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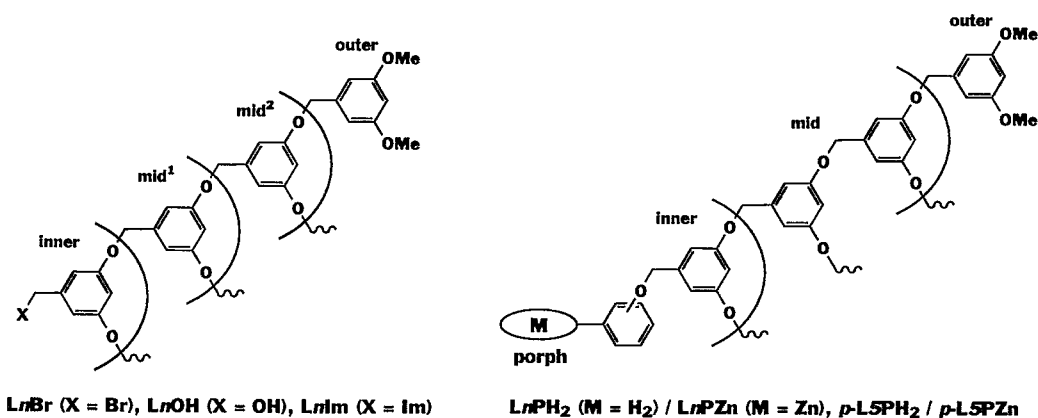
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## Supporting Information

### Schematic Representations of Dendrimers for NMR Assignments



### Synthesis and Analytical Data of Dendritic Benzyl Bromides (**LnBr**, *n* = 1 - 4) and Dendritic Benzyl Alcohols (**LnOH**, *n* = 2 - 4)

**L1Br**: To a THF solution (40 mL) of a mixture of 3, 5-dimethoxybenzyl alcohol (**L1OH**, 134.6 mmol) and CBr<sub>4</sub> (168.2 mmol) was slowly added PPh<sub>3</sub> (168.2 mmol) under N<sub>2</sub>, and the reaction mixture was stirred for 30 min and evaporated to dryness. The residue was poured into water (150 mL) and extracted with CHCl<sub>3</sub> (3 x 150 mL). The combined extracts were dried over anhydrous MgSO<sub>4</sub> and chromatographed on silica gel with CHCl<sub>3</sub> / hexane (4 / 1 v/v) as eluent. The second fraction collected was recrystallized from CHCl<sub>3</sub> / hexane to give **L1Br** (108.6 mmol) as white crystals in 80.7 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.8 (s, 6H;

OCH<sub>3</sub>), 4.45 (s, 2H; Ar-CH<sub>2</sub>-Br), 6.4 (t, 1H; Ar-*p*-H), 6.55 (d, 2H; Ar-*o*-H); mp: 71 - 72 °C.

**L2OH:** An acetone (150 mL) solution of a mixture of L1Br (31.6 mmol), 3, 5-dihydroxybenzyl alcohol (15.8 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (60 mmol), and 18-crown-6 (3.2 mmol) was refluxed for 72 h under N<sub>2</sub>. Then, the reaction mixture was evaporated to dryness, and the residue was poured into water (150 mL) and extracted with CHCl<sub>3</sub> (3 x 150 mL). The combined extracts were dried over MgSO<sub>4</sub> and chromatographed on silica gel with CHCl<sub>3</sub> as eluent, where the first fraction collected was evaporated to dryness, and recrystallized from CHCl<sub>3</sub> / hexane to give L2OH (13.7 mmol) as white crystalline solid in 86.7 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.67 (s, 1H; OH), 3.81 (s, 12H; OCH<sub>3</sub>), 4.65 (d, 2H; Ar-CH<sub>2</sub>-OH), 5.0 (s, 4H; Ar-CH<sub>2</sub>-OAr), 6.42 (t, 2H; outer Ar-*p*-H), 6.53 (t, 1H; inner Ar-*p*-H), 6.60 (d, 4H; outer Ar-*o*-H), 6.63 (d, 2H; inner Ar-*o*-H); mp: 88 - 91 °C.

**L2Br:** L2OH (32.9 mmol), CBr<sub>4</sub> (49.9 mmol), and PPh<sub>3</sub> (49.9 mmol) were reacted in THF (40 mL), and the reaction mixture was treated in a manner similar to that for L1Br, to give L2Br (30.8 mmol) as white crystalline solid in 93.6 % yield. FAB-HRMS for C<sub>25</sub>H<sub>28</sub>O<sub>6</sub>Br *m/z*: calcd: 503.1069 [MH<sup>+</sup>]; found: 503.1089; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.8 (s, 12H; OCH<sub>3</sub>), 4.43 (s, 2H; Ar-CH<sub>2</sub>-Br), 4.98 (s, 4H; Ar-CH<sub>2</sub>-OAr), 6.41 (t, 2H; outer Ar-*p*-H), 6.51 (t, 1H; inner Ar-*p*-H), 6.55 (d, 4H; outer Ar-*o*-H), 6.61 (d, 2H; inner Ar-*o*-H); mp: 117 - 120 °C.

**L3OH:** L2Br (31.2 mmol) and 3, 5-dihydroxybenzyl alcohol (15.4 mmol) were reacted in refluxing acetone (160 mL) in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> (21.8 mmol) and 18-crown-6 (3.1 mmol), and the reaction mixture was treated in a manner similar to that for L2OH, to give L3OH (14.5 mmol) as white crystalline solid in 92.9 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.80 (s, 1H; OH), 3.80 (s, 24H; OCH<sub>3</sub>), 4.70 (d, 2H; Ar-CH<sub>2</sub>-OH), 5.00 (s, 12H; mid Ar-CH<sub>2</sub>-OAr), 6.42 (t, 4H; outer Ar-*p*-H), 6.51 (t, 1H; inner Ar-*p*-H), 6.58 (t, 2H; mid Ar-*p*-H), 6.60 (d, 8H; outer Ar-*o*-H), 6.65 (d, 2H; inner Ar-*o*-H), 6.70 (d, 4H; mid Ar-*o*-H); mp: 88 - 91 °C.

**L3Br:** L3OH (5.5 mmol), CBr<sub>4</sub> (11.1 mmol), and PPh<sub>3</sub> (11.1 mmol) were reacted in THF (20 mL), and the reaction mixture was treated in a manner similar to that for L2Br, to give L3Br (3.2 mmol) as white solid in 58.2 % yield. FAB-HRMS for C<sub>57</sub>H<sub>59</sub>O<sub>14</sub>Br *m/z*: calcd: 1046.3090 [MH<sup>+</sup>]; found: 1046.3140; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.8 (s, 24H; OCH<sub>3</sub>), 4.43 (s, 2H; Ar-CH<sub>2</sub>-Br), 5.0 (s, 12H; mid Ar-CH<sub>2</sub>OAr), 6.4 (t, 4H; outer Ar-*p*-H), 6.55 (t, 1H; inner Ar-*p*-H), 6.57 (t, 2H; mid Ar-*p*-H), 6.59 (d, 8H; outer Ar-*o*-H), 6.65 (d, 2H; inner Ar-*o*-H), 6.7 (d, 4H; mid Ar-*o*-H); mp: < 30 °C.

**L4OH:** L3Br (16.9 mmol) and 3, 5-dihydroxybenzyl alcohol (8.4 mmol) were reacted in refluxing acetone (90 mL) in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> (31.6 mmol) and 18-crown-6 (1.7 mmol), and the reaction mixture was treated in a manner similar to that for L3OH, to give L4OH (8.2 mmol) as white crystalline

solid in 97 % yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.85 (s, 1H; OH), 3.8 (s, 48H;  $\text{OCH}_3$ ), 4.60 (d, 2H; Ar- $\text{CH}_2$ -OH), 4.98 (s, 28H; mid Ar- $\text{CH}_2$ -OAr), 6.42 (t, 8H; outer Ar-*p*-H), 6.51 (t, 1H; inner Ar-*p*-H), 6.53 (t, 6H; mid Ar-*p*-H), 6.56 (d, 16H; outer Ar-*o*-H), 6.62 (t, 8H; mid<sup>2</sup> Ar-*o*-H), 6.65 (d, 2H; inner Ar-*o*-H), 6.68 (d, 4H; mid<sup>1</sup> Ar-*o*-H); mp: 88 - 91 °C.

**L4Br:** L4OH (8.6 mmol),  $\text{CBr}_4$  (15.4 mmol), and  $\text{PPh}_3$  (15.4 mmol) were reacted in THF (14 mL), and the reaction mixture was treated in a manner similar to that for L3Br, to give L4Br (7.0 mmol) as white solid in 81.4 % yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.8 (s, 48H;  $\text{OCH}_3$ ), 4.43 (s, 2H; Ar- $\text{CH}_2$ -Br), 4.98 (s, 28H; mid Ar- $\text{CH}_2$ -OAr), 6.42 (t, 8H; outer Ar-*p*-H), 6.52 (t, 1H; inner Ar-*p*-H), 6.54 (t, 6H; mid Ar-*p*-H), 6.56 (t, 16H; outer Ar-*o*-H), 6.59 (t, 8H; mid<sup>2</sup> Ar-*o*-H), 6.64 (d, 2H; inner Ar-*o*-H), 6.68 (d, 4H; mid<sup>1</sup> Ar-*o*-H); mp: < 30 °C.

### Synthesis and Analytical Data of $\text{LnPH}_2$ ( $n = 1 - 5$ )

**L1PH<sub>2</sub>:** To a refluxing propionic acid solution (200 mL) of 3, 5-dimethoxybenzaldehyde (0.05 mol) was slowly added a propionic acid solution (30 mL) of pyrrole (0.05 mol), and the mixture was further refluxed for 30 min and then allowed to cool to room temperature overnight, whereupon crude crystals formed. The crystals collected were washed successively with EtOH and hot water, and recrystallized from  $\text{CHCl}_3$  / MeOH to give L1PH<sub>2</sub> as purple

crystals in 25.5 % yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -2.8 (s, 2H; NH), 4.0 (s, 24H;  $\text{OCH}_3$ ), 6.95 (t, 4H; Ar-*p*-H), 7.45 (d, 8H; Ar-*o*-H), 8.95 (s, 8H; pyrrole- $\beta$ -H); UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  421.0, 515.0, 551.0, 589.0, 644.0.

**5, 10, 15, 20-Tetrakis(2', 6'-dihydroxyphenyl)porphine ( $\text{T(OH)}_8\text{PPH}_2$ ):**

To a dry  $\text{CH}_2\text{Cl}_2$  solution (50 mL) of  $\text{L1PH}_2$  (2.1 mmol) at  $-78^\circ\text{C}$  was dropwise added a  $\text{CH}_2\text{Cl}_2$  solution (30 mL) of  $\text{BBr}_3$  (24.8 mmol) with vigorous stirring under  $\text{N}_2$ . After 30-min stirring at  $-78^\circ\text{C}$ , the reaction mixture was allowed to stand overnight at room temperature, and poured into ice - water (300 mL), which was then extracted with ethyl acetate (3 x 300 mL). The combined extracts were washed successively with water, brine, and aq.  $\text{NaHCO}_3$ , and evaporated to dryness after dried over anhydrous  $\text{MgSO}_4$ . The residue was recrystallized from  $\text{CHCl}_3$  / MeOH to give  $\text{T(OH)}_8\text{PPH}_2$  (2.0 mmol) as dark purple crystals in 95.2 % yield. FAB-HRMS for  $\text{C}_{44}\text{H}_{30}\text{O}_8\text{N}_4$   $m/z$ : calcd: 743.2142 [ $\text{MH}^+$ ]; found: 743.2100;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  -3.0 (s, 2H; NH), 6.65 (d, 4H; Ar-*p*-H), 6.95 (t, 8H; Ar-*o*-H), 8.95 (s, 8H; pyrrole- $\beta$ -H), 9.80 (s, 8H; OH).

**L2PH<sub>2</sub>**: An acetone solution (20 mL) of a mixture of  $\text{T(OH)}_8\text{PPH}_2$  (0.06 mmol),  $\text{L1Br}$  (0.58 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (2.6 mmol), and 18-crown-6 (0.06 mmol) was refluxed under  $\text{N}_2$  for 72 h in the dark. Then, the reaction mixture was evaporated to dryness, and the residue was poured into water (100 mL) and extracted with  $\text{CHCl}_3$  (3 x 100 mL). The combined extracts were dried over

anhydrous  $\text{Na}_2\text{CO}_3$  and chromatographed on silica gel with  $\text{CHCl}_3$  as eluent. The second band collected was subjected to flash column chromatography on silica gel with  $\text{CHCl}_3$  as eluent, and the crude product was recrystallized from  $\text{CH}_2\text{Cl}_2$  / hexane to give  $\text{L2PH}_2$  (0.02 mmol) as purple crystals in 33.3 % yield. FAB-MS for  $\text{C}_{116}\text{H}_{110}\text{O}_{24}\text{N}_4$   $m/z$ : calcd: 1943.8  $[\text{MH}^+]$ ; found: 1944;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -2.82 (s, 2H; NH), 3.80 (s, 48H;  $\text{OCH}_3$ ), 5.52 (s, 16H; Ar- $\text{CH}_2$ -OAr), 6.47 (t, 8H; Ar- $p$ -H), 6.68 (d, 16H; Ar- $o$ -H), 7.09 (t, 4H; porph-Ar- $p$ -H), 7.42 (d, 8H; porph-Ar- $o$ -H), 8.87 (s, 8H; pyrrole- $\beta$ -H); UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  423.0, 517.0, 551.0, 588.0, 645.0; SEC (polystyrene standards): PDI = 1.02.

**L3PH<sub>2</sub>**:  $\text{T(OH)}_8\text{PPH}_2$  (0.05 mmol) was reacted with  $\text{L2Br}$  (0.44 mmol) in acetone (9.2 mL) in the presence of anhydrous  $\text{K}_2\text{CO}_3$  (2.24 mmol) and 18-crown-6 (0.018 mmol) upon refluxing under  $\text{N}_2$  for 6 days in the dark, and the reaction mixture was treated in a manner similar to the above, affording  $\text{L3PH}_2$  (0.014 mmol) as purple crystalline solid in 28 % yield. FAB-MS for  $\text{C}_{244}\text{H}_{238}\text{O}_{56}\text{N}_4$   $m/z$ : calcd: 4120.6  $[\text{MH}^+]$ ; found: 4120;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -2.78 (s, 2H; NH), 3.74 (s, 96H;  $\text{OCH}_3$ ), 5.13 (s, 32H; outer Ar- $\text{CH}_2$ -OAr), 5.30 (s, 16H; inner Ar- $\text{CH}_2$ -OAr), 6.42 (t, 16H; outer Ar- $p$ -H), 6.58 (d, 32H; outer Ar- $o$ -H), 6.65 (t, 8H; inner Ar- $p$ -H), 6.84 (d, 16H; inner Ar- $o$ -H), 7.15 (t, 4H; porph-Ar- $p$ -H), 7.58 (d, 8H; porph-Ar- $o$ -H), 8.97 (s, 8H; pyrrole- $\beta$ -H); UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  423.0, 517.0, 551.0, 588.0, 645.0; SEC (polystyrene standards): PDI = 1.03.

**L4PH<sub>2</sub>**: T(OH)<sub>8</sub>PPH<sub>2</sub> (0.25 mmol) was reacted with L3Br (2.97 mmol) in acetone (50 mL) in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> (21.7 mmol) and 18-crown-6 (0.1 mmol) upon refluxing under N<sub>2</sub> for 14 days in the dark, and the reaction mixture was treated in a manner similar to the above (CHCl<sub>3</sub> / MeOH as eluent for chromatography), to give L4PH<sub>2</sub> (0.045 mmol) as purple crystalline solid in 18 % yield. FAB-MS for C<sub>500</sub>H<sub>494</sub>O<sub>120</sub>N<sub>4</sub> *m/z*: calcd: 8479.3 [M + 6H<sup>+</sup>]; found: 8480; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -2.85 (s, 2H; NH), 3.65 (s, 192H; OCH<sub>3</sub>), 4.83 (s, 64H; outer Ar-CH<sub>2</sub>-OAr), 4.88 (s, 32H; mid Ar-CH<sub>2</sub>-OAr), 5.10 (s, 16H; inner Ar-CH<sub>2</sub>-OAr), 6.31 (t, 32H; outer Ar-*p*-H), 6.45 (d, 64H; outer Ar-*o*-H), 6.47 (t, 16H; mid Ar-*p*-H), 6.55 (t, 8H; inner Ar-*p*-H), 6.58 (d, 32H; mid Ar-*o*-H), 6.73 (d, 16H; inner Ar-*o*-H), 7.06 (t, 4H; porph-Ar-*p*-H), 7.52 (d, 8H; porph-Ar-*o*-H), 8.95 (s, 8H; pyrrole-β-H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 424.0, 518.0, 553.0, 592.0, 648.0; SEC (polystyrene standards): PDI = 1.03.

**L5PH<sub>2</sub>**: T(OH)<sub>8</sub>PPH<sub>2</sub> (0.16 mmol) was reacted with L4Br (1.93 mmol) in acetone (60 mL) in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> (14.5 mmol) and 18-crown-6 (0.06 mmol) upon refluxing under N<sub>2</sub> for 21 days in the dark, and the reaction mixture was treated in a manner similar to the above, to give L5PH<sub>2</sub> (0.08 mmol) as purple solid in 50 % yield. MALDI-TOF-MS for C<sub>1012</sub>H<sub>1006</sub>N<sub>4</sub>O<sub>248</sub> *m/z*: calcd: 17186; found: 17180; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -2.90 (s, 2H; NH), 3.4 - 3.7 (br. s, 384H; OCH<sub>3</sub>), 4.5 - 5.0 (br., 224H; mid and outer Ar-CH<sub>2</sub>-OAr), 5.03 (br., 16H; inner



Ar-CH<sub>2</sub>-OAr), 6.1 - 6.7 (br., 360H; dendritic Ar-H), 7.02 (br, 4H; porph-Ar-*p*-H), 7.51 (br, 8H; porph-Ar-*o*-H), 8.99 (br, 8H; pyrrole- $\beta$ -H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  425.0, 520.0, 551.0, 592.5, 649.0; SEC (polystyrene standards): PDI = 1.04.

### Synthesis and Analytical Data of L $n$ PZn ( $n = 1 - 5$ )

**L1PZn:** To a CH<sub>2</sub>Cl<sub>2</sub> solution (10 mL) of L1PH<sub>2</sub> (0.006 mmol) was added a saturated MeOH solution of Zn(OAc)<sub>2</sub> (3 mL), and the mixture was refluxed for 2 h in the dark. Then, the reaction mixture was evaporated to dryness, and the residue dissolved in CHCl<sub>3</sub> was washed with water and dried over anhydrous MgSO<sub>4</sub>. The resulting crude product was purified by flash column chromatography on silica gel with CHCl<sub>3</sub> as eluent and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / hexane, to give L1PZn (0.004 mmol) in 66.7 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.94 (s, 24H; OCH<sub>3</sub>), 6.88 (t, 4H; Ar-*p*-H), 7.40 (d, 8H; Ar-*o*-H), 8.95 (s, 8H; pyrrole- $\beta$ -H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  400.0, 421.5, 506.5, 548.0.

**L2PZn:** L2PH<sub>2</sub> (0.021 mmol) was reacted with Zn(OAc)<sub>2</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub> / MeOH (10 mL / 2 mL) in a manner similar to the above. Flash column chromatography of the crude product on silica gel with CHCl<sub>3</sub> as eluent followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> / hexane gave L2PZn (0.020 mmol) in 95.2 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.78 (s, 48H; OCH<sub>3</sub>), 5.10 (s, 16H; Ar-CH<sub>2</sub>-OAr), 6.38 (t, 8H; Ar-*p*-H), 6.59 (d, 16H; Ar-*o*-H), 7.98 (t, 4H; porph-Ar-*p*-H), 7.51 (d, 8H;

porph-Ar-*o*-H), 9.0 (s, 8H; pyrrole- $\beta$ -H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  402.0, 423.0, 506.5, 549.5, 594.5.

**L3PZn:** L3PH<sub>2</sub> (0.016 mmol) was reacted with Zn(OAc)<sub>2</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub> / MeOH (10 mL / 3 mL) overnight in the dark, and the reaction mixture was treated in a manner similar to the above, to give L3PZn (0.013 mmol) in 81.3 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.65 (s, 96H; OCH<sub>3</sub>), 4.95 (s, 32H; outer Ar-CH<sub>2</sub>-OAr), 5.15 (s, 16H; inner Ar-CH<sub>2</sub>-OAr), 6.29 (t, 16H; outer Ar-*p*-H), 6.47 (d, 32H; outer Ar-*o*-H), 6.56 (t, 8H; inner Ar-*p*-H), 6.76 (d, 16H; inner Ar-*o*-H), 7.06 (t, 4H; porph-Ar-*p*-H), 7.49 (d, 8H; porph-Ar-*o*-H), 8.99 (s, 8H; pyrrole- $\beta$ -H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  404.0, 423.5, 506.5, 550.5, 590.5.

**L4PZn:** L4PH<sub>2</sub> (0.017 mmol) was reacted with Zn(OAc)<sub>2</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub> / MeOH (30 mL / 10 mL) overnight in the dark, and the reaction mixture was treated in a manner similar to the above, to give L4PZn (0.013 mmol) in 76.5 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.61 (s, 192H; OCH<sub>3</sub>), 4.78 (s, 64H; outer Ar-CH<sub>2</sub>-OAr), 4.90 (s, 32H; mid Ar-CH<sub>2</sub>-OAr), 5.12 (s, 16H; inner Ar-CH<sub>2</sub>-OAr), 6.25 (t, 32H; outer Ar-*p*-H), 6.38 (d, 64H; outer Ar-*o*-H), 6.44 (t, 16H; mid Ar-*p*-H), 6.57 (d, 32H; mid Ar-*o*-H), 6.55 (t, 8H; inner Ar-*p*-H), 6.73 (d, 16H; inner Ar-*o*-H), 7.04 (t, 4H; porph-Ar-*p*-H), 7.51 (d, 8H; porph-Ar-*o*-H), 8.99 (s, 8H; pyrrole- $\beta$ -H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  426.5, 552.0, 594.0.

**L5PZn:** L5PH<sub>2</sub> (0.0031 mmol) was reacted with Zn(OAc)<sub>2</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub> / MeOH (30 mL / 10 mL) overnight in the dark, and the reaction mixture was treated in a manner similar to the above, to give L5PZn (0.003 mmol) in 96.8 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.2 - 3.8 (br. s, 384H; OCH<sub>3</sub>), 4.2 - 5.0 (br., 224H; mid and outer Ar-CH<sub>2</sub>-OAr), 5.05 (br., 16H; inner Ar-CH<sub>2</sub>-OAr), 6.0 - 6.8 (br., 360H; dendritic Ar-H), 7.01 (br, 4H; porph-Ar-*p*-H), 7.55 (br, 8H; porph-Ar-*o*-H), 9.02 (br, 8H; pyrrole- $\beta$ -H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  427.0, 516.0, 552.0, 590.5.

### Synthesis and Analytical Data of *p*-L5PH<sub>2</sub> and *p*-L5PZn

***p*-L5PH<sub>2</sub>:** 5, 10, 15, 20-tetrakis(4'-hydroxyphenyl)porphine (T(OH)<sub>4</sub>PPH<sub>2</sub>) was prepared in a manner similar to that for T(OH)<sub>8</sub>PPH<sub>2</sub>. An acetone solution (10 mL) of a mixture of T(OH)<sub>4</sub>PPH<sub>2</sub> (0.1 mmol), L4Br (0.65 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (4.34 mmol), and 18-crown-6 (0.02 mmol) was refluxed under N<sub>2</sub> for 7 days in the dark. Then, the reaction mixture was evaporated to dryness, and the residue was subjected to repeated reprecipitations from CHCl<sub>3</sub> / hexane. The precipitates collected were poured into water (100 mL) and extracted with CHCl<sub>3</sub> (3 x 100 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>CO<sub>3</sub> and chromatographed on silica gel with CHCl<sub>3</sub> / MeOH (100 / 1 v/v) as eluent. The second fraction collected was subjected to flash column chromatography on silica gel with CHCl<sub>3</sub> as eluent, and further purified by precipitation from CH<sub>2</sub>Cl<sub>2</sub> /

hexane to give *p*-L5PH<sub>2</sub> (0.036 mmol) as purple crystalline solid in 36 % yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -2.80 (s, 2H; NH), 3.6 - 3.8 (br. s, 192H; OCH<sub>3</sub>), 4.8 - 5.0 (br. s, 112H; mid and outer Ar-CH<sub>2</sub>-OAr), 5.05 (s, 8H; inner Ar-CH<sub>2</sub>-OAr), 6.2 - 6.9 (br. m, 180H; dendritic Ar-H), 7.31 (d, 8H; porph-Ar-*m*-H), 8.21 (d, 8H; porph-Ar-*o*-H), 8.99 (s, 8H; pyrrole-β-H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 424.5, 511.0, 554.0, 593.0; SEC (polystyrene standards): PDI = 1.03.

***p*-L5PZn:** To a CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) of *p*-L5PH<sub>2</sub> (0.011 mmol) was added a saturated MeOH solution (10 mL) of Zn(OAc)<sub>2</sub>, and the mixture was refluxed overnight in the dark. The reaction mixture was evaporated to dryness, and the residue dissolved in CHCl<sub>3</sub> was washed with water and dried over anhydrous MgSO<sub>4</sub>. The resulting crude product was subjected to flash column chromatography on silica gel with CHCl<sub>3</sub> as eluent and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / hexane, affording *p*-L5PZn (0.01 mmol) in 90.9 % yield.

MALDI-TOF-MS for C<sub>528</sub>H<sub>516</sub>N<sub>4</sub>O<sub>124</sub>Zn *m/z*: calcd: 8963; found: 8960; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.6 - 3.8 (br. s, 192H; OCH<sub>3</sub>), 4.8 - 5.2 (br. s, 112H; mid and outer Ar-CH<sub>2</sub>-OAr), 5.25 (s, 8H; inner Ar-CH<sub>2</sub>-OAr), 6.2 - 6.9 (br. m, 180H; dendritic Ar-H), 7.31 (d, 8H; porph-Ar-*m*-H), 8.12 (d, 8H; porph-Ar-*o*-H), 8.99 (s, 8H; pyrrole-β-H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 426.5, 553.0, 593.5, 686.0.

## Synthesis and Analytical Data of Dendritic Imidazoles (**L<sub>n</sub>Im**, *n* = 1, 2, and 4)

Typically, to a refluxing toluene solution (120 mL) of a mixture of imidazole (1.26 mmol) and KOH (1.51 mmol) was slowly added a toluene solution (20 mL) of **L4Br** (1.26 mmol). After 15 min, the reaction mixture was evaporated to dryness, and the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was washed with saturated aqueous NH<sub>4</sub>Cl, dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The residue was chromatographed on silica gel with CHCl<sub>3</sub> as eluent, and the crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / MeOH to give **L4Im** (0.81 mmol) as white crystalline solid in 64 % yield. Likewise, **L1Im** and **L2Im** were synthesized by the reaction of potassium imidazolate with **L<sub>n</sub>Br** in 67 and 98 % yield, respectively.

**L1Im**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.67 (s, 6H; OCH<sub>3</sub>), 4.96 (s, 2H; ArCH<sub>2</sub>Im), 6.20 (d, 2H; Ar-*o*-H), 6.32 (t, 1H; Ar-*p*-H), 6.84 (s, 1H; Im-4-H), 7.02 (s, 1H; Im-5-H), 7.48 (s, 1H; Im-2-H); FAB-HRMS for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> *m/z*: calcd: 219.1133 [MH<sup>+</sup>]; found: 219.1172; Mp: 54 - 56 °C.

**L2Im**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.80 (s, 12H; OCH<sub>3</sub>), 4.94 (s, 4H; ArCH<sub>2</sub>OAr), 5.06 (s, 2H; ArCH<sub>2</sub>Im), 6.36 (d, 2H; inner Ar-*o*-H), 6.45 (t, 2H; outer Ar-*p*-H), 6.55 (overlapped, 5H; inner Ar-*p*-H + outer Ar-*o*-H), 6.90 (s, 1H; Im-4-H), 7.10 (s, 1H; Im-5-H), 7.53 (s, 1H; Im-2-H); FAB-HRMS for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub> *m/z*: calcd: 491.2182

[MH<sup>+</sup>]; found: 491.2231; Mp: 109 - 111 °C.

**L4Im:** <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.78 (s, 48H; OCH<sub>3</sub>), 4.9 - 5.0 (br., 30H; ArCH<sub>2</sub>OAr + ArCH<sub>2</sub>Im), 6.35 (d, 2H; inner Ar-*o*-H), 6.43 (t, 8H; outer Ar-*p*-H), 6.5 - 6.7 (overlapped, 35H; other dendritic Ar-H), 6.89 (s, 1H; Im-4-H), 7.08 (s, 1H; Im-5-H), 7.53 (s, 1H; Im-2-H); FAB-HRMS for C<sub>124</sub>H<sub>126</sub>N<sub>2</sub>O<sub>30</sub> *m/z*: calcd: 2123.8473 [MH<sup>+</sup>]; found: 2123.8466.

## Molecular Modelling Calculations

Molecular mechanics and dynamics calculations were performed with the DREIDING force field (version 2.21) as implemented in CERIUS<sup>2</sup> software (version 1.5; Molecular Simulations Inc., Burlington, MA) running on an Indigo<sup>2</sup> Extreme graphics workstation (Silicon Graphics). First, a full energy minimization of the initial input structures was performed by a conjugate gradient method using the DREIDING force field until the root mean square value became less than 0.1 kcal mol<sup>-1</sup> Å. Then, molecular dynamics calculations were run for 2 ps with a step size of 1 fs at 300 K (L3PH<sub>2</sub>), for 2 ps at 1,000 K (L4PH<sub>2</sub>), for 20 ps at 1,000 K (L5PH<sub>2</sub>), and for 20 ps at 300 K (*p*-L5PH<sub>2</sub>). These structures were again optimized by the same energy minimization method to obtain the final structures: (a) Mayo, S. L.; Olafson, B. D.; Goddard III, W. A. *J. Phys. Chem.* **1990**, *94*, 8897; (b) Rappe, A. K.; Goddard III, W. A. *ibid.* **1991**, *95*,

3358.

### **Titration of $L_n$ PZn ( $n = 1 - 5$ ) and $p$ -L5PZn with $L_n$ Im ( $n = 1, 2$ , and $4$ )**

Titration of  $L_n$ PZn ( $n = 1 - 5$ ) and  $p$ -L5PZn with  $L_n$ Im ( $n = 1, 2$ , and  $4$ ) was carried out in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  using a quartz cell of 0.1-cm path length. The concentrations of the zinc porphyrins were kept at  $3 - 15\ \mu\text{M}$ , while those of the dendritic imidazoles were varied in the ranges  $4 - 436\ \mu\text{M}$  for L1PZn and L2PZn,  $4 - 711\ \mu\text{M}$  for L3PZn,  $4 - 3,180\ \mu\text{M}$  for L4PZn and  $p$ -L5PZn, and  $80 - 16,800\ \mu\text{M}$  for L5PZn. The spectral changes at the Soret region ( $400 - 450\ \text{nm}$ ) were monitored for evaluation of binding constants ( $K$ ). In each case, the spectral change upon titration showed clear isosbestic points, and the plots of  $\ln[(A_{\text{obsd}} - A_{[L_n\text{Im}] = 0}) / (A_{[L_n\text{Im}] = \infty} - A_{\text{obsd}})]$  versus  $\ln[L_n\text{Im}]$  gave a straight line with the slope close to unity (correlation factor;  $0.98 - 0.99$ ), indicating one-to-one complexation. The quantities of non-complexed and complexed zinc porphyrins were measured at 6 - 8 different concentrations of  $L_n$ Im, and the obtained binding constants ( $K$ ) were averaged (SD =  $10 \sim 20\%$ ) as summarized in **Table 1**.

**Table 1.** Binding Constants ( $K$ ,  $M^{-1}$ ) of  $L_nPZn$  ( $n = 1 - 5$ ) and  $p$ - $L5PZn$  toward  $LnIm$  ( $n = 1, 2, 4$ ) in  $CH_2Cl_2$  at 20 °C.

	L1Im	L2Im	L4Im
L1PZn	92,000	44,000	36,000
L2PZn	61,000	34,000	31,000
L3PZn	28,000	23,000	14,000
L4PZn	6,400	5,300	2,700
L5PZn	1,400	350	240
$p$ -L5PZn	8,900	4,300	3,100