Supporting information

Pincer-Porphyrin Hybrids

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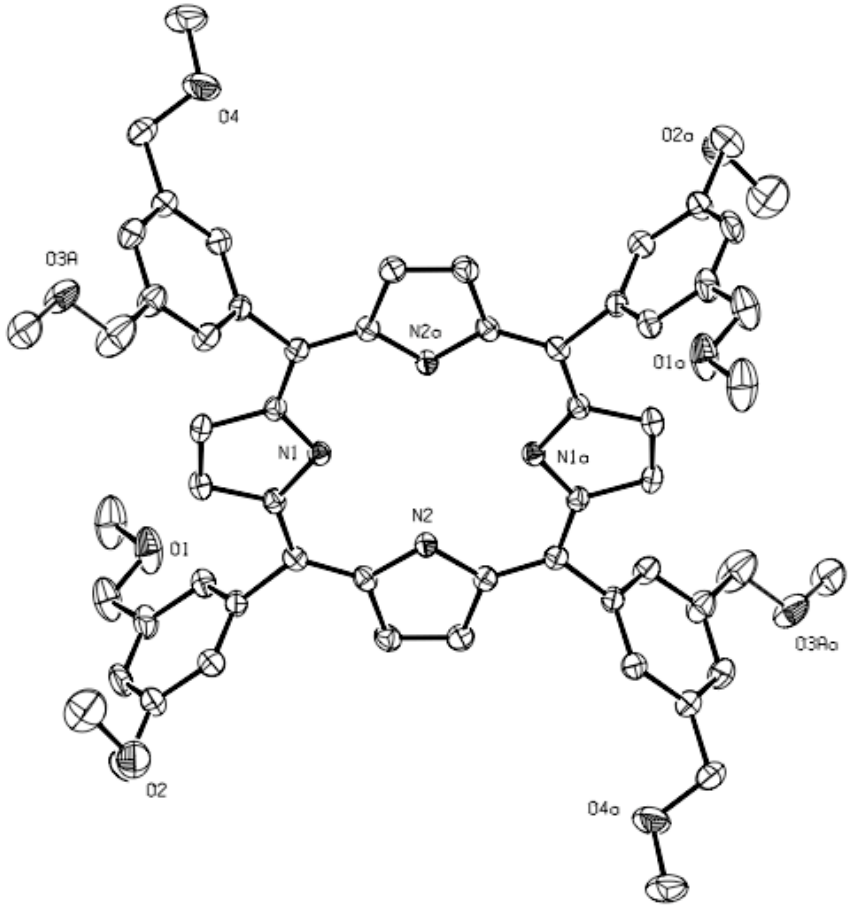

Figure S1. Crystal structure of tetrakis(3,5-bis(methoxymethyl)phenyl)porphyrin **2**.

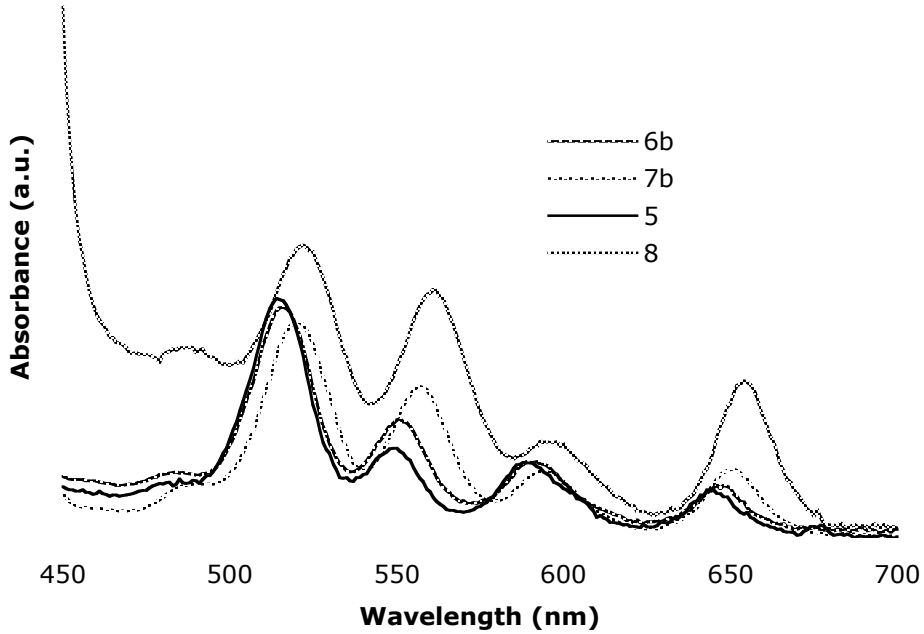

Figure S2. Q band region of the UV-vis spectra of **5** through **8**

Experimental Section

General. All air-sensitive reactions were performed under a nitrogen atmosphere using standard Schlenck techniques. All reactions involving porphyrin compounds were shielded from ambient light using aluminum foil. Et_2O and THF were carefully dried and distilled from sodium/benzophenone prior to use. MeCN and CH_2Cl_2 were distilled from CaH_2. Other solvents and all standard reagents were purchased and used as received. Column chromatography was performed using ACROS silicagel for column chromatography, 0.060–0.200 mm, pore diameter ca 4 nm. ^1H and $^{13}C\{^1H\}$ were recorded on a Varian 300 spectrometer, and ^{31}P NMR spectra were recorded on a Varian AC 200 spectrometer. Due to extreme line-broadening, in most cases the ^{13}C NMR signals for the porphyrin α- and β-carbon atoms were not detected. When the signals were detected, they are denoted by (b). UV/Vis spectra were recorded on a Cary 50 scan UV-visible spectrophotometer and fluorescence spectra were recorded on a Spex 1680 0.22m double spectrometer. ESI-MS measurements were performed by the Department of Biomolecular Mass Spectrometry, Bijvoet Centre for Biomolecular Research Utrecht, The Netherlands. Elemental microanalyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Müllheim a/d Ruhr, Germany.

3,5-bis(methoxymethyl)benzaldehyde (**1**)

A cooled (-78 °C), colorless solution of 3,5-bis(methoxymethyl)iodobenzene[1] (6.75 g, 23.1 mmol) in dry Et_2O (280 mL) was treated dropwise with *t*-Buli (31.2 mL of a 1.5 M solution in pentane, 46.8 mmol) during 15 min. The resulting white suspension was

stirred for an additional 30 min after which dry DMF (3.89 mL, 50.0 mmol) was added and the yellow solution was allowed to reach RT. Water (200 mL) was subsequently added, the biphasic system was strirred overnight, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic fractions were washed with brine (200 mL), dried ($MgSO_4$), filtered, and evaporated to leave a yellow oil. Careful bulb-to-bulb distillation afforded **1** as a colorless oil.

Yield: 4.20 g (94%).

^{1}H NMR ($CDCl_3$): δ = 10.02 (s, 1H, C*H*O), 7.78 (s, 2H, Ar*H*), 7.59 (s, 1H, Ar*H*), 4.52 (s, 4H, ArCH_2O), 3.42 (s, 6H, OCH_3) ppm;

^{13}C NMR ($CDCl_3$): δ = 192.3, 139.9, 136.9 132.5, 128.0, 73.9, 58.9 ppm;

GC-MS: *m*/*z* 194 (M^+), calcd for $C_{11}H_{14}O_3$ 194.2;

Elem. an. calc. for $C_{11}H_{14}O_3$: C 68.02, H 7.27%; found: C 68.13, H 7.20%.

For an other synthetic route to **1**, see: Tanner, M. E.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1992**, *57*, 40–46

5,10,15,20-Tetrakis(3,5-bis(methoxymethyl)phenyl)porphyrin (**2**)

A colorless solution of **1** (9.56 g, 49.2 mmol) in propionic acid (185 mL) was heated to reflux and subsequently treated with neat pyrrole (3.44 mL, 49.2 mmol), whereupon the mixture immediately turned black. After half an hour at reflux temperature, the solution was allowed to settle overnight and the volatiles were removed *in vacuo*. The remaining black, tarry oil was dissolved in CH_2Cl_2 (200 mL), washed with a saturated $NaHCO_3$ solution (2 × 100 mL), dried ($MgSO_4$), filtered and evaporated to dryness. The remaining purplish tar was loaded onto a silicagel column, which was subsequently eluted with 2%

MeOH in CH_2Cl_2. The purple fractions were collected, evaporated and subsequently triturated with MeOH to furnish **2** as a purple microcrystalline solid. Oxidation with *p*-chloranil gave the chlorin-free porphyrin.

Yield: 1.40 g (12%).

^{1}H NMR ($CDCl_3$): δ = 8.83 (s, 8H, *β-H*), 8.11 (s, 8H, Ar*H*), 7.78 (s, 4H, Ar*H*), 4.76 (s, 16H, ArCH_2O), 3.54 (s, 24H, OCH_3), -2.80 (s, 2H, N*H*) ppm;

^{13}C NMR ($CDCl_3$): δ = 146.0 (b), 142.4, 137.1, 133.3 131.4 (b), 126.5, 120.0, 74.9, 58.7 ppm;

ESI-HRMS *m/z* 967.4637 $(M + H)^+$, calcd. for $C_{60}H_{63}N_4O_8$ 967.4646;

UV-vis ($\lambda_{max}(\varepsilon)$, CH_2Cl_2): 420 (384,000), 515 (14,500), 549 (6,300), 590 (4,200), 650 (3,700) nm.

Elem. an. calc. for $C_{60}H_{62}N_4O_8$: C 74.51, H 6.46, N 5.79%; found: C 74.39, H 6.37, N 5.64%.

5,10,15,20-Tetrakis(3,5-bis(bromomethyl)phenyl)porphyrin (**3**)

A dark red solution of **2** (98 mg, 101 μmol) in CH_2Cl_2 (20 mL) was treated with FRESH! HBr/AcOH (30 mL) and after 5 h of stirring at RT, H_2O (30 mL) was added. The phases were separated and the organic layer was treated with a saturated $NaHCO_3$ solution (2 × 50 mL), dried ($MgSO_4$) and evaporated. The resulting purple solid was dissolved in CH_2Cl_2 (10 mL) and pentane (80 mL) was added to induce precipitation of a purple solid. This solid was purified using column chromatography (silicagel, CH_2Cl_2/pentane 1:1) and the first, fast-running band was finally recrystallized from CH_2Cl_2/pentane to yield **3** as a purple, crystalline solid.

Yield: 92 mg (67%).

Note: due to its suspected toxicity, this compound was immediately used in the subsequent steps.

^{1}H NMR ($CDCl_3$): δ = 8.88 (s, 8H, *β-H*), 8.19 (s, 8H, Ar*H*), 7.86 (s, 4H, Ar*H*), 4.77 (s, 16H, ArCH_2Br), -2.84 (s, 2H, N*H*) ppm;

^{13}C NMR ($CDCl_3$): δ = 143.2, 137.3, 135.1, 129.2, 119.1, 34.3 ppm;

ESI-MS *m/z* 1358.95 $(M + H)^+$, calcd. for $C_{52}H_{39}Br_8N_4$ 1359.14;

UV-vis ($\lambda_{max}(\varepsilon)$, CH_2Cl_2): 420 (531,000), 515 (20,900), 550 (8,200), 589 (6,400), 644 (4,300) nm.

Elem. an. calc. for $C_{52}H_{38}Br_8N_4$: C 45.99, H 2.82, N 4.13%; found: C 45.82, H 2.92, N 4.04%.

5,10,15,20-Tetrakis(3,5-bis((dimethylamino)methyl)phenyl)porphyrin (**4**)

Octabromide **3** (95 mg, 70 μmol) was dissolved in CH_2Cl_2 (30 mL) and Me_2NH (1.5 mL, excess) was added at once. After stirring for 16 h at RT, H_2O (10 mL) was added and the biphasic system was stirred for 1 h. The organic phase was separated, dried ($MgSO_4$), and filtered. Hexane (30 mL) was added and the purple solution was concentrated to 15 mL and stored at –30 ºC. After 3 days, the resulting purple crystals were collected.

Yield: 72 mg (96%).

^{1}H NMR ($CDCl_3$): δ = 8.87 (s, 8H, *β-H*), 8.10 (s, 8H, Ar*H*), 7.75 (s, 4H, Ar*H*), 3.75 (s, 16H, ArCH_2NMe_2), 2.45 (s, 48H, N(CH_3)$_2$), -2.84 (s, 2H, N*H*) ppm;

^{13}C NMR ($CDCl_3$): δ = 147.0 (b), 142.0, 137.3, 134.1 131.1 (b), 129.4, 120.2, 64.5, 45.7 ppm;

ESI-HRMS *m/z* 1071.7210 $(M + H)^+$, calcd. for $C_{68}H_{87}N_{12}$ 1071.7176;

UV-vis ($\lambda_{max}(\varepsilon)$, CH_2Cl_2): 419 (452,000), 515 (16,000), 551 (8,300), 590 (5,000), 648 (4,200) nm.

Elem. an. calc. for $C_{68}H_{86}N_{12}$: C 76.22, H 8.09, N 15.69%; found: C 76.31, H 8.16, N 15.61%.

5,10,15,20-Tetrakis(3,5-bis((borane-diphenylphosphino)methyl)phenyl)porphyrin (**5BH$_3$**)

$LiPPh_2$-BH_3 was prepared by treating a cooled (-78 ºC) solution of $HPPh_2$-BH_3 (690 mg, 3.45 mmol) in dry THF (30 mL) with *n*-BuLi (2.1 mL of a 1.6 M solution in hexane, 3.36 mmol) in a dropwise manner. The resulting colorless solution was stirred at -78 ºC for 10 min and then allowed to reach RT, at which it was stirred for 2 h. The resulting faintly yellow solution was subsequently added to a precooled solution (-40 ºC) of **3** (284 mg, 209 μmol) in dry THF (40 mL). Upon addition, the resulting solution slightly darkened and acquired a yellow tinge. After 40 h, the solution was treated with H_2O (20 mL) and the volatiles were evaporated. The resulting purple solid was redissolved in CH_2Cl_2 (40 mL) and washed with H_2O (60 mL), brine (50 mL), dried ($MgSO_4$), filtered, and concentrated to 10 mL. Addition of EtOH (80 mL) induced the precipitation of a fluffy red solid, which was collected by means of centrifugation.

Yield: 442 mg (99%).

^{1}H NMR ($CDCl_3$): δ = 8.43 (s, 8H, *β-H*), 7.75 (m, 32H, PAr*H*), 7.59 (s, 8H, Ar*H*), 7.41 (m, 48H, PAr*H*), 7.19 (s, 4H, Ar*H*), 3.77 (d, $^2J_{PH}$ = 12.3 Hz, 16H, ArCH_2P), 1.15 (br, 24H, BH_3), -3.23 (s, 2H, N*H*) ppm;

^{13}C NMR ($CDCl_3$): δ = 142.1, 134.8, 132.7 (d, $^1J_{PC}$ = 9.1 Hz), 131.6, 130.5, 129.3, 129.0 (d, $^2J_{PC}$ = 9.7 Hz), 128.6, 118.9, 34.0 (d, $^1J_{PC}$ = 31.6 Hz) ppm;

^{31}P NMR ($CDCl_3$): δ = 19.2 (b);

ESI-MS *m/z* 2312.0 $(M + H)^+$, calcd. for $C_{148}H_{143}B_8N_4P_8$ 2312.9;

UV-vis (λ_{max}, CH_2Cl_2): 420, 514, 550, 588, 643 nm.

Elem. an. calc. for $C_{148}H_{142}B_8N_4P_8$: C 76.92, H 6.19, N 2.42, P 10.72%; found: 76.78, H 6.25, N 2.34, P 10.85%.

5,10,15,20-Tetrakis(3,5-bis((diphenylphosphino)methyl)phenyl)porphyrin (**5**)

Freshly distilled and degassed $HNEt_2$ (20 mL) was added to a degassed solution of **5BH$_3$** in dry THF (20 mL) and the red solution was heated to reflux for 2 h. All volatiles were subsequently evaporated *in vacuo* to leave a mixture of **5** and $HNEt_2{\cdot}BH_3$, which was used without further purification.

^{1}H NMR ($CDCl_3$): δ = 8.43 (s, 8H, *β-H*), 7.63 (s, 8H, Ar*H*), 7.50 (m, 32H, PAr*H*), 7.43 (s, 4H, Ar*H*), 7.30 (m, 48H, PAr*H*), 3.63 (s, 16H, ArCH_2P), -3.12 (s, 2H, N*H*) ppm;

^{31}P NMR ($CDCl_3$): δ = -7.17 ppm

UV-vis (λ_{max}, CH_2Cl_2): 420, 514, 550, 588, 643 nm.

5,10,15,20-Tetrakis(-3,5-bis((diphenylphosphino)methyl) 4-chloroplatino(II) phenyl)porphyrin (**8**)

To a clear red solution of **5** (250.0 mg, 113.6 μmol) in dry toluene (15 mL) was added PtCl-NCN (191.6 mg, 454.4 μmol), which immediately resulted in the formation of a purple precipitate. The mixture was heated to reflux and after 72 h it was allowed to

reach room temperature. The purple precipitate was isolated by means of centrifugation and the remaining solid was washed with toluene (80 mL), pentane (80 mL), and CH_2Cl_2 (20 mL), and dried *in vacuo*. Yield: 354 mg (quantitative).

^{1}H NMR ($CDCl_3$): δ = 8.85 (s, 8H, *β-H*), 8.06 (m, 32H, PAr*H*), 7.91 (s, 8H, Ar*H*), 7.51 (m, 48H, PAr*H*), 4.16 (s, 16H, ArCH_2P), -2.79 (s, 2H, N*H*) ppm;

^{31}P NMR ($CDCl_3$): δ = 38.4 ($^1J_{PtP}$ = 2937 Hz);

MALDI-TOF MS *m/z* 3119.67 $(M + H)^+$, calcd. for $C_{132}H_{139}Cl_4N_4Pd_4S_8$ 3119.20;

UV-vis (λ_{max}, CH_2Cl_2): 420, 514, 550, 588, 643 nm. Due to the extreme insolubility of this compound, an accurate determination of the *ε* was impossible

Elem. an. calc. for $C_{148}H_{118}Cl_4N_4P_8Pt_4$: C 56.93, H 3.81, N 1.79, P 7.94%; found: 56.93, H 3.74, N 1.73, P 7.88%.

5,10,15,20-Tetrakis(3,5-bis((4-tert-butylphenylsulphido)methyl)phenyl)porphyrin (**6b**)

To a solution of **3** (330 mg, 243 μmol) in dry THF (30 mL) under nitrogen were added 4-*tert*-butylthiophenol (400 μL, 2.37 mmol), K_2CO_3 (660 mg, 4.78 mmol), and 18-crown-6 (10 mg) and the dark red solution was subsequently stirred for 16 h. The volatiles were evaporated and the resulting solid was redissolved in CH_2Cl_2 (40 mL) and washed with $NaHCO_3$ (10% in H_2O, 50 mL), and H_2O (50 mL), dried ($MgSO_4$), filtered, and concentrated to 15 mL. Upon addition of MeOH (80 mL) a purple solid precipitated which was collected by centrifugation.

Yield: 459 mg (93%).

^{1}H NMR ($CDCl_3$): δ = 8.66 (s, 8H, *β-H*), 7.85 (s, 8H, Ar*H*), 7.68 (s, 4H, Ar*H*), 7.37 (d, $^{3}J_{HH}$ = 7.2 Hz, 16H, Ar*H*), 7.33 (d, $^{3}J_{HH}$ = 7.2 Hz, 16H, Ar*H*), 4.30 (s, 16H, ArCH_2S), 1.12 (s, 72H, C(CH_3)$_3$), -3.00 (s, 2H, N*H*) ppm;

^{13}C NMR ($CDCl_3$): δ = 150.3, 142.2, 136.7, 134.0, 132.2, 131.2, 129.1, 126.1, 119.5, 40.0, 34.6, 31.3 ppm;

ESI-MS *m/z* 1021.6 $(M + H)^{2+}$, calcd. for $(C_{132}H_{143}N_4S_8)^{2+}$ 1021.5;

UV-vis (λ_{max} (ε), CH_2Cl_2): 420 (533,000), 514 (21,000), 549 (10,000), 591 (7,400), 645 (6,000) nm.

Elem. an. calc. for $C_{132}H_{142}N_4S_8$: C 77.67, H 7.01, N 2.74; found: C 77.55, H 6.86, N 2.61%.

5,10,15,20-Tetrakis(3,5-bis((4-tert-butylphenylsulphido)methyl)-4-chloropalladio(II)phenyl)porphyrin (**7b)**

To a red solution of **6b** (350 mg, 172 μmol) in CH_2Cl_2/MeCN (4/3, 50 mL) was added $[Pd(MeCN)_4](BF_4)_2$ (310 mg, 698 μmol) and the yellow suspension was stirred overnight at reflux temperature. The resulting dark green solution was transferred to a centrifuge vessel and concentrated to 15 mL. Upon addition of Et_2O (75 mL) a green solid precipitated. This solid was collected, redissolved in MeCN (40 mL) and Et_3N (5 mL) was added, whereupon the solution turned purple. LiCl (200 mg, large excess) was added and the mixture was stirred overnight, centrifuged, and the solid was washed with H_2O, MeOH and Et_2O (all 2 × 80 mL). The resulting brown solid was dissolved in CH_2Cl_2 and chromatographed on silica using 5% MeOH in CH_2Cl_2. The first band was collected, concentrated and upon addition of Et_2O, a brown/red solid precipitated. Yield: 401 mg

(90%). X-ray quality crystals were grown by slow evaporation of a saturated solution of **7b** in a 1:1 mixture of toluene/CH_2Cl_2.

^{1}H NMR ($CDCl_3$): δ = 8.84 (s, 8H, *β-H*), 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 16H, Ar*H*), 7.77 (s, 8H, Ar*H*), 7.49 (d, $^3J_{HH}$ = 8.4 Hz, 16H, Ar*H*), 4.83 (br s, 16H, ArCH_2S), 1.34 (s, 72H, C(CH_3)$_3$), -2.86 (s, 2H, N*H*) ppm;

^{13}C NMR ($CDCl_3$): δ = 160.8, 153.7, 148.0, 138.8, 131.9, 129.1, 128.4, 127.1, 119.7, 53.0, 35.1, 31.3 ppm;

ESI-MS *m/z* 2599.7 $(M + H)^+$, calcd. for $C_{132}H_{139}Cl_4N_4Pd_4S_8$ 2599.4;

UV-vis (λ_{max} (ε), CH_2Cl_2): 426 (616,000), 520 (21,000), 557 (14,000), 596 (5,500), 650 (7,300) nm.

Elem. an. calc. for $C_{132}H_{138}Cl_4N_4Pd_4S_8$: C 60.87, H 5.34, N 2.15, S 9.85%; found: C 60.85, H 5.42, N 2.08, S 9.72%.

Crystal structure determination of 2:

$C_{60}H_{62}N_4O_8$, Fw = 967.14, dark purple block, 0.45 x 0.36 x 0.21 mm^3. Monoclinic crystal system, space group $P2_1/c$ (no. 14). Cell parameters: a = 14.0191(2), b = 9.9445(1), c = 18.9747(3) Å, β = 102.5709(13)°, V = 2581.90 $Å^3$. Z = 2, D_x = 1.244 g cm^{-3}, μ = 0.083 mm^{-1}. 41793 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (Mo-K_α, λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.61 $Å^{-1}$. An absorption correction was not considered necessary. The reflections were merged using the program SortAV[2], resulting in 4830 unique reflections (R_{int} = 0.0404), of which 3691 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97[3], and refined with the program SHELXL-97[4] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The N-H hydrogen atom was located in the difference Fourier map and kept fixed in that position. All other hydrogen atoms were refined as rigid groups. The methoxy group at C27 was disordered over two positions. 343 refined parameters, 28 restraints. R (obs. data): R1 = 0.0443, wR2 = 0.1184. R (all data): R1 = 0.0611, wR2 = 0.1299. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.8100P]$, where $P = (F_o^2+2F_c^2)/3$. GoF = 1.096. Residual density between -0.26 and 0.34 e/$Å^3$. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON[5].

Crystal structure determination of 7b:

$C_{132}H_{137.93}Cl_4N_4Pd_{0.04}S_8 \cdot 4C_7H_8$ + disordered solvent, Fw = 2977.07[*], dark red plate, 0.24 x 0.21 x 0.06 mm^3. Triclinic crystal system, space group $P\bar{1}$ (no. 2). Cell parameters: a

= 15.0209(2), b = 17.1924(2), c = 17.7209(3) Å, α = 68.0524(7), β = 86.0962(7), γ = 89.2137(7)°, V = 4234.49(10) Å^3. Z = 1, D_x = 1.167 g cm$^{-3[*]}$, μ = 0.628 mm$^{-1[*]}$. 58270 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (Mo-K_α, λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.60 Å^{-1}. An absorption correction was not considered necessary. 14915 reflections were unique (R_{int} = 0.0903), of which 9456 were observed [$I > 2\sigma(I)$]. The structure was solved with automated Patterson methods using the program DIRDIF-99[6], and refined with the program SHELXL-97[4] against F^2 of all reflections. Toluene solvent molecules were refined with isotropic displacement parameters, all other non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. Three of the ^{t}butyl groups were rotationally disordered. Additionally to the ordered toluene molecules, the structure contains voids of 836.1 Å^3/unit cell, containing disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier-transformation using the SQUEEZE routine of the program PLATON[5] resulting in 191 e/unit cell. The small electron density at the center of the porphyrin system was assigned to a Pd-center with an occupancy of 0.04. The vast majority is the N-H derivative of the porphyrin system. 832 refined parameters, 744 restraints. R (obs. data): R1 = 0.0506, wR2 = 0.1170. R (all data): R1 = 0.0918, wR2 = 0.1277. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$, where $P = (F_o^2+2F_c^2)/3$. GoF = 0.994. Residual density between -0.53 and 0.82 e/Å^3. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON[5].

[*] Derived quantities (Fw, D_x, μ) do not contain the contribution of the disordered solvent.

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