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Synthesis of extremely soluble precursors of tetrabenzoporphyrins

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Abstract

This paper describes the preparation of dimethylbicyclo[2.2.2]octadiene-fused porphyrins as extremely soluble precursors of tetrabenzoporphyrins and thermal conversion of the precursors to tetrabenzoporphyrins.

1. Introduction

Recently, much attention has been focused on the organic semiconducting molecules due to their potential applications in electronics as large-area, low-cost, and flexible materials. Many kinds of π-conjugated systems provided suitable materials for such applications. The organic semiconductors are classified into two groups: polymers and low-molecular-weight materials. Polymers are attractive as organic field effect transistors (OFETs) because their thin films are easily fabricated by the solution processes such as spin-coating or printing techniques. On the other hand, the vacuum deposition technique was employed for low-molecular-weight materials. However, only a few polymers exhibited good performance with high carrier mobility beyond 0.1 cm^2/V s even after structural optimization or annealing.[1–4] Most of them showed low mobility compared with small molecules due to their poor molecular ordering and low crystallinity by the solution process. Therefore, a development of solution-processible low-molecular-weight semiconductors is necessary in order to provide low-cost and large-area OFET devices with the high performance.

For the fabrication of small semiconducting molecules by the solution process, their poor solubility is the obstacle. For example, pentacene is one of the most widely studied organic semiconductors because of its high charge mobility up to 3 cm^2/V s.[5] Improvement of the performance was achieved by optimization of the device structure. In many cases, the thin films have been fabricated by vacuum deposition. Recently, the solution-processed organic thin-film transistors (OTFTs) of pentacene were reported by Afzali et al.[6] and Müllen et al.[7] The OTFTs were fabricated by spin-coating of the Diels–Alder adducts of pentacene followed by annealing. The devices exhibited good charge mobilities of 0.2–0.9 cm^2/V s. Their performance depended on the loss of weight in retro Diels–Alder reaction and optimization of conversion conditions.

Phthalocyanines and porphyrins are also the promising semiconductors for practical OFETs.[8,9] They were very attractive for the fabrication of OFETs due to the easy optimization of molecular structure and the thermal and chemical stabilities compared to pentacene. Little is known about solution-processed organic semiconductors of phthalocyanines and porphyrins. Only a few examples of soluble precursors of tetrabenzoporphyrins (TBPs) synthesized utilizing the masked isoindole method have been reported by Cavaleiro et al.[10] Recently, we have also reported the convenient and highly efficient synthesis of insoluble benzoporphyrin derivatives by the retro Diels–Alder reaction.[11,12] TBPs (**1**) were prepared quantitatively by heating soluble bicyclo[2.2.2]octadiene(BCOD)-fused porphyrins **2** as solids

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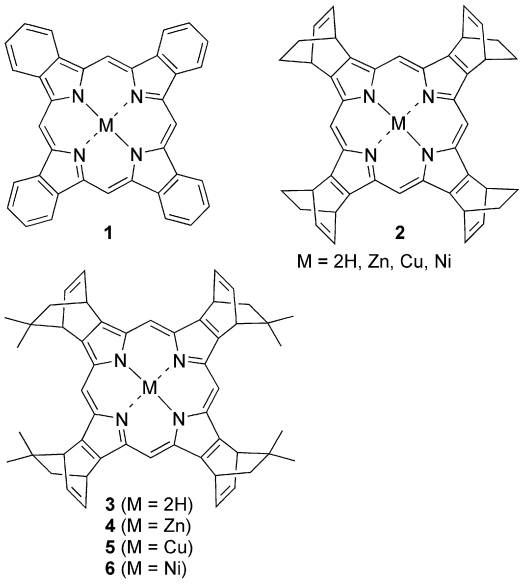


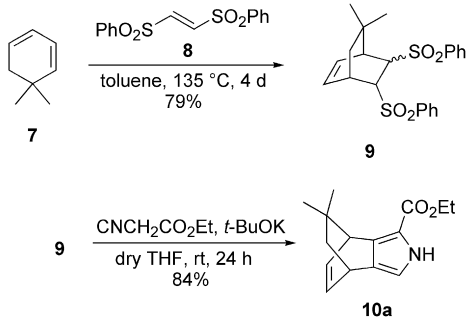
Chart 1.

(Chart 1). We have succeeded in preparation of a polycrystalline thin film of **1** by heating an amorphous thin film of **2** at 200 °C followed by spin-coating of **2**. The thin film of **1** showed good transistor properties ($\mu = \sim 10^{-1}$ cm^2/V s).[13] However, chloroform was used as a solvent for the spin-coating of **2**. Chlorinated solvents are unfavorable for an application in electronics due to their toxicity. The plastic substrates are dissolved in such solvents. To produce the practical solution-processible organic semiconductors, the solubility of the precursors should be improved. Herein, we report an efficient preparation of extremely soluble TBP precursors **3**–**6** from dimethyl BCOD-fused pyrrole derivatives and thermal conversion of the precursors to TBPs.

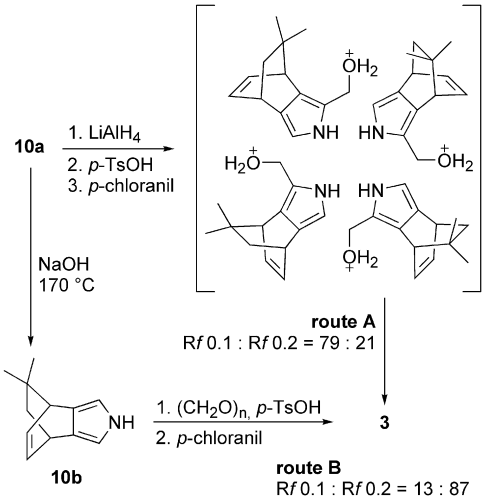
2. Results and discussion

*2.1. Synthesis of TBP precursors **3**–**6** and thermal conversion to TBP*

The synthesis of pyrrole **10a** is summarized in Scheme 1. 5,5-Dimethyl-1,3-cyclohexadiene (**7**) was prepared by the procedure described in the literature.[14] The Diels–Alder reaction of **7** with *trans*-1,2-bis(phenylsulfonyl)ethylene (**8**) gave the adduct **9** in 79% yield.[15] The adduct **9** was treated with



Scheme 1.



Scheme 2.

ethyl isocyanoacetate in the presence of potassium *tert*-butoxide to give dimethyl BCOD-fused pyrrole **10a** in 84% yield. Porphyrin **3** was synthesized as a mixture of diastereomers by reduction of **10a** with $LiAlH_4$ followed by tetramerization and oxidation with *p*-chloranil in good yield as shown in Scheme 2. Porphyrin was purified by column chromatography on silica gel with $CHCl_3$ to give two fractions of R_f=0.1 and 0.2 ($CHCl_3$). After further purification by preparative GPC and recrystallization from $CHCl_3$/methanol, the isolated yields of **3a** (R_f 0.1) and **3b** (R_f 0.2) were 57 and 15% yields, respectively, and the relative ratio of **3a**/**3b** was 79:21. Metal porphyrins **4**–**6** were readily prepared by the reaction of **3** with the corresponding metal acetates in almost quantitative yields.

The retro Diels–Alder reaction of **3** was carried out in a glass tube oven at 210 °C under reduced pressure for 20 min. TBP was quantitatively obtained from both **3a** and **3b**. The TG analysis of **2** (2H) and **3b** is shown in Figure 1. The weight loss of both **2** and **3b** started at around 150 °C and stopped after 200 °C. The loss of weight of **3b** was 37%, which corresponds to the elimination of four isobutene molecules and the including solvents. After the measurement of TG, the pure **1** was obtained. Metal porphyrins **4**–**6** were also converted into metal complexes of TBP by heating under the same conditions quantitatively.

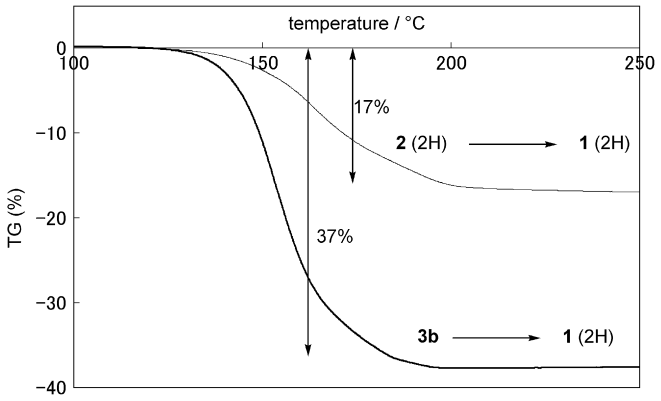


Figure 1. Thermogravimetric analysis of **2** (2H) (solid line) and **3b** (bold line).

The absorption spectra of dimethyl BCOD-fused porphyrins **3**–**6** in $CHCl_3$ were similar to those of **2**.[11b] For example, **3** showed the Soret band at 385 nm and the Q bands at 496, 527, 564, and 616 nm. The Soret bands of metal complexes **4**–**6** appeared at 402, 399, and 392 nm, respectively (see Supplementary data). A glass plate coated with **3b** was prepared by spin-coating of a solution of **3b**. The Soret band of **3b** was observed at 402 nm. After heating the glass at 210 °C for 20 min, the absorption maxima showed a consistent bathochromic shift on changing the fused bicyclic rings to benzene rings. The broad Soret band appeared at 415 nm, which corresponded to the Soret band of TBP.

2.2. Characterization, solubility, and the optimized preparation of porphyrin *3*

Porphyrins **3**–**6** were characterized by physical and spectral methods including the X-ray crystallographic analysis in the case of **3a**, **4a**, and **5a**. The stereochemistry of **3** was investigated by ^{1}H NMR spectroscopy. ^{1}H NMR spectra of **3a** and **3b** are shown in Figure 2. The methyl signals of **3a** are observed as a pair of singlet absorptions at 0.7 (*endo* methyl) and 1.5 (*exo* methyl) ppm, while those of **3b** are observed as complex numbers of singlet absorptions at 0.6–0.8 and 1.6 ppm. This indicates that **3a** consists of a single isomer and has either 4 or $\bar{4}$ symmetry. On the other hand, **3b** consists of other isomers. The prediction is confirmed by the X-ray crystallographic analysis of **3a** as described in Section 2.3.

The solubility of porphyrins **3**, which were expected to show good solubility due to their bulky bicyclic rings was determined by the absorptions in UV–vis spectroscopy. The saturated solutions of BCOD-fused porphyrins **2** (M=2H), **3a**, and **3b** were prepared and then diluted for measuring their absorption. Toluene, methanol, and hexane were used as the solvents. The dimethyl BCOD-fused porphyrin mixture **3b** showed over 100 times higher solubility compared to **2** for toluene while the symmetrical **3a** showed only higher solubility (3 times) compared to **2**. The ratio of solubility was 1:0.6:>100 (methanol) and 1:2:60 (hexane) for **2/3a/3b**. The dimethyl BCOD-fused porphyrin mixture **3b** is much more soluble in organic solvents compared with **2**, while **3a** showed similar solubility as **2**. Since soluble isomeric mixture **3b** was a minor component by route A, another synthetic route should be searched to increase the yield of isomeric mixture **3b**. Removal of the ethoxycarbonyl group by heating **10a** with NaOH in ethylene glycol at 170 °C gave α-free pyrrole **10b** in 71% yield. The reaction of **10b** with paraformaldehyde in the presence of *p*-TsOH followed by the oxidation with *p*-chloranil gave **3a** and **3b** in 4 and 29% yields, respectively. The ratio of **3a** and **3b** was 13:87. ^{1}H NMR spectrum of **3b** from route B is shown in Figure 2. The ratio of isomeric mixtures from route B is different from that from route A due to the different reaction routes. However, the solubility of **3b** from route B was similar to route A. Therefore, the extremely soluble TBP precursor **3b** was prepared by route B (Scheme 2).

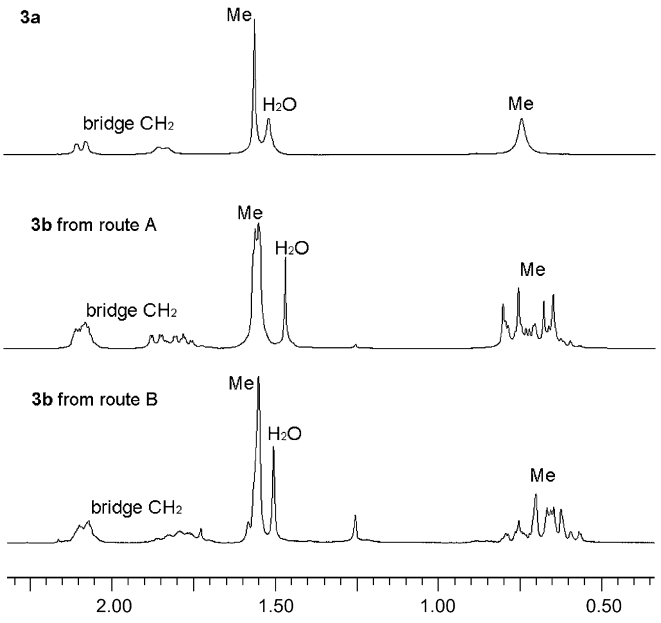


Figure 2. ^{1}H NMR spectra of **3a** and **3b** from route A and B.

2.3. Crystal structure of *10a*, *3a*, *4a*, and *5a*

The crystal structure of **10a** was determined by X-ray diffraction analysis. Single crystals for the X-ray structural determination were obtained by recrystallization from methanol/$CHCl_3$. Dimethyl BCOD-fused pyrrole **10a** crystallizes in a monoclinic cell, space group $P2_1/n$, and Z=4 (Table 1). The ORTEP drawing is shown in Figure 3. The structure of the product in the Barton–Zard reaction of **9** was apparently not 9,9-dimethyl but 8,8-dimethylisoindole **10a**. The formation of **10a** was well rationalized as follows: the sulfonyl group at

Table 1
Crystallographic summary of pyrrole **10a** and porphyrins **3a**–**5a**

	10a	**3a**	**4a**	**5a**
Formula	$C_{15}H_{19}NO_2$	$C_{52}H_{54}N_4\cdot 2CHCl_3$	$C_{52}H_{52}N_4Zn\cdot CH_3OH\cdot CHCl_3$	$C_{52}H_{52}N_4Cu\cdot CHCl_3$
FW	245.32	973.78	949.8	915.89
System	Monoclinic	Tetragonal	Tetragonal	Monoclinic
Space group	$P2_1/n$	$I\bar{4}$	$I\bar{4}$	$C2$
a/Å	6.1731 (6)	15.0927 (14)	15.004 (5)	20.431 (16)
b/Å	31.764 (2)	15.0927 (14)	15.004 (5)	9.762 (7)
c/Å	7.3136 (7)	10.4558 (17)	10.039 (5)	14.778 (11)
α/°	90.00	90.00	90.00	90.00
β/°	108.216 (5)	90.00	90.00	132.948 (6)
γ/°	90.00	90.00	90.00	90.00
V/Å^3	1362.2 (2)	2381.7 (5)	2260.0 (15)	2157 (3)
Z	4	2	2	2
μ (Mo Kα) /mm^{-1}	0.079	0.403	0.766	0.736
Unique	3043	2722	2570	4130
R_{int}	0.0250	0.0244	0.0432 [0.0444]	0.0690
Obsd	2273	1710	2198 [2167]	3194
Param.	164	325	186 [168]	290
R_1	0.0675	0.0760	0.0724 [0.0668]	0.0980
wR_2 (all)	0.1872	0.2223	0.1897 [0.1930]	0.2455
GOF	1.143	1.082	1.088 [1.090]	1.128
T/K	298	100	173	100
CCDC No.	661511	661512	661513, 661514	661628

[a] Values in brackets are obtained by removal of solvent chloroform using the PLATON-SQUEEZE program.[16]

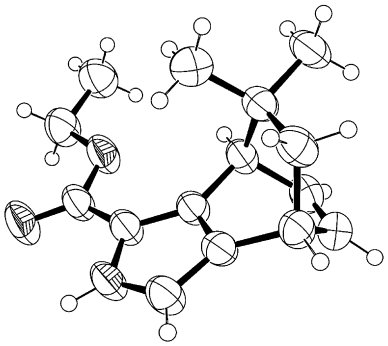


Figure 3. ORTEP drawing of **10a**.

7-position in **9** was removed by potassium *tert*-butoxide selectively due to the steric hindrance of two methyl groups and then the reaction with ethyl isocyanoacetate afforded **10a**.

The crystallographic data of isomerically pure porphyrins **3a**–**5a** with lower solubilities are summarized in Table 1.[16] Free base porphyrin **3a** and Zn complex **4a** crystallize in a tetragonal cell, and Cu complex **5a** crystallizes in a monoclinic cell. We encountered the difficulty in determination of the space groups of **3a** and **4a**. From the extinction law and intensity statistics, the space group of **3a** was firstly suggested as a centric space group *I*4/*m*. The structure could be solved and refined as a heavily disordered form with rather high R_1 and wR_2 values. As there were two other noncentrosymmetric space groups with the same extinction law with *I*4/*m*, we examined the possibility of these space groups $I\bar{4}$ and *I*4. Next, we solved and refined the structure of **3a** in $I\bar{4}$, which was more common than *I*4. The result was, however, almost the same as in *I*4/*m*. Finally, by treatment as a twin crystal, we obtained the satisfactory result in *I*4 (Table 1). Similarly, the space groups of **4a** and **5a** were determined as chiral *I*4 and *C*2, respectively. The porphyrin rings adopted a domed conformation like a saucer. The dimethylethano moiety is under the saucer and a methanol molecule coordinates to the center zinc atom from the top side as shown in Figure 4. Cu complex **5a** also has a domed structure. The displacements of β-pyrrole from the mean planes are 0.31 and 0.33 Å for **3a**, 0.14 and 0.17 Å for **4a**, and 0.070, 0.070, 0.11, and 0.19 Å for **5a**. Inner zinc in **4a** is pulled from porphyrin plane toward top side owing to the coordination of methanol.

The symmetrical **3a**–**6a** showed lower solubility than **3b**–**6b** as described in Section 2.2. The solubility of porphyrins **3**–**6** depended on their stereochemistry. In the molecular packing, **4a** showed the regular configuration to minimize the steric hindrance (Fig. S-23, Supplementary data). On the other hand, the similar configuration of asymmetrical **3b**–**6b** is unfavorable and their π-stacking is prevented at both sides of porphyrin plane due to the bulky bridge moieties with two methyl groups.

3. Conclusion

We have demonstrated that the extremely soluble TBP precursors **3b**–**6b** were prepared by Lindsey porphyrin synthesis from dimethyl BCOD-fused pyrrole **10b**. The X-ray diffraction analysis revealed that **3a** with low solubility had *C*4

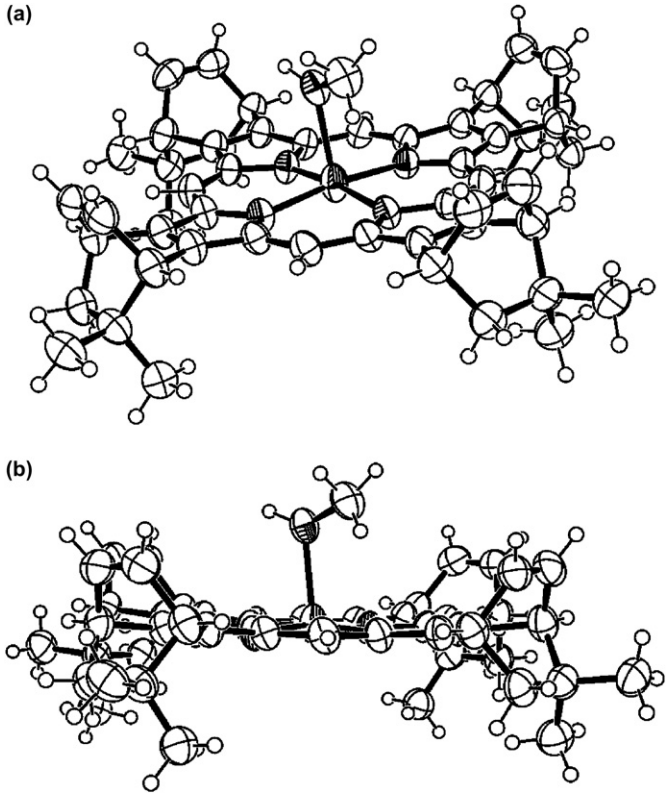


Figure 4. (a) ORTEP drawing and (b) side view of **4a**. This structure is obtained by removal of solvent chloroform using the PLATON-SQUEEZE program.[16]

symmetry in the stereochemistry of bicyclic rings. The retro Diels–Alder reaction of **3**–**6** afforded pure TBPs efficiently by heating at 200 °C in a solid. This study shows the potential utility of the novel TBP precursors **3**–**6** for applications in solution-processible electronics as large-area, low-cost, and flexible materials because the precursors are dissolved not only in $CHCl_3$ but also in hexane, methanol, and toluene. Further investigations of solution-processed fabrication method and OFET performance are under way.

4. Experimental

4.1. General

Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. DI-EI and FAB mass spectra were recorded on a JEOL JMS-700. IR spectra were recorded on a Horiba FT-720 Infrared Spectrophotometer. UV–vis spectra were recorded on a JASCO V-570 spectrophotometer. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL AL-400 at 400 MHz (100 MHz). Gel permeation chromatography (GPC) was performed on a JAIGEL 2-H and a JAIGEL 1-H. Elemental analyses were performed at Integrated Center for Sciences, Ehime University.

4.1.1. 7,8-Bis(phenylsulfonyl)-5,5-dimethylbicyclo[2.2.2]oct-2-ene (**9**)

A solution of **7** (7.21 g, 61.3 mmol, purity 92%) and **8** (9.25 g, 30.0 mmol) in toluene (70 ml) was heated at 135 °C

for 4 days in an autoclave. The solvent was removed under reduced pressure. The residue was washed with ether to give **9** (9.88 g, 79%). White powder; mp 172.0–173.1 °C; MS (FAB) *m/z* (relative intensity) 417 (M^++1, 59%); IR (KBr disk) ν_{max} 3066, 2972, 2935, 2870, 1446, 1306, 1217, 1147, and 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 2H, C-2′,6′), 7.83 (m, 2H, C-2′,6′), 7.64–7.70 (m, 2H, C-4′), 7.58 (m, 2H, C-3′,5′), 7.56 (m, 2H, C-3′,5′), 6.29 (dd, 1H, *J*=7.3, 6.5 Hz, H-3), 6.20 (dd, 1H, *J*=7.3, 6.5 Hz, H-2), 4.37 (dd, 1H, *J*=6.3, 2.0 Hz, H-7), 3.67 (ddd, 1H, *J*=6.3, 2.4, 2.0 Hz, H-8), 3.12 (m, 1H, H-1), 2.57 (d, 1H, *J*=6.5 Hz, H-4), 2.16 (dd, 1H, *J*=13.7, 2.0 Hz, H-6), 1.15 (s, 3H, 5-Me), 1.00 (ddd, 1H, *J*=13.7, 2.4, 2.0 Hz, H-6), and 0.86 (s, 3H, 5-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.60 (C-1′), 138.84 (C-1′), 134.77 (C-3), 133.79 (C-4′), 133.75 (C-4′), 130.22 (C-2), 129.12 (C-3′,5′), 129.06 (C-3′,5′), 128.49 (C-2′,6′), 128.48 (C-2′,6′), 63.76 (C-8), 62.35 (C-7), 44.08 (C-4), 34.09 (C-7′), 33.87 (C-6), 33.24 (C-1), 31.56 (5-Me), and 26.83 (5-Me). Anal. Calcd for $C_{22}H_{24}O_4S_2$: C, 63.43; H, 5.81. Found: C, 63.21; H, 5.78.

4.1.2. Ethyl 4,7-dihydro-8,8-dimethyl-4,7-ethano-2H-isoindole-1-carboxylate (*10a*)

To a stirred solution of **9** (16.66 g, 40.00 mmol) and ethyl isocyanoacetate (5.6 ml) in dry THF (190 ml) was added dropwise a solution of potassium *tert*-butoxide (13.61 g) in dry THF (120 ml) at 0 °C under an Ar atmosphere. The resulting mixture was stirred at room temperature under an Ar atmosphere for 1 day. The reaction mixture was poured into 1 M HCl (10 ml), evaporated, and extracted with $CHCl_3$. The organic layer was washed with water, satd aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **10a** (8.285 g, 84%). Colorless crystals; mp 127.2–128.0 °C; MS (70 eV) *m/z* (relative intensity) 245 (M^+, 0.1%), 189 (100); IR (KBr disk) ν_{max} 3309 (N–H), 3051, 2974, 2929, 2859, 1685 (C=O), 1608, 1587, 1494, 1458, 1427, 1369, 1315, 1259, 1211, 1155, 1116, and 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (br s, 1H, NH), 6.55 (d, 1H, *J*=2.7 Hz, H-3), 6.47–6.56 (m, 2H, H-5,6), 4.36 (dq, 1H, *J*=10.7, 7.1 Hz, 1-CO_2Et), 4.27 (dq, 1H, *J*=10.7, 7.1 Hz, 1-CO_2Et), 3.81 (d, 1H, *J*=5.9 Hz, H-7), 3.73 (m, 1H, H-4), 1.40 (m, 1H, H-9), 1.36 (t, 3H, *J*=7.1 Hz, 1-CO_2Et), 1.22 (dd, 1H, *J*=11.7, 2.7 Hz, H-9), 1.07 (s, 3H, 8-Me), and 0.70 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.63 (1-CO_2Et), 136.49 (C-7a), 135.96 (C-6), 135.22 (C-5), 130.02 (C-3a), 116.20 (C-1), 112.67 (C-3), 59.73 (1-CO_2Et), 46.42 (C-7), 43.82 (C-9), 37.77 (C-8), 34.61 (C-4), 30.82 (8-Me), 30.29(8-Me), and 14.63 (1-CO_2Et). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.53; H, 7.82; N, 5.67.

4.1.3. 4,7-Dihydro-8,8-dimethyl-4,7-ethano-2H-isoindole (*10b*)

A solution of **10a** (496 mg, 2.02 mmol) and NaOH (617 mg) in ethylene glycol (35 ml) was heated at 170 °C for 80 min under an Ar atmosphere in a shaded vessel. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **10b** (250 mg, 71%). Colorless crystals; mp >90 °C (decomp.); MS (70 eV) *m/z* (relative intensity) 173 (M^+, 3%) and 117 (100); IR (KBr disk) ν_{max} 3365 (N–H), 3039, 2964, 2929, 2861, 1602, 1508, 1428, 1340, 1288, 1255, 1197, 1155, 1122, 1089, 1047 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (br s, 1H, NH), 6.54 (m, 1H, H-6), 6.48 (m, 1H, H-5), 6.47 (m, 1H, H-1 or H-3), 6.41 (m, 1H, H-1 or H-3), 3.70 (m, 1H, H-4), 3.22 (d, 1H, *J*=5.9 Hz, H-7), 1.41 (dd, 1H, *J*=11.5, 2.7 Hz, H-9), 1.24 (dd, 1H, *J*=11.5, 2.7 Hz, H-9), 1.04 (s, 3H, 8-Me), and 0.72 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.97, 135.23, 128.65, 127.87, 110.28, 107.67, 46.03, 44.32, 37.39, 34.52, 31.00, and 30.73. Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.97; H, 8.55; N, 8.04.

4.1.4. Tetrakis(dimethylBCOD)porphyrin *3a*

Route A: to a solution of **10a** (487 mg, 1.99 mmol) in dry THF (30 ml), $LiAlH_4$ (352 mg, 9.27 mmol) was added at 0 °C under an Ar atmosphere. The resulting mixture was stirred at the same temperature for 2 h. The reaction mixture was poured into water, filtrated with Celite, and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was diluted with $CHCl_3$ (400 ml) and *p*-TsOH·H_2O (30 mg) was added. After stirring at room temperature for 1 day, *p*-chloranil (291 mg, 1.18 mmol) was added. The resulting mixture was stirred at the same temperature for 1 day. The mixture was poured into water. The organic layer was washed with satd aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on alumina with $CHCl_3$, column chromatography on silica gel with $CHCl_3$ and EtOAc/$CHCl_3$, and recrystallization from methanol/$CHCl_3$ to give **3a** (207 mg, 57%) and **3b** (56 mg, 15%).

Route B: **10b** (173 mg, 0.999 mmol) and paraformaldehyde (36 mg) were dissolved in $CHCl_3$ (200 ml) in a shaded vessel. After stirring at room temperature for 10 min under an Ar atmosphere, *p*-TsOH·H_2O (34 mg) was added. The resulting mixture was stirred at the same temperature for 24 h. After addition of *p*-chloranil (100 mg, 0.407 mmol), the mixture was stirred for 2 h and poured into satd aqueous $NaHCO_3$. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on alumina with $CHCl_3$ and on silica gel with $CHCl_3$ to give **3a** (8 mg, 4%) and **3b** (53 mg, 29%).

Porphyrin **3a**: purple crystals; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 736 (M^++2, 12%) and 511 (100); HRMS calcd for $C_{52}H_{55}N_4$ 735.4427, found 735.4425; UV–vis ($CHCl_3$) λ_{max}, nm: 385, 496, 527, 564, and 616; ^1H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 4H, *meso*-H), 7.16 (m, 8H, olefin), 5.62 (m, 4H, bridge head), 5.12 (d, 1H, *J*=5.9 Hz, bridge head), 2.09 (dd, 4H, *J*=11.7, 2.4 Hz, bridge CH_2), 1.84 (m, 4H, bridge CH_2), 1.56 (s, 12H, Me), 0.75 (s, 12H, Me), and −4.66 (br s, 2H, NH). Porphyrin **3b**: purple

powder; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 736 (M^++2, 23%), 735 (M^++1, 9), and 510 (100); HRMS calcd for $C_{52}H_{55}N_4$ 735.4427, found 735.4427; UV–vis ($CHCl_3$) λ_{max}, nm: 385, 496, 527, 564, and 616; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26–10.33 (m, 4H, *meso*-H), 7.11–7.26 (m, 8H, olefin), 5.63 (m, 4H, bridge head), 5.12–5.16 (m, 4H, bridge head), 2.06–2.11 (m, 4H, bridge CH_2), 1.75–1.88 (m, 4H, bridge CH_2), 1.55–1.56 (m, 12H, Me), 0.59–0.80 (m, 12H, Me), and −4.63 (br, 4H, NH). Anal. Calcd for $C_{52}H_{54}N_4 \cdot 3/2CHCl_3$: C, 70.30; H, 6.12; N, 6.13. Found: C, 70.08; H, 6.06; N, 6.18.

4.1.5. [Tetrakis(dimethylBCOD)porphyrinato]zinc(II) **4a** and **4b**

Porphyrins **3a** and **3b** were prepared by reduction of **10a** (490 mg, 2.00 mmol) with $LiAlH_4$ (300 mg, 7.90 mmol) in THF (30 ml) at 0 °C for 2 h, tetramerization in the presence of *p*-TsOH·H_2O (20 mg) in $CHCl_3$ (400 ml) at room temperature for 21 h, and oxidation with *p*-chloranil (314 mg, 1.28 mmol) for 1 h. After column chromatography the crude free base porphyrins **3a** and **3b** were used without further purification.

To a solution of crude **3a** in $CHCl_3$ (60 ml) was added a satd solution of $Zn(OAc)_2 \cdot 2H_2O$ in methanol (15 ml) at room temperature under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was poured into water. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and recrystallization from methanol/$CHCl_3$ to give **4a** (194 mg, 49%). Reddish purple crystals; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 797 (M^++1, 9%), 796 (M^+, 10), and 572 (100); HRMS calcd for $C_{52}H_{53}N_4Zn$ 797.3562, found 797.3558; UV–vis ($CHCl_3$) λ_{max}, nm: 402, 529, and 563; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 4H, *meso*-H), 7.18 (ddd, 4H, *J*=6.1, 5.9, 1.2 Hz, olefin), 7.13 (ddd, 4H, *J*=6.1, 5.9, 1.2 Hz, olefin), 5.65 (m, 4H, bridge head), 5.15 (dd, 4H, *J*=5.9, 1.2 Hz, bridge head), 2.13 (dd, 4H, *J*=11.5, 2.7 Hz, bridge CH_2), 1.94 (dd, 4H, *J*=11.5, 2.7 Hz, bridge CH_2), 1.59 (s, 12H, Me), and 0.84 (s, 12H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.83, 148.26, 143.97, 142.24, 137.85, 136.16, 97.94, 49.64, 44.24, 40.69, 37.88, 31.83, and 31.52.

To a solution of crude **3b** in $CHCl_3$ (20 ml) was added a satd solution of $Zn(OAc)_2 \cdot 2H_2O$ in methanol (5 ml) at room temperature under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was poured into water. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and recrystallization from methanol/$CHCl_3$ to give **4b** (62 mg, 15%). Red powder; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 797 (M^++1, 8%), 796 (M^+, 7), and 572(100); HRMS calcd for $C_{52}H_{53}N_4Zn$ 797.3562, found 797.3562; UV–vis ($CHCl_3$) λ_{max}, nm: 402, 529, and 563; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31–10.38 (m, 4H, *meso*-H), 7.10–7.27 (m, 8H, olefin), 5.65 (m, 4H, bridge head), 5.14–5.20 (m, 4H, bridge head), 2.07–2.14 (m, 4H, bridge CH_2), 1.76–1.95 (m, 4H, bridge CH_2), 1.55–1.58 (m, 12H, Me), and 0.61–0.85 (m, 12H, Me).

4.1.6. [Tetrakis(dimethylBCOD)porphyrinato]copper(II) **5a** and **5b**

Porphyrins **3a** and **3b** were prepared by reduction of **10a** (489 mg, 1.99 mmol) with $LiAlH_4$ (310 mg, 8.17 mmol) in THF (30 ml) at 0 °C for 4 h, tetramerization in the presence of *p*-TsOH·H_2O (24 mg) in $CHCl_3$ (400 ml) at room temperature for 18 h, and oxidation with *p*-chloranil (304 mg, 1.24 mmol) for 22 h. After column chromatography the crude free base porphyrins **3a** and **3b** were used without further purification.

To a solution of crude **3a** in $CHCl_3$ (60 ml) was added a satd solution of $Cu(OAc)_2$ in methanol (15 ml) at room temperature. The resulting mixture was stirred at room temperature for 23 h. The reaction mixture was poured into water. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$, GPC with $CHCl_3$, and recrystallization from methanol/$CHCl_3$ to give **5a** (201 mg, 51%). Red powder; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 796 (M^++1, 5%), 795 (M^+, 4), and 571 (100); HRMS calcd for $C_{52}H_{53}N_4Cu$ 796.3666, found 796.3567; UV–vis ($CHCl_3$) λ_{max}, nm: 399, 522, and 556.

To a solution of crude **3b** in $CHCl_3$ (20 ml) was added a satd solution of $Cu(OAc)_2$ in methanol (5 ml) at room temperature. The resulting mixture was stirred at room temperature for 18 h. The reaction mixture was poured into water. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$, GPC with $CHCl_3$, and recrystallization from methanol/$CHCl_3$ to give **5b** (64 mg, 16%). Red powder; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 796 (M^++1, 22%), 795 (M^+, 17), and 571(100); HRMS calcd for $C_{52}H_{53}N_4Cu$ 796.3666, found 796.3567; UV–vis ($CHCl_2$) λ_{max}, nm: 399, 522, and 556.

4.1.7. [Tetrakis(dimethylBCOD)porphyrinato]nickel(II) **6a** and **6b**

Porphyrins **3a** and **3b** were prepared by reduction of pyrrole (490 mg, 2.00 mmol) with $LiAlH_4$ (300 mg, 7.90 mmol) in THF (30 ml) at 0 °C for 2 h, tetramerization in the presence of *p*-TsOH·H_2O (20 mg) in $CHCl_3$ (400 ml) at room temperature for 20 h, and oxidation with *p*-chloranil (314 mg, 1.28 mmol) for 1 h. After column chromatography, the crude free base porphyrins **3a** and **3b** were used without further purification.

To a solution of crude **3a** in $CHCl_3$ (60 ml) was added a satd solution of $Ni(OAc)_2 \cdot 4H_2O$ in methanol (20 ml) at room temperature. The resulting mixture was refluxed for 10 h. The reaction mixture was poured into water. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and recrystallization from methanol/$CHCl_3$ to give **6a**

(195 mg, 49%). Purple crystals; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 791 (M^++1, 7%), 790 (M^+, 5), and 566 (100); UV–vis ($CHCl_3$) λ_{max}, nm: 392, 513, and 547; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 4H, *meso*-H), 7.09 (dd, 4H, *J*=6.3, 6.0 Hz, olefin), 7.04 (dd, 4H, *J*=6.3, 6.0 Hz, olefin), 5.44 (m, 4H, bridge head), 4.95 (d, 4H, *J*=6.0 Hz, bridge head), 2.02 (dd, 4H, *J*=11.5, 2.4 Hz, bridge CH_2), 1.78 (dd, 4H, *J*=11.5, 2.4 Hz, bridge CH_2), 1.51 (s, 12H, Me), and 0.75 (s, 12H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.05, 147.58, 137.60, 137.06, 97.02, 49.29, 44.15, 40.66, 37.53, 31.52, and 31.44. Anal. Calcd for $C_{52}H_{52}N_4Ni\cdot 3/2CHCl_3$: C, 66.19; H, 5.55; N, 5.77. Found: C, 65.93; H, 5.65; N, 5.84.

To a solution of crude **3b** in $CHCl_3$ (20 ml) was added a satd solution of $Ni(OAc)_2\cdot 4H_2O$ in methanol (10 ml) at room temperature. The resulting mixture was refluxed for 8 h. The reaction mixture was poured into water. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and recrystallization from methanol/$CHCl_3$ to give **6b** (69 mg, 17%). Red powder; mp >200 °C (decomp.); MS (FAB) *m/z* (relative intensity) 791 (M^++1, 12%), 790 (M^+, 10), and 566 (100); HRMS calcd for $C_{52}H_{53}N_4Ni$ 791.3624, found 791.3622; UV–vis ($CHCl_3$) λ_{max}, nm: 392, 513, and 547; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (m, 4H, *meso*-H), 7.00–7.16 (m, 8H, olefin), 5.46 (m, 4H, bridge head), 4.95 (m, 4H, bridge head), 1.99–2.03 (m, 4H, bridge CH_2), 1.72–1.82 (m, 4H, bridge CH_2), 1.45–1.52 (m, 12H, Me), and 0.60–0.83 (m, 12H, Me).

4.1.8. X-ray crystallography

A summary of the crystallographic data and details of the structural determination are given in Table 1. The data were obtained using a Rigaku/MSC Mercury CCD. The diffraction data were processed with Crystal Clear, solved with SIR-97 or DIRDIF-99, and refined with SHELXL-97. In the event of the solvent molecules not being adequately modeled, the core porphyrin molecules were refined without the solvent molecules by a combination of the SHELXL-97 and PLATON-SQUEEZE programs. Crystallographic data (excluding structural factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.01.014.

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