

## Supporting Information

### **Novel One-Pot Synthesis of 5-Alkenyl-15-alkynyl-porphyrins and Their Derivatisation to a Butadiyne-Linked Benzoporphyrin Dimer**

*Hiroko Yamada, \* Kayo Kushibe, Tetsuo Okujima, Hidemitsu Uno, and Noboru Ono\**

[\*]Dr. H. Yamada, K. Kushibe, Dr. T. Okujima, Prof. N. Ono

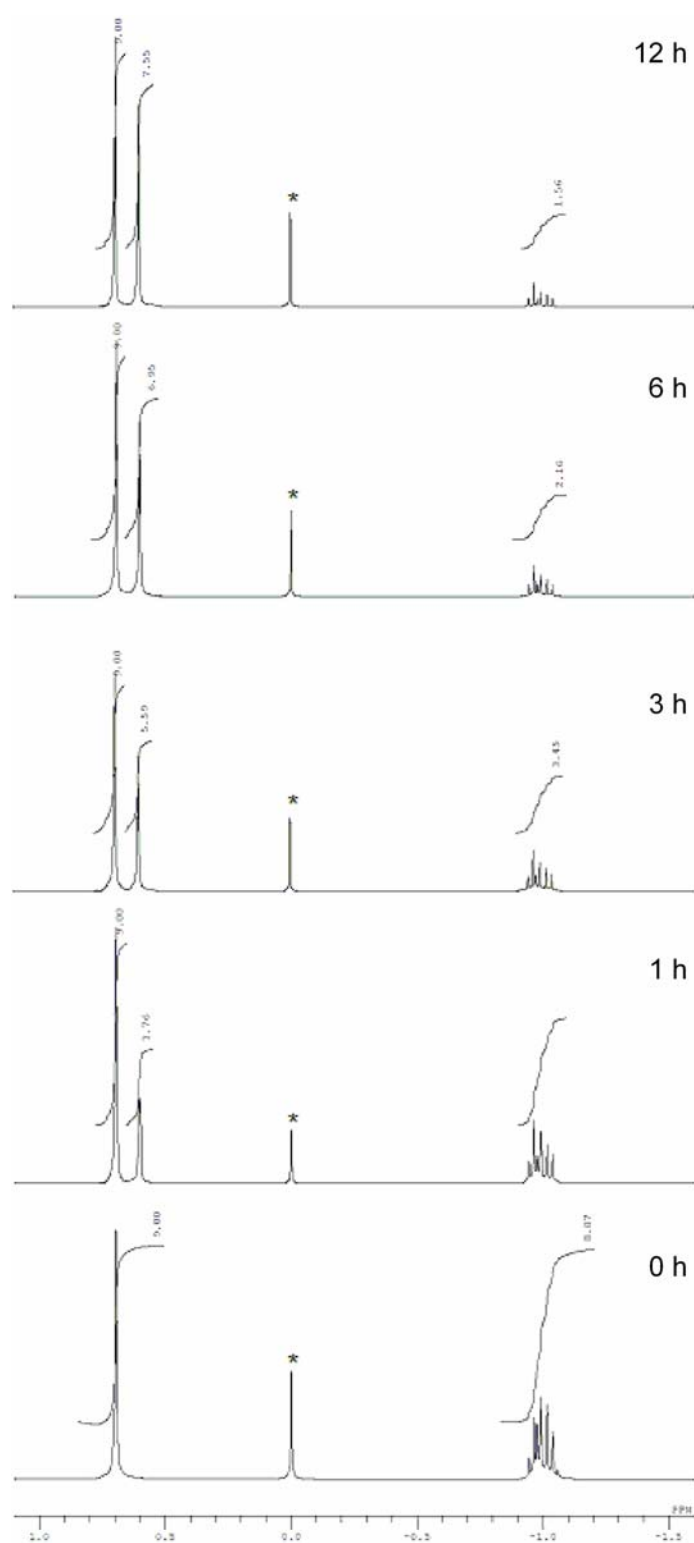
Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho 2-5, Matsuyama  
790-8577, Japan.

Fax: (+81) 89-927-9615

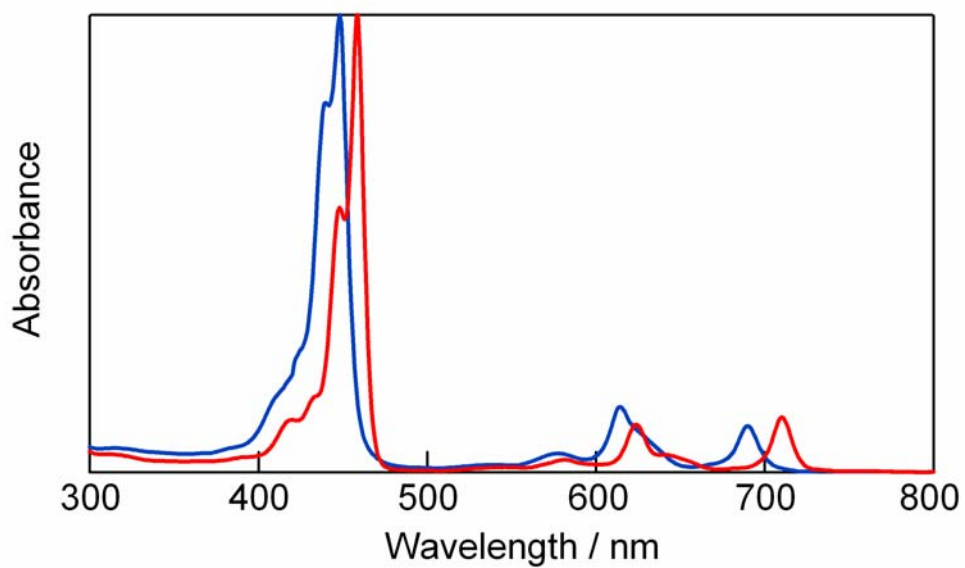
E-mail: [yamada@chem.sci.ehime-u.ac.jp](mailto:yamada@chem.sci.ehime-u.ac.jp), [ono@dpc.ehime-u.ac.jp](mailto:ono@dpc.ehime-u.ac.jp)

Prof. H. Uno

Division of Synthesis and Analysis, Department of Molecular Science, Integrated Center for  
Sciences, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, and CREST, Japan Science  
Technology Corporation (JST), Japan



**Figure S1** The photoconversion of *cis* porphyrin **3a** to *trans* porphyrin **2a** monitored by NMR spectra.  $\lambda_{\text{EX}} = 420 \text{ nm}$ ; solvent:  $\text{CDCl}_3$ . \* = TMS as an internal standard..



**Figure S2** Absorption spectra of benzoporphyrins **4b** (red) and **5b** (blue) in THF containing 5% pyridine. The absorbance was normalised at Soret peaks.

**Table S1** Yields of porphyrin synthesis with propynals

(7)	TIPS (13)	<b>14</b> : 14 %	<b>15</b> : 10%
(7)		<b>16</b> : 3 %	-
-H	TMS (9)	<b>17</b> : 3 %	-
-CH <sub>2</sub> CH <sub>3</sub>	TMS (9)	<b>18</b> : 34 %	-

## Experimental

**General** Melting points were measured with a Yanaco M-500D melting point apparatus.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Hitachi 270-30 as KBr disks. FAB mass spectra were measured on JEOL JMS-MS700V spectrometer. MALDI-TOF mass spectra were measured on Voyager DE Pro (Applied Biosystems). Elemental analyses were performed on Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. For photoreactions or spectral measurements, spectral grade of toluene and chloroform were purchased from Nakalai tesque co. Thin-layer chromatography (TLC), flush column chromatography, and gravity column chromatography were performed on Art. 5554 (Merck KGaA), Silica Gel 60 (Merck KGaA), and Silica Gel 60N (Kanto Chemical Co.), respectively. Alminum, activated (200 mesh, Wako Pure Chemical Industries, Ltd) and Bio-Beads S-X1 (Bio-Rad Lab.) were also used for purification.

**Bis(4,7-dihydro-4,7-ethano-2H-isoindol-1-yl)methane (7) (1) Bis(3-ethoxycarbonyl-4,7-dihydro-4,7-ethano-2H-isoindol-1-yl)methane:** Methylal (0.54 ml, 6.0 mmol) and acetic acid (24 ml) were added to a solution of pyrrole **6**<sup>1</sup> (2.17 g, 10.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (12 ml). After the addition of conc.  $\text{H}_2\text{SO}_4$  (10 drops), the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was poured into water to quench and then extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with water,  $\text{NaHCO}_3$  aq., and brine, then dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure. Recrystallisation from  $\text{CH}_2\text{Cl}_2$ -hexane yielded bis(3-ethoxycarbonyl-4,7-dihydro-4,7-ethano-2H-isoindol-1-yl)methane as pale yellow powder (2.23 g, quant.). m.p.: 91-92 °C;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$ =1.32 (t, 3H,  $J$ =7.1 Hz), 1.34 (t, 3H,  $J$ =7.1 Hz), 1.36-1.58 (m, 8H), 3.66 (m, 1H), 3.72 (m, 1H), 3.84-3.99 (m, 2H), 4.25-4.31 (m, 4H), 4.32

(m, 2H), 6.44-6.49 (m, 4H), 9.05 (brs, 1H), 9.11 (brs, 1H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$ =14.50, 14.56, 23.22, 23.30, 26.29, 26.99, 32.35, 32.40, 32.45, 33.89, 33.92, 59.96, 112.55, 112.60, 124.03, 124.17, 128.27, 128.35, 135.29, 135.91, 137.45, 161.98; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1045, 1088, 1142, 1223, 1265, 1311, 1446, 1512, 1670, 2341, 2360, 2866, 2950, 3047, 3317, 3734; MS (FAB)  $m/z$  (%): 447 (38) [ $\text{M}^++1$ ]; Anal. calcd for  $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_4$ : C, 72.62; H, 6.77; N, 6.27; Found: C, 72.58; H, 6.75; N, 6.25. (2) **Bis(4,7-dihydro-4,7-ethano-2H-isoindol-1-yl)methane** : A mixture of the obtained compound (0.45 g, 1.00 mmol), NaOH (0.48 g, 12.0 mmol), and ethylene glycol (30 ml) was heated to 175 °C for 3 h under an argon atmosphere in the dark. The reaction mixture was allowed to cool to room temperature and poured into water, then was extracted with  $\text{CHCl}_3$ . The organic layer was washed with water and brine. After dried over  $\text{Na}_2\text{SO}_4$ , the solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography ( $\text{CHCl}_3$ ) to yield **3** as deep brown powder (0.28 g, 92%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$ =1.45-1.56 (m, 8H), 3.56-3.60 (m, 2H), 3.79 (m, 2H), 3.89 (s, 2H), 6.29-6.31 (m, 2H), 6.43-6.51 (m, 4H), 7.16 (brs, 2H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$ =23.23, 23.29, 27.59, 27.61, 27.62, 32.11, 32.14, 33.39, 77.20, 106.27, 106.29, 125.94, 129.54, 136.15, 136.17, 136.20; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1051, 1084, 1153, 1207, 1269, 1342, 1458, 1601, 1675, 1861, 2947, 3041, 3378; MS (FAB)  $m/z$  (%): 303 (26) [ $\text{M}^++1$ ].

**Trimethylsilylpropynal (9) (1) Trimethylsilylpropynoic acid methyl ester** : To a solution of trimethylsilylacetylene (**8**) (5.6 ml, 40 mmol) in *dry* THF (60 ml) under an argon atmosphere, *n*-BuLi (27.6 ml, 44.0 mmol) was added dropwise at -78 °C. After stirring for 30 min at -78 °C, the reaction mixture was allowed to warm up to room temperature. Methyl chlorocarbonate (3.4 ml, 44 mmol) was added and stirring was continued for 2.5 h. The mixture was poured into  $\text{NH}_4\text{Cl}$  aq. to quench the reaction then extracted with ether. The organic layer was washed with water and brine. After dried over  $\text{Na}_2\text{SO}_4$ , solvent was removed under reduced pressure. The crude product

was purified on silica gel column chromatography (5% ethyl acetate / hexane) to yield trimethylsilylpropynoic acid methyl ester as orange oil (5.44 g, 87%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.24 (m, 9H), 3.77 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ=-0.79, 52.70, 94.25, 153.34; HRMS (FAB<sup>+</sup>) calcd for C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>Si 157.0685, found 157.0681. (2)

**Trimethylsilylpropynal :** To a solution of **5** (4.72 g, 30.2 mmol) in *dry* CH<sub>2</sub>Cl<sub>2</sub> (100 ml) under an argon atmosphere, DIBAL (35.3 ml, 35.5 mmol) was added dropwise at -78 °C. After stirring for 15 min at -78 °C, methanol (9 ml) was added at -78 °C to quench. Stirring was continued for 2 h at room temperature and the insoluble materials were removed by filtration. The organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to yield **6** as yellow oil (2.98 g, 78%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.27 (m, 9H), 9.17 (s, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ=-0.44, -0.13, 0.07, 77.31, 102.12, 102.99, 176.58; HRMS (FAB<sup>-</sup>) calcd for C<sub>6</sub>H<sub>10</sub>OSi 125.0423, found 125.0422.

**5,15-bis(trimethylsilylethynyl)tetrakis(bicyclo[2,2,2]octadieno)porphyrin (1a) and trans-5-alkenyl-15-alkynyltetrabicycloporphyrin (2a)** After trimethylsilylpropynal **9** (0.96 ml, 6.4 mmol) was added to a solution of **7** (1.81 g, 6.00 mmol) in methanol (600 ml) under an argon atmosphere at 0 °C, *p*-toluenesulfonic acid monohydrate (0.28 g, 1.5 mmol) was added. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and DDQ (2.68 g, 11.8 mmol) was added. After the additional stirring for 30 min, the mixture was neutralised with triethylamine (2 ml) and the solvent was removed under reduced pressure. The reaction mixture was purified on aluminum column chromatography (CHCl<sub>3</sub>) and then on silica gel column chromatography (CHCl<sub>3</sub>). Porphyrin **1a** came off as the first green band and porphyrin **2a** as the second red band. Recrystallisation from CHCl<sub>3</sub>-methanol yielded **1a** as deep purple crystals (1.48 g, 30%) and **2a** as reddish purple crystals (0.50 g, 10%). **1a**: m.p.: 168-170 °C

(decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 422 (5.39), 507 (3.85), 535 (4.13), 575 (4.67), 603 (3.94), 662 (4.24); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =-3.07 (s, 2H), 0.69 (s, 18H), 1.87-2.03 (m, 8H), 2.11-2.18 (m, 8H), 5.68 (s, 4H), 6.53 (s, 4H), 7.09 (m, 8H), 10.22 (m, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ =0.03, 0.09, 0.15, 0.21, 27.07, 27.31, 36.17, 38.57, 99.97, 98.81, 104.17, 107.87, 135.96, 136.47, 137.20, 141.82, 147.94, 147.96, 147.98, 148.00, 148.02, 151.39, 151.43; MS (FAB)  $m/z$  (%): 815 (45) [M<sup>+</sup>+1], 816 (64) [M<sup>+</sup>+2], 703 (47); Anal. calcd for C<sub>54</sub>H<sub>54</sub>N<sub>4</sub>Si<sub>2</sub>: C, 79.56; H, 6.68; N, 6.87; Found: C, 79.47; H, 6.65; N, 6.89. **2a**: m.p.: 170-172 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 419 (5.26), 521 (4.13), 559 (4.19), 590 (3.82), 646 (3.69); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =-3.24 (brs, 1H), -3.19 (brs, 1H), 0.60 (s, 9H), 0.69 (s, 9H), 1.89-2.16 (m, 16H), 5.70 (s, 4H), 5.78 (s, 2H), 6.56 (s, 2H), 6.67 and 6.68 (a mixture of diastereomers, d, 1H,  $J$ =19.0 Hz), 6.96-7.01 (m, 2H), 7.09-7.25 (m, 6H), 9.68 and 9.69 (a mixture of diastereomers, d, 1H,  $J$ =19.0 Hz), 10.22 (m, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ =-0.93, 0.16, 26.97, 27.07, 27.34, 27.37, 27.52, 27.60, 36.09, 36.24, 38.55, 39.52, 39.56, 39.61, 77.20, 77.53, 97.95, 103.23, 108.22, 120.18, 120.20, 135.95, 136.13, 136.56, 136.68, 136.73, 137.06, 137.30, 138.78, 142.27, 144.68, 144.83, 145.97, 147.51, 147.55, 147.72, 147.78, 150.45, 151.47; MS (FAB)  $m/z$  (%): 817 (26) [M<sup>+</sup>+1], 818 (48) [M<sup>+</sup>+2], 705 (23); Anal. calcd for C<sub>54</sub>H<sub>54</sub>N<sub>4</sub>Si<sub>2</sub>·CHCl<sub>3</sub>: C, 70.53; H, 6.13; N, 5.98; Found: C, 70.48; H, 6.15; N, 6.07.

**Zinc 5,15-bis(trimethylsilylethynyl)tetrakis(bicyclo[2,2,2]octadieno)porphyrin (1b)** A solution of **1a** (0.200 g, 0.246 mmol) in CHCl<sub>3</sub> (25 ml) was stirred at 75 °C with Zn(OAc)<sub>2</sub>·H<sub>2</sub>O (0.154 g, 0.700 mmol) in methanol (2.1 ml) for 2 h. The reaction mixture was poured into water and extracted with CHCl<sub>3</sub>. The organic layer was washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. Recrystallisation from CHCl<sub>3</sub>-methanol yielded **1b** as purple crystals (0.190 g, 88%). m.p.: 157-158°C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 433 (5.68), 563 (4.20), 599 (4.50), 611 (4.45); <sup>1</sup>H-NMR



(CDCl<sub>3</sub>, 400 MHz):  $\delta$ =0.69 (s, 18H), 1.93-2.20 (m, 16H), 5.69 (s, 4H), 6.68 (s, 4H), 7.09 (s, 8H), 10.23 (s, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ =0.12, 27.08, 27.14, 27.27, 27.35, 36.20, 39.36, 77.21, 97.90, 99.52, 104.28, 104.47, 109.02, 136.09, 136.14, 137.42, 137.48, 137.56, 140.80, 142.23, 144.58, 149.03, 149.65, 149.72, 151.83, 151.90; MS (FAB) *m/z* (%): 879 (0.53) [M<sup>+</sup>+3], 878 (0.51) [M<sup>+</sup>+2], 877 (0.47) [M<sup>+</sup>+1], 765 (0.51); Anal. calcd for C<sub>54</sub>H<sub>52</sub>N<sub>4</sub>Si<sub>2</sub>Zn□1/2H<sub>2</sub>O: C, 73.07; H, 6.02; N, 6.31; Found: C, 73.24; H, 6.04; N, 6.16.

**Zinc *trans*-5-(2-trimethylsilylethenyl)-15-trimethylsilylethynyltetrabicycloporphyrin (2b)**

The porphyrin **2b** was prepared from porphyrin **2a** in 85 % yield as purple crystals following the procedure described for porphyrin **1b**. m.p.: 158-160 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 425 (5.59), 554 (4.24), 594 (4.09); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =0.59 (s, 9H), 0.70 (s, 9H), 1.91-2.23 (m, 16H), 5.71 (s, 4H), 5.87 (m, 2H), 6.51, 6.52, 6.53 and 6.54 (a mixture of diastereomers, d, 1H, *J*=19.0 Hz), 6.72 (m, 2H), 6.97-7.02 (m, 2H), 7.07-7.14 (m, 6H), 9.83, 9.83 and 9.86 (a mixture of diastereomers, d, 1H, *J*=19.0 Hz), 10.24 (s, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ =-1.02, -0.97, -0.94, 0.10, 0.17, 0.23, 1.12, 26.94, 27.10, 27.19, 27.38, 27.53, 27.64, 36.09, 36.26, 39.32, 39.36, 40.18, 40.27, 77.21, 95.39, 98.71, 103.43, 103.45, 109.35, 121.27, 121.35, 126.32, 128.25, 136.07, 136.13, 136.73, 136.88, 136.93, 137.52, 137.60, 140.47, 141.40, 141.53, 144.27, 145.04, 146.64, 149.23, 149.47, 149.54, 150.72, 151.90; MS (FAB) *m/z* (%): 881 (18) [M<sup>+</sup>+3], 880 (17) [M<sup>+</sup>+2], 879 (17) [M<sup>+</sup>+1], 767 (26); Anal. calcd for C<sub>54</sub>H<sub>52</sub>N<sub>4</sub>Si<sub>2</sub>Zn□2H<sub>2</sub>O: C, 70.76; H, 6.38; N, 6.11; Found: C, 70.50; H, 6.09; N, 6.02.

***cis*-5-alkenyl-15-alkynyltetrabicycloporphyrin (3a)** Trimethylsilylpropynal **9** (0.16 ml, 1.04 mmol) was added to a solution of **7** (0.29 g, 0.97 mmol) in methanol (100 ml) under an argon atmosphere at 0 °C, then *p*-toluenesulfonic acid monohydrate (0.05g, 0.24 mmol) was added in the dark. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and DDQ (0.43 g, 1.91 mmol) was added. After the additional stirring for 30 min, the

mixture was neutralised with triethylamine (0.4 ml) and the solvent was removed under reduced pressure. The residue was purified on aluminum column chromatography (CHCl<sub>3</sub>) and on silica gel column chromatography (CHCl<sub>3</sub>) in the dark. The product **1a** came off as the first green band and the product **3a** came off as the second red band. Recrystallisation from CHCl<sub>3</sub>-methanol yielded **1a** as deep purple crystals (0.17 g, 43%) and **3a** as reddish purple crystals (0.08 g, 19%). **3a**: m.p.: 163-165 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 416 (5.27), 520 (4.20), 556 (4.21), 588 (3.87), 644 (3.72); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =-3.31 (brs, 2H), -1.06--0.94 (m, 9H), 0.70 (s, 9H), 1.64-1.79 (m, 16H), 5.70 (s, 4H), 5.91-5.95 (m, 2H), 6.57 (s, 2H), 6.97-7.11 (m, 6H), 7.17-7.22 (m, 1H), 9.78 and 9.92 (a mixture of diastereomers, d, 1H,  $J$ =14.9 Hz), 10.25 (m, 2H); MS (FAB)  $m/z$  (%): 818 (23) [ $M^{+2}$ ], 705 (49).

**5,15-bis(trimethylsilylethynyl)tetrabenzoporphyrin (4a)** Porphyrin **1a** (0.010 g, 0.012 mmol) was heated in a sample tube under reduced pressure at 200 °C for 10 min to give **4a** as deep green crystals (0.008 g, 100 %). m.p.: >300 °C; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 450 (5.50), 460 (5.74), 583 (4.13), 625 (4.71), 710 (4.76); MS (FAB)  $m/z$  (%): 703 (31) [ $M^{+1}$ ], 704 (30) [ $M^{+2}$ ]; Anal. calcd for C<sub>46</sub>H<sub>38</sub>N<sub>4</sub>Si<sub>2</sub>: C, 78.59; H, 5.45; N, 7.97; Found: C, 78.37; H, 5.51; N, 7.95.

**trans-5-alkenyl-15-alkynyltetrabenzoporphyrin (5a)** Porphyrin **5a** was prepared from porphyrin **2a** quantitatively as deep green crystals following the procedure described for porphyrin **4a**. m.p.: >300 °C; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 441 (5.50), 450 (5.65), 577 (4.19), 616 (4.75), 689 (4.61); MS (FAB)  $m/z$  (%): 705 (2.6) [ $M^{+1}$ ], 706 (2.4) [ $M^{+2}$ ]; Anal. calcd for C<sub>46</sub>H<sub>40</sub>N<sub>4</sub>Si<sub>2</sub>: C, 78.37; H, 5.72; N, 7.95; Found: C, 78.23; H, 5.66; N, 8.04.

**Zinc 5,15-bis(trimethylsilylethynyl)tetrabenzoporphyrin (4b)** Porphyrin **4b** was prepared from porphyrin **1b** quantitatively as deep green crystals following the procedure described for

porphyrin **4a**. m.p.: >300 °C; UV-vis (DMF)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 467 (6.76), 633 (5.28), 649 (5.33), 682 (5.99); HRMS (FAB<sup>+</sup>)  $m/z$ : calcd for C<sub>46</sub>H<sub>37</sub>N<sub>4</sub>Si<sub>2</sub><sup>64</sup>Zn 765.1848, found 765.1844.

**Zinc trans-5-(2-trimethylsilylethenyl)-15-trimethylsilylethynyltetrabenzoporphyrin (5b)**

Porphyrin **5b** was prepared from porphyrin **2b** quantitatively as deep green crystals following the procedure described for porphyrin **4a**. m.p.: >300 °C; UV-vis (DMF)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 454 (5.55), 603 (4.06), 639 (4.58), 659 (4.72); HRMS (FAB<sup>+</sup>)  $m/z$ : calcd for C<sub>46</sub>H<sub>39</sub>N<sub>4</sub>Si<sub>2</sub><sup>68</sup>Zn 771.1962; Found 771.1958.

**Zinc trans-5-(2-trimethylsilylethenyl)-15-ethynyltetrabicycloporphyrin (10)**

The product **2b** (0.137 g, 0.156 mmol) was dissolved in *dry* THF (195 ml) and treated with K<sub>2</sub>CO<sub>3</sub> (0.207 g, 1.50 mmol) and methanol (48 ml) under an argon atmosphere. The mixture was refluxed at 70 °C for 5 h then cooled to room temperature. The solvent was evaporated and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and solvent was removed under reduced pressure. Recrystallisation from CHCl<sub>3</sub>-methanol yielded **15** as reddish purple crystals (0.125 g, 99%). m.p.: 153-154 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 421 (5.57), 549 (4.23), 591 (4.09); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =0.60 (s, 9H), 1.92-2.19 (m, 16H), 4.42 (s, 1H), 5.71 (s, 4H), 5.88 (m, 2H), 6.53, 6.54 and 6.54 (a mixture of diastereomers, d, 1H,  $J$ =19.0 Hz), 6.66 (m, 2H), 6.98-7.02 (m, 2H), 7.09-7.14 (m, 6H), 9.83 and 9.86 (a mixture of diastereomers, d, 1H,  $J$ =19.0 Hz), 10.25 (s, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ =-3.07, -0.97, -0.94, 0.09, 1.11, 26.96, 27.10, 27.54, 27.64, 36.11, 36.26, 39.44, 40.22, 40.29, 77.21, 86.01, 87.55, 98.63, 136.05, 136.73, 136.78, 136.87, 136.92, 137.73, 140.50, 141.44, 141.56, 144.37, 145.09, 146.60, 149.09, 149.61, 150.76, 152.09, 152.10; MS (FAB)  $m/z$  (%): 809 (70.8) [M<sup>+</sup>+3], 808 (70.7) [M<sup>+</sup>+2], 807 (67.2) [M<sup>+</sup>+1], 694 (53.7); Anal. calcd for C<sub>54</sub>H<sub>52</sub>N<sub>4</sub>Si<sub>2</sub>Zn·3H<sub>2</sub>O: C, 71.02; H, 6.08; N, 6.08; Found: C, 71.02; H, 5.81; N, 6.28.

**Zinc tetrabicycloporphyrin dimer (11)** To a solution of **10** (0.050 g, 0.061 mmol) in *dry* CH<sub>2</sub>Cl<sub>2</sub> (140 ml) and pyridine (1.4 ml) stirring vigorously in a 1 L round-bottomed flask under an O<sub>2</sub> atmosphere at room temperature, CuCl (0.49 g, 4.9 mmol) and TMEDA (0.74 ml, 4.9 mmol) were added. After 20 min, the reaction mixture was washed repeatedly with water to remove Cu<sup>2+</sup> salts. The organic layer was separated and washed with brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under a reduced pressure. The residue was purified on flush silica gel column chromatography with eluents of CHCl<sub>3</sub> and then 3% MeOH in CHCl<sub>3</sub>. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>-methanol and a rinse with hexane yielded **16** as green powder (0.016 g, 33%). m.p.: 161-162 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>, nm (log ε): 413 (5.11), 437 (5.06), 480 (5.09), 538 (4.28), 565 (4.25), 649 (4.54); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.63 (s, 18H), 1.99-2.36 (m, 32H), 5.75-5.90 (m, 12H), 6.55-6.60 (m, 2H), 7.04-7.44 (m, 20H), 9.82-9.89 (m, 2H), 10.31 (s, 4H); HRMS (FAB<sup>+</sup>) *m/z*: calcd for C<sub>102</sub>H<sub>91</sub>N<sub>8</sub>Si<sub>2</sub><sup>66</sup>Zn<sup>68</sup>Zn: 1617.5414; Found: 1617.5417.

**Zinc tetrabenzoporphyrin dimer (12)** Porphyrin **11** (0.010 g, 0.006 mmol) was heated in a sample tube under reduced pressure at 200 °C for 10 min to give **17** as green powder (0.009 g, quant.). m.p.: >300 °C; UV-vis (DMF) λ<sub>max</sub>, nm (log ε): 321 (4.31), 458 (4.92), 487 (4.79), 530 (5.01), 593 (4.26), 637 (4.56), 680 (4.59); HRMS (FAB<sup>+</sup>) *m/z*: calcd for C<sub>86</sub>H<sub>59</sub>N<sub>8</sub>Si<sub>2</sub><sup>66</sup>Zn<sup>68</sup>Zn: 1391.2941; found: 1391.2947.

**Triisopropylsilylpropynal (13)** (1) **Triisopropylsilylpropynoic acid methyl ester** : To a solution of triisopropylacetylene (5.0 ml, 22.5 mmol) in *dry* THF (30 ml) under an argon atmosphere, *n*-BuLi (15.6 ml, 24.8 mmol) was added dropwise at -78 °C. After stirring for 30 min at -78 °C, the reaction mixture was allowed to warm up to room temperature. Methyl chlorocarbonate (1.9 ml, 24.8 mmol) was added and stirring continued for 2.5 h. The mixture was poured into aqueous NH<sub>4</sub>Cl to quench and the reaction mixture was extracted with ether. The organic layer was washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was

removed under reduced pressure to yield triisopropylsilylpropynoic acid methyl ester as pale yellow oil (5.39 g, quant.). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ=1.07-1.15 (m, 21H), 3.77 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ=11.02, 11.14, 18.49, 52.62, 91.45, 96.44, 153.32; HRMS (FAB<sup>+</sup>) calcd for C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>Si, 241.1624, found 241.1621. (2) **Triisopropylsilylpropynal** To a solution of the obtained methyl ester (5.39 g, 22.4 mmol) in *dry* CH<sub>2</sub>Cl<sub>2</sub> (75 ml) under an argon atmosphere, DIBAL (26.1 ml, 24.8 mmol) was added dropwise at -78 °C. After stirring for 15 min at -78 °C, methanol (7 ml) was added at -78 °C to quench. Stirring continued for 2 h at room temperature and the insoluble materials were removed by filtration. The organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure to yield **13** as colorless oil (4.36 g, 93%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ=1.07-1.14 (m, 21H), 9.21 (s, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ=11.02, 11.08, 11.26, 18.52, 18.61, 18.65, 51.73, 100.74, 104.52, 176.47; HRMS (FAB<sup>+</sup>) calcd for C<sub>6</sub>H<sub>10</sub>OSi 211.1518, found 211.1524.

**5,15-bis(triisopropylsilylethynyl)tetrakis(bicyclo[2,2,2]octadieno)porphyrin (14) and *trans*-5-alkenyl-15-alkynyltetrabicycloporphyrin (15)** Triisopropylsilylpropynal **13** (0.249 g, 1.19 mmol) was added to a solution of **7** (0.334 g, 1.11 mmol) in methanol (110 ml) under an argon atmosphere at 0 °C then *p*-toluenesulfonic acid monohydrate (0.05 g, 0.3 mmol) was added. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and stirred with DDQ (0.493 g, 2.17 mmol) for 30 min. The mixture was neutralised with triethylamine (0.4 ml) and the organic solvent was removed under reduced pressure. The residue was purified on aluminum chromatography (CHCl<sub>3</sub>) and silica gel column chromatography (CHCl<sub>3</sub>). The product **14** came off as the first green band and the product **15** came off as the second red band. Recrystallisation from CHCl<sub>3</sub>-methanol yielded **14** (0.078 g, 14%) as deep purple crystals and **15** as reddish purple crystals (0.055 g, 10%). **Porphyrin 14**: m.p.: 176-178 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>, nm (log ε): 423 (5.37), 507 (3.82), 536 (4.09), 576 (4.67),

604 (3.92), 661 (4.24);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ =-2.88 (s, 2H), 1.50 (s, 36H), 1.65 (m, 6H), 1.93-2.18 (m, 16H), 5.69 (s, 4H), 6.62 (s, 4H), 7.07 (s, 8H), 10.23 (s, 2H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$ =0.09, 12.13, 19.05, 27.31, 27.36, 36.25, 38.39, 77.21, 98.75, 109.00, 136.02, 136.20, 137.23, 142.06, 148.00, 151.39; MS (FAB)  $m/z$  (%): 985 (63) [ $\text{M}^++2$ ], 984 (81) [ $\text{M}^++1$ ], 871 (49); Anal. calcd for  $\text{C}_{66}\text{H}_{78}\text{N}_4\text{Si}_2\cdot\frac{3}{4}\text{CHCl}_3$ : C, 74.71; H, 7.40; N, 5.22; Found: C, 74.70; H, 7.44; N, 5.29. **Porphyrin 15**: m.p.: 183-185 °C (decomp.); UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 421 (5.32), 524 (4.12), 563 (4.26), 592 (3.93), 648 (3.81);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ =-2.94 (brs, 1H), -2.88 (brs, 1H), 1.42-1.49 (m, 36H), 1.65 (m, 6H), 1.88-2.18 (m, 16H), 5.71 (s, 4H), 5.90 (s, 2H), 6.64 (s, 2H), 6.72 and 6.73 (a mixture of diastereomers, d, 1H,  $J$ =19.5 Hz), 6.97-7.02 (m, 2H), 7.08 (m, 6H), 9.79 and 9.80 (a mixture of diastereomers, d, 1H,  $J$ =19.0 Hz), 10.22 (m, 2H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$ =0.10, 12.04, 12.15, 19.07, 19.25, 19.28, 19.31, 27.40, 27.47, 27.64, 36.16, 36.30, 38.36, 39.57, 50.11, 77.21, 95.61, 98.01, 99.69, 109.23, 120.08, 136.00, 136.50, 136.73, 137.31, 139.01, 142.26, 142.53, 145.45, 147.50, 147.59, 150.60, 151.48; MS (FAB)  $m/z$  (%): 986 (9) [ $\text{M}^++1$ ], 873 (3); Anal. calcd for  $\text{C}_{66}\text{H}_{80}\text{N}_4\text{Si}_2\cdot\frac{1}{2}\text{H}_2\text{O}\cdot\frac{1}{2}\text{CHCl}_3$ : C, 75.76; H, 7.79; N, 5.31; Found: C, 75.82; H, 7.81; N, 5.24.

**5,15-bis(phenylethynyl)tetrakis(bicyclo[2,2,2]octadieno)porphyrin (16)** Phenylpropynal (0.39 ml, 0.94 mmol) was added to a solution of **7** (0.26 g, 0.88 mmol) in methanol (90 ml) under an argon atmosphere at 0 °C, then *p*-toluenesulfonic acid monohydrate (0.04g, 0.2 mmol) was added. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and DDQ (0.39 g, 1.7 mmol) was added. After the additional stirring for 30 min, the mixture was neutralised with triethylamine (0.3 ml) and the solvent was removed under the reduced pressure. The residue was dissolved in  $\text{CHCl}_3$  and the organic layer was washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was removed under reduced pressure. The crude product was purified on aluminum column chromatography ( $\text{CHCl}_3$ ) and silica gel column

chromatography (CHCl<sub>3</sub>). Recrystallisation from CHCl<sub>3</sub>-methanol yielded **16** as deep purple crystals (0.010 g, 3%). m.p.: 193-195 °C (decomp.); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>, nm (log ε): 435 (5.37), 512 (3.83), 545 (3.95), 588 (4.64), 670 (4.26); <sup>1</sup>H-NMR (1%TFA/CDCl<sub>3</sub>, 400 MHz): δ=-1.92 (brs, 4H), 1.86-2.54 (m, 16H), 5.57 (s, 4H), 6.20 (s, 4H), 6.77-7.26 (m, 8H), 7.68-7.73 (m, 6H), 8.14-8.16 (m, 4H), 10.58 (m, 2H); <sup>13</sup>C-NMR (1%TFA/CDCl<sub>3</sub>, 100 MHz): δ=0.08, 26.11, 26.24, 26.48, 26.74, 29.77, 36.31, 36.37, 37.27, 37.39, 37.50, 77.21, 77.59, 100.63, 100.77, 109.73, 112.62, 115.42, 118.28, 122.54, 129.33, 130.37, 132.08, 134.52, 135.13, 135.87, 135.92, 136.10, 136.19, 138.62, 147.48, 147.51, 147.54, 147.71, 150.77; MS (FAB) *m/z* (%): 823 (1.3) [M<sup>+</sup>+1], 824 (2.8) [M<sup>+</sup>+2], 711 (2.9); Anal. calcd for C<sub>60</sub>H<sub>46</sub>N<sub>4</sub>·1/2H<sub>2</sub>O·1/2CHCl<sub>3</sub>: C, 81.49; H, 5.37; N, 6.28; Found: C, 81.44; H, 5.51; N, 6.10.

**5,15-bis(trimethylsilylethynyl)porphyrin (17)** Trimethylsilylpropynal **9** (0.35 ml, 2.4 mmol) was added to a solution of β-unsubstituted dipyrromethane<sup>2</sup> (0.32 g, 2.2 mmol) in methanol (220 ml) under an argon atmosphere at 0 °C then *p*-toluenesulfonic acid monohydrate (0.10g, 0.55 mmol) was added. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and DDQ (0.98 g, 4.3 mmol) was added. After the additional stirring for 30 min, the mixture was neutralised with triethylamine (0.7 ml) and the solvent was removed under the reduced pressure. The residue was dissolved in CHCl<sub>3</sub> and the organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified on aluminum column chromatography (CHCl<sub>3</sub>) and silica gel column chromatography (CHCl<sub>3</sub>). The product came off as the first green band. Recrystallisation from CHCl<sub>3</sub>-methanol yielded **17** as deep purple crystals (0.017 g, 3%). m.p.: >300 °C; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>, nm (log ε): 429 (5.41), 512 (3.79), 538 (4.05), 579 (4.55), 607 (3.94), 665 (4.13); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ=-2.86 (brs, 2H), 0.65 (s, 18H), 9.27 (d, 4H, *J*=4.4 Hz), 9.66 (d, 4H, *J*=4.4 Hz), 10.07 (s, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ=0.09, 0.44, 1.11, 77.20, 99.64,

102.61, 106.04, 106.71, 130.37, 131.80; MS (FAB)  $m/z$  (%): 503 (60.0)  $[M^+ + 1]$ ; Anal. calcd for  $C_{30}H_{30}N_4Si_2 \cdot 1/4H_2O \cdot 1/4CHCl_3$ : C, 67.64; H, 5.77; N, 10.43; Found: C, 67.53; H, 6.09; N, 10.20.

**5,15-bis(trimethylsilylethynyl)octaethylporphyrin (18)** Trimethylsilylpropynal **9** (0.45 ml, 3.0 mmol) was added to a solution of all- $\beta$ -ethyl-dipyrromethane<sup>3</sup> (0.72 g, 2.8 mmol) in methanol (250 ml) under an argon atmosphere at 0 °C, then *p*-toluenesulfonic acid monohydrate (0.14g, 0.75 mmol) was added. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and DDQ (1.25 g, 5.5 mmol) was added. After the additional stirring for 30 min, the mixture was neutralised with triethylamine (0.8 ml) and the solvent was removed under the reduced pressure. The residue was dissolved in  $CHCl_3$  and the organic layer was washed with water and brine, dried over  $Na_2SO_4$ , and the solvent was removed under reduced pressure. The crude product was purified on aluminum column chromatography ( $CHCl_3$ ) and silica gel column chromatography ( $CHCl_3$ ). The product came off as the first green band. Recrystallisation from  $CHCl_3$ -methanol yielded **18** as deep purple crystals (0.348 g, 34%). m.p.: 261-262 °C; UV-vis ( $CH_2Cl_2$ )  $\lambda_{max}$ , nm (log  $\epsilon$ ): 429 (5.41), 512 (3.79), 538 (4.05), 579 (4.55), 607 (3.94), 665 (4.13);  $^1H$ -NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = -1.51 (brs, 2H), 0.58 (s, 18H), 1.81 (t, 12H,  $J$ =7.8 Hz), 1.86 (t, 12H,  $J$ =7.8 Hz), 4.04 (q, 8H,  $J$ =7.8 Hz), 4.31 (q, 8H,  $J$ =7.8 Hz), 10.08 (s, 2H);  $^{13}C$ -NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 17.61, 18.49, 19.77, 21.63, 77.21, 96.99, 98.38, 105.92, 106.68, 140.13, 142.12, 144.39, 147.01; MS (FAB)  $m/z$  (%): 727 (100)  $[M^+ + 1]$ ; Anal. calcd for  $C_{46}H_{62}N_4Si_2$ : C, 75.98; H, 8.59; N, 7.70; Found: C, 75.90; H, 8.52; N, 7.76.

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