Synthesis of 3,4-diarylpyrroles and conversion into dodecaarylporphyrins; a new approach to porphyrins with altered redox potentials

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3,4-Diarylpyrroles (1) have been directly prepared in 20–50% yield by the reaction of β-nitrostyrenes with aqueous $TiCl_3$ in 1,4-dioxane. Pyrroles 1 were also prepared *via* Barton–Zard pyrrole synthesis using the reaction of α-nitrostilbenes with ethyl isocyanoacetate followed by de-ethoxycarbonylation. 3,4-Diarylpyrroles have been converted into dodecaarylporphyrins by reaction with aromatic aldehydes. Various aryl groups are readily introduced at the periphery of porphyrins by this method. Phenyl substitution at any of the positions of pyrroles decreases $E_{1/2}^{ox}$, while $E_{1/2}^{red}$ is almost unchanged. On the other hand, substitution of the 2-thienyl group affects both the HOMO and LUMO energies, and the UV-vis spectra of dodeca-2-thienylporphyrins (4f or 4i) are extremely red-shifted.

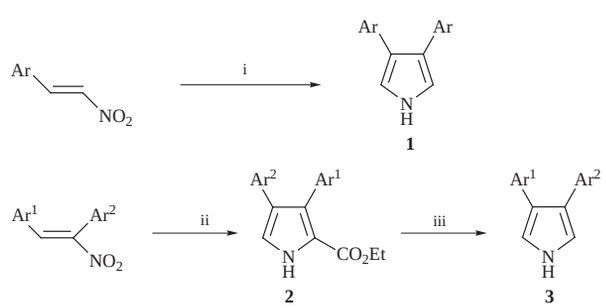
Much attention has been devoted to the synthesis of new porphyrins to elucidate the main factors in controlling the redox, spectroscopic, and catalytic properties of metalloenzymes involving porphyrins or related molecules.[1] The effects of peripheral substituents in porphyrins are especially important in controlling the properties of porphyrins. For example, porphyrins and their metal derivatives with strong electron withdrawing groups such as nitroporphyrins or halporphyrins show excellent catalytic properties in metalloporphyrin catalyzed oxygenation reactions due to their stability and reactivity.[2] The electronegative substituents lower the energy of the highest occupied molecular orbital (HOMO) to increase the reactivity of the high-valent metal-oxo intermediates involved in these reactions. Introduction of substituents into porphyrin rings affects the steric interactions between the β- and *meso*-substituents, which induces distorting of the macrocycles from planarity.[3] Such conformational distortion may serve to fine-tune the porphyrin properties. For example, dodecaphenylporphyrin has a non-planar macrocycle with a saddle-type distortion which causes changes in redox potentials, optical absorption spectra and spin delocalization. Non-planarity of porphyrins induces destabilization of the porphyrin HOMO to facilitate porphyrin radical cation formation. Now sufficient data about such dodecasubstituted porphyrins are available for elucidation, some conclusions regarding the conformational preferences and flexibility of these novel macrocycles can be drawn.

In the present work, we investigate the possibility of varying the aryl groups in dodecaarylporphyrins to affect the properties of porphyrins in electronic and steric ways. These compounds promise to be useful models for investigating the effects of conformational changes and electronic states.[4] In order to prepare dodecaarylporphyrins with variously substituted aryl groups, general synthetic methods to 3,4-diarylpyrroles are required. 3,4-Diarylpyrroles have been prepared so far by the condensation reaction of benzil with dimethyl *N*-acetyliminodiacetate,[5] or Knorr-type condensation of amino ketones.[6] Although 3,4-diphenylpyrrole or its simple variants can be prepared by these methods, they lack generality and suffer from the difficulty of changing the aryl groups in the pyrroles. More general and simpler routes to 3,4-diarylpyrroles are required for our purpose. In 1986, Sera reported that reduction of β-nitrostyrene with $TiCl_3$ gave 3,4-diphenylpyrrole directly in 20–30% yield.[7] As substituted β-nitrostyrenes are readily prepared by the reaction of aromatic aldehydes with nitromethane, this method is very attractive as a general route to 3,4-diarylpyrroles if it works in the case of substituted nitrostyrenes. The Barton–Zard pyrrole synthesis using nitroalkenes is now well established for the preparation of β-arylpyrroles.[8] So the reaction of α-nitrostilbenes with ethyl isocyanoacetate is also a good candidate as an alternative route to 3,4-diarylpyrroles. Here we report details on the preparation of 3,4-diarylpyrroles by these two methods and their conversion into dodecaarylporphyrins **4**. The effect of substituents of **4** on absorption spectra and redox potentials of these new porphyrins is also investigated. Recently, the Suzuki cross-coupling reaction of β-bromotetraarylporphyrins with arylboronic acids has been demonstrated to be an efficient route to β-arylporphyrins.[9] The route described here is a complementary approach.

Results and discussion

Synthesis of 3,4-diarylpyrroles

The synthesis of 3,4-diarylpyrroles **1** or **3** is shown in Scheme 1. The former method is based on the reduction of β-nitrostyrenes



Scheme 1 *Reagents and conditions*: i, $TiCl_3$ aq, 1.4-dioxane, pH 6.5, 12 h, room temp.; ii, $CNCH_2CO_2Et$, DBU, THF, room temp. 14 h; iii, KOH, $HOCH_2CH_2OH$, reflux, 2 h

with $TiCl_3$ and the latter one is based on the Barton–Zard reaction. The requisite β-nitrostyrenes were prepared in good yields by the reaction of aromatic aldehydes with nitromethane in methanol in the presence of NaOH.[10] Although many

Table 1 Preparation of 3,4-diarylpyrroles **1**

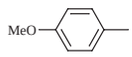
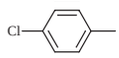
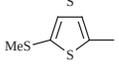
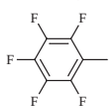
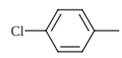
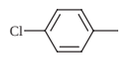
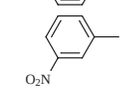
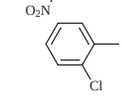
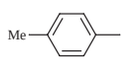
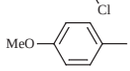
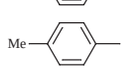
Ar		Yield %	Ar		Yield %
Ph	**1a**	50		**1f**	32
	**1b**	19		**1g**	19
	**1c**	20		**1h**	13
	**1d**	30			
	**1e**	28		**1i**	32

Table 2 Preparation of ethyl 3,4-diarylpyrrole-2-carboxylates **2** and 3,4-diarylpyrroles **1** or **3**

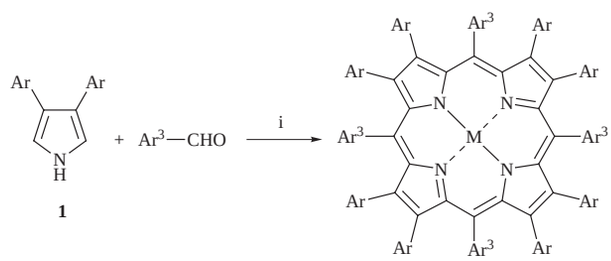
Ar^1	Ar^2	**2**	Yield %	**1** or **3**	Yield %
Ph	Ph	**2a**	71	**1a**	85
		**2b**	70	**1c**	50
	Ph	**2c**	74	**3c**	45
		**2d**	70	**3d**	70
		**2e**	64	**3e**	75

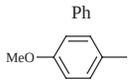
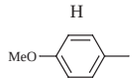
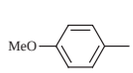
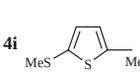
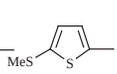
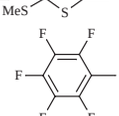
modified methods for the preparation of nitroalkenes have been reported recently, [11] the conventional procedures using NaOH as a base work well for the preparation of most β-nitrostyrenes. The conversion of β-nitrostyrene into 3,4-diphenylpyrroles **1a** was carried out by stirring with $TiCl_3$ in 1,4-dioxane–water at pH 6.5 to give **1a** in 50% yield. Although THF was used as a solvent in the original literature, replacement of THF by 1,4-dioxane increased the yield of **1a** from 25 to 50%. Various pyrroles **1** were readily prepared by this method as shown in Table 1. Although the yields by this method are modest, the simplicity and generality of this procedure are very attractive. Thus, pyrroles with electron-withdrawing or -donating aryl groups were directly prepared from β-nitrostyrenes by a one-pot reaction. As aryl groups in **1** are derived from aromatic aldehydes, various aryl groups are readily introduced at the β-position of the pyrroles.

Recently the Barton–Zard pyrrole synthesis [8] using nitroalkenes and ethyl isocyanoacetate has been widely recognized as a useful tool for porphyrin synthesis.[12] If the requisite nitroalkenes are available, it provides a reliable method for pyrrole synthesis. The reaction of α-nitrostilbene with ethyl isocyanoacetate was carried out in THF in the presence of DBU to give ethyl 3,4-diphenylpyrrole-2-carboxylate **2a** in 71% yield. The ester function was removed by heating with KOH in ethylene glycol at 170 °C to give 3,4-diphenylpyrrole **1a** in 85% yield. 3,4-Diarylpyrroles **3** with two different aryl groups could be prepared by this procedure as shown in Table 2. The requisite α-nitrostilbenes were prepared either by the reaction of α-nitrotoluene with aromatic aldehydes or by the nitration of stilbenes.[13] Although these starting materials are not so easily available as β-nitrostyrenes, this route provides a general synthesis of 3,4-diarylpyrroles. Different substitution patterns are accessible; in particular the aryl groups at the β-positions can be easily varied by the choice of α-nitrostilbenes. The ester function at the 2-position in **2** can play an important role for further conversion into other derivatives. The reduction of **2** with $LiAlH_4$ gave a very reactive 2-hydroxymethylpyrrole, which was readily converted into the corresponding octaarylporphyrin.[12] Furthermore, the pyrroles **2** are potential precursors for pyrrole alkaloids such as lukianol A and lamellalin O which have been isolated in recent years from marine sources.[6] Thus, the pyrrole syntheses from nitroalkenes shown in Scheme 1 provide a useful method for the preparation of 3,4-diarylpyrroles, which are compatible with other recent synthetic methods towards them.[6]

Synthesis of dodecaarylporphyrins and octaarylporphyrins

Recently, much attention has been devoted to the synthesis of highly substituted porphyrins in order to clarify the effect of conformational variations on the properties of porphyrin macrocycles. Although the substituents at the *meso*-positions are easily changed, the substituents of the β-position are mostly limited to simple alkyl or aryl groups due to the difficulty of synthesis of β-substituted pyrroles. Since the aryl groups in the β-position of pyrroles can now be varied as shown in Table 1, porphyrins with various substituents can be prepared from 3,4-diarylpyrroles **1**. Tsuchiya has reported the preparation of various dodecaarylporphyrins by the reaction of 3,4-diphenylpyrrole with aromatic aldehydes such as benzaldehyde, *p*-nitrobenzaldehyde, pentafluorobenzaldehyde and 2,5-dichlorobenzaldehyde.[14] Thus, the introduction of aryl groups at the *meso*-position of porphyrins is generally easy as shown in the preparation of *meso*-tetraarylporphyrins.[15] According to a similar procedure, pyrroles **1** were converted into various types of 2,3,5,7,8,10,12,13,15,17,18,20-dodecaarylporphyrins **4** by acid-catalyzed condensation with aromatic aldehydes followed by oxidation with chroranil (Scheme 2). Metal com-



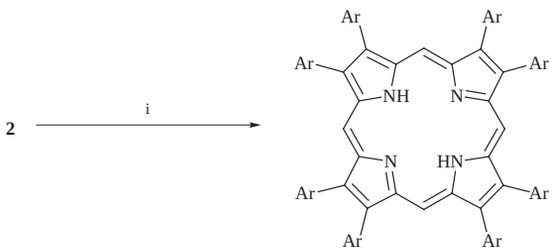
	Ar	Ar^3		Ar	Ar^3
4a	Ph	Ph	**4f**		
4b	H	Ph			
4c	Ph	H	**4g**	H	
4d			**4h**		
4e	H		**4i**		
			4j	H	

Scheme 2 *Reagents and conditions*: i, Trifluoroacetic acid, MXn, *p*-chloranil, 24 h, room temp.

plexes were also prepared by treatment with the appropriate metal salts according to the literature method.[1] Thus, various dodecaarylporphyrins **4** and their metal complexes can be prepared from aromatic aldehydes in a very simple way: all aryl groups in **4** are derived from readily available aromatic aldehydes.

2,3,7,8,12,13,17,18-Octaarylporphyrins **4c** or **5** were also prepared by the reaction of pyrroles **1** with formaldehyde.

In the literature, they were prepared from the Mannich bases of **1**.[5] However, they could be prepared more conveniently from **2**. The reduction of the ester group in pyrrole **2** with $LiAlH_4$ followed by acid-catalyzed tetramerization and oxidation gave **5** in 20–30% yield (Scheme 3).



Scheme 3 *Reagents and conditions*: i, $LiAlH_4$, THF, 0 °C, 1 h, *p*-TsOH, *p*-chloranil, 24 h, room temp.

The porphyrins **4** and their metal complexes were identified by the ^{1}H NMR, FAB mass and absorption spectra summarized in Tables 3 and 4. Some of them, namely, **4a**, **4b** and **4c** are known compounds, and their spectral data were in good agreement with reported ones.[3,9,14] The conformation of these porphyrins can be assigned from their ^{1}H NMR spectra. It has been well known that internal NH protons are strongly deshielded by the ring current effect of the porphyrin ring. The NH protons of planar porphyrins such as **4b** or **4c** were observed at about −3 ppm. On the other hand, the NH protons of dodecaarylporphyrins **4a**, **4f** and **4h** were less deshielded and observed at about −1 ppm. The NH protons appear as broad peaks at 20 °C, and they become sharp at −80 °C. The NMR spectra at −80 °C suggest the saddle-shaped conformation of **4a** and **4d**. As pointed out by Smith, *ortho* protons of the pyrrole phenyl rings appear at an unusually wide range of chemical shifts at low temperature.[3] The same conclusion was obtained for our new dodecasubstituted porphyrins by measurement of their NMR spectra at low temperature. Such dodecasubstituted porphyrins exhibit a severe non-planar saddle conformation, and increasing non-planarity is shown by the shift of the NH protons in the ^{1}H NMR spectrum to lower field.[3,9] Published crystal structures of such dodecasubstituted porphyrins provide conclusive evidence for non-planar conformations.[3]

Recent studies on the effects of non-planarity on the visible absorption spectra of porphyrins have shown that the optical spectra of non-planar porphyrins are shifted to longer wavelength when compared to planar porphyrins.[3] A direct correlation between the red-shift of the absorption bands and the porphyrin distortion has been shown in many cases. The optical data show that the absorption maximum for all dodecaarylporphyrins and their metal complexes are shifted to lower energy compared to tetraaryl- or octaaryl-porphyrins. However, the magnitudes of the shifts in the absorption of porphyrins with thiophenes as aryl groups are quite different from those of **4a**. In particular the absorption maximum of **4f** and **4i** are remarkable. The Soret bands appeared at about 500 nm and the Q bands are about at 800 nm, so that they are shifted by over 100 nm compared to TPP (**4b**). The red-shifts observed for **4f** and **4i** are larger than those of **4a**. The non-planarity of **4f** and **4i** should be smaller than that of **4a**, since porphyrins with thienyl groups are less crowded than phenyl substituted porphyrins. This fact suggests that another factor also must be considered for the red-shift of dodecathienyl porphyrins. Such red-shifted porphyrinoid chromophores promise potential uses as opto-electronic materials.[16] Porphyrins with dodecathienyl groups provide a new class of red-shifted porphyrins.[17]

The redox properties of the copper porphyrins were measured by the cyclic voltammetry (CV) method (Fig. 1). Copper complexes were selected owing to their stability. The CV studies were performed on a Pt electrode using CH_2Cl_2 as a solvent and 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. The redox potential data of **Cu-4** are summarized in Table 5. The one-electron redox potentials of porphyrins reflect the energy levels of their HOMO and LUMO. The difference ($\Delta E_{1/2}$) between the first oxidation ($E^{ox}_{1/2}$) and first reduction ($E^{red}_{1/2}$) potentials reflects the energy difference between the HOMO and LUMO. Redox potentials of **Cu-4a** and **Cu-4b** (TPP) are in good agreement with reported values.[18] The energy difference of most planar porphyrins, such as TPP, are almost constant at about 2.2–2.3 V, and they are not much affected by either the substituents or the central metals of the porphyrins.[1] Therefore, Soret bands appear at *ca.* 400 nm and Q bands appear at 500–600 nm for most planar porphyrins and their metal complexes. It is well established that non-planarity of sterically crowded porphyrins causes destabilization of the HOMO energy to decrease the energy gap between the HOMO and LUMO.[19] Thus, dodecasubstitution decreases $E^{ox}_{1/2}$, while $E^{red}_{1/2}$ is less affected in the cases of **4a** and **4d**. $\Delta E_{1/2}$ values of **Cu-4a** and **Cu-4d** are almost constant (1.90 and 1.83 V, respectively) so that substituents on the phenyl rings do not much affect $\Delta E_{1/2}$ of dodecaarylporphyrins. On the other hand, porphyrins with dodeca-2-thienyl groups such as **4f** and **4i** show different behaviour. Substitution with 2-thienyl groups causes both stabilization of the LUMO and destabilization of the HOMO to give small $\Delta E_{1/2}$ values such as 1.63 V (**Cu-4f**)

Table 3 Preparation of porphyrins **4**[a] and their ^{1}NMR spectra in CD_2Cl_2 and FAB mass spectra

		δ_{NH}/ppm		FAB mass		
Porphyrin	Yield %	25 °C	−80 °C		calc. (M^+)	found
H_2**4a**		−1.0	−1.5	$C_{92}H_{62}N_4$	1222	1224 (M + 2)
Cu**4a**	20			$C_{92}H_{60}N_4Cu$	1284	1285 (M + 1)
H_2**4b** (TPP)		−2.8	−3.2			
H_2**4c**		−3.0				
H_2**4d**		−0.8	−1.5	$C_{104}H_{86}N_4O_{12}$	1583	1584 (M + 1)
Cu**4d**	15			$C_{104}H_{84}N_4O_{12}Cu$	1645	1646 (M + 1)
H_2**4f**			−0.85	$C_{68}H_{38}N_4S_{12}$	1294	1297 (M + 3)
Cu**4f**	15			$C_{68}H_{36}N_4S_{12}Cu$	1356	1357 (M + 1)
Zn**4f**	10			$C_{68}H_{36}N_4S_{12}Zn$	1357	1358 (M + 1)
Ni**4f**				$C_{68}H_{36}N_4S_{12}Ni$	1351	1382 (M + 1)
H_2**4h**		−0.8	−1.3	$C_{68}H_{38}N_4S_{12}$	1294	1296 (M + 1)
Cu**4h**	20			$C_{68}H_{36}N_4S_{12}Cu$	1356	1357 (M + 1)
Cu**4i**	12			$C_{80}H_{60}N_4S_{24}Cu$	1908	1910 (M + 2)
Cu**4j**	15			$C_{92}F_{20}H_{40}N_4$	1643	1644 (M + 1)

[a] Porphyrins were prepared and purified as metal salts. Metal free porphyrins were prepared by treatment with acid in quantitative yields.

Table 4 UV-visible spectral data for porphyrins **4** and their metal complexes

Porphyrin	M	λ_{max} (log ε) in CH_2Cl_2 (nm)
4a (DPP)	2H	466 (5.18), 562 (4.05), 613 (3.99), 719 (3.76)
	Cu	443 (5.32), 577 (4.27), 615 (3.95)
	Zn	459 (5.36), 584 (4.11), 636 (3.78)
4b (TPP)	2H	417 (5.65), 515 (4.16), 548 (3.65), 588 (3.34), 647 (3.33)
	Cu	414 (5.70), 533 (4.11)
	Zn	423 (6.07), 553 (4.37), 594 (3.85)
4c (5)	2H	420 (5.14), 515 (5.23), 545 (4.04), 581 (3.95), 638 (3.48)
	Zn	430 (5.40), 554 (4.40), 588 (4.18)
4d	2H	477, 566, 627, 730
	Cu	450 (5.12), 581 (4.19), 625 (4.00)
4e	2H	418 (5.71), 516 (4.18), 548 (3.73), 589 (3.50), 648 (3.45)
4f	2H	508 (4.98), 681 (4.05), 794 (3.69)
	Cu	472 (4.97), 610 (4.14), 660 (3.93)
4g	2H	425 (5.70), 521 (4.30), 558 (3.80), 594 (3.48), 659 (3.42)
4h	2H	482 (5.14), 581 (3.82), 638 (4.01), 747 (3.73)
	Cu	453 (5.17), 588 (4.18), 632 (3.93)
4i	2H	520 (4.74), 720 (4.12), 830 (3.85)
	Cu	483 (4.80), 679 (4.20), 670 (4.00)
	Zn	508 (4.95), 635 (4.85), 706 (4.21)
4j	Cu	430 (5.23), 562 (4.05), 597 (3.95)

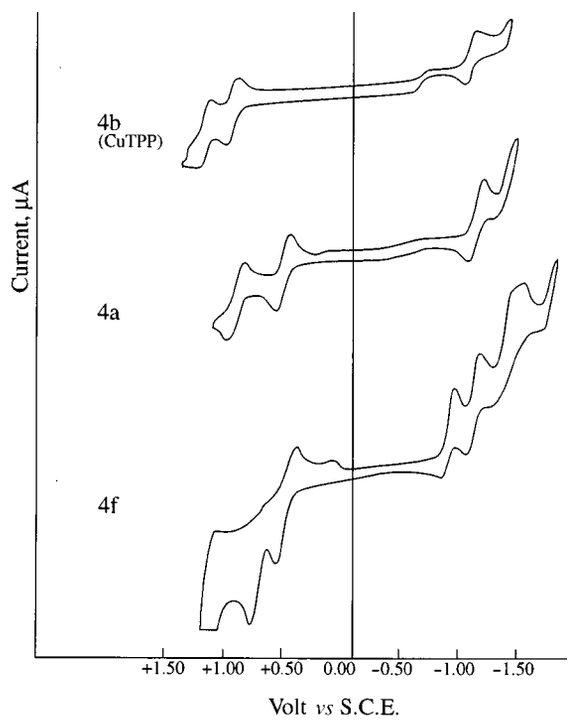


Fig. 1 Cyclic voltammogram of 4.5×10^{-3} M porphyrins in CH_2Cl_2 0.1 M TBAP; scan rate, 0.2 V s^{-1}

and 1.48 V (**Cu-4i**). This is evidenced by the strongly red-shifted Soret and Q bands of these porphyrins. It is interesting that the red-shift of **4i** is larger than that of **4f**, where substituents of thiophene rings affect the electronic properties of thiophene-substituted porphyrins. This finding is very important, for it is generally difficult to modulate the electronic property of porphyrins by changing the substituents of 5,10,15,20-tetrakis-(aryl-substituted)porphyrins. Recently electronic modulation of porphyrins through *meso*-arylethynyl groups has been attained.[20] Our method using 2-thienyl groups as an electronic modulator affords another strategy for control of the electronic properties of porphyrin π-systems.[21] Further application of porphyrins with a thiophene ring for new devices in opto-electronic materials is now in progress in our group.

Table 5 Redox properties of metal porphyrines **4**

Porphyrin	$E^{ox}_{1/2}$ (1)	$E^{ox}_{1/2}$ (2)	$E^{red}_{1/2}$ (1)	$E^{red}_{1/2}$ (2)	$\Delta E_{1/2}$ (1)
Cu-4a	0.52	0.96	−1.38	−1.71	1.90
Cu-4b	0.90	1.16	−1.44	—	2.34
Cu-4d	0.28	0.84	−1.55	—	1.83
Cu-4e	0.80	1.15	−1.46	—	2.26
Cu-4f	0.55	—	−1.08	−1.35	1.63
Cu-4g	0.98	—	−1.22	−1.62	2.20
Cu-4h	0.55	1.04	−1.34	−1.69	1.89
Cu-4i	0.53	0.81	−0.95	−1.23	1.48

Experimental

Mps were measured with a Yanagimoto BY-1 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a JEOL-JNM-GSX 270 or JNM-EX 400 spectrometer using tetramethylsilane as an internal standard. *J* Values are given in Hz. IR and UV-visible spectra were obtained with a Hitachi 270-30 and Shimazu UV-2200 spectrometer, respectively. Mass spectra and high resolution mass spectra were measured with a Hitachi M80B spectrometer. FAB mass spectra of porphyrins were measured with a JEOL JMS-DX-300 spectrometer; samples were dissolved in $CHCl_3$ and *m*-nitrobenzyl alcohol was used as a matrix.

Nitroalkenes

β-Nitrostyrenes were prepared according to the published methods from the corresponding aldehydes and nitromethane in 60–80% yields.[10] α-Nitrostilbenes were prepared by the literature method using α-nitrotoluene and aromatic aldehydes.[13] The requisite aldehydes are commercially available except for 5-methylthiothiophene-2-carboxyaldehyde which was prepared in 85% yield by the reaction of 2-methylthiothiophene with phosphorous chloride with *N*-methylformamide according to the literature procedure.[22]

General procedure for the preparation of 3,4-diarylpyrroles 1

To a solution of aqueous $TiCl_3$ (39 ml, 1.76 M solution, Wako Chemical) and aqueous solution of NH_4OAc (300 ml, 2 M solution) was added NH_4OH (24 ml, 10% solution). The pH of the solution was adjusted to be 6.5. To this solution was added a solution of β-nitrostyrenes (20 mmol) in dioxane (50 ml), and the mixture was stirred at room temperature for 12 h. Extraction with diethyl ether was followed by washing with saturated aqueous sodium hydrogen carbonate, water and saturated aqueous sodium chloride. The organic layer was dried with sodium sulfate and concentrated. The residue was subjected to column chromatography (silica gel, hexane–ethyl acetate) to give **1**.

3,4-Diphenylpyrrole 1a. Colorless needles, mp 99–101 °C (lit.,[5] 99 °C); $\delta_H(CDCl_3)$ 8.06 (1 H, br s), 7.28–7.12 (10 H, m), 6.79 (2 H, d, *J* 1.8); δ_C 135.71, 128.40, 128.13, 125.62, 123.18, 117.43; ν_{max}/cm^{-1} 3420 (NH); *m*/*z* (EI) 219 (M^+) (Found: M^+, 219.1063. $C_{16}H_{13}N$ requires 219.1048).

3,4-Bis(4′-methoxyphenyl)pyrrole 1b. Mp 115–117 °C (lit.,[5] 116 °C); $\delta_H(CDCl_3)$ 8.26 (1 H, br s), 7.18 (2 H, d, *J* 8.9), 6.80 (2 H, d, *J* 2.8), 6.79 (2 H, d, *J* 2.7), 3.77 (6 H, s); ν_{max}/cm^{-1} 3400 (NH); *m*/*z* (EI) 279 (M^+) (Found: M^+, 279.1241. $C_{18}H_{17}N_1O_2$ requires 279.1260).

3,4-Bis(4′-chlorophenyl)pyrrole 1c. Mp 143–145 °C; $\delta_H(CDCl_3)$ 8.38 (1 H, NH), 7.21 (4 H, d, *J* 8.5), 7.14 (4 H, d, *J* 8.5), 6.84 (2 H, d, *J* 2.8); ν_{max}/cm^{-1} 3444 (NH); *m*/*z* (EI) 287 (M^+) (Found: C, 66.61; H, 3.79; N, 4.69. $C_{16}H_{11}NCl_2$ requires C, 66.69; H, 3.85; N, 4.86%).

3,4-Bis(2′-thienyl)pyrrole 1d. Mp 91–93 °C; $\delta_H(CDCl_3)$ 7.97 (1 H, s), 7.11 (2 H, d, *J* 5.2), 6.94–6.87 (4 H, m), 6.77 (2 H, d, *J* 2.8); $\delta_C(CDCl_3)$ 136.65, 127.12, 124.96, 123.63, 117.96, 116.60; *m*/*z* (EI) 231 (M^+) (Found: C, 62.44; H, 3.97; N, 6.29. $C_{12}H_9NS_2$ requires C, 62.31; H, 3.92; N, 6.05%).

3,4-Bis[2′-(5′-methylthio)thienyl]pyrrole 1e. Oil; $\delta_H(CDCl_3)$ 8.28 (1 H, s), 6.92 (2 H, d, *J* 3.7), 6.81 (2 H, d, *J* 2.4), 6.75 (2 H, d, *J* 3.7), 2.44 (6 H, s); $\delta_C(CDCl_3)$ 139.44, 134.47, 131.51, 125.16, 116.31, 22.17; *m*/*z* (EI) 323 (M^+) (Found: C, 51.87; H, 4.18; N, 4.27; $C_{14}H_{13}NS_4$ requires C, 51.98; H, 4.05; N, 4.33%).

3,4-Bis(3′-thienyl)pyrrole 1f. Mp 106–108 °C; $\delta_H(CDCl_3)$ 8.02 (1 H, NH), 7.18 (2 H, d, *J* 8.9), 6.80 (2 H, d, *J* 8.9), 6.79 (2 H, d, *J* 2.7), 3.77 (6 H, s); $\delta_C(CDCl_3)$ 135.94, 128.26, 128.37, 124.73, 120.01, 118.35, 117.03; ν_{max}/cm^{-1} 3375 (NH); *m*/*z* (EI) 231 (M^+) (Found: C, 62.09; H, 4.06; N, 6.02. $C_{12}H_9NS_2$ requires C, 62.31; H, 3.92; N, 6.05%).

3,4-Bis(2′-furyl)pyrrole 1g. Oil; $\delta_H(CDCl_3)$ 8.14 (1 H, br s), 7.35 (2 H, d, *J* 1.8), 6.85 (2 H, d, *J* 2.7), 6.37 (2 H, d, *J* 3.4), 6.28 (2 H, *J* 4.0); $\delta_C(CDCl_3)$ 149.63, 140.46, 117.57, 112.97, 111.01, 105.41 (Found: M^+, 199.0640. $C_{12}H_{93}NO_2$ requires 199.0634).

3,4-Bis(1′-naphthyl)pyrrole 1h. Mp >250 °C; $\delta_H([^2H]_6$-DMSO); 11.44 (1 H, NH), 8.10 (2 H, d, *J* 8.6), 7.77 (2 H, d, *J* 7.9), 7.63 (2 H, d, *J* 7.6), 7.37–7.18 (8 H, m), 7.13 (2 H, d, *J* 2.8); $\delta_C([^2H]_6$DMSO) 134.88, 133.53, 132.08, 127.86, 127.49, 126.20, 125.99, 125.33 (Found: M^+, 319.1366. $C_{24}H_{17}N$ requires 319.1361).

3,4-Bis(pentafluorophenyl)pyrrole 1i. Mp 179–181 °C; $\delta_H(CDCl_3)$ 8.82 (1 H, NH), 7.10 (2 H, d, *J* 2.8); $\delta_F(CDCl_3)$ −142.69 (dd, *J* 23.7 and 8.5), −156.96 (t, *J* 21.4), −163.03 (dt, *J* 22.8 and 7.5); *m*/*z* (EI) 399 (M+) (Found: M^+, 399.0108. $C_{16}F_{10}H_3N$ requires 399.0106).

Ethyl 3,4-diphenylpyrrole-2-carboxylate 2a. To a solution of α-nitrostilbene (2.3 g, 10 mmol) and ethyl isocyanoacetate (1.7 g, 15 mmol) in the THF (30 ml) was added slowly DBU (2.3 g, 15 mmol) and the resulting solution was stirred at room temperature for 12 h. The reaction mixture was poured into water containing dilute aqueous HCl, and extracted with ethyl acetate. The extracts were washed with water and evaporated to give the crude material which was purified by column chromatography (silica gel, hexane–ethyl acetate to give **2a** (2.1 g, 71%); mp 131–132 °C; $\delta_H(CDCl_3)$ 9.57 (NH, 1 H), 7.27 (d, 1 H, *J* 6.1), 7.21–7.07 (m, 10 H), 4.18 (q, 2 H, *J* 7.0), 1.14 (t, 3 H, *J* 7.0); ν_{max}/cm^{-1} 3300, 1670, 1412, 1386, 1292, 1260, 1186, 1140, 770; *m*/*z* (EI) 291 (M^+) (Found: C, 78.38; H, 5.76; N, 4.73. $C_{19}H_{17}NO_2$ requires C, 78.32: H, 5.88; N, 4.81%).

Ethyl 3,4-bis(4′-chlorophenyl)pyrrole-2-carboxylate 2b. Colorless crystals, mp 175–176 °C; $\delta_H(CDCl_3)$ 9.28 (NH, 1 H), 7.28–6.98 (m, 9 H), 4.20 (q, 2 H, *J* 7.0), 1.18 (t, 3 H, *J* 7.0); ν_{max}/cm^{-1} 3304, 1680, 1418, 1380, 1283, 1180, 1134, 1016, 838; *m*/*z* (EI) 359 (M^+) (Found: C, 63.48; H, 4.17; N, 3.68. $C_{19}H_{15}NO_2Cl$ requires C, 63.36; H, 4.20; N, 3.80%).

Ethyl 3-(3′-nitrophenyl)-4-phenylpyrrole-2-carboxylate 2c. Mp 194–195 °C; $\delta_H(CDCl_3)$ 9.57 (NH, 1 H), 8.26 (1 H, s), 8.14 (1 H, d, *J* 7.9), 7.52 (1 H, d, *J* 7.6), 7.41 (1 H, t, *J* 8.2), 7.32–7.04 (5 H, m), 7.13 (1 H, d, *J* 3.1), 4.20 (2 H, q, *J* 7.0), 1.14 (3 H, t, *J* 7.0); ν_{max}/cm^{-1} 3230, 1675, 1520, 1340; *m*/*z* (EI) 336 (M^+) (Found: M^+, 336.1118. $C_{19}H_{16}N_2O_4$ requires 336.1111).

Ethyl 3-(2′-chlorophenyl)-4-(4′-methylphenyl)pyrrole-2-carboxylate 2d. Mp 134–136 °C; $\delta_H(CDCl_3)$ 9.58 (1 H, NH), 7.41 (2 H, d, *J* 7.6), 7.22 (2 H, d, *J* 7.6), 7.13 (1 H, d, *J* 7.6), 7.13 (1 H, d, *J* 3.1), 7.01 (2 H, d, *J* 8.6), 6.97 (2 H, d, *J* 8.6), 4.10 (2 H, q, *J* 7.0), 2.26 (3 H, s), 1.04 (3 H, t, *J* 7.0); ν_{max}/cm^{-1} 3240, 1675; *m*/*z* (EI) 339 (M^+) (Found: M^+, 339.1062, $C_{20}H_{18}NO_2Cl$ requires 339.1027).

Ethyl 3-(4′-methoxyphenyl)-4-(4′-methylphenyl)pyrrole-2-carboxylate 2e. Mp 88–89 °C; $\delta_H(CDCl_3)$ 9.78 (1 H, NH), 7.75 (2 H, d, *J* 8.2), 7.19 (2 H, d, *J* 9.5), 7.06 (2 H, d, *J* 8.2), 6.97 (1 H, d, *J* 4.0), 6.81 (2 H, d, *J* 8.9), 4.17 (2 H, q, *J* 7.0), 4.73 (3 H, s), 2.23 (3 H, s), 1.13 (3 H, t, *J* 7.0); ν_{max}/cm^{-1} 3250, 1670; *m*/*z* (EI) 335 (M^+) (Found: M^+, 335.1514. $C_{21}H_{21}NO_3$ requires 335.1522).

Preparation of 1a by de-ethoxycarbonylation of 2a

A stirring mixture of **2a** (2.91 g, 10 mmol) and NaOH (0.6 g, 15 mmol) in ethylene glycol (20 ml) was heated at reflux under Ar for 2 h. The reaction mixture was poured into saturated aqueous NaCl. Extraction with diethyl ether followed by the usual work-up gave crude **1a**, which was purified by column chromatography (silica gel, ethyl acetate–hexane) to give pure **1a** (1.86 g, 85% yield). The spectra were identical with those of **1a** prepared by the reaction of β-nitrostyrene with $TiCl_3$. The following pyrroles were prepared by the same procedures.

3,4-Bis(4-chlorophenyl)pyrrole 1c. Spectral data were identical with those of **1c** prepared by the reaction of β-nitro-*p*-chlorostyrene with $TiCl_3$.

3-(3′-Nitrophenyl)-4-phenylpyrrole 3a. Mp 45 °C; $\delta_H(CDCl_3)$ 8.51 (1 H, NH), 8.17 (1 H, s), 7.99 (1 H, d, *J* 8.2), 7.48 (1 H, d, *J* 7.6), 7.31 (1 H, d, *J* 7.9), 7.30–7.18 (5 H, m), 6.98 (1 H, s), 6.89 (1 H, s); $\delta_C(CDCl_3)$ 148.25, 137.70, 134.99, 134.49, 128.84, 128.55, 128.49, 126.18, 123.59, 122.58, 121.17, 120.35, 118.07, 118.03; ν_{max}/cm^{-1} 3380 (NH); *m*/*z* (EI) 264 (M^+) (Found: M^+, 264.0893. $C_{16}H_{12}N_2O_2$ requires 264.0899).

3-(2′-Chlorophenyl)-4-(4′-methylphenyl)pyrrole 3b. Mp 87–89 °C; $\delta_H(CDCl_3)$ 8.22 (1 H, NH), 7.38 (1 H, d, *J* 6.4), 7.23–7.14 (3 H, m), 7.05 (2 H, d, *J* 8.2), 6.99 (2 H, d, *J* 8.2), 6.90 (1 H, s), 6.95 (1 H, s), 2.27 (3 H, s); $\delta_C(CDCl_3)$ 134.99, 133.92, 132.81, 132.72, 129.60, 129.50, 128.93, 127.64, 127.27, 126.31, 124.45, 120.08, 118.80, 115.95, 21.06; ν_{max}/cm^{-1} 3400 (NH); *m*/*z* (EI) 267 (M^+) (Found: C, 76.37; H, 5.21; N, 5.28. $C_{17}H_{14}NCl$ requires C, 76.26; H, 5.27; N, 5.23%).

3-(4′-Methoxyphenyl)-4-(4′-methylphenyl)pyrrole 3c. Oil; $\delta_H(CDCl_3)$ 8.20 (1 H, NH), 7.19 (2 H, d, *J* 8.6), 7.17 (2 H, d, *J* 13.7), 7.06 (2 H, d, *J* 8.2), 6.84–6.79 (4 H, m), 3.78 (3 H, s), 2.31 (3 H, s); $\delta_C(CDCl_3)$ 157.78, 135.09, 132.88, 129.59, 128.88, 128.40, 128.36, 123.31, 123.06, 117.02, 116.85, 113.60, 55.14, 21.10; ν_{max}/cm^{-1} 3360 (NH); *m*/*z* (EI) 263 (M^+) (Found: C, 82.36; H, 6.46; N, 6.15. $C_{18}H_{17}NO$ requires C, 82.10; H, 6.51; N, 6.08%).

Preparation of dodecaarylporphyrins 4 and their metal complexes

A solution of the relevant aromatic aldehyde (10 mmol) and the relevant 3,4-diarylpyrrole (10 mmol) in CH_2Cl_2 (700 ml) was stirred at 0 °C for 30 min and then trifluoroacetic acid (10 mmol) was added. The resulting solution was stirred at room temperature for 24 h and heated at reflux for 1 h. Chloranil (0.5 mmol) was added to the reaction mixture and then it was further refluxed for 1 h. To the reaction mixture was added 5% aqueous NaOH (100 ml) and the organic layer was washed with 5% aqueous NaOH and water. The organic layer was dried with anhydrous sodium carbonate, and the solvent was evaporated. The residue was subject to column chromatography (silica gel, CH_2Cl_2–2% MeOH) to collect the red solution. The porphyrins were further converted into the corresponding Zn or Cu complexes on treatment with zinc acetate or copper acetate, respectively, in CH_2Cl_2, which were purified by column chromatography (silica gel, CH_2Cl_2–2% MeOH) followed by recrystallization from CH_2Cl_2–MeOH to give pure **Zn-4** or **Cu-4** in 10–20% yield (see Table 3). The metals were removed on treatment with acid to give **4** in quantitative yields. Some spectral data of **4** and the metal complexes are summarized in Tables 3 and 4. Porphyrins **4a**, **4b**, **4c**, **4e**, **4g** and **4j** are known and spectral data for them are in good agreement with those reported.[3,14]

$H_2$4a. $\delta_H(CD_2Cl_2)$ at 20 °C: 7.62 (d, 8 H *meso*-Ph_o), 6.75–6.62 (m, 52 H), −1.0 (br s, 2 H); at −80 °C: 7.90 (d, 4 H, β-Ph_o), 7.88 (d, 4 H, *meso*-Ph_o), 7.66 (d, 4 H, *meso*-Ph_o), 7.44 (d, 4 H, β-Ph_o), 6.95 (t, 4 H, *meso*-Ph_m), 6.77–6.44 (m, 32 H), 6.02 (d, 4 H, β-Ph_o), 5.63 (d, 4 H, β-Ph_o), −1.5 (br s, 2 H) (HRMS found: 1223.56. $C_{92}H_{63}N_4$ + H requires 1223.5052).

$H_2$4d. $\delta_H(CD_2Cl_2)$ at 20 °C: 7.45 (d, 8 H, *meso*-Anisyl), 6.64 (d, 16 H, β-Anisyl), 6.36 (d, 8 H, *meso*-Ph), 6.27 (d, 16 H, β-Anisyl), 3.64 (s, 12 H, OMe), 3.55 (s, 24 H, OMe), −0.8 (br s, 2 H); at −80 °C: 7.72 (d, 4 H, β-Anisyl), 7.62 (d, 4 H, *meso*-Anisyl), 7.45 (d, 4 H, *meso*-Anisyl), 7.40 (d, 4 H, β-Anisyl),

6.50–5.92 (m, 28 H), 5.30 (d, 4 H, β-Anisyl), 3.69 (s, 12 H, OMe), 3.55 (s, 12 H, OMe), 3.52 (s, 12 H, OMe), −1.5 (s, 2 H) (HRMS found: 1583.69. $C_{104}H_{86}N_4O_{12}$ + H requires 1583.6324).

$H_2$4f. $\delta_H(CD_2Cl_2)$ at 20 °C: 7.42 (d, 4 H), 7.32 (d, 8 H), 6.90 (d, 8 H), 6.66–6.56 (m, 16 H), −0.8 (br, 2 H); −80 °C: 7.65 (m, 4 H, *meso*-thiophene), 7.45–7.35 (m, 8 H), 6.96–6.54 (m, 24 H), −0.8 (m, 2 H). The NMR spectra at −80 °C were very complicated due to the presence of many isomers; *m*/*z* 1295 (M^+ + 1), 1297 (M^+ + 3) (HRMS: found 1295.10, 1297.11. $C_{68}H_{38}N_4S_{12}$ + 2 H requires 1295.9902).

$H_2$4h. $\delta_H(CD_2Cl_2)$ at 20 °C: 7.54 (d, 4 H), 7.36 (d, 4 H), 6.86–6.78 (m, 28 H), −0.8 (br s, 2 H); −80 °C: 7.78 (d, 4 H), 7.1–7.5 (m, 4 H), 7.4–7.3 (m, 4 H), 6.8–6.9 (m, 24 H), −1.32 (m, 2 H). The NMR spectra at −80 °C were very complicated due to the presence of many isomers. *m*/*z* 1296 (M^+ + 2) (HRMS found 1296.06. $C_{68}H_{38}N_4S_{12}$ + 2 H requires 1295.9902); **$H_2$4i**: $\delta_H(CD_2Cl_2)$ at 20 °C: 7.4–7.7 (m, 24 H), 2.31 (s, 12 H, SMe), 2.35 (s, 24 H, SMe), −0.8 (br, 2 H); mass spectrum for **Cu4i**: *m*/*z* 1910 (M^+ + 2) (HRMS: found: 1910.48. $C_{80}H_{60}N_4S_{24}Cu$ + 2 H requires 1910.5132).

Preparation of octaphenylporphyrin from 2a

To a stirred mixture of $LiALH_4$ (5 mmol) in THF (30 ml) was added **2a** (3 mmol) in THF (5 ml) at 0–5 °C. The reaction mixture was stirred for 1 h at this temperature then poured into saturated aqueous NH_4Cl, and extracted with CH_2Cl_2 (100 ml × 3). To the combined extracts was added toluene-*p*-sulfonic acid (0.02 g), and the resulting solution was stirred for 12 h at room temperature and then chroranil (0.4 g) was added. The mixture was stirred for 8 h, and washed with 5% aqueous sodium hydrogen carbonate, and the organic layer was dried with anhydrous sodium carbonate. After evaporation, column chromatography of the residue (silica gel, CH_2Cl_2) gave **5** (0.21 g, 30% yield); $\delta_H(CD_2Cl_2)$ −3.03 (NH, 2 H), 6.4–6.9 (m, Ph, 40 H), 10.32 (*meso*-H, 4 H); $\lambda_{max}(CH_2Cl_2)$/nm 420, 515, 645, 580, 638; *m*/*z* (EI) 918 (M^+). The zinc complex of **5** was prepared on treatment with a saturated solution of $Zn(OAc)_2$ in methanol.

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