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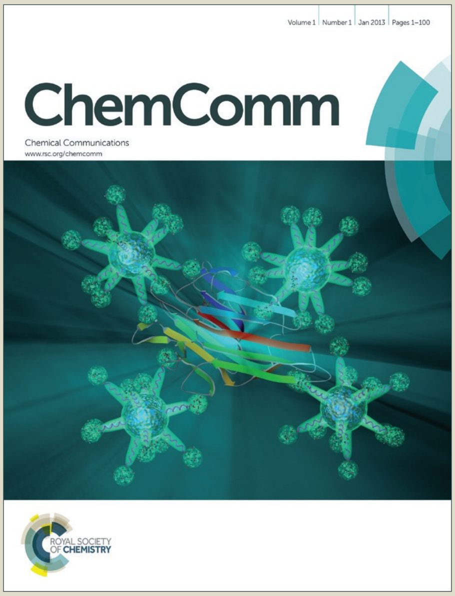

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ARTICLE TYPE

1, 4, 8, 11, 15, 18, 22, 25-Alkylsulfanyl phthalocyanines. Effect of macrocycle distortion on spectroscopic and packing properties

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The effect of phthalocyanine macrocycle distortion on their spectroscopic and packing properties is studied, by comparing two phthalocyanines octa non-peripherally substituted by alkanethiols of different bulkiness (*n*-hexyl and *tert*-butyl). Their X-ray structures evidence their core shape, respectively planar and strongly distorted, inducing a 55 nm shift of their maximum absorption wavelength. Comparison of frontier orbital energies revealed that this distortion decreases the conjugation potency of the benzo rings to the central pyrrolic rings. Also the *tert*-butyl derivative presents a MOF-like porous crystalline assembly with 22.2 % void.

Since their first use as dyes and pigments, phthalocyanines have gained technological recognition, as their electronic and optical properties are desired in a large number of highly specialized applications.[1] Controlled modulation of their photophysical properties is crucial and must be tailored accordingly to the targeted applications. The effect of substituent nature, number and position on the Q band maximum absorption wavelength of phthalocyanines is well known.[2] NIR (Near Infra-Red) absorption is desired in several fields,[3] such as photodynamic therapy,[3b-c] imaging or light havesting.[3d] Non-peripheral substitution[4] and sulfanyl grafting[5] are both known to red-shift the maximum absorption wavelength of phthalocyanine Q-band, and have been previously combined to shift the maximum electronic absorption up to 800 nm.[6] Aggregation (dimerization then oligomerization of phthalocyanine macrocycle via their π-π stacking[7]) limits or even inhibits the electronic events inducing the desired properties. The steric hindrance of bulky substituents prevents macrocycles to come close to each other enough to aggregate, and are commonly used to lower aggregation and retain phthalocyanine electronic properties. Phthalocyanines **1** and **2**, respectively octa non-peripherally substituted by hexylsulfanyl and *tert*-butylsulfanyl moieties (Fig. 1) were selected as potential non-aggregated NIR absorbing molecules, with the aim to explore the effect of the substituent bulkiness. **1** and **2** were prepared by previously reported lithium-assisted templating method from the corresponding phthalonitriles (Scheme S1).[8] Phthalocyanine **2** proved to be much less stable than **1**, during the course of the reaction as well as over time. Suitable crystals of **1** were grown by recrystallization from DCM whereas crystals of **2** were obtained by diffusion of ethanol into dichloromethane. As revealed by X-ray diffraction (Fig. 1), **1** is planar whereas the macrocycle of **2** is remarkably distorted.

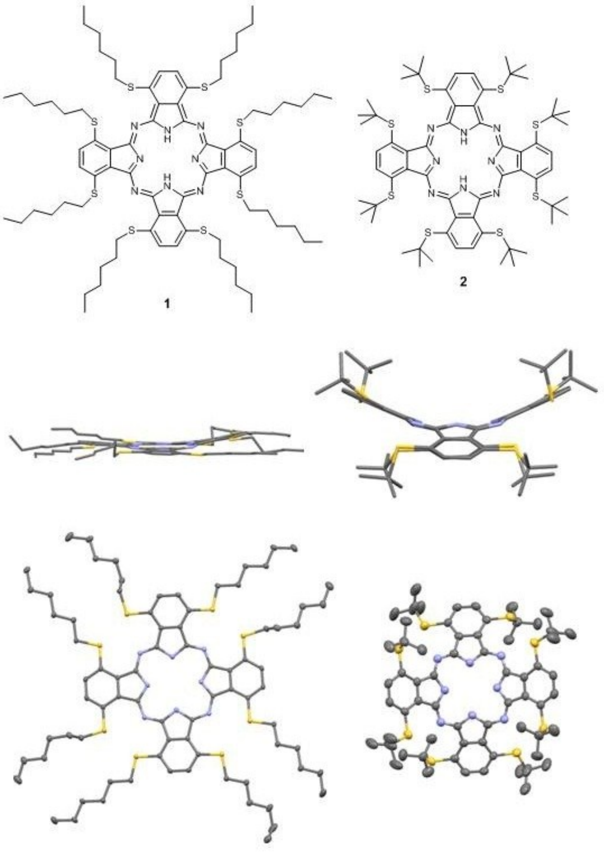

Fig. 1 a) Molecular structure, b) side view, c) face-on view (displacement ellipsoids drawn at the 30% probability level, H atoms omitted for clarity) of **1** (left) and **2** (right). See the atom numbering scheme on Fig. S1

1 crystallizes in centrosymmetric triclinic *P*-1 space group. The dihedral angles between the four isoindole rings and the mean plane formed by the four pyrrole nitrogens that goes through N_4(isoindole) atoms (N8, N12, N16 and N20) are 3.41°, 5.59°, 4.72°, 9.64°, respectively. The ring planarity is similar to that of previously published nonperipherally octasubstituted phthalocyanines (Table S2, entries 2,[9] 4,[10] 5[11] and 7[12]). **2** crystallizes in the non-centrosymmetric cubic space group *P*-43n.

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The great steric hindrance of bulky *tert*-butylthiol groups leads to an extremely distorted conformation (Fig. 1). The asymmetric unit consists of 1/4 of the phthalocyanine molecule. One of the butylsulfanyl groups is nearly situated in the same plane as the isoindole ring system with an angle of 11.29° between the mean plane of the isoindole and the plane that goes through atoms C5, S6, and C7. The second butylsulfanyl group is nearly perpendicular to the isoindole with an angle of 79.71° between the plane formed by C2, S1, and C17 and isoindole ring. The crystallographically equal isoindole rings make angles at 24.08° with the mean plane generated by the four pyrrole nitrogens. The dihedral angle between the pair of the planes generated by the isoindole unites on either side of the phthalocyanine is 48.15° (Fig. S2). Similar phthalocyanine ring distortions were observed in related 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines[13-16] (Table S2).

The electronic absorption spectra of both phthalocyanines in THF at same concentration (Fig 2) evidenced a significant shift between the two compounds, which have very different colours: greyish violet for **1** and green for **2**. Given the same alkylsulfanyl nature of the substituents for both compounds, the distortion of the macrocycle due to the bulkiness of the *tert*-butyl moieties seems to be the reason of this 55 nm blue shift for **2**. As the relative spatial disposition of the substituents may not be the same in solution and on their crystalline form, UV-vis solid state spectra of each molecule has been recorded (Fig. S8, top). If the spectra were not fully unequivocal, probably due to the proximity of the molecules having an aggregation-like effect, colour of the powder of phthalocyanine **1** and **2** spread out on a white sheet of paper is similar to those of the solutions colour (Fig. S8, bottom). These observations are in contradiction with reported statements asserting the red-shifting effect of phthalocyanine ring distortion.[17] Anyway, there is only a limited number of reports of phthalocyanine structures (all summarized in Table S2) along with their UV-vis data, and no systematic interpretation of the effect of the distortion of the macrocycle could be extracted from these data, as no “all being equal” data are available: either the substituent grafting atom is different, or the nature of the substituents (alkyl *vs* aromatic). It was therefore decided to corroborate our experimental UV-vis observations with DFT calculations. Geometries of **1** and **2** were optimized at various levels, all of which predicted an unexpected distortion in the core of **2**, while **1** adopted an essentially planar geometry (see Table S3). We presumed this large degree of distortion as (i) the most significant difference of **2** compared to **1** and (ii) the source of the 55 nm blue-shift in λ_{max} abs of **2**. Therefore frontier orbitals of **1** and **2** were analyzed. As seen from MO plots and energies depicted in Fig. 3, both HOMOs and LUMOs for both species show similar spatial distribution and LUMOs are energetically very close lying. On the other hand, there is a small but significant difference in energies of HOMOs. This difference results in a 50 nm blue shift in the absorption wavelength of **2** which is in excellent agreement with the spectroscopic data of 55 nm.

In addition to a quantitative match between experiment and theory, a sound explanation of the underlying electronic structure principles that may help rational designing of related systems is also obtained. Previous experience in accessing long wave-length absorbing dyes suggest that the frontier orbitals are fine-tuned by imposing π-electrons to the π-framework of the dye.[18] This rationale operates by shifting the HOMO to higher energies while the LUMO is usually left unchanged due to being empty. Hence the HOMO - LUMO gap is decreased and λ_{abs} is red-shifted. Applying this view to the pyrrolic rings of the phthalocyanine core and treating the benzylic rings as fused π-electron injection agents, the degree of planarity of the phthalocyanine core impacts the efficiency of π-injection which in turn dictates the rise in HOMO level. The more planar phthalocyanine core of **1** possesses an effectively conjugated π-framework whereas π-electrons in **2** are localized on highly perturbed constituents of the phthalocyanine core.

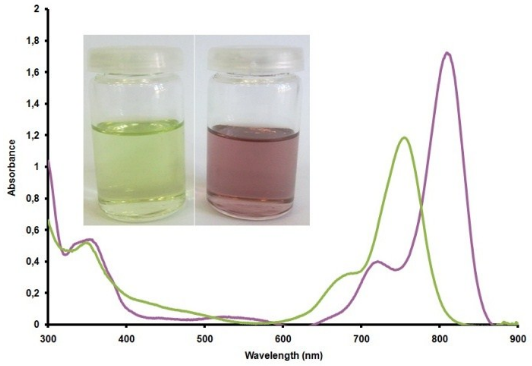

Fig. 2 UV-vis spectra of **1** (violet) and **2** (green) in THF (10 µM)

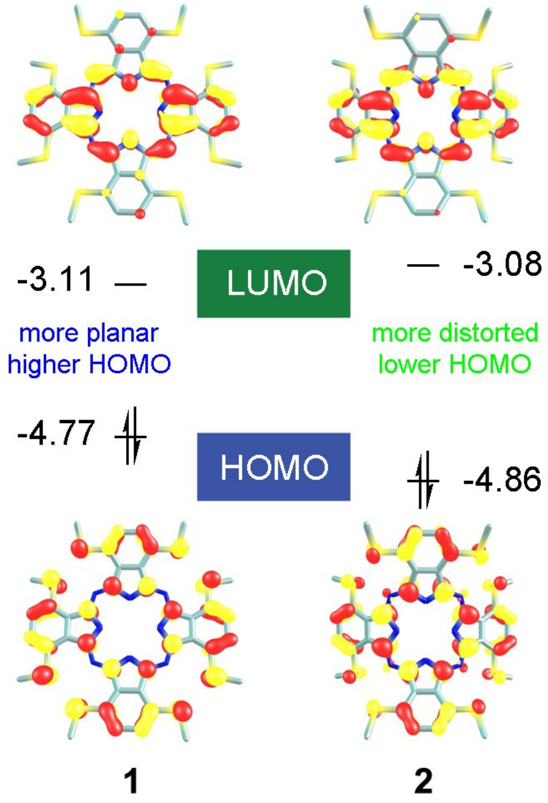

Fig. 3 Frontier orbital energies (eV) and plots (isosurface at 0.03) of **1** and **2** at (U)B3LYP/cc-pVTZ, SCRF (Solvent = THF) level of theory. Alkyl chains and hydrogens are excluded for clarity.

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Our quantum chemical calculations suggest that HOMO of distorted **2** does not experience an appreciable amount of π-electron injection, whereas the planarity of **1** allows an efficient π-system extension. Conformations of the Salkyl groups also modulate the inductively transferred charge density to the phthalocyanine core as evidenced by computed charges (Table S4). Although the source of the spectroscopic difference is dictated by structural means, the resultant electronic effect is neatly seen on frontier orbital levels where an $S_0 \rightarrow S_1$ excitation that is mainly of the HOMO → LUMO type is computed to be 50 nm blue shifted for **2** (measured 55 nm).

Having a look at the packing of the phthalocyanines, one can see that the hexylsulfanyl chains of **1** are nearly planar to the plane of macrocycle, thereby allowing the formation of abundant face-to-face π-π stacking (shortest centroid-to centroid distance of 3.570 Å) interactions, which help to consolidate the packing lattice, with no solvent-accessible void in the crystal structure. The shortest distance between planes of phthalocyanine molecules within the crystal structure is 3.440 Å (Fig. S1), whereas in the case of **2**, the shortest distance between planes of phthalocyanine molecules was 11.311 Å. Interestingly, **2** has 3-D channel voids encapsulated by phthalocyanines with different pore size (approx. 1.12 and 1.14 nm) in its crystal structure (Fig. 4a and 4b), with solvent-accessible void being 22.2 % (2565.1 Å^3) of the unit cell volume (11576.5 Å^3) obtaining using the PLATON "CALC SOLV".[19] It should be noted that free guest molecules using X-ray single-crystal data could not be modelled. Recently, McKeown and co-workers reported the nanoporous structures of phthalocyanine-based nanoporous crystals with important voids, but generated by co-crystallization with introduction of axial coordinating ligands.[20]

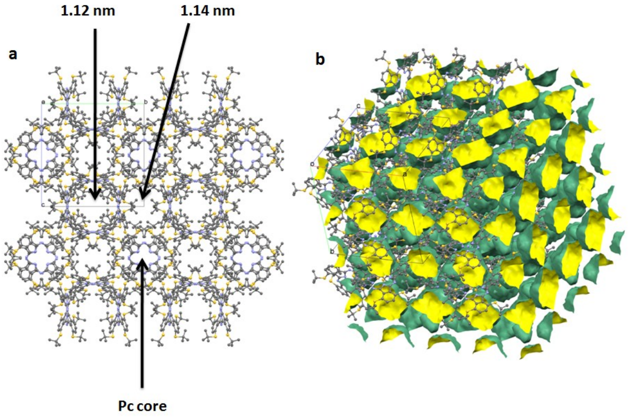

Fig. 4 a) Channels with different size and b) Perspective view of the 3-D channel voids encapsulated by phthalocyanine units in the unite cell.

To conclude, these two molecules are the first example of a comparison between a planar and a distorted phthalocyanine derivative with the same substitution pattern, as both compounds carry alkylsulfanyl substituents. This allows to attribute the observed shift in UV-vis absorption to the macrocycle distortion. More derivatives with substituents of other sizes and bulkiness are being synthesized. We plan as well to investigate the effect of metalation of the phthalocyanine core. Besides, the distorted *tert*-butylsulfanyl substituted derivative **2** crystallized in a very rare porous configuration with a remarkable solvent-accessible void, likely to be of extreme interest for materials applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterizations, crystallographic data collection and refinement details, computational details, coordinates of all calculated structures, and energy components checkcif files CCDC 894420 (for **1**) and CCDC 894419 (for **2**) and contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See DOI: 10.1039/b000000x/

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