Solution-processed, highly-oriented supramolecular architectures of functionalized porphyrins with extended electronic states†

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Thin films of aligned supramolecular architectures built from newly synthesized thiophene-substituted porphyrins have been processed from solution on surfaces.

Solution-processible, well-aligned nanostructures with special electronic functions are highly desired for future high-performance electronics, where fast charge separation and transport are required.[1,2]

Metal-complexed porphyrins are among the best systems for such electronic devices, since they allow fast charge transfer processes, as employed in nature[3a] and technological applications like catalysts,[3b] gas sensors[3c] and photovoltaic cells.[3d] Their disk-like (discotic) character with π-orbitals extending out of the plane of the molecules enables intrinsically good stacking. While porphyrin stacks might provide efficient charge separation and fast transport of charges away from dissociation sites, specific opto-electronic functions can be added by attaching selectively chosen side groups. For example, varying the length of oligo-thiophene chains, or a combination of thiophene and other functional units, does allow tuning of the wavelength of light absorbed.

For this study, we prepared a new porphyrin, 5,10,15,20-tetrakis(5-bromothien-2-yl)porphyrin ($H_2$5BrTTP, **1**), and its zinc complex (Zn5BrTTP, **2**)†. The non-brominated analogue of **1** has been synthesized before, in low to moderate yields,[4] and was for us difficult to purify and process, due to its low solubility. Much to our surprise, however, we found that compounds **1** and **2**, with bromines at all peripheral α-positions of the thiophenes, are well soluble in common organic solvents. This special feature, which we cannot yet rationalize (bromination of organic compounds usually lowers the solubility), greatly facilitates the processing of these materials. In addition, it adds liquid crystalline properties to the film-forming mesogens. These thienyl bromides should also be well suited for further functionalizations via, for instance, Suzuki or Stille coupling methods, to give more extended systems.

In this communication, we report on solution-processed, few-nanometers thick films of compound **2**, as studied by angle-resolved photoelectron spectroscopy (ARUPS) and quantum-chemical calculations. For the preparation of thin films, molecules were dissolved in *p*-xylene, in concentrations of about 0.01–0.1 mg mL^{-1}. Varying the concentrations allows the

processing of films of various thicknesses, between nominally about 3 and 15 nm, as determined from the suppression of substrate core level photoelectron lines.[2] The solutions were then deposited onto freshly cleaved MoS_2 [0001] substrates (JEOL, B. V. Belgium) held at temperatures of 40–50 °C.
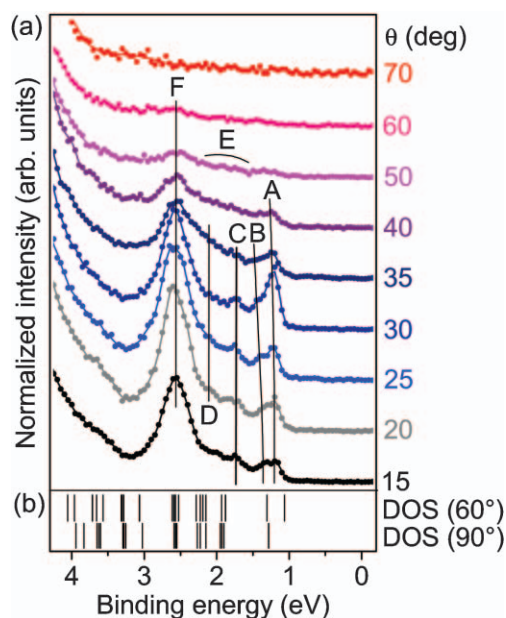
ARUPS valence-band spectra (photon energy hv = 60 eV, resolution *ca.* 25 meV) have been recorded with the Scienta SES-200 spectrometer at the beamline I411 at the synchrotron radiation research facility MAX-Lab in Lund, Sweden‡.[2a] Spectra are plotted with respect to the Fermi level of the spectrometer, and as a function of the angle between the substrate normal and the photoelectron emission direction θ. The morphology of the films was studied in air by tapping-mode scanning force microscopy (TF-SFM) in a Nanoscope IIIa system (Digital Instruments, Santa Barbara, CA), under conditions used for other thin films of discotic materials.[2a] Geometry optimization and electronic structure calculations were performed with the Gaussian 98 program using B3LYP DFT and a D95V basis set.[5] The Stuttgart/Dresden effective core potential (ECP)[5] is used to model the inner core electrons of the Zn and Br atoms§.

Fig. 1b shows a TM-SFM image of a nominally about 10 nm thick, as-prepared **2** film. The film is flat within 1–2 nm but exhibits small grains on the top of the film that are slightly higher. Since the nominal thickness is higher than the depth of surface structures, it is concluded that the surface is completely covered. Morphological and structural transitions are not observed by TM-SFM and photoelectron spectroscopy when heating the films up to 200 °C in ultrahigh vacuum. This is different from thin film systems of polycyclic, "graphene-like"[2a] or nitrogen-rich[2b] mesogens.
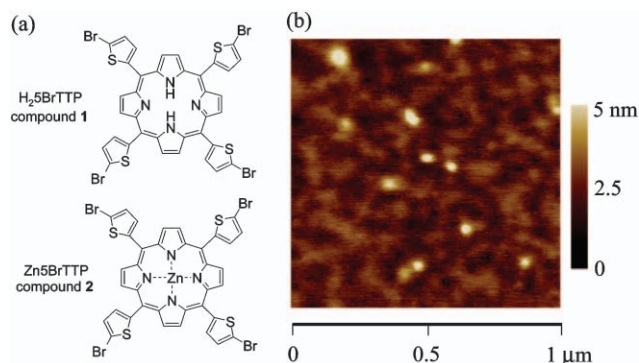

Fig. 1 (a) The chemical structure of thiophene-substituted porphyrins. (b) Topographical TM-SFM image of an as-prepared **2** film.

Fig. 2 (a) ARUPS spectra of as-prepared **2** films, as a function of the photoelectron emission angle θ. (b) Density of states for a free molecule (DOS 90°), and for twist angles between the thiophene groups and the porphyrin aromatic core of 60° (DOS 60°).

The ARUPS spectra (Fig. 2a), measured with the films held at about 25 °C, display a pronounced dependence on θ that indicates a high degree of order in such films. Cone-like photoelectron emission around the molecular axis is typical for π-electronic states of discotic molecules,[2,6] and indicates a flat orientation of the individual porphyrin rings face-to-face to the substrate surface. Relatively sharp individual features at 1.20 eV (at $\theta = 15°$, labelled A, highest occupied molecular orbital HOMO, ionization potential IP = 5.7 eV)¶, 1.35 eV (labelled B, HOMO-1), 1.75 eV (labelled C) and 2.0 eV (labelled D) are related to the highest occupied π-electronic orbitals. As revealed by the calculations,† feature E at energies between *ca.* 1.8 to 2.5 eV is dominated by π states with large contributions at the thiophene units—the HOMO-11 to HOMO-14. Feature F at about 2.55 eV contains a number of states, all of π character as well.
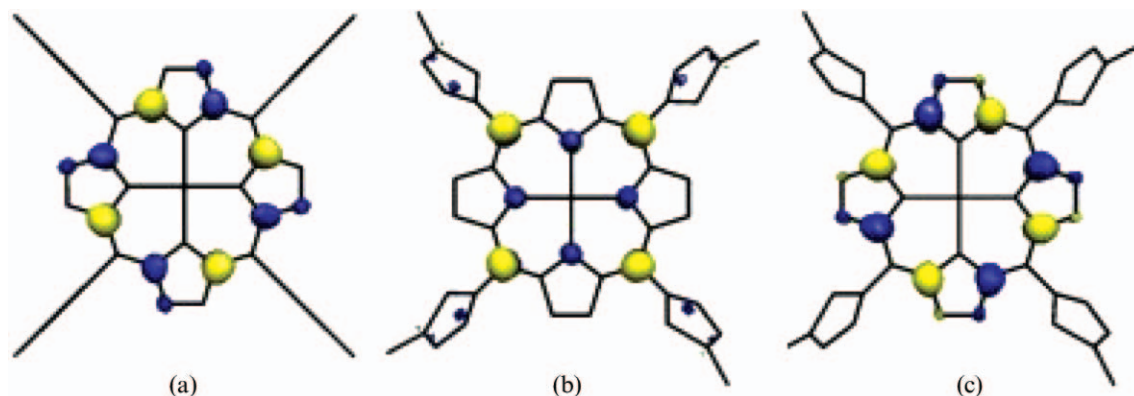
Features A and B are separated by only *ca.* 150 meV. Interestingly, at angles close to 30°, enhanced intensity is found for A but not for B. This strong dependence of the photoelectron cross-section on θ indicates a different character of two highest occupied orbitals.

In the free molecule, the thiophene groups are oriented perpendicular to the porphyrin ring. In this geometry, denoted DOS 90°, the HOMO and HOMO-1 are almost degenerate (Fig. 2b) and exclusively localized at the porphyrin unit (Fig. 3a). The HOMO-2 to HOMO-5 are, on the other hand, only at the thiophene groups.† The HOMO-6 is the first orbital with contributions at the Zn site. A different character of the two highest occupied orbitals, and a lifting of the degeneracy of the two highest occupied levels (Fig. 2b, DOS 60°) is introduced if the thiophene groups are partially planarised, allowing a coupling of the electronic systems of the thiophene units to that of the porphyrin ring. In such a case, like for instance at a twist angle of 60°, the HOMO is extended all over the molecule, including the thiophene group (Fig. 3b), while the HOMO-1 is almost exclusively localized at the porphyrin ring (Fig. 3c). Regarding the stacking mechanism, it can be concluded that intermolecular interactions are strong enough to tilt the functional groups as compared to the free molecule.

A dispersion of features A and B with θ indicating the formation of intermolecular bands[2] with a width of at least 100 meV for A and 150 meV for B in the direction out of the surface plane. For discotic materials, a high intermolecular π–π overlap is only realized for a face-to-face arrangement of the aromatic molecular cores of neighbouring molecules.[2a,7] Therefore, it can be concluded that such extended electronic states are formed along stacks[2] standing on the substrate surface. With an alignment of stacks as optimal for solar cell applications,[1c] these new mesogens emerge as promising candidates for a solution-processed fast electronics.

Fig. 3 Molecular wavefunctions of **2** for different twist angles between the thiophene groups and the porphyrin aromatic core: (a) HOMO at 90°; (b) HOMO at 60°; and (c) HOMO-1 at 60°.

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Notes and references

‡ The time of exposure to X-rays was minimized in order to avoid damages in the film. Within each series measured at one spot no change of spectral features was observed.

§ The eigenvalues were multiplied by a factor of 0.8, in order to account for correlation effects, and shifted rigidly towards lower binding energy. In the calculations for twist angle of 60°, beside twisting the thiophene groups, the molecular geometry was kept fixed in the structure of the free molecule.

¶ IP is obtained by adding the workfunction ϕ = 4.7 eV, measured on similarly prepared films in a home-built spectrometer, to the energy of the onset of the spectral weight.

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