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Synthesis of flexible dimeric *meso*-tetrakis-porphyrins

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Abstract—Monofunctionalisation of *meso*-tetrakis-porphyrins through introduction of a carboxylic group in the *meso* position of the phenyl group confers the necessary characteristics to anchor them through stable amide bonds to functionalised supports or to molecules. In this Letter we describe the synthesis, characterisation and photophysical evaluation of such a functionalised flexible dimeric porphyrin, bis-(*meso*-tetrakis-5,10,15-triphenyl-20-(*p*-carboxyphenyl)-porphyrinyl)-1,6-hexanediamide.

The unique photophysical and photochemical properties of porphyrins and related macrocycles make them an extremely versatile class of compounds for a variety of applications in medicine, catalysis, conversion of solar energy and nanotechnology.[1–7]

Dimeric porphyrin arrays (bis-porphyrins) in particular are important for supramolecular recognition and energy or electron donor–acceptor systems. The bis-porphyrins are the simplest elements in porphyrin based nanostructures and consequently several methods have been developed to achieve efficient and controlled synthesis of porphyrin-spacer-porphyrin systems. Since the nature of the linker has a strong influence on the overall properties of the porphyrin dimers, affecting both physical (solubility, aggregation behaviour or photo response) and chemical properties (reactivity or thermal stability) a large amount of work has been done over the last four decades on the synthesis and evaluation of the physical properties of a number of bis-porphyrins. The actual bis-porphyrin based design of *porphyrin-spacer-porphyrin* systems, with organic ionic, metal ionic or organic covalent linked spacers constitutes a diverse set of molecular types, involving *meso*-free porphyrins, *meso*-tetrakis-porphyrins and a combination of both, with spacers ranging from a few atoms to complex spacers of lengths extending to dozens of angstroms, having saturated molecules, aromatics or other highly conjugated motifs as spacers.[8–13]

In spite of this intense activity, synthesis of new bis-porphyrins is still an area of high potential, both in terms of improving low yields generally obtained in the synthetic process as well as discovering novel properties from new assemblies of porphyrins and spacers, as in the case of the long saturated spacers between *meso*-phenyl-porphyrins. Since most of the work has been done with conjugated spacers to favour the electronic interaction among the two porphyrins, mostly with restricted rotation, there is a lack in the evaluation of the interaction of two porphyrins restricted in the same volume but without direct conjugation between their electronic systems. This has led us to plan and synthesise the title compound, whose photophysical properties are also presented.

Optical absorption spectra of porphyrins were recorded on a Jasco V-560 UV–vis absorption spectrophotometer. Fluorescence measurements were made on a Perkin–Elmer LS50B spectrofluorometer. The instrumental response at each wavelength was corrected by means of a curve obtained using appropriate fluorescence standards. The sample holders of both instruments were thermostated at 25.0 °C and all measurements were performed with [Porphyrin] $\sim 4\ \mu\text{M}$ in acetonitrile using 10 mm path length quartz cells. MM2 calculations were performed in a Pentium 4 workstation at 3.2 GHz, via CambridgeSoft Chem3D Pro 7, 2001, USA, using a conjugated gradient algorithm for

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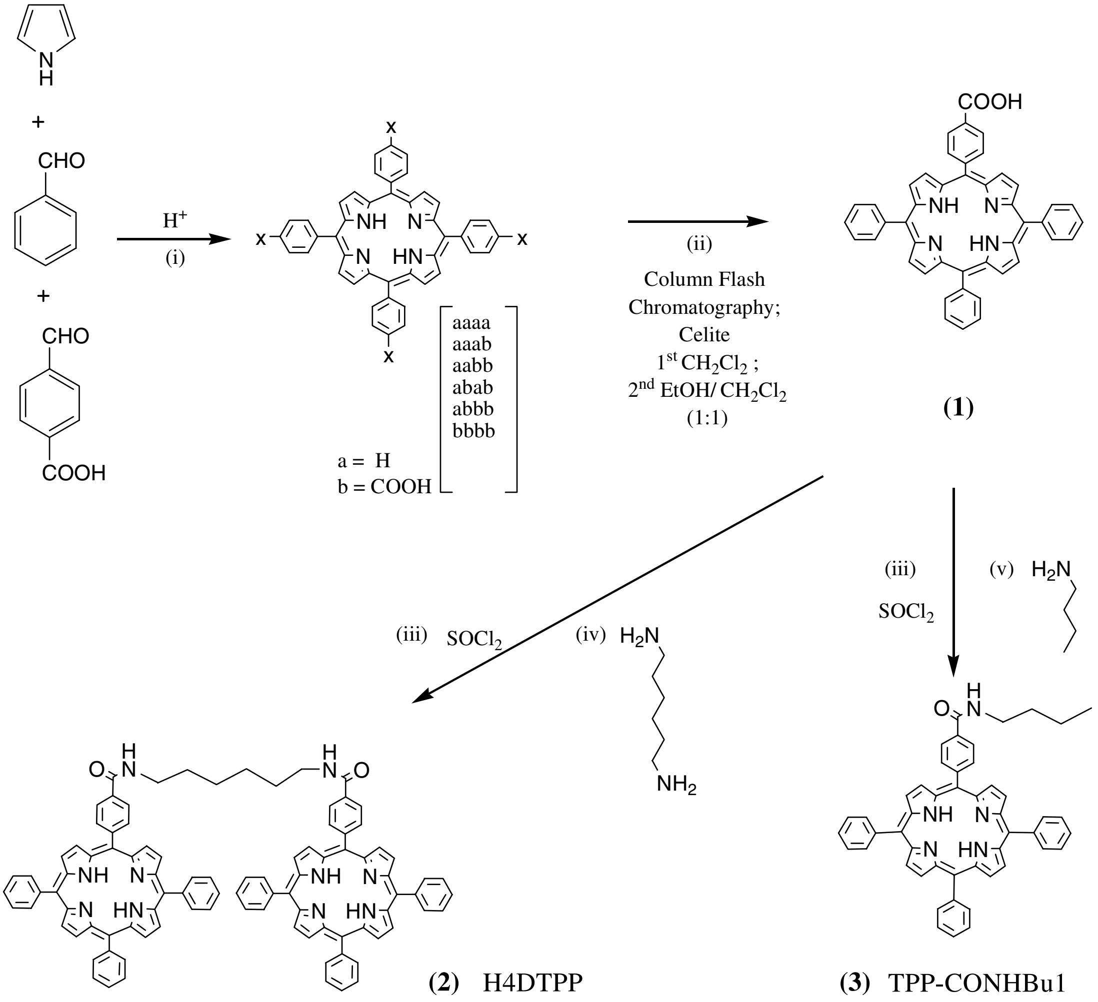
energy minimisation in vacuum, with a final gradient of 0.05 kcal/(Å mol).

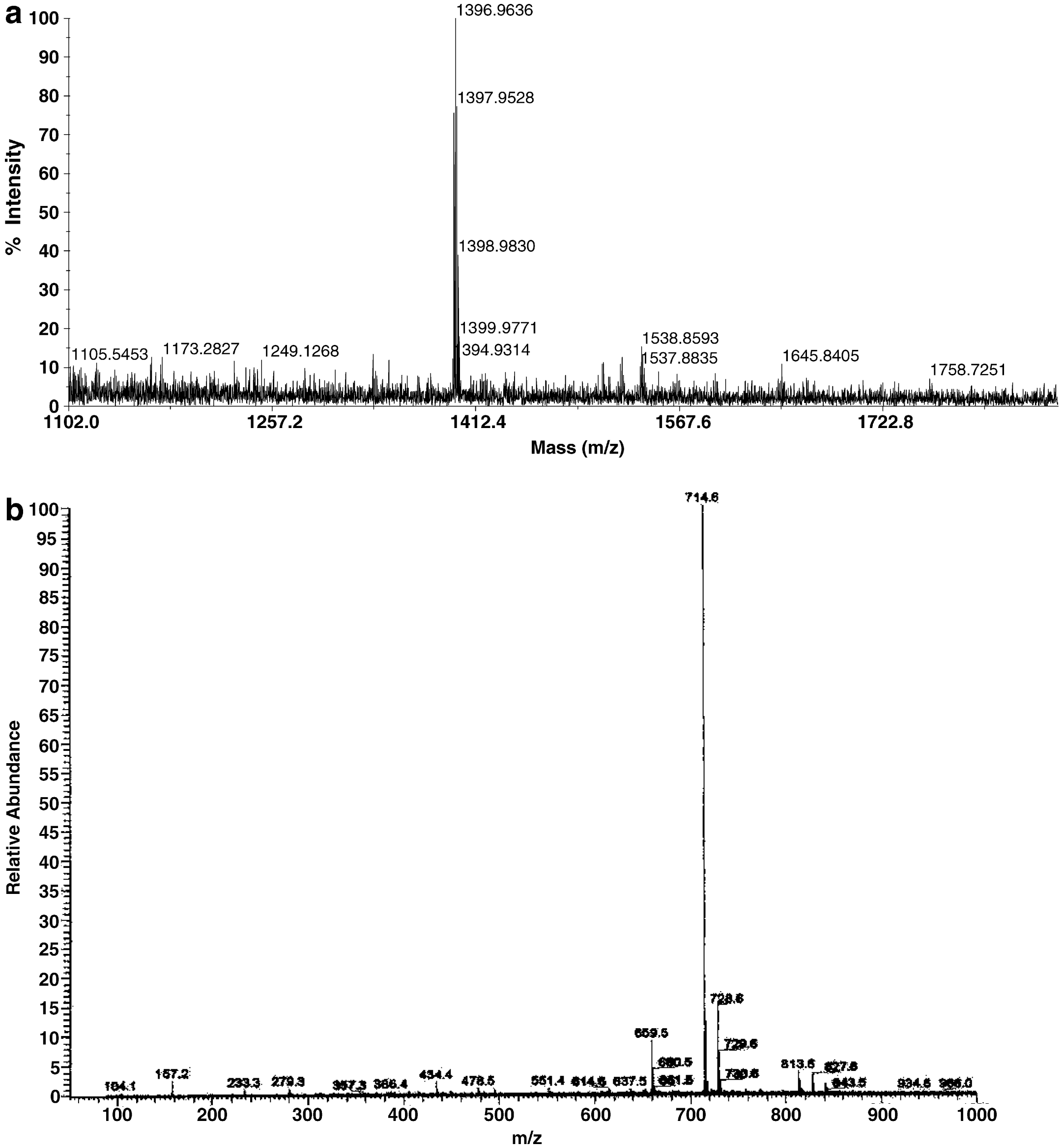
We isolated the mono functionalised porphyrin (**1**) in a 5% yield from the statistical mixture of porphyrins resulting from the cross condensation of benzaldehyde and 4-carboxy-benzaldehyde with 1*H*-pyrrole, in aerated propionic acid and acetic anhydride solution at 130 °C. After conversion of the carboxyl group to its acyl chloride by $SOCl_2$, the porphyrin was coupled with hexane-1,6-diamine to give dimeric porphyrin (**2**) (H4DTPP) or with *n*-butylamine to give porphyrin (**3**) (TPP-CONHBu1), as shown in Scheme 1. All compounds gave the expected spectroscopic and analytical data for the suggested structures.

The electronic absorption spectra were examined in acetonitrile and compared with that of TPP-CONHBu1 under similar conditions. Figure 1 shows the absorption spectra of H_4DTPP (in bold) and of TPP-CONHBu1. These display common features, with both exhibiting a single Soret (B) and four Q-bands. The similar spectra and lack of splitting of the bands indicate that no distortions occur in ring planarity. The lack of splitting of the Soret band suggests that the electronic states of the dimer are not perturbed compared with that of the monomeric porphyrins.

According to exciton coupling theory, the transition dipole moments for each moiety interact electrostatically to create two exciton states, $\Psi^{|}$ and Ψ^{-}. The $\Psi^{|}$ state corresponds to the case where both monomeric units are excited in phase, while for the Ψ^{-} state, both monomers are out of phase. The absorption energies of the transitions depend on the angle between the transition dipoles and the relative phase of their excitations. The exciton is expected to be strong in directly *meso*-linked arrays because of the short interconnection between porphyrin moieties. However, in the present case the interconnection between units is large enough to allow



Scheme 1. Reagents and conditions: (i) Propionic acid, acetic anhydride, benzaldehyde, 4-carboxy-benzaldehyde, 1*H*-pyrrole; (1)/(2)/(3) (0.0144 mol/7.0×10^{-3} mol/7.0×10^{-3} mol), 130 °C, 3 h, 4%; (ii) column flash chromatography (first run CH_2Cl_2; second run $EtOH/CH_2Cl_2$ (1:1)); (iii) K_2CO_3 anhydrous, CH_2Cl_2, 32 °C, $SOCl_2$, 6 h; (iv) hexane-1,6-diamine, 32 °C, 2 h, 10%; (v) 1-butylamine, 32 °C, 1 h, 5%. (**1**) *m/z* (FAB MS, NBA) 659.9 (100%, $[M+H]^+$, $C_{45}H_{30}N_4O_2$ requires 658.7), ^1H NMR 500 MHz (0.01 M in $CDCl_3$): δ 11.1 (br s, 1H, COOH), δ 8.88 (m, 6H, βH_a), δ 8.83 (m, 2H, βH_b), 8.51 (dd, *J* 2.8 Hz, 2H, Subst. ArH_o), 8.36 (dd, *J* 2.8 Hz, 2H, Subst. ArH_m), δ 8.24 (m, 6H, ArH_m) δ 7.80 (m, 9H, $ArH_{o,p}$), δ −2.51 (m, 2H, NH). Inset: (a) MALDI-TOF mass spectra for (**2**), DHB matrix with calibration mixture Pepmix 1, $M^{+\cdot}$ at *m/z* 1396.96 ($C_{96}H_{72}N_{10}O_2$ requires 1396.58) and (b) ESI MS for (**3**) *m/z* (FAB, NBA) $[M+H]^+$ at 714.6 ($C_{49}H_{39}N_5O$ requires 713.4).



Scheme 1 (*continued*)

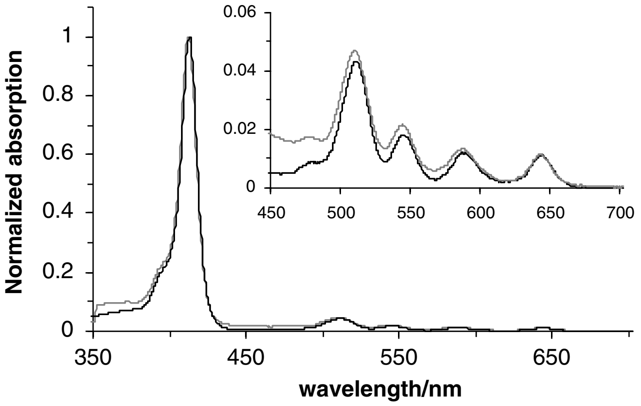


Figure 1. Normalised UV–vis absorption spectra of H_4DTPP (black line) and TPP-CONHBu1 (grey line) in acetonitrile. Inset: Expanded absorption spectra in Q-band region.

for a considerable angular distribution, such that exciton coupling is weak (or nonexistent). The perturbations sensed in the Q-band region are even less marked due to the much smaller transition dipole moments compared with those of B-bands.

The fluorescence emission spectrum of TPP-CONHBu1 in acetonitrile exhibits two vibronic emission bands centred at 650.5 and 717.5 nm (see Table 1) independent of the excitation wavelength, Figure 2. In the case of H_4DTPP, however, besides two similar vibronics, a totally new band is detected at higher energies (centred at 543 nm) with an intensity (INT) that, in contrast to the two longer wavelength emissions, depends on the excitation wavelength, with $\mathrm{INT}(\lambda_{\mathrm{exc}} = 375\ \mathrm{nm}) > \mathrm{INT}(\lambda_{\mathrm{exc}} = 508\ \mathrm{nm}) > \mathrm{INT}(\lambda_{\mathrm{exc}} = 420\ \mathrm{nm})$.

The excitation spectra also show a dependence on the emission wavelength. The spectrum obtained collecting emission at the usual vibronic bands (650 or 712 nm) is clearly superimposable on the absorption spectrum, both in Soret and Q-band regions. However, when the

Table 1. Comparison of photophysical parameters of H_4DTPP and TPP-CONHBu1 in acetonitrile

	Absorption maxima (nm)					Emission maxima (nm)			ϕ_f[a]
	B(Soret)	Qy(1,0)	Qy(0,0)	Qx(1,0)	Qx(1,0)				
H_4DTPP	413.5(2.54)[b]	512.0	546.0	589.0	644.0	542.0	650.0	716.0	0.12
TPP-CONHBu1	413.0(2.02)[b]	512.5	545.5	588.0	643.0	—	650.5	717.5	0.10

[a] $\lambda_{exc} = 508$ nm using for reference TPP in benzene with $\phi_f = 0.11$.

[b] Molar extinction coefficient, $\varepsilon/10^5$ M^{-1} cm^{-1}.

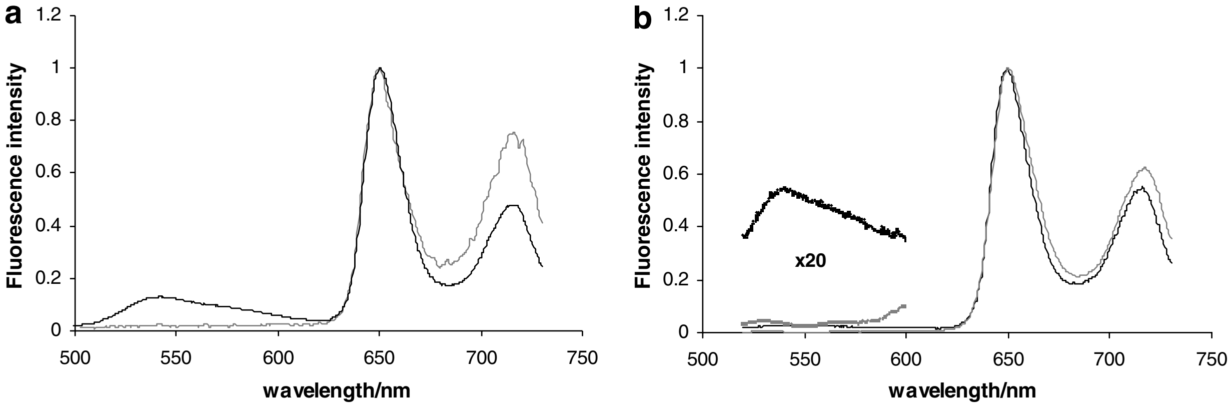


Figure 2. Normalised fluorescence spectra of H_4DTPP (black line) and of TPP-CONHBu1 (grey line) in acetonitrile obtained upon excitation at (a) 375 nm and at (b) 508 nm (inset: amplification of fluorescence intensity in the high energy region).

emission is observed at shorter wavelengths (e.g., 610 nm and 540 nm, in Fig. 3) a new band is detected in the corresponding excitation spectra with a maximum at 375 nm. In contrast, the intensity of the band common to absorption (centred at 413 nm) decreases, and it is not detectable when emission is collected near the new emission band maximum (540 nm). It is possible that upon excitation, a different configuration of the two porphyrin moieties is achieved, probably facilitated by the polar aliphatic solvents.

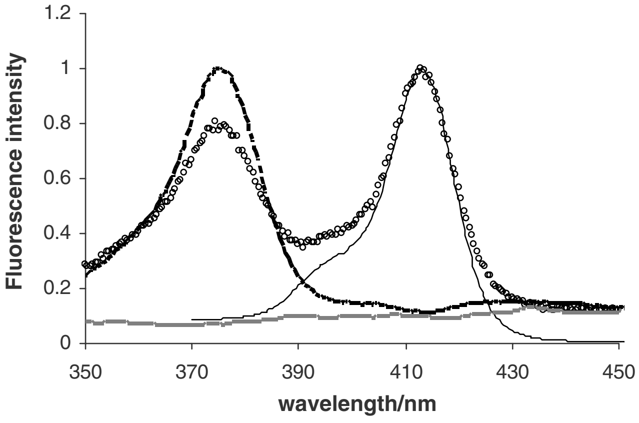
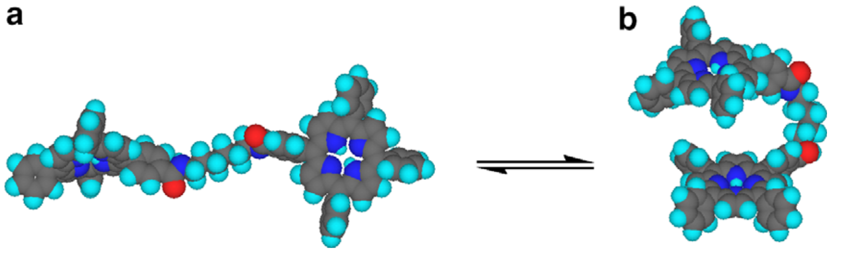


Figure 3. Normalised excitation spectra of H_4DTPP in acetonitrile collected at different emission wavelengths: 712 nm (black thin line); 610 nm (○○○); 540 nm (- - -) and (grey bold line for TPP-CONHBu1).

This broad band at higher energies than the monomer emission appears in many aprotic and protic polar aliphatic solvents and decreases with the temperature, but is absent in the aromatic apolar toluene. Work is in progress in order to clarify these features in the fluorescence emission.

Preliminary molecular mechanic calculations in vacuum of the open and closed forms (Scheme 2) show that the 'closed form' is 26 kcal/mol more stable than the 'open form', due to favourable $\pi\cdots\pi$ stacking interactions. Although this calculated vacuum value is too high to correspond to solution conditions, and would dramatically favour the stability of closed form, in contrast to what is observed, this suggests a favourable interaction between the linked macrocycles, which will be diminished by the solvent molecules and could even be totally



Scheme 2. Minimised conformational structures from molecular mechanical calculations (MM2) (a) 'open form' and (b) 'closed form'.

quenched by aromatic molecules that would create competing $\pi\cdots\pi$ interactions with the macrocycles. This is in line with the observed photophysical behaviour.

Acknowledgements

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