

## Experimental

A suspension of **Zn-1** (91.3 mg, 63.6  $\mu\text{mol}$ ) and **Sn-2** (69.1 mg, 63.6  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (ca. 10 mL) was stirred at room temperature for 24 h, after which the solution was filtered and the solvent removed under reduced pressure. The residue was recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give [**Sn-2/Zn-1**] as a purple solid. Yield: 92%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 300K):  $\delta$  10.25 (s, 2H, Zn-*meso*-H), 10.18 (s, 2H, Sn-*meso*-H), 8.43 (s, 2H, Zn-H<sub>8</sub>), 8.27 (d,  $J$  = 7.6 Hz, 2H, Zn-H<sub>9</sub>), 7.98 (d,  $J$  = 7.6 Hz, 2H, Zn-H<sub>11</sub>), 7.87 (s, 2H, Sn-H<sub>b</sub>), 7.83 (s, 1H, Sn-H<sub>a</sub>), 7.78 (t,  $J$  = 7.7 Hz, 2H, Zn-H<sub>10</sub>), 7.35 (s, 4H, tolyl H<sub>6</sub> & H<sub>7</sub>), 7.01 (s, 2H, tolyl-H<sub>5</sub>), 6.61 (d,  $J$  = 7.6 Hz, 2H, benzoate-H<sub>4</sub>), 6.50 (d,  $J$  = 5.9 Hz, 2H, Sn-pyridyl-H <sub>$\beta$</sub> ), 6.09 (t,  $J$  = 7.6 Hz, 2H, benzoate-H<sub>3</sub>), 4.93 (s, 2H, benzoate-H<sub>1</sub>), 4.47 (d,  $J$  = 7.6 Hz, 2H, benzoate-H<sub>2</sub>), 4.14-3.96 (m, 8H, Zn- $^1\text{CH}_2$ ), 3.82 (t, 4H,  $^1\text{CH}_2$  on the side of *t*-Bu<sub>2</sub> phenyl in Sn), 3.66 (t, 4H,  $^1\text{CH}_2$  on the side of pyridine in Sn), 2.76 (d,  $J$  = 6.1 Hz, 2H, Sn-pyridyl-H <sub>$\alpha$</sub> ), 2.63 (s, 12H, Zn-CH<sub>3</sub>), 2.41 (s, 6H, CH<sub>3</sub> on the side of *t*-Bu<sub>2</sub> phenyl in Sn), 2.32 (s, tolyl-CH<sub>3</sub>), 1.58 - 1.21 (the remaining protons of the hexyl groups appear as a complex overlay of multiplets), 1.48 (s, 18H, *t*-Bu), 1.13 (s, 6H, CH<sub>3</sub> on the pyridyl-side of the Sn porphyrin), 0.92 (t, 12H, Zn- $^6\text{CH}_3$ ), 0.85 (t, 6H,  $^6\text{CH}_3$  on the phenyl di-*t*-Bu<sub>2</sub>-side of the Sn porphyrin), 0.83 (t, 6H,  $^6\text{CH}_3$  on the pyridyl-side of the Sn porphyrin).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 300K):  $\delta$  161.5, 150.3, 147.6, 146.6, 145.2, 143.5, 137.6, 137.4, 132.0, 130.0, 130.7, 130.1, 127.7, 126.7, 125.8, 120.8, 117.5, 110.6, 97.3, 96.7, 35.2, 33.6, 32.9, 32.7, 32.1, 31.8, 31.6, 30.2, 30.1, 31.6, 30.2, 30.1, 29.9, 28.7, 27.0, 26.8, 26.6, 22.9, 22.7, 21.1, 15.8, 14.9, 14.4, 14.2, 14.1. UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 414 (5.30), 422 (5.17), 546 (4.28), 582 (4.07) nm. MALDI-MS:  $m/z$  2523.05 ( $\text{M}+\text{K}$ )<sup>+</sup>, ( $\text{C}_{161}\text{H}_{177}\text{N}_9\text{O}_4\text{SnZn}+\text{K}$ ) requires 2523.18.

[**Sn-3/(Zn-4)**]<sub>2</sub> was prepared by mixing two equiv. of **Zn-4** with one equiv. of **Sn-3** according to the procedure reported for [**Sn-2/Zn-1**]. Yield: 90 %.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 280K):  $\delta$  10.22 (s, 4H, Zn-*meso*-H), 10.07 (s, 2H, Sn-*meso*-H), 8.61 (s, 1H, Zn-iodophenyl-H<sub>12</sub>), 8.56 (s, 1H, Zn-iodophenyl-H<sub>12'</sub>), 8.44 (s, 2H, Zn-H<sub>8</sub>), 8.17 (d, 1H, Zn-iodophenyl-H<sub>15</sub>), 8.15 (d, 3H, Zn-iodophenyl-H<sub>15'</sub> & Zn-H<sub>9</sub>), 7.99 (d, 2H, Zn-H<sub>11</sub>), 7.76 (t, 2H, Zn-H<sub>10</sub>), 7.50 (m, 4H, Zn-iodophenyl-H<sub>12'</sub> & Zn-iodophenyl-H<sub>13</sub>), 7.40 (t, 2H, tolyl-H<sub>7</sub>), 7.28 (t, 2H, tolyl-H<sub>5</sub>), 7.05 (t, 2H, tolyl-H<sub>6</sub>), 6.56 (d, 2H, benzoate-H<sub>4</sub>), 6.04 (q, 2H, benzoate-), 4.73-4.57 (m, 4H, benzoate-H<sub>1</sub> & benzoate-H<sub>2</sub>), 4.10-3.93 (m, 8H, Zn-CH<sub>2</sub>), 3.60

(t, 4H, Sn-CH<sub>2</sub>), 2.59 (s, 12H, Zn-CH<sub>3</sub>), 2.57 (s, 12H, Zn-CH<sub>3</sub>), 2.35 (s, 6H, tolyl-CH<sub>3</sub>), 2.23 (m, 16H, Zn-<sup>2</sup>CH<sub>3</sub>), 1.78-1.21 (several multiplets, rest of hexyl groups), 0.98 (s, 12H, Sn-CH<sub>3</sub>), 0.90-0.81 (m, 36H, Zn- & Sn-CH<sub>3</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 412 (5.25), 422 (5.16), 544 (4.32), 576 (4.14) nm. MALDI-MS: m/z 3588.59 (M+Na)<sup>+</sup>, (C<sub>214</sub>H<sub>234</sub>N<sub>14</sub>O<sub>4</sub>I<sub>2</sub>SnZn<sub>2</sub>+Na) requires 3588.41.

A suspension of **Zn-1** (31.8 mg, 22.2 mmol) and **Sn-3** (23.2 mg, 23.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (ca. 10 mL) was stirred at room temperature. After 24 h, the solution was evaporated under reduced pressure. The residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give [**Sn-3/Zn-1**] as a purple solid. Yield: 90 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 300K): δ 10.25 (s, 2H, Zn-*meso*-H), 10.22 (s, 2H, Sn-*meso*-H), 8.38 (s, 2H, Zn-H<sub>8</sub>), 8.29 (d, 2H, Zn-H<sub>9</sub>), 7.99 (d, 2H, Zn-H<sub>11</sub>), 7.80 (t, 2H, Zn-H<sub>10</sub>), 7.36 (s, 2H, tolyl-H<sub>6</sub>), 7.33 (s, 2H, tolyl-H<sub>7</sub>), 7.03 (s, 2H, tolyl-H<sub>5</sub>), 6.63 (d, 2H, benzoate-H<sub>4</sub>), 6.13 (t, 2H, benzoate-H<sub>3</sub>), 4.71 (s, 2H, benzoate-H<sub>1</sub>), 4.59 (d, benzoate-H<sub>2</sub>), 4.13 (m, 4H, Zn-<sup>1</sup>CH<sub>2</sub>), 4.01 (m, 4H, Zn-<sup>1</sup>CH<sub>2</sub>), 3.74 (t, 8H, Sn-<sup>1</sup>CH<sub>2</sub>), 2.63 (s, 12H, Zn-CH<sub>3</sub>), 2.61 (s, 12H, Sn-CH<sub>3</sub>), 2.33 (s, 6H, tolyl-CH<sub>3</sub>), 2.26 (m, 8H, Zn-<sup>2</sup>CH<sub>2</sub>), 1.91 (m, 8H, Sn-<sup>2</sup>CH<sub>2</sub>), 1.81-1.26 (several multiplets, the rest hexyl groups of Zn and Sn), 0.91 (t, 12H, Zn-<sup>6</sup>CH<sub>2</sub>), 0.85 (t, 12H, Sn-<sup>6</sup>CH<sub>2</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 414 (5.27), 422 (5.12), 546 (4.30), 582 (4.10) nm. MALDI-MS: m/z 2414.57 (M+K)<sup>+</sup>, (C<sub>152</sub>H<sub>160</sub>N<sub>10</sub>O<sub>4</sub>SnZn+K) requires 2414.19.

A solution of **Ru-5** (7.4 mg, 7.3 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added to a solution of [**Sn-3/Zn-1**] (17.3 mg, μmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The mixture was stirred at room temperature for 30 min. after which the solution was concentrated to 1 mL and layered with methanol (10 mL) to give [**Ru-5/Sn-3/Zn-1**] as a red solid. Yield: 96 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 300K): δ 10.18 (s, 2H, Zn-*meso*-H), 9.95 (s, 2H, Ru-*meso*-H), 9.92 (s, 2H, Sn-*meso*-H), 8.33 (s, 2H, Zn-H<sub>8</sub>), 8.23 (d, 2H, Zn-H<sub>9</sub>), 8.14 (d, 2H, Ru-H<sub>16</sub>), 8.09 (d, 2H, Ru-H<sub>12</sub>), 7.94 (d, 2H, Zn-H<sub>10</sub>), 7.77-7.74 (m, 6H, Zn-H<sub>11</sub>, Ru-H<sub>14</sub> & Ru-H<sub>15</sub>), 7.64 (d, 2H, Ru-H<sub>13</sub>), 7.31 (s, 2H, tolyl-H<sub>7</sub>), 7.23 (s, 2H, tolyl-H<sub>5</sub>), 6.96 (s, 2H, tolyl-H<sub>6</sub>), 6.50 (d, 2H, benzoate-H<sub>4</sub>), 6.36 (d, 2H, Sn-pyridyl-H<sub>β</sub>), 5.87 (m, 4H, benzoate-H<sub>3</sub> & Sn-pyridyl-H<sub>β</sub>), 4.52 (s, 2H, benzoate-H<sub>1</sub>), 4.09 (m, 6H, benzoate-H<sub>2</sub> & Zn-<sup>1</sup>CH<sub>2</sub>), 3.91 (m, 12H, Zn-<sup>1</sup>CH<sub>2</sub> & Ru-<sup>1</sup>CH<sub>2</sub>), 3.50 (m, 8H, Sn-<sup>1</sup>CH<sub>2</sub>), 2.70 (d, 2H, Sn-pyridyl-H<sub>α</sub>), 2.57 (s, 12H, Zn-CH<sub>3</sub>), 2.43 (s, 12H, Ru-CH<sub>3</sub>), 2.19 (s, 6H, tolyl-CH<sub>3</sub>), 1.72 (d, 2H, Sn-pyridyl-H<sub>α'</sub>), 1.80-1.15 (several multiplets, the rest hexyl

groups of Zn, Sn and Ru), 1.02 (s, 6H, Sn-CH<sub>3</sub> facing Zn), 0.90-0.86 (m, 36H, Zn-, Sn- & Ru-<sup>6</sup>CH<sub>3</sub>), 0.85. (s, 6H, Sn-CH<sub>3</sub> facing Ru). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 414 (5.33), 424 (5.17), 548 (4.26), 580 (4.02) nm. MALDI-MS: m/z 3368.57 (M-CO+K)<sup>+</sup>, (C<sub>213</sub>H<sub>236</sub>N<sub>14</sub>O<sub>5</sub>RuSnZn-CO+K) requires 3368.58.