F11): $\delta$ = –63.48 (m, 4 F), –75.18 (s, 4 F) ppm. MS (MALDI): $m/z$ = 1314.1 with an isotope distribution pattern that is the same as the calculated one. UV/Vis: $\lambda_{max}$ = 585 nm, 557, 449, 415. HRMS (MALDI): $m/z$ calcd. for $C_{68}H_{37}Cl_2F_8N_8Zn_2$ [MH$^+$] 1315.0968; found 1315.1007.

**Compound Zn-2c:** A sample of zinc(II) 5-(4-chlorooctafluorobutyl)-10,20-diphenylporphyrin (38 mg, 0.05 mmol) and PIFA (13 mg, 0.03 mmol) in 30 mL of CHCl$_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$/hexanes = 1:1) to give **Zn-2c** (36 mg, 95%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.66 (m, 12 H, Ph), 8.09 (d, $J$ = 4.5 Hz, 4 H, β), 8.18 (d, $J$ = 5.1 Hz, 8 H, Ph), 8.60 (d, $J$ = 4.8 Hz, 4 H, β), 9.10 (d, $J$ = 5.1 Hz, 4 H, β), 9.69 (s, 4 H, β) ppm. $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ = –67.25 (t, $J$ = 14.66 Hz, 4 F), –76.72 (s, 4 F), –113.9 (m, 4 F), –118.96 (t, $J$ = 13.8 Hz, 4 F) ppm. MS (MALDI): $m/z$ = 1514.1 with an isotope distribution pattern that is the same as the calculated one. UV/Vis: $\lambda_{max}$ = 586 nm, 557, 449, 415. HRMS (MALDI): calcd. for $C_{72}H_{36}Cl_2F_{16}N_8Zn_2\cdot H^+$ 1515.0840; found 1515.0845.

**Compound Zn-2d:** A sample of zinc(II) 5-perfluorohexyl-10,20-diphenylporphyrin (21 mg, 0.025 mmol) and PIFA (7 mg, 0.015 mmol) in 20 mL of CHCl$_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$/hexanes = 1:1) to give **Zn-2d** (19 mg, 92%). $^1$H NMR (CDCl$_3$): $\delta$ = 9.73 (s, 4 H, β), 9.16 (d, $J$ = 4.7 Hz, 4 H, β), 8.65 (d, $J$ = 4.7 Hz, 4 H, β), 8.23 (s, 8 H, Ph), 8.14 (d, $J$ = 3.1 Hz, 4 H, β), 7.71 (m, 12 H, Ph) ppm. $^{19}$F NMR (CDCl$_3$): $\delta$ = –77.06 (s, 4 F), –80.82 (m, 6 F), –114.9 (s, 4 F), –121.1 (m, 4 F), –122.47 (s, 4 F), –126.03 (s, 4 F) ppm. MS (MALDI): $m/z$ = 1682.1 [M$^+$]. UV/Vis: $\lambda_{max}$ = 414 nm, 449, 558, 586. HRMS (MALDI): calcd. for $C_{76}H_{36}F_{26}N_8Zn_2\cdot H^+$ 1683.1303; found 1683.1281. $C_{76}H_{36}F_{26}N_8Zn_2$: calcd. C 54.09, H 2.14, N 6.6; found C 53.73, H 2.67, N 6.02.

**Compound Zn-2e:** A sample of zinc(II) 5-(3-oxa-ω-fluorosulfonyl perfluoropentanyl)-10,20-diphenylporphyrin (21 mg, 0.025 mmol) and PIFA (7 mg, 0.015 mmol) in 20 mL of CHCl$_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$/hexanes = 1:1) to give **Zn-2e** (19 mg, 95%). $^1$H NMR (CDCl$_3$): $\delta$ = 9.72 (s, 4 H, β), 9.12 (d, $J$ = 4.8 Hz, 4 H, β), 8.62 (d, $J$ = 4.7 Hz, 4 H, β), 8.21 (d, $J$ = 5.7 Hz, 8 H, Ph), 8.11 (d, $J$ = 4.4 Hz, 4 H, β), 7.69 (m, 12 H, Ph) ppm. $^{19}$F NMR (CDCl$_3$): $\delta$ = 45.64 (m, 2 F), –80.44 (s, 4 F), –81.3 (m, 4 F), –81.79 (s, 4 F), –112.1 (m, 4 F) ppm. MS (MALDI): $m/z$ = 1642.1 [M$^+$]. UV/Vis: $\lambda_{max}$ = 414 nm, 448, 556, 585. HRMS (MALDI): calcd. for $C_{72}H_{36}F_{18}N_8O_6S_2Zn_2\cdot H^+$ 1643.0568; found 1643.0543.

**Compound Zn-4aa. Method A:** A sample of 5,10,20-triphenylporphyrinatozinc(II) (30 mg, 0.05 mmol) and PIFA (13 mg, 0.03 mmol) in 30 mL of CHCl$_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$/hexanes = 1:1) to give **Zn-4aa** (29 mg, 98%).

**Method B:** A sample of 5,10,15-triphenylporphyrinatozinc(II) (30 mg, 0.05 mmol) and PIDA (18 mg, 0.05 mmol) in 30 mL of CHCl$_3$ was stirred at room temperature for 4 h. The mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography through silica gel to yield pure coupling product **Zn-4aa**[5b] (29 mg, 98%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.05 (d, $J$ = 4.5 Hz, 4 H, β), 9.02 (d, $J$ = 4.8 Hz, 4 H, β), 8.69 (d, $J$ = 4.7 Hz, 4 H, β), 8.34–8.23 (m, 12 H, Ph), 8.15 (d, $J$ = 4.8 Hz, 4 H, β), 7.832–7.67 (m, 18 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 559 nm, 454, 417. MS (MALDI): $m/z$ = 1198.3 with an isotope distribution pattern that is the same as the calculated one.

**Compound Zn-4ac:** Following the same procedure for **Zn-4aa** described in Method A, 10,20-diphenyl-5-[4-(trifluoromethyl)phenyl]-porphyrinatozinc(II) (66 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in CHCl$_3$ for 1 min. The product was obtained as a purple solid after chromatography (silica gel, CH$_2$Cl$_2$/hexane = 1:1). Yield: 63 mg (95%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.04 (d, $J$ = 4.7 Hz, 4 H, β), 8.97 (d, $J$ = 4.6 Hz, 4 H, β), 8.70 (d, $J$ = 4.8 Hz, 4 H, β), 8.46 (d, $J$ = 8 Hz, 4 H, *p*-CF$_3$-C$_6$H$_4$), 8.23 (m, 8 H, Ph), 8.16 (d, $J$ = 4.8 Hz, 4 H, β), 8.10 (d, $J$ = 7.9 Hz, 4 H, *p*-CF$_3$-C$_6$H$_4$), 7.69 (m, 12 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 557 nm, 454, 416. MS (MALDI): $m/z$ = 1334.2 with an isotope distribution pattern that is the same as the calculated one. $C_{78}H_{44}F_6N_8Zn_2\cdot H_2O$: calcd. C 69.23, H 3.4, N 8.28; found C 69.18, H 4.29, N 7.86.

**Compound Zn-4ad:**[7] Following the same procedure for **Zn-4aa** described in Method A, 5-(4-methoxyphenyl)-10,20-diphenylporphyrinatozinc(II) (63 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in CHCl$_3$ for 1 min. The product was obtained as a purple solid after chromatography (silica gel, CH$_2$Cl$_2$/hexane = 1:1). Yield: 60 mg (95%). $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 8.88 (d, $J$ = 4.5 Hz, 4 H, β), 8.79 (d, $J$ = 4.4 Hz, 4 H, β), 8.48 (d, $J$ = 4.3 Hz, 4 H, β), 8.17 (m, 12 H, Ph, *p*-CH$_3$O-C$_6$H$_4$), 7.94 (d, $J$ = 4.6 Hz, 4 H, β), 7.70 (m,12 H, Ph), 7.39 (d, $J$ = 8.1 Hz, 4 H, *p*-CH$_3$O-C$_6$H$_4$), 4.07 (s, 6 H, CH$_3$O) ppm. UV/Vis: $\lambda_{max}$ = 559 nm, 455, 418. MS (MALDI): $m/z$ = 1258.3 with an isotope distribution pattern that is the same as the calculated one.

**Compound Zn-4ae:** Following the same procedure for **Zn-4aa** described in Method A, 5-(4-methylphenyl)-10,20-diphenylporphyrinatozinc(II) (61 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in CHCl$_3$ for 1 min. The product was obtained as a purple solid after chromatography (silica gel, CH$_2$Cl$_2$/hexane = 1:1). Yield: 60 mg (98%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.07 (d, $J$ = 4.7 Hz, 4 H, β), 9.00 (d, $J$ = 4.7 Hz, 4 H, β), 8.67 (d, $J$ = 4.4 Hz, 4 H, β), 8.23 (m, 12 H, Ph, *p*-CH$_3$-C$_6$H$_4$), 8.13 (d, $J$ = 4.8 Hz, 4 H, β), 7.67 (m, 16 H, Ph, *p*-CH$_3$-C$_6$H$_4$), 2.76 (s, 6 H, CH$_3$). UV/Vis: $\lambda_{max}$ = 417 nm, 455, 559. MS (MALDI): $m/z$ = 1226.3 (calcd. for $C_{78}H_{50}N_8Zn_2$: 1226.3). HRMS (MALDI): calcd. for $C_{78}H_{50}N_8Zn_2$ 1226.2736; found 1226.2787.

**Compound Zn-4af:**[5b,23] Following the same procedure for **Zn-4aa** described in Method A, 5-bromo-10,20-diphenylporphyrinatozinc(II) (60 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in CHCl$_3$ for 1 min. The product was obtained as a purple solid after chromatography (silica gel, CH$_2$Cl$_2$/hexane = 1:1). Yield: 57 mg (95%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.82 (d, $J$ = 4.8 Hz, 4 H, β), 9.01 (d, $J$ = 4.5 Hz, 4 H, β), 8.58 (d, $J$ = 4.9 Hz, 4 H, β), 8.17 (m, 8 H, Ph), 8.03 (d, $J$ = 4.7 Hz, 4 H, β), 7.66 (m, 12 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 561 nm, 454, 421. MS (MALDI): $m/z$ =

1202.0 with an isotope distribution pattern that is the same as the calculated one. HRMS (MALDI): calcd. for $C_{64}H_{36}Br_2N_8Zn_2{\cdot}H^+$ 1203.0085; found 1203.0127.

**Compound Zn-4bb:** Following the same procedure for **Zn-4aa** described in Method A, 5,10,20-tris(4-chlorophenyl)porphyrinatozinc(II) (70 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in $CHCl_3$ for 1 min. The product was obtained as a purple solid after chromatography (silica gel, $CH_2Cl_2$/hexane = 1:1). Yield: 66 mg (95%). $^1H$ NMR (300 MHz, [D6]DMSO): $\delta$ = 8.87 (d, $J$ = 4.6 Hz, 4 H, β), 8.84 (d, $J$ = 4.8 Hz, 4 H, β), 8.52 (d, $J$ = 5 Hz, 4 H, β), 8.26 (d, $J$ = 8.3 Hz, 4 H, $p$-Cl-$C_6H_4$), 8.19 (d, $J$ = 8.3 Hz, 8 H, $p$-Cl-$C_6H_4$), 7.95 (d, $J$ = 4.8 Hz,4 H, β), 7.89 (d, $J$ = 8.4 Hz, 4 H, $p$-Cl-$C_6H_4$), 7.75 (d, $J$ = 8.3 Hz, 8 H, $p$-Cl-$C_6H_4$) ppm. UV/Vis: $\lambda_{max}$ = 559 nm, 455, 418. MS (MALDI): $m/z$ = 1402.0 with an isotope distribution pattern that is the same as the calculated one. HRMS (MALDI): calcd. for $C_{76}H_{40}Cl_6N_8Zn_2$ 1402.0085; found 1402.0098.

**Compound Cu-4aa:** Following the same procedure for **Zn-4aa** described in Method A, 5,10,20-triphenylporphyrinatocopper(II) (60 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in $CHCl_3$ for 10 min. The product was obtained as a red-brown solid after chromatography (silica gel, $CH_2Cl_2$/hexane = 1:1). Yield: 53 mg (90%). UV/Vis: $\lambda_{max}$ = 548 nm, 447, 412. MS (MALDI): $m/z$ = 1196.3 with an isotope distribution pattern that is the same as the calculated one. **Cu-4aa** (20 mg, 0.017 mmol) was treated with several drops of neat $H_2SO_4$ in 30 mL of $CH_2Cl_2$ at room temperature for 30 min. The resulting mixture was washed with saturated aq. $NaHCO_3$ (30 mL × 2), then the organic phase was evaporated to dryness and the residue was recrystallised from $CH_2Cl_2/CH_3OH$ to give free-base bisporphyrin **4aa** (17 mg, 95%).[6] $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.93 (d, $J$ = 4.4 Hz, 4 H, β), 8.90 (d, $J$ = 4.6 Hz, 4 H, β), 8.59 (d, $J$ = 4.8 Hz, 4 H, β), 8.30–8.20 (m, 12 H, Ph), 8.08 (d, $J$ = 4.6 Hz, 4 H, β), 7.81–7.66 (m, 18 H, Ph), –2.19 (s, 4 H, NH) ppm. UV/Vis: $\lambda_{max}$ = 651 nm, 595, 524, 450, 416. MS (ESI): $m/z$ = 1075.45.

**Compound Ni-4aa:** Following the same procedure for **Zn-4aa** described in Method A, 5,10,20-triphenylporphyrinatonickel(II) (59 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in $CHCl_3$ for 10 min. The product was obtained as a red-brown solid after chromatography (silica gel, $CH_2Cl_2$/hexane = 1:1). Yield: 53 mg (90%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.82 (br. s, 8 H, β), 8.55 (br. s, 4 H, β), 8.10 (s, 8 H, Ph), 8.03 (s, 8 H, Ph + β, overlapped), 7.74 (s, 6 H, Ph), 7.64 (s, 12 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 535 nm, 444, 412. MS (MALDI): $m/z$ = 1186.3 with an isotope distribution pattern that is the same as the calculated one. **Ni-4aa** (30 mg, 0.025 mmol) was treated with several drops of neat $H_2SO_4$ in 50 ml of $CH_2Cl_2$ at room temperature for 30 min, the resulting mixture was washed with saturated aq. $NaHCO_3$ (50 mL × 3), then the organic phase was evaporated to dryness and the residue was recrystallised from $CH_2Cl_2/CH_3OH$ to give free-base bisporphyrin **4aa** (24 mg, 90%).[6]

**Compound Pd-4aa:** Following the same procedure for **Zn-4aa** described in Method A, 5,10,20-triphenylporphyrinatopalladium(II) (64 mg, 0.1 mmol) was treated with PIFA (26 mg, 0.06 mmol) in $CHCl_3$ for 10 min. The product was obtained as a red-brown solid after chromatography (silica gel, $CH_2Cl_2$/hexane = 1:1). Yield: 57 mg (90%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.89 (s, 8 H, β), 8.56 (d, $J$ = 4.8 Hz, 4 H, β), 8.24 (m, 12 H, Ph), 8.03 (d, $J$ = 4.9 Hz, 4 H, β), 7.70 (m, 18 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 531 nm, 443, 417. MS (MALDI): $m/z$ = 1277.2 with an isotope distribution pattern that is the same as the calculated one.

**Reaction Between 5,15-Diphenylporphinatozinc(II) and PIFA:** A solution of PIFA (0.074 mmol, 32 mg, 0.3 mol equiv.) in 30 mL of $CHCl_3$ was added dropwise at room temperature to a solution of 5,15-diphenylporphinatozinc(II) (**5**; 0.25 mmol, 130 mg) in 60 mL of $CHCl_3$, and the mixture was stirred for a further 30 min. The mixture was dried on a rotary evaporator and purified by flash column chromatography on silica gel using THF/hexanes as eluent to yield five fractions. The first fraction afforded the unconverted starting porphyrin **5** (53 mg, 41%), the second fraction gave **6a** (22 mg, 17%), the third fraction afforded **6b** (20 mg, 16%), the fourth fraction afforded **6c** (14 mg, 11%) and the fifth fraction afforded **6d** (9 mg, 7%).

**Dimer 6a:**[5a] $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 10.05 (s, 2 H, *meso*), 9.19 (d, $J$ = 4.2 Hz, 4 H, β), 8.83 (d, $J$ = 4.8 Hz, 4 H, β), 8.37 (d, $J$ = 4.8 Hz, 4 H, β), 8.00 (m, 8 H, Ph), 7.80 (d, $J$ = 4.8 Hz, 4 H, β), 7.43 (m, 12 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 552 nm, 445, 410. MS (MALDI): $m/z$ = 1046.2 with an isotope distribution pattern that is the same as the calculated one.

**Trimer 6b:**[24] $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 10.42 (s, 2 H, *meso*), 9.52 (d, $J$ = 4.2 Hz, 4 H, β), 9.18 (d, $J$ = 4.5 Hz, 4 H, β), 8.77 (d, $J$ = 4.5 Hz, 4 H, β), 8.69 (d, $J$ = 4.5 Hz, 4 H, β), 8.28 (m, 16 H, Ph + β, overlapped), 8.17 (d, $J$ = 4.2 Hz, 4 H, β), 7.73 (m, 18 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 562 nm, 470, 408. MS (MALDI): $m/z$ = 1568.4 with an isotope distribution pattern that is the same as the calculated one. HRMS (MALDI): calcd. for $C_{96}H_{56}N_{12}Zn_3$ 1568.2620; found 1568.2642.

**Tetramer 6c:** $^1H$ NMR (300 MHz, [D6]DMSO): $\delta$ = 10.44 (s, 2 H, *meso*), 9.57 (d, $J$ = 4.2 Hz, 4 H, β), 8.96 (d, $J$ = 4.5 Hz, 4 H, β), 8.62 (d, $J$ = 4.5 Hz, 4 H, β), 8.59 (d, $J$ = 4.5 Hz, 4 H, β), 8.53 (d, $J$ = 4.2 Hz, 4 H, β), 8.24 (m, 16 H), 8.11 (m,8 H), 7.98 (d, $J$ = 4.2 Hz, 4 H, β), 7.78 (m, 12 H, Ph), 7.64 (m, 12 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 569 nm, 481, 409. MS (MALDI): $m/z$ = 2090.4 with an isotope distribution pattern that is the same as the calculated one. HRMS (MALDI): calcd. for $C_{128}H_{74}N_{16}Zn_4$ 2090.3443; found 2090.3423.

**Pentamer 6d:** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 10.43 (s, 2 H, *meso*), 9.54 (d, $J$ = 4.1 Hz, 4 H, β), 9.20 (d, $J$ = 4.5 Hz, 4 H, β), 8.80 (m, 8 H, β), 8.73 (d, $J$ = 4.6 Hz, 4 H, β), 8.30 (m, 36 H, Ph + β), 8.20 (d, $J$ = 4.5 Hz, 4 H, β), 7.74 (m, 15 H, Ph), 7.61 (m, 15 H, Ph) ppm. UV/Vis: $\lambda_{max}$ = 571 nm, 486, 415. MS (MALDI): $m/z$ = 2615.5 with an isotope distribution pattern that is the same as the calculated one. HRMS (MALDI): calcd. for $C_{160}H_{92}N_{20}Zn_5$ 2612.4266; found 2612.4232.

**Reaction between 2-(2-Chlorotetrafluoroethyl)-5,15-diphenylporphinatozinc(II) (7) and PIFA:** A sample of 2-(2-chlorotetrafluoroethyl)-5,15-diphenylporphinatozinc(II) (**7**; 22 mg,0.03 mmol) and PIFA (8 mg, 0.02 mmol) in 20 mL of $CHCl_3$ was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water several times, the organic layer was dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, $CH_2Cl_2$/hexanes = 1:1) to give **8** as the sole product (18 mg, 95%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 10.60 (s, 2 H, *meso*), 9.53 (d, $J$ = 4.5 Hz, 2 H, β), 9.41 (s, 2 H, β), 9.13 (d, $J$ = 4.8 Hz, 2 H, β), 8.68 (d, $J$ = 1.8 Hz, 2 H, β), 8.67 (d, $J$ = 2.1 Hz, 2 H, β), 8.21 (m, 8 H, Ph), 8.09 (d, $J$ = 3.3 Hz, 2 H, β), 8.06 (d, $J$ = 5.1 Hz, 2 H, β), 7.70 (m, 12 H, Ph) ppm. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ = –68.30 (s, 4 F), –99.48 (s, 4 F) ppm. UV/Vis: $\lambda_{max}$ = 557 nm, 449, 415. MS (MALDI): $m/z$ = 1314.1 with an isotope distribution pattern that is the same as the calculated one. HRMS (MALDI): calcd. for $C_{68}H_{36}Cl_2F_8N_8Zn_2{\cdot}H^+$ 1315.0968; found 1315.0994.

**Supporting Information** (see footnote on the first page of this article): Selected characterisation data ($^{1}H$ NMR, $^{19}F$ NMR and MALDI mass spectra) for **Zn-2a–2d**, **3ac**, **Zn-4ac**, **3ae**, **Zn-4ae**, **3bb**, **Zn-4bb**, **Ni-4aa**, **Pd-4aa**, **4aa** and **6b**–**6d** and AFM images for **6c** and **6d**.

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