Supplementary Information

For

Porphyrin nanochannels reinforced by

hydrogen bonding

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Experimental Section

General. All commercially available chemicals were purchased from appropriate sources and used as received unless otherwise mentioned. 5,15-Bis(4-methoxy-carbonylphenyl)porphyrin,¹ 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin² and 5,10,15,20-tetrakis(3,5-diethoxycarbonylphenyl)porphyrin³ were synthesized and characterized with modified procedures reported in the literature. All ¹H NMR measurements were performed on a JEOL EX270 and JEOL EX400 spectrometers. UV-vis absorption spectra were measured in spectroscopic-grade solvents on a Shimadzu UV-3600 spectrophotometer at room temperature. Fluorescence spectra were recorded on a Hamamatsu Photonics C9920-02 spectrometer at room temperature. MALDI-TOF-MS spectra were measured on a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer using dithranol as a matrix.

Synthesis.



Scheme S1. Synthesis of diprotonated 2,3,7,8,12,13,17,18-octaphenyl-5,15-bis-(4-carboxyphenyl)porphyrin diperchlorate ([H₂**2**](ClO₄)₂).

Copper(II) 5,15-bis(4-methoxycarbonylphenyl)porphyrinato: 5,15-bis(4-methoxycarbonylphenyl)porphyrin (47 mg, 6.5 μ mol) was dissolved in CHCl₃ (50 mL) and to the solution was added the suspension of Cu(OAc)₂·H₂O (49.6 mg, 0.25 mmol) in methanol (5 mL) and the mixture was refluxed for 45 min. The volatile was evaporated to dryness under vacuum and the residue was dissolved in CHCl₃ (25 mL). The solution was washed with water (25 mL) to remove excess copper salt and dried over Na₂SO₄. The crude product was purified on a silica gel column by eluting with CHCl₃ and the collected fraction was evaporated to dryness to yield reddish-purple powder. The obtained powder was dried under vacuum for 5 h. Yield: 50 mg (100%). UV-vis (CHCl₃): λ_{max} [nm] = 417, 540. MS (MALDI-TOF): m/z = 791.7 (Calcd. for C₄₈H₃₂N₄O₈Cu [M]⁺: 791.17).

2,3,7,8,12,13,17,18-Octabromo-5,15-bis(4-methoxycarbonylphenyl)porphyrin: To the solution of copper(II) 5,15-bis(4-methoxycarbonylphenyl)porphyrinato (46.8 mg, 59 µmol) in CHCl₃ (20 mL) was added dropwise the solution of Br₂ (58 µL, 1.1 mmol) in CHCl₃ (10 mL) over 4 h and then the solution of pyridine (0.11 mL) in CHCl₃ (10 mL) was added. The mixture was allowed to stir for further 8 h at room temperature. The excess Br_2 was quenched using saturated $Na_2S_2O_5(aq)$ (25 mL), and then the solution was transferred to a separating funnel, washed with water (50 mL \times 3 times), dried over Na_2SO_4 and evaporated to dryness under vacuum. It was found that the product contained partially brominated Cu-porphyrins and thus the crude mixture (53 mg) was dissolved in CHCl₃ (20 mL). To the solution was added dropwise the solution of Br₂ (0.2 mL) in CHCl₃ (15 mL) and stirred for 2 d at room temperature to complete bromination. The excess Br_2 was quenched by using saturated $Na_2S_2O_5$ (aq) (50 mL), and the mixture was washed thoroughly with water (150 mL \times 3 times), dried over Na₂SO₄ and evaporated to dryness under vacuum. The obtained crude porphyrin was dissolved in CHCl₃ (40 mL) and cooled to 0 °C on ice. To the cooled solution was added conc. H₂SO₄ (1 mL) and stirred for 20 min. Then, water (50 mL) was added slowly with caution and the organic layer was washed with water (150 mL \times 2 times) and neutralized with NH₃(aq) (12.5%, 14 mL) followed by washing with water (150 mL) to remove excess NH_3 and the salts. The organic layer was dried over Na_2SO_4 , concentrated to a minimum volume, and loaded on a silica gel column. The desired product was eluted with CHCl₃ and the collected fraction was evaporated to dryness under vacuum. The crude product was recrystallized from CHCl₃/CH₃OH mixture (1:6, v/v) and dried under vacuum. Yield: 40.5 mg (56%). UV-vis (CH₂Cl₂): λ_{max} [nm] = 369, 471, 581, 626, 738. ¹H NMR (CDCl₃): δ 8.45 (d, 4H, J = 8.1 Hz, o-Hs of meso-esterPh), 8.31 (d, 4H, J = 8.1 Hz, m-Hs of meso-esterPh), 8.20 (dd, 4H, J = 7.6, 1.3 Hz, o-Hs of meso-Ph), 7.8-7.6 (m, 6H, m- & p-Hs of meso-Ph), 4.10 (s, 6H, -COOCH₃). MS (MALDI-TOF): m/z = 1345.1 (Calcd. for $C_{47}H_{26}N_4O_4Br_8 [M-CH_3]^+$: 1346.51).

$\label{eq:2,3,7,8,12,13,17,18-octaphenyl-5,15-bis (4-methoxycarbonylphenyl) porphyrin: 2,3,$

7,8,12,13,17,18-octabromo-5,15-bis(4-methoxycarbonylphenyl)porphyrin (38.5 mg, 28 µmol), phenylboronic acid (82.7 mg, 0.68 mmol), Pd(PPh₃)₄ (6.5 mg, 5.6 µmol), and K₂CO₃ (176 mg, 1.3 mmol) were charged in a 50 mL Schrenk tube and dried under vacuum for 30 min. Freshly distilled toluene (10 mL) was added to the flask under Ar and the flask was degassed with three freeze-pump-thaw cycles. The mixture was heated around 90-100 °C for 12 h and the toluene was removed *in vacuo*. The residue was dissolved in CHCl₃ (50 mL), washed with water (40 mL), dried over Na₂SO₄, and concentrated to dryness. Yield: 28 mg (74%). UV-vis (CH₂Cl₂): λ_{max} [nm] = 386, 467, 561, 612, 713. ¹H NMR (CDCl₃): δ 7.7-7.5 (m, 8H, *o*-Hs of *meso*-esterPh and *meso*-Ph), 7.60 (d, 8H, J = 7.9 Hz, *o*-Hs of *meso*-Ph), 7.38 (d, 4H, J = 8.2 Hz, *m*-Hs of *meso*-esterPh), 6.8–6.6 (m, 46H, β -PhHs), 3.49 (s, 6H, -COOCH₃). MS (MALDI-TOF): m/z = 1340.4 (Calcd. for C₉₆H₆₈N₄O₄ [M+2H]⁺: 1340.52).

2,3,7,8,12,13,17,18-Octaphenyl-5,15-bis(4-carboxyphenyl)porphyrin (**2**): To the solution of 2,3,7,8,12,13,17,18-octaphenyl-5,15-bis(4-methoxycarbonylphenyl) porphyrin (28 mg, 21 µmol) in THF/EtOH mixture (2:1 v/v, 24 mL) was added the solution of KOH (0.4 g, 7 mmol) in water (0.2 mL) and degassed with Ar bubbling. The reaction mixture was heated to reflux for 18 h and then the solvent was removed under vacuum. HCl(aq) (2 M, 40 mL) was added and the resultant green precipitate was filtered, washed with water (10 mL × 10 times), and dried under vacuum. To the residual solid was added a few drops of NEt₃ and the remaining volatile was removed under vacuum. The resulting crystalline green solid was recrystallized from THF/diethyl ether mixture (1:6, v/v) and dried under vacuum. Yield: 20 mg (15 µmol, 73%). UV-vis (THF/MeOH with one drop of NEt₃): λ_{max} [nm] = 381, 465, 557, 612, 732. MS (MALDI-TOF): m/z = 1312.1 (Calcd. for C₉₄H₆₄N₄O₄ [M+2H]⁺: 1312.49).

Diprotonated-2,3,7,8,12,13,17,18-octaphenyl-5,15-bis(4-carboxyphenyl)porphyrin diperchlorate ([H₂2](ClO₄)₂): To a suspension of 2,3,7,8,12,13,17,18-octaphenyl-5,15bis(4-carboxyphenyl)porphyrin (20 mg, 14 µmol) in THF (10 mL), was added HClO₄(aq) (60%, 60 µL) and stirred for a few minutes. The mixture was evaporated to dryness in vacuo. The residual solid was dissolved in CHCl₃ (20 mL), filtered through a celite pad, and the subsequent evaporation yielded dark-green solid. The solid was recrystallized from THF and diethyl ether (1:7, v/v) and dried under vacuum at room temperature. Yield: 15 mg (9.9 µmol, 68%). UV-vis (THF): λ_{max} [nm] = 489, 708.¹H NMR (DMSO-*d*₆): δ 8.12 (d, 4H, J = 8 Hz, *o*-*H*s of *meso*-carboxyPh), 8.10 (m, 4H, *o*-*H*s of *meso*-Ph), 7.66 (d, 4H, J = 8 Hz, *m*-*H*s of *meso*-carboxyPh), 7.08 (m, 4H, *o*-*H*s of *meso*-carboxyPh), 6.84–6.66 (m, 42H, β-PhHs). MS (MALDI-TOF): m/z = 1311.9 (Calcd. for C₉₄H₆₄N₄O₄ [M–2ClO₄]⁺: 1312.49).



Scheme S2. Synthesis of diprotonated 2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin dichloride ([H₂**3**]Cl₂).

Copper(II) 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrinato: 5,10,15, 20-Tetrakis(4-carbomethoxyphenyl)porphyrin (0.78 g, 0.86 mmol) was dissolved in CHCl₃ (60 mL) and, to the solution, was added Cu(OAc)₂·H₂O (1.71 g, 8.6 mmol) dispersed in methanol (10 mL). After refluxing for 10 min, the reaction mixture was evaporated to dryness. The residue was dissolved in CHCl₃ (30 mL) and washed with water (100 mL) to remove excess metal salts and then dried over Na₂SO₄. The crude product was purified on a silica gel column by eluting with CHCl₃ containing 3-4% acetone. The collected fraction was evaporated to dryness to yield purple powder and dried under vacuum for 5 h. Yield: 0.832 g (100%). UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 416 (5.75), 539 (4.41), 573 (sh). MS (MALDI-TOF): m/z = 908.77 (Calcd. for C₅₂H₃₆N₄O₈Cu [M]⁺: 908.43). Anal. Calcd. for C₅₂H₃₆N₄O₈Cu: C; 68.75, H; 3.99, N; 6.17, Found: C; 68.75, H; 3.75, N; 5.99.

2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-methoxycarbonylphenyl) porphyrin:⁴ To the solution of copper(II) 5,10,15,20-tetrakis (4-methoxycarbonylphenyl)porphyrinato (0.96 g, 1.13 mol) in CHCl₃ (200 mL), was added dropwise the solution of Br₂ (5.9 mL, 0.11 mol) in CHCl₃ (150 mL) over 4 h and the mixture was allowed to stir for 2 d at room temperature. The excess Br₂ was quenched using saturated $Na_2S_2O_5(aq)$ (150 mL), and then the solution was transferred to a separating funnel, washed with water (150 mL \times 4 times), dried over Na₂SO₄ and evaporated to dryness under vacuum. UV-vis (CHCl₃) λ_{max} [nm] = 350, 452, 548, 698, 703. It was found that the product contained partially brominated Cu-porphyrin and the demetallated derivatives and thus the porphyrin mixture was metallated again with Cu(OAc)₂·H₂O in CHCl₃/CH₃OH mixed solvent. The crude mixture of partially brominated Cu-porphyrins (1.20 g) was dissolved in CHCl₃ (200 mL). To the solution, the solution of Br₂ (5.9 mL, 0.11 mol) in CHCl₃ (200 mL) was added dropwise and stirred for 2 d at room temperature to complete bromination. The excess Br₂ was quenched using saturated Na₂S₂O₅ (aq) (150 mL), and the mixture was washed with water (250 mL \times 4 times), dried over Na₂SO₄ and evaporated to dryness under vacuum. The crude porphyrin obtained (1.15 g) was dissolved in CHCl₃ (100 mL) and cooled to 0 °C on ice. To the cooled solution was added conc. H₂SO₄(5 mL) and stirred for 30 min. Then, water (50 mL) was added slowly with caution and the organic layer was washed with water (250 mL \times 3 times) and neutralized with NH₃(aq) (28%, 50 mL) followed by washing with water (100 mL) to remove excess NH₃ and the salts. The organic layer was dried over Na₂SO₄, concentrated to a minimum volume, and loaded on a silica gel column. The desired product was eluted with CHCl₃ containing 6-9% EtOAc and the collected fraction was evaporated to dryness under vacuum. The crude product was recrystallized from CHCl₃/CH₃OH mixture (1:6, v/v) and dried under vacuum. Yield: 1.09 g (65%). UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) = 372 (4.33), 471 (5.15), 571 (3.90), 626 (4.01), 738 (3.71). ¹H NMR (CDCl₃): δ 8.45 (d, 8H, J = 8.2 Hz, *o-H*s of *meso-Ph*), 8.30 (d, 8H, *J* = 8.2 Hz, *m-H*s of *meso-Ph*), 4.10 (s, 12H, -COOCH₃). MS (MALDI-TOF): m/z = 1478.1 (Calcd. for $C_{52}H_{30}N_4O_8Br_8$ [M]⁺: 1478.57). Anal. Calcd. for C₅₂H₃₀N₄O₈Br₈·H₂O: C; 41.75, H; 2.16, N; 3.74, Found: C; 41.80, H; 2.11, N; 3.66.

2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)

porphyrin:⁴ 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (0.24 g, 0.16 mmol), phenylboronic acid (0.48 g, 3.9 mmol), $Pd(PPh_3)_4$ (37.7 mg, 32.6 µmol), and K_2CO_3 (1.01 g, 7.32 mmol) were added in a three-necked 100 mL-round-bottomed flask and dried under vacuum for 30 min. Freshly distilled toluene (50 mL) was added to the flask under Ar and the flask was degassed with three freeze-pump-thaw cycles. The mixture was heated around 90-100 °C for 2 d and the toluene was removed *in vacuo*. The residue was dissolved in CHCl₃ (100 mL), washed with saturated NaHCO₃(aq) (50 mL), water (80 mL × 3 times) and brine (60 mL), and dried over Na₂SO₄, concentrated to a minimum volume and loaded on a silica gel column. The desired porphyrin was eluted with CHCl₃ containing 5-10% EtOAc and the obtained fraction was evaporated. The crude product was recrystallized from CHCl₃/EtOH mixture (1:6, v/v) and dried under vacuum to yield brown powder (0.16 g, 68%). UV-vis (CH₂Cl₂): λ_{max} [nm] (log ε) = 383 (4.64), 471 (5.30), 565 (4.26), 618 (4.24), 720 (4.02). ¹H NMR (CDCl₃): δ 7.60 (d, 8H, *J* = 7.9 Hz, *o*-*H*s of *meso*-Ph), 7.38 (d, 8H, *J* = 8.1 Hz, *m*-*H*s of *meso*-Ph), 6.76 – 6.57 (m, 40H, β -PhHs), 3.94 (s, 12H, -COOCH₃), -0.93 (s, 2H, inner NH). MS (MALDI-TOF): *m/z* = 1455.7 (Calcd. for C₁₀₀H₇₀N₄O₈ [M]⁺: 1455.71). Anal. Calcd. for C₁₀₀H₇₀N₄O₈: C; 82.52, H; 4.85, N; 3.85, Found: C; 82.51, H; 5.00, N; 3.81.

2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (3):⁴ 2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)-

porphyrin (0.36 g, 0.25 mmol) was dissolved in of THF (50 mL) and, to the solution, was added 2 M KOH(aq) (30 mL) and the mixture was stirred vigorously at room temperature for 2 d. The reaction mixture was heated around 80-85 °C overnight and THF was removed under vacuum. To the residue was added 2M HCl(aq) (60 mL) and the resulting green precipitate was filtered, washed with water (30 mL × 4 times), and dried under vacuum. The obtained solid was added into NH₃(aq) (25%, 60 mL) and the volatile was carefully removed under vacuum. The resulting green crystalline solid was washed with water and dried under vacuum. Yield: 0.31 g (0.22 mmol, 90%). UV-vis (THF with one drop of NEt₃): λ_{max} [nm] = 384, 470, 562, 626, 741. ¹H NMR (DMSO-*d*₆): δ 7.75 (bs, 8H, *o*-Hs of *meso*-Ph), 7.44 (bs, 8H, *m*-Hs of *meso*-Ph), 6.90–6.55 (m, 40H, β -PhHs). MS (MALDI-TOF): *m/z* = 1399.5 (Calcd. for C₉₆H₆₂N₄O₈ · 5H₂O: C; 77.40, H; 4.87, N; 3.76, Found: C; 77.57, H; 4.88, N; 4.02.

Diprotonated-2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin dichloride ($[H_23]Cl_2$): 2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis (4-carboxyphenyl)porphyrin (0.20 g, 0.14 mmol) was dispersed in THF (100 mL) and to the suspension was added conc. HCl(aq) (38%, 0.2 mL) and stirred for a few minutes and evaporated to dryness *in vacuo*. The residual solid was dissolved in THF (20 mL), filtered through a celite pad, and the subsequent evaporation yielded dark-green solid. The solid was recrystallized from THF/diethyl ether (1:7, v/v) and dried under vacuum at room temperature for 2 h. Yield: 0.19 g (0.13 mmol, 90%). UV-vis (THF): λ_{max} [nm] (log ε) = 437 (sh), 498 (5.23), 655 (sh), 715 (4.54). ¹H NMR (CD₃OD): δ 8.28 (d, 8H, *J* = 7 Hz, *o*-Hs of *meso*-Ph), 7.38 (d, 8H, *J* = 8 Hz, *m*-Hs of *meso*-Ph), 6.96–6.69 (m, 40H, β -PhHs). MS (MALDI-TOF): *m*/*z* = 1401.67 (Calcd. for C₉₆H₆₄N₄O₈ [M]⁺: 1401.56). Anal. Calcd. for C₉₆H₆₄N₄O₈Cl₂·4H₂O: C; 74.65, H; 4.70, N; 3.63, Found: C; 74.37, H; 4.44, N; 3.32.



Scheme S3. Synthesis of diprotonated 2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(3,5-dicarboxyphenyl)porphyrin dichloride ([H₂4]Cl₂).

Copper(II) 5,10,15,20-Tetrakis(3,5-dicarboethoxyphenyl)porphyrinato: 5,10,15, 20-Tetrakis(3,5-diethoxycarbonylphenyl)porphyrin (0.72 g, 0.61 mmol) was dissolved in CHCl₃ (150 mL) and to the solution was added the solution of $Cu(OAc)_2$ ·H₂O (0.90 g, 4.5 mmol) in CH₃OH (30 mL). The mixture was refluxed for 2 h, and then cooled to room temperature. The solvent of the mixture was removed under vacuum, and the residue was dissolved in CHCl₃ (100 mL), washed with water (100 mL), and dried over anhydrous Na₂SO₄. The crude porphyrin was purified by column chromatography on silica gel using CHCl₃ containing 6-8% EtOAc as an eluent and recrystallized from

CHCl₃/CH₃OH (1:5, v/v). Yield: 0.74 g (0.59 mmol, 98 %). UV-vis (CH₂Cl₂): λ_{max} [nm] (log ε) = 419 (5.83), 540 (4.48), 574 (sh). MS (MALDI-TOF): m/z = 1252.31 (Calcd. for C₆₈H₆₀N₄O₁₆Cu [M]⁺: 1252.77). Anal. Calcd. for C₆₈H₆₀N₄O₁₆Cu: C; 65.19, H; 4.83, N; 4.47, Found: C; 65.12, H; 4.65, N; 4.41.

2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(3,5-diethoxycarbonylphenyl)

porphyrin: Copper(II) 5,10,15,20-tetrakis(3,5-diethoxycarbonylphenyl)porphyrinato (0.864 g, 0.67 mmol) was dissolved in CHCl₃ (180 mL) and to the solution was added dropwise the solution of Br₂ (1.2 mL, 0.023 mol) in CHCl₃ (100 mL) for 1 h at room temperature and the mixture was stirred for 4 h. Pyridine (2.3 mL, 0.028 mol) in CHCl₃ (100 mL) was added dropwise to the solution, which was stirred for further 18 h at room temperature. The excess Br₂ was quenched with Na₂S₂O₅(aq) (30%, 200 mL), and the mixture was washed with water (200 mL \times 3 times), dried over Na₂SO₄ and evaporated to dryness *in vacuo*. UV-vis (CHCl₃): λ_{max} [nm] = 368, 443, 575, 609 (sh). It was found that the product involved the mixture partially-brominated Cu-porphyrinate. The crude mixture of the porphyrins (1.30 g) was dissolved in CHCl₃ (280 mL) and to the solution was added dropwise the solution of Br₂ (3.6 mL, 0.07 mol) in CHCl₃ (100 mL) over 2 h and stirred for 2 d at room temperature. The excess Br₂ was quenched by using Na₂S₂O₅(aq) (30%, 150 mL), and the mixture was washed with water (200 mL \times 3 times), dried over Na₂SO₄ and evaporated to dryness in vacuo to give green solid. The obtained crude porphyrin (1.35 g) was dissolved in CHCl₃ (100 mL) and cooled to 0 °C. To the solution was added conc. H_2SO_4 (6 mL) and the mixture was stirred for 15 min till the CHCl₃ layer become colorless. Then, water (50 mL) was added slowly with caution and the organic layer was washed with water (250 mL × 3 times) and neutralized with NH₃(aq) (13%, 180 mL) followed by washing with water (200 mL) to remove excess ammonia and the salts. The CHCl₃ layer was dried over Na₂SO₄, concentrated to a minimum volume and loaded on a silica gel column. The desired product was eluted with CHCl₃ containing 8% EtOAc and the collected fraction was evaporated to dryness, followed by drying under vacuum for 2 h. Yield (1.01 g, 81%). UV-vis (CH₂Cl₂): λ_{max} [nm] (log ε) = 372 (3.38), 465 (5.28), 562 (4.07), 613 (4.01), 725 (3.70). ¹H NMR (CDCl₃, 270 MHz): δ 9.16 (t, 4H, J = 1.7 Hz, *p*-Hs of meso-Ph), 9.02 (d, 8H, J = 1.3 Hz, o-Hs of meso-Ph), 4.60 (q, 16H, J = 6.9 Hz, -OCH₂), 1.51 (t, 24H, J = 7.1 Hz, -CH₂CH₃). MS (MALDI-TOF): m/z = 1823.49 (Calcd. for C₆₈H₅₄N₄O₁₆Br₈ [M+H]⁺: 1823.41). Anal. Calcd. for C₆₈H₅₄N₄O₁₆Br₈·0.5 H₂O: C; 44.60, H; 3.03, N; 3.06, Found: C; 42.35, H; 2.99, N; 2.78.

2,3,7,8,12,13,17,18-Octaphenyl-5,10,15,20-tetrakis(3,5-diethoxycarbonylphenyl)-

porphyrin: 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(3,5-diethoxycarbonylphenyl)porphyrin (1.01 g, 0.55 mmol), phenylboronic acid (1.62 g, 13.3 mmol), $Pd(PPh_3)_4$ (0.13g, 0.11 mmol) and K_2CO_3 (3.45 g, 25 mmol) were charged into a 500 mL three-necked round-bottomed flask and dried under vacuum for 45 min. Freshly-distilled toluene (200 mL) was added to the flask under Ar and the mixture was degassed with two freeze-pump-thaw cycles. The reaction mixture was heated around 90-100 °C for 36 h and toluene was removed under vacuum. The residue was dissolved in CHCl₃ (150 mL) and washed with water (150 mL), NH₃(aq) (12.5%, 100 mL), water (150 mL), and brine (150 mL). The organic phase was dried over anhydrous Na₂SO₄, concentrated to a minimum volume and loaded on a silica gel column. The desired porphyrin was eluted with CHCl₃ containing 10% EtOAc and the collected fraction was dried under vacuum to yield brown powder (0.92 g, 92%). UV-vis (CH₂Cl₂): λ_{max} [nm] $(\log \varepsilon) = 384 (4.75), 465 (5.44), 558 (4.38), 609 (4.30), 708 (4.02).$ ¹H NMR (CDCl₃): δ 8.35 (d, 8H, J = 1.7 Hz, o-Hs of meso-Ph), 8.12 (t, 4H, J = 1.7 Hz, p-Hs of meso-Ph), 6.75-6.58 (m, 40H, β -PhHs), 4.44 (q, 16H, J = 7.1 Hz, -OCH₂), 1.47 (t, 24H, J = 7.1 Hz, $-CH_2CH_3$, -1.00 (bs, 2H, NH). MS (MALDI-TOF): m/z = 1800.41 (Calcd. for C₁₁₆H₉₄N₄O₁₆ [M]⁺: 1800.00). Anal. Calcd. for C₁₁₆H₉₄N₄O₁₆·EtOAc: C; 76.33, H; 5.45, N; 2.97, Found: C; 76.54, H; 5.44, N; 2.94.

2,3,7,8,12,13,17,18-Octaphenyl-5,10,15,20-tetrakis(3,5-dicarboxyphenyl)porphyrin (4): To the solution of 2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(3,5-diethoxy-carbonylphenyl)porphyrin (0.372 g, 0.207 mmol) in THF/EtOH mixture (1:1 v/v, 100 mL) was added the solution of KOH (1.74 g, 0.031 mol) in water (10 mL) and degassed with Ar bubbling. The reaction mixture was heated to reflux for overnight and then THF was removed under vacuum. HCl(aq) (2 M, 40 mL) was added and the resulting green precipitate was filtered, washed with water (20 mL × 5 times), and dried under vacuum. To the residual solid was added a few drops of NEt₃ and the remaining volatile was removed under vacuum. The resulting crystalline green solid was recrystallized from THF/diethyl ether mixture (1:6, v/v) and dried under vacuum. Yield: 0.316 g (0.20 mmol, 97%). UV-vis (THF/MeOH with one drop of NEt₃): λ_{max} [nm] = 381, 465, 557, 612, 732. ¹H NMR (DMSO-*d*₆): δ 8.70 (bs, 8H, *o*-Hs of *meso*-Ph), 8.24 (bs, 4H, *p*-Hs of

meso-Ph), 6.94–6.61 (m, 40H, β -Ph*H*s).MS (MALDI-TOF): m/z = 1575.52 (Calcd. for C₁₀₀H₆₂N₄O₁₆ [M]⁺: 1575.58). Anal. Calcd. for C₁₀₀H₆₂N₄O₁₆·4.5H₂O·2NH₃: C; 67.79, H; 4.89, N; 4.74, Found: C; 67.55, H; 4.71, N; 4.97.

Diprotonated-2,3,7,8,12,13,17,18-Octaphenyl-5,10,15,20-tetrakis(3,5-dicarboxyphenyl)porphyrin dichloride ([H₂4]Cl₂): 2,3,7,8,12,13,17,18-Octaphenyl-5,10,15,20tetrakis(3,5-dicarboxyphenyl)porphyrin (0.13 g, 83 µmol) was dispersed in THF (100 mL) and to the suspension was added conc. HCl(aq) (38%, 0.1 mL) and stirred for a few minutes. The THF solvent was removed and dried under vacuum to yield green solid. The solid was recrystallized from THF/diethyl ether (1:7, v/v) and dried under vacuum at room temperature for 5 h. Yield: 0.126 g (76.43 µmol, 93%). UV-vis (THF): λ_{max} [nm] (log ε) = 431 (4.55), 493 (5.20), 647 (sh), 706 (4.44). ¹H NMR (CD₃OD): δ 8.89 (bs, 8H, *o*-Hs of *meso*-Ph), 8.32 (bs, 4H, *p*-Hs of *meso*-Ph), 7.10–6.61(m, 40H, β -PhHs). MS (MALDI-TOF): m/z = 1577.92 (Calcd. for C₁₀₀H₆₄N₄O₁₆ [M]⁺: 1577.59). Anal. Calcd. for C₁₀₀H₆₄N₄O₁₆Cl₂·THF·3H₂O: C; 70.39, H; 4.43, N; 3.16, Found: C; 70.04, H; 4.71, N; 2.89.

TG/DTA measurements and N₂ isotherm.

TG/DTA data were recorded on an SII TG/DTA 7200 instrument. Each sample (~1.0 mg) was heated from 25 °C to 400 °C with a ramp rate of 2 °C/min. A certain amount (~1.0 mg) of γ -Al₂O₃ was used as a reference for DTA measurements. Nitrogen adsorption-desorption at -196 °C was performed with a Belsorp-mini (BEL Japan, Inc.) within a relative pressure range from 0.01 to 101.3 kPa. A sample mass was used for adsorption analysis after pretreatment at 80 °C for 30 min under vacuum conditions and kept in N₂ atmosphere until N₂-adsorption measurements. The sample was exposed to a mixed gas of He and N₂ with a programmed ratio and adsorbed amount of N₂ was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min).

X-ray crystallography

The crystal structures of diprotonated forms of **1**, **2**, **3**, and **4**, were determined by X-ray crystallography. The single crystals were mounted on mounting loops. All diffraction data were collected by using a Bruker APEXII diffractometer at -153 °C equipped with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) by the ω -2 θ scan. The structures

were solved by direct methods by using SIR97 and SHELX-97.⁵ Crystallographic data for these compounds are summarized in Table S1. CCDC-866776 ($[H_21](ClO_4)_2$), -866777 ($[H_22](ClO_4)_2$), -866778 ($[H_23]Cl_2$), and -866779 ($[H_24]Cl_2$) contain the supplementary crystallographic data. In the structure refinements, we could not determine the exact positions of the solvent molecules of crystallization because of their severe disorder. Their contribution was thus subtracted from the diffraction pattern by the "Squeeze" program.⁶ These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

compound	$[\mathrm{H}_{2}1](\mathrm{ClO}_{4})_{2}$	$[\mathrm{H}_{2}2](\mathrm{ClO}_{4})_{2}$	[H ₂ 3]Cl ₂	[H ₂ 4]Cl ₂
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P \overline{1}$	$P2_{1}/n$	$P \overline{1}$	<i>C</i> 2/ <i>m</i>
<i>T</i> [K]	120	120	120	120
formula	$C_{92}H_{64}N_4{\cdot}2ClO_4{\cdot}$	$C_{94}H_{64}N_4O_4{\cdot}2ClO_4$	$C_{94}H_{64}N_4O_8{\cdot}2Cl{\cdot}$	$C_{100}H_{64}N_4O_{16}\cdot 2Cl\cdot$
	$\mathrm{C_4H_8O}{\cdot}\mathrm{C_2H_6O}{\cdot}\mathrm{H_2O}$	$\cdot 6.5 C_2 H_6 O$	5CH ₄ O·4H ₂ O	$8C_{2}H_{6}O\cdot 5C_{6}H_{12}$
FW	1560.56	1811.83	1868.89	2437.78
<i>a</i> [Å]	15.0586(16)	20.917(4)	15.306(5)	36.043(11)
<i>b</i> [Å]	15.9050(18)	21.983(4)	15.402(5)	18.849(6)
c [Å]	18.483(2)	22.099(4)	19.612(7)	20.929(7)
α [°]	96.275(2)	90	81.772(5)	90
β[°]	98.0870(10)	115.546(2)	74.657(5)	115.756(4)
γ[°]	109.4310(10)	90	89.895(5)	90
V [Å ³]	4075.0(8)	9168(3)	4410(3)	12806(7)
Ζ	2	4	2	4
λ (MoK α) [Å]	0.71073			
$D_{\rm c} [{\rm g}{\rm cm}^{-3}]$	1.272	1.313	1.408	1.264
reflns measured	22945	32702	18643	19439
reflns unique	17635	11141	13197	6576
$R1 \ (I > 2\sigma(I))$	0.0678	0.0720	0.0698	0.0757
$wR2 \ (I > 2\sigma(I))$	0.1922	0.1900	0.1838	0.2041
GOF	1.125	1.019	1.026	1.010

Table S1. Crystallographic data for diprotonated dodecaphenylporphyrin derivatives.

Reference and Notes.

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Figure S1. Crystal structure of $[H_2\mathbf{1}](\text{ClO}_4)_2$. (a) A top view, (b) a side view, (c) a packing diagram viewed from the *b*-axis.



Figure S2. Crystal structure of $[H_2 2](ClO_4)_2$. ORTEP diagrams in the top view (a) and the side view (b) as drawn with 50% probability thermal ellipsoids, and a hydrogen bonding pair in the top view (c) and the side view (d).



Figure S3. Crystal structure of $[H_23]Cl_2$. ORTEP diagrams in the top view (a) and the side view (b) as drawn with 50% probability thermal ellipsoids, and a hydrogen bonding pair in the top view (c) and the side view (d).



(c)



Figure S4. Crystal structure of $[H_24]Cl_2$. (a) A top view, (b) a side view, and (c) a ladder-like hydrogen-bonding diagram. The top and side views were displayed as the crystallographically-imposed structure based on the mirror symmetry.



Figure S5. Schematic description of linking manners of the nanochannels by hydrogen bonds in (a) $[H_22](ClO_4)_2$, (b) $[H_23]Cl_2$, (c) and (d) $[H_24]Cl_2$.



Figure S6. Powder X-ray diffraction patterns of thermally treated samples for (a) $[H_23]Cl_2$ (at 250 °C) and (b) $[H_24]Cl_2$ (at 150 °C) (red lines) and simulated diffraction patterns by the single crystal structures for each sample (black lines).



Figure S7. N₂-adsorption and desorption isotherm at 77 K of (a) $[H_21](ClO_4)_2$, (b) $[H_22](ClO_4)_2$, (c) $[H_23]Cl_2$ and (d) $[H_24]Cl_2$.