Synthesis of perialkynylated tetrapyrazinoporphyrazines and its optical properties

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Some phthalocyanines soluble in organic solvents have been developed by peripheral introduction of substituent groups. We report a new method for preparation of the polyphenyl-substituted dicyanopyrazines based on the [2 + 4] Diels–Alder cycloaddition of the tetraphenylcyclopentadienone to an ethynyl compound. The synthesised tetrapyrazinoporphyrazinato metal complexes were characterised by UV-visible spectroscopy, MALDI-TOF-Ms (matrix-assisted laser desorption ionisation time-of-flight mass) spectroscopy, and ^{1}H NMR spectroscopy.

Keywords: porphyrazine, spectral change, aggregation, fluorescence, perialkynyl substituent

Phthalocyanine derivatives have found wide applications as traditional dyes[1] in liquid crystallinity,[2] chemical sensors,[3] and non-linear optical materials.[4] In addition, they can be applied to the electronics industry. For instance, they may be used for optical data storage, colour display technology, and biological technology (*e.g.* photodynamic tumour therapy (PDT)).[5-6]

The properties of phthalocyanines are influenced by the nature of the peripheral substituents and the central metal ion. Unsubstituted phthalocyanine has poor solubility. However, alkyl chain substituents can increase the solubility in common organic solvents and facilitate the formation of discotic mesophases. It promises high potential for high charge mobilities in sufficiently ordered rod-like structures. The phthalocyanine transferred films or patterning have been actively researched. Zangmeister *et al.* transferred peripherally ethylene oxide substituted copper phthalocyanines to bilayer films by Langmuir–Blodgett (LB) films.[7,8]

Faust *et al.* researched phthalocyanines or tetrapyrazinoporphyrazines that contained acetylene groups as their peripheral substituents. Peripheral alkynyl substitution of strongly absorbent chromophores, such as porphyrins and phthalocyanines, is becoming an increasingly popular strategy for the design of functional dyes.

We now report a general synthesis of 2,3-dicyanopyrazines and their conversion to tetrapyrazinoporphyrazines equipped with polyphenyl dendrons. The perialkynyl substituent can modify the chromophores in two different ways. First, it can cause bathochromic shifts in the electron absorption and emission spectra, due to the expansion of the π-electron systems of the chromophores. Second, it can act as a monomer and can be linked to form delocalised multichromophore chains or two-dimensional polymer networks.[9,10]

Result and discussion

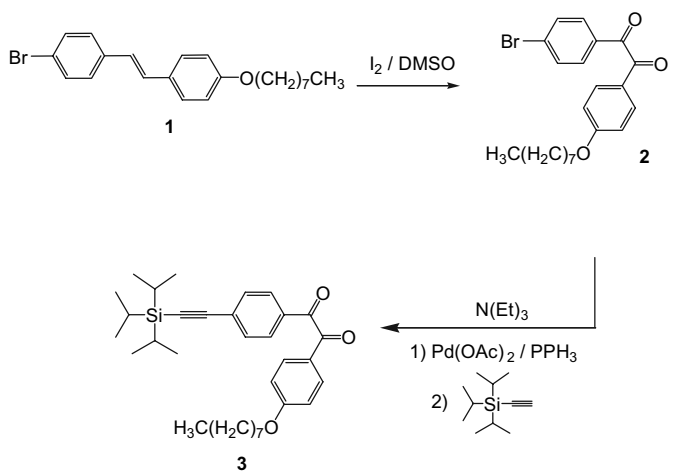
Synthesis

The preparation method of 1-bromo-4-(4-(octyloxy)styryl) benzene (**1**) has been described in previous literature.[11,12] 1-(4-Bromophenyl)-2-[4-(octyloxy)phenyl]ethane-1,2-dione (**2**) was prepared by refluxing **1** in dimethyl sulfoxide (DMSO) and 0.4 equiv. of iodine with a 69% yield. 1-[4-(Octyloxy) phenyl]-2-[4-((trimethylsilyl)ethynyl)phenyl]ethane-1,2-dione (**3**) was synthesised by palladium-catalysed ethynylation in triethylamine. Scheme 1 shows these steps for preparing an acetylene group containing an α-diketone.

Compound **3** can be a precursor of various compounds, which are used for preparing peripheral substituents of phthalocyanines, as shown in Scheme 2. The reaction of **3** with 2,3-diaminomaleonitrile (DAMN) in ethanol, in the presence of *p*-toluenesulfonic acid produced the 2,3-dicyanopyrazine derivative **4**.

Treatment of **4** with tetrabutylammonium fluoride in THF, under mild conditions, with subsequent removal of the triisopropyl silyl group resulted in a high conversion to 5-(4-ethynylphenyl)-6-(4-(octyloxy)phenyl)pyrazine-2,3-dicarbonitrile (**5**).

The compounds **6** were prepared by the condensation between dibenzyl ketone and α-diketones, in the presence of potassium hydroxide in ethanol.[13] However, the reaction conditions were highly basic and this meant that the reaction rate was too fast. A low yield, with various by-products,



Scheme 1 Synthesis method of acetylene-containing α-diketone.

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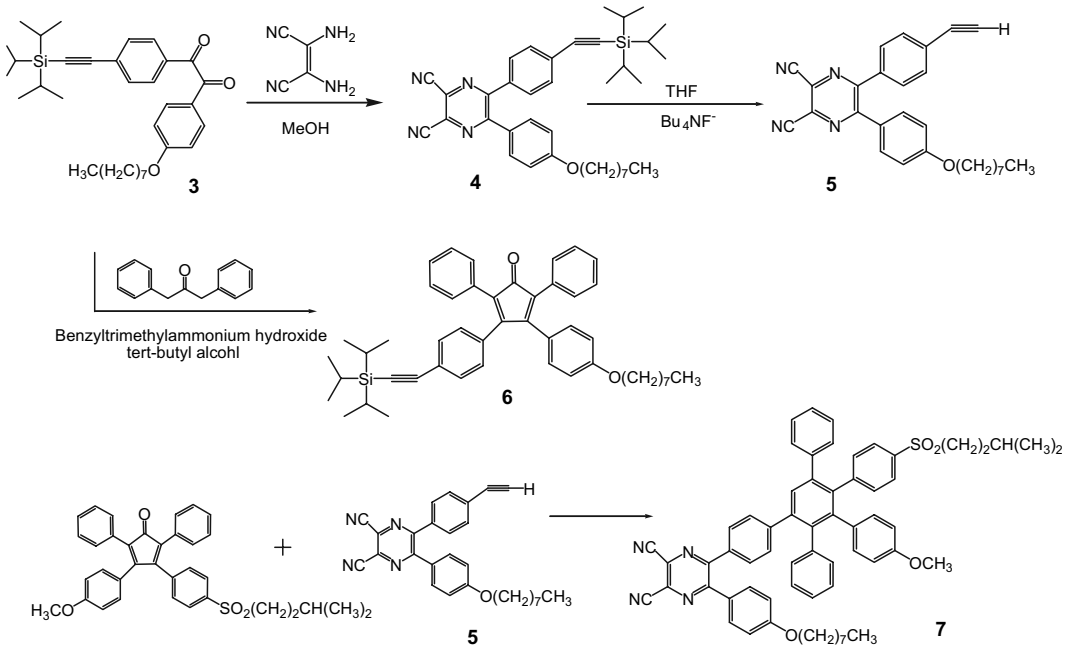


Scheme 2 Preparation of 2,3-dicyanopyrazines.

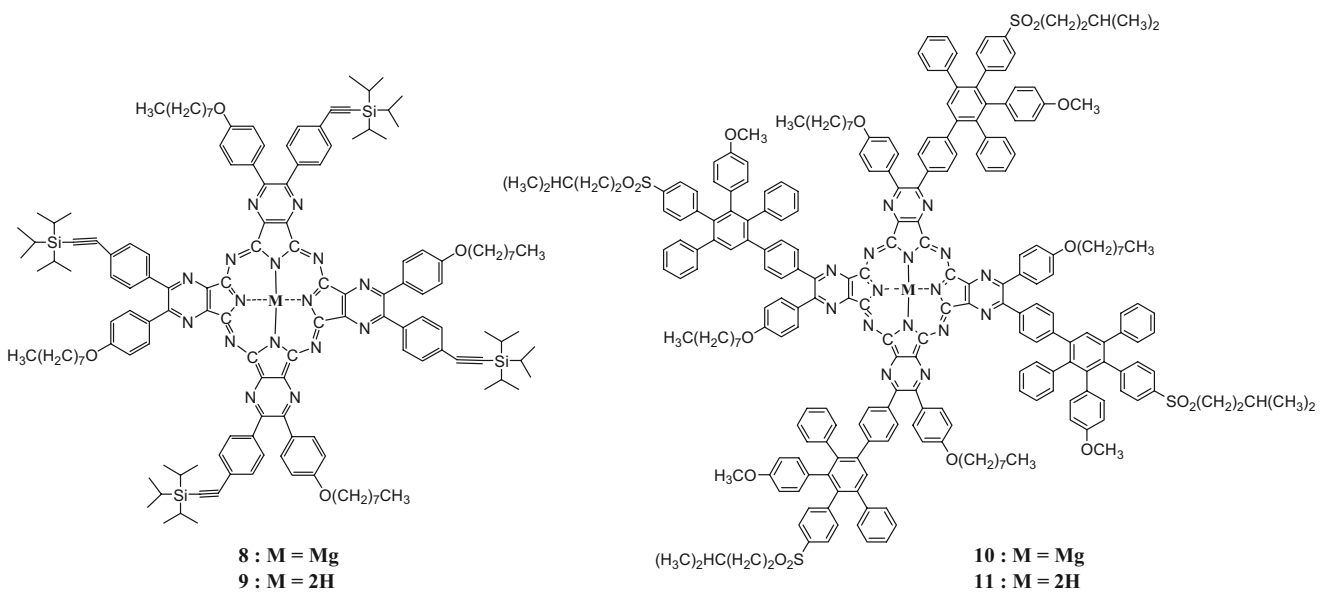
resulted. But in an improvement the base and solvent used were benzyltrimethyl ammonium hydroxide and *tert*-butyl alcohol respectively and as a result even though the reaction rate was slightly slower a more favourable yield (72%) resulted. A [2 + 4] Diels–Alder cycloaddition reaction between tetraphenylcyclopentadienone **6** and the acetylene-group-containing compound **5** was used, and the polyphenylene substituent-containing 2,3-dicyanopyrazine **7** was created by refluxing in degassed *p*-xylene, followed by the elimination of carbon monoxide. The advantage of this cycloaddition is that it is practically free of side reactions, and the equilibrium is shifted toward the products due to the irreversible loss of CO and the formation of a benzene ring. Therefore, a retro Diels–Alder reaction cannot occur.[14]

The synthesised 2,3-dicyanopyrazine compounds **4** and **7** are precursors of tetrapyrazinoporphyrazines. 2,3-Dicyanopyrazines undergo cyclotetramerisation with a magnesium metal ion, which was prepared from a magnesium butoxide emulsion to afford magnesium complexes **8** and **10**. The magnesium derivatives were demetallised by stirring them with excess *p*-toluenesulfonic acid in THF at room temperature for 30 min to produce **9** and **11**, as shown in Scheme 3.

UV-visible spectra

The maximum absorption wavelength and molar absorptivity (ε) values for compounds **8–11** are shown in Table 1. The typical B-band (Soret band, around 400nm), and Q-band (in 600–700nm region) of phthalocyanines were identified in this study. The metal-free tetrapyrazinoporphyrazine generally have two narrow splitting Q_x/Q_y bands. These are not related to their peripheral substituents.

The compound **8** shows the highest molar absorptivity of all of the products. Even if compounds **8** and **9** have only TIPS groups attached, the wavelengths of the Q-bands are almost the same as those for **10** and **11**, which have polyphenylene



Scheme 3 Structure of tetrapyrazinoporphyrazines.

Table 1 Absorption and molar absorptivity of tetrapyrazinoporphyrazines

Compd.	Solvent	λ_{max}(nm)		ε(l/mol·cm)[a]
		Soret band (B-band)	Q-band	
8	$CHCl_3$	383	667	3.68×10^5
	THF	385	661	3.77×10^5
	CCl_4	380	666	2.79×10^5
9	$CHCl_3$	379	650, 679	8.98×10^4
	THF	373	650, 673	7.55×10^4
	CCl_4	374	681	4.45×10^4
10	$CHCl_3$	384	662	7.20×10^4
	THF	380	660	9.16×10^4
	CCl_4	381	661	4.53×10^4
11	$CHCl_3$	377	650,679	1.55×10^5
	THF	371	679,673	1.49×10^5
	CCl_4	374	649, 679	1.24×10^5

[a]Molar absorptivity of Q-band or Q_y band.

groups attached as their peripheral substituents.

The aggregation behaviour of phthalocyanines is a specific property due to the intermolecular stacking of the planar and rigid core structures of the molecules. Sometimes this can become a significant problem for their various applications. The synthesised products aggregated in solution, and this tendency was varied by controlling the products' environments, such as the solvents, their concentration and the basicity. Figure 1 shows spectra of compounds **8** and **9** in CCl_4, chloroform, and THF all at the same concentration. Spectra of **10** and **11** show almost the same behaviour. The absorbance of the spectra was significantly decreased in CCl_4. Especially comparing with **9** and **11**, spectral peaks of compound **10** were severely broadened. However, spectral peaks of compound **11** remain as narrow peaks, although the absorptivity is decreased. It is assumed that the rigidity of the phthalocyanine structure is decreased because of the out-of-twisted peripheral phenyl components.

The aggregation behaviour of **8** was investigated at different concentrations in $CHCl_3$. In $CHCl_3$, as the concentration was decreased, the intensity of absorption of the Q-band increased as shown in Fig. 2, because of reduction of aggregation.

There has been a great deal of research focusing on the optical sensitivity of phthalocyanines due to their acidic or basic properties. In this paper, the synthesised products also experience an anion effect, especially with the F^- anion,

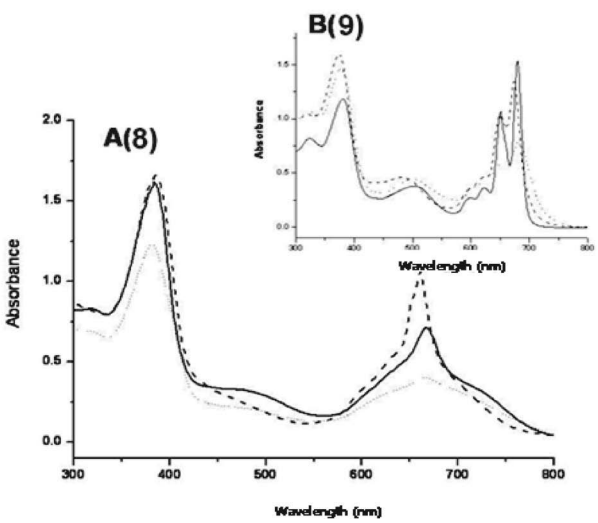


Fig.1 Absorption spectra of **8** (A, 4.4×10^{-6} M) and **9** (B, 1.78×10^{-5} M) in CCl_4 (dot line), tetrahydrofuran (dashed line), and chloroform (solid line).

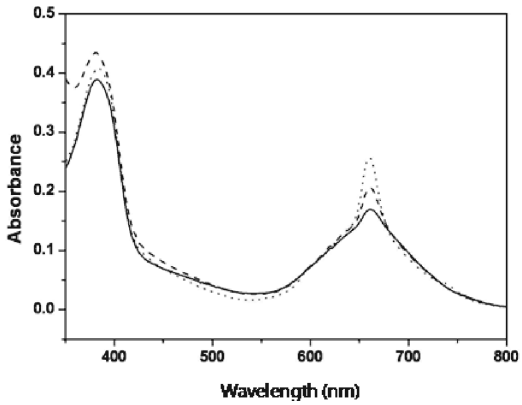


Fig 2 Effect of concentration on the absorption spectra of compound 8 (solid line: 2.8×10^{-5} M, dashed line: 2.8×10^{-6} M, dotted line: 0.7×10^{-6} M).

which was added to the nonaqueous solvents in the form of tetra-*n*-butylammonium salts. The spectra were found to rapidly change. Previous researchers showed that the fluoride anion can bind within the cores of metallophthalocyanines. Strictly speaking, it forms F^- coordinated complexes[15] or causes deprotonation of the proton on the pyrrole group of metal-free phthalocyanines.[16] In our case, Figure 3 shows the UV-visible spectral changes of **10** and **11** upon adding tetrabutylammonium fluoride monohydrate (TBAF). The spectra showed a sharp peak in the Q-band and the molar absorptivity was higher than that for the initial solution.

Fluorescence property

Tetrapyrazinoporphyrazine derivatives show fluorescence properties which vary according to different environments around the molecule. The excitation wavelengths used in the experiments were the λ_{max} of B and Q-bands.

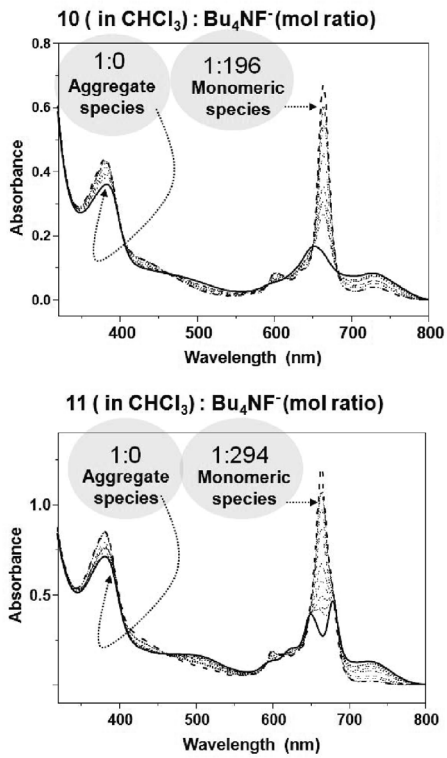


Fig.3 UV-vis absorption spectral change upon adding a base to **10** (1.74×10^{-5} M) and **11** (1.75×10^{-5} M).

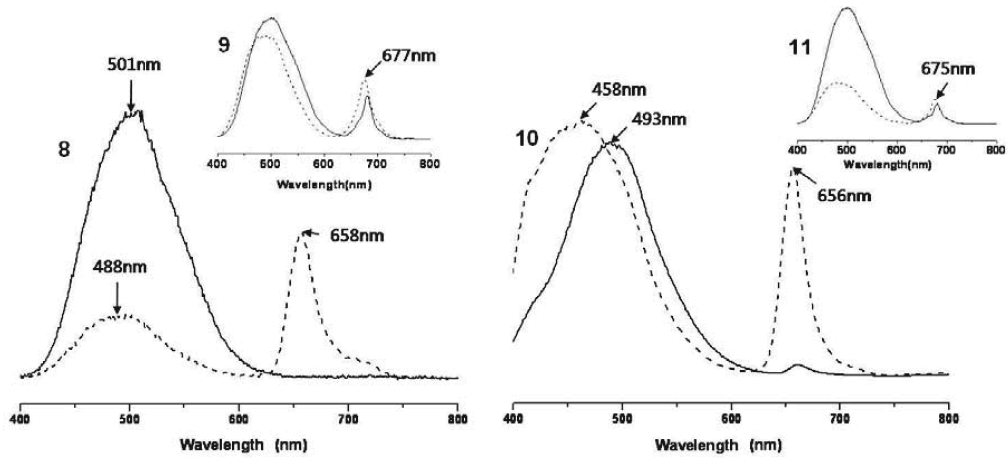


Fig. 4 Fluorescence spectra in chloroform (solid line) and THF (dashed line) at the same concentration (**8**: 2.6×10^{-7} M, **9**: 2.6×10^{-7} M, **10**: 1.74×10^{-7}M, **11**: 1.75×10^{-7} M).

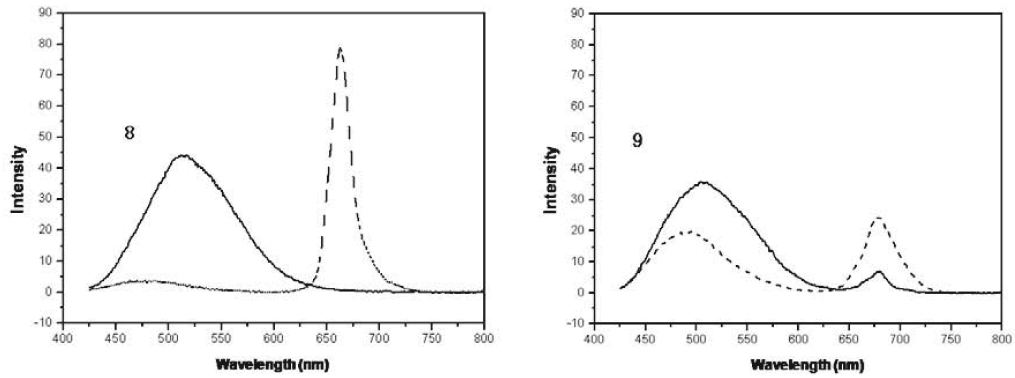


Fig. 5 Fluorescence change upon adding a base to **8** (**8**:TBAF = 1:0 (solid line), **8**:TBAF = 1:108 (dashed line) mol ratio), and **9** (**9**:TBAF = 1:0 (solid line), **9**:TBAF = 1:150 (dashed line) mol ratio).

Figure 4 shows fluorescence spectra of the synthesised products in chloroform and THF, from the emission peak in the B-band. Generally, the emission peak around 450–550 nm was more intense in chloroform. However, the emission peak around 650–750 nm which shows a red fluorescence, was significantly more intense in THF than in chloroform.

The appearance of the long wavelength region can be examined by the fluorescence quenching effect, due to the intermolecular π–π interaction relatively decreasing in solution.

Figure 5 displays the emission spectra of compounds **8** and **9** when tetra-*n*-butylammonium fluoride (TBAF) was added in chloroform. The F_{max} was significantly changed and Fig. 5 also shows the strong fluorescence in the 650–750nm region.

Conclusion

In this study, the peripheral acetylene group was successfully attached in the pyrazine unit, and it could be used as a precursor of various compounds by using condensation and cycloaddition reactions. We also designed and synthesised metal and metal-free tetrapyrazinoporphyrazines, which show that the polyphenylene dendrimers increase the solubility of porphyrazines in common organic solvents. The aggregation behaviour in solution was investigated through their absorption and emission spectra.

Experimental

General

Compounds were identified and their properties were measured using the following techniques. Flash chromatography was performed with Merck-EM type 60 (230–400 mesh) silica gel (flash). Melting points were obtained with a capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a VARIAN UnityInova 300 MHz FT-NMR Spectrometer. UV-visible and fluorescence spectra were measured using a SCINCO S-4100 and a SHIMADZU RF-5301PC spectrophotometer. MALDI-TOF-Ms (matrix-assisted laser desorption ionisation time-of–flight mass) spectra were obtained on a Waters Limited MALDI-TOF spectrometer with dithranol as a matrix. All chemicals were used of reagent grade without further purification unless otherwise specified.

Tetrapyrazinoporphyrazinato magnesium complex (**8**)

A suspension of Mg turning (200 mg, 8.4 mmol), one small crystal of iodine and *n*-butanol 20 mL were heated under reflux for 4 h. The reaction mixture was then cooled to room temperature, and dicyanopyrazine **4** (1.2 g, 2.1 mmol) was added in one portion. The reaction mixture was quickly reheated to reflux for 1 h. After approximately 10 min, the reaction mixture had become dark green. The mixture was cooled and the solvent was removed *in vacuo*, yielding crude product as a dark green solid. The crude product was purified using chloroform/methanol (30/1) as an eluent. **8** (dark green solid, 48%): m.p >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 0.40–1.85 (m, $–CH_3$, 12H), 1.08–1.55 (m, –Si–C–CH_3, 72H; methylene, 40H; –Si–CH, 12H), 1.90–2.21 (m, –O–C–CH_2, 8H,), 3.90–4.38 (m, O–CH_2, 8H,), 6.6–8.3 (m, aryl protons, 32H); MALDI-TOF mass-spectra: *m/z* 2387.1 (Calcd 2387.8)

Demetallised tetrapyrazinoporphyrazine (**9**)

p-Toluenesulfonic acid (0.81 g, 4.23 mmol) was added to a solution of Mg tetrapyrazinoporphyrazine **8** (200 mg, 0.08 mmol) in tetrahydrofuran (THF, 10 mL) and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo*, yielding the crude product as a dark green solid. The crude product was purified by column chromatography on silica gel using chloroform/methanol (30/1) as an eluent. **9** (dark green solid, 58%): m.p >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ : –0.80 (s, N–H, 2H), 0.98–1.08 (m, CH_3, 12H), 1.20 (s, –Si–C–CH_3, 72H), 1.36–1.58 (m,

methylene, 40H), 1.59–1.68(m, –Si–CH, 12H), 1.83–2.13 (m, –O–C–CH_2, 8H), 3.90–4.20 (m, O–CH_2, 8H), 6.92–7.05 (m, ArH, 8H), 7.62–7.80 (m, ArH, 16H), 7.87–8.10(m, ArH, 8H); MALDI-TOF mass-spectra: *m/z* 2364.9 (Calcd 2365.51)

Tetrapyrazinoporphyrazinato magnesium complex (**10**)
This compound was prepared by the procedure described for **8** but from magnesium (0.11 g, 4.5 mmol), 10 mL of *n*-butanol and **7** (0.72 g, 0.75 mmol). The mixture was cooled and the solvent was removed *in vacuo*, yielding crude product as a dark green solid. The crude product was purified using chloroform/methanol (30/1) as an eluent. **10** (dark green solid, 59%): m.p >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ : 0.80–1.08 (m, –CH_3, 36 protons), 1.22–1.53 (m, methylene, 40H), 1.53–1.75 (m, O–C–CH_2, 8H), 1.80–2.20 (m, –S–C–CH_2–CH, 12H), 2.90–3.10 (m, –S–CH_2, 8H), 3.62–3.80 (m, –O–CH_3, 12 protons), 4.00–4.24 (m, –O–CH_2, 8H), 6.2–8.2 (m, Aryl protons, 108H); MALDI-TOF mass-spectra: *m/z* 3841.4 (Calcd 3845.16)

Demetallised tetrapyrazinoporphyrazine (**11**)
This compound was prepared by the procedure described for **9** but from compound **10** (100 mg, 0.04 mmol), *p*-toluenesulfonic acid (0.4 g, 2.12 mmol). The solvent was removed *in vacuo*, yielding the crude product as a dark green solid. The crude product was purified by column chromatography on silica gel using chloroform/methanol (30/1) as an eluent. **11** (dark green solid, 70%): m.p >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ : –0.64 (s, N–H, 2H), 0.90–1.00 (m, CH_3, 36H), 1.25–1.50 (m, methylene, 40H), 1.53–1.65 (m, O–C–CH_2, 8H), 1.80–2.00 (m, –S–C–CH_2–CH, 12H), 2.90–3.02 (m, –S–CH_2, 8H), 3.62 (s, –O–CH_3, 12 protons), 4.08–4.15 (m, –O–CH_2, 8H), 6.46 (d, *J* = 9.0 Hz, ArH, 8H), 6.53 (d, *J* = 9.0 Hz, ArH, 8H), 6.71 (d, *J* = 9.0 Hz, ArH, 8H), 6.77 (d, *J* = 9.0 Hz, ArH, 8H), 6.90–7.05 6.46(m, ArH, 30H), 7.09 (d, *J* = 9.0 Hz, ArH, 8H), 7.20 (s, ArH, 4H), 7.35 (d, *J* = 9.0 Hz, ArH, 8H), 7.47 (d, *J* = 9.0 Hz, ArH, 8H), 7.53 (d, *J* = 9.0 Hz, ArH, 8H), 7.77(d, *J* = 12.0 Hz, ArH, 4H), 7.95–8.03 (m, ArH, 6H); MALDI-TOF mass-spectra: *m/z* 3822.7 (Calcd 3822.87)

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