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Aromatic fused heterocyclic [22] macrocycles with NIR absorption[†]

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Cite this: Chem. Commun., 2014, 50, 9094

Received 14th April 2014, Accepted 20th May 2014

DOI: 10.1039/c4cc02749c

www.rsc.org/chemcomm

Three related aromatic [22] heteroporphyrins have been synthesized and characterized, with the target of achieving NIR absorption. The propensity of these smallest π -conjugated macrocycles to absorb in the NIR region is benefitted from the fusion/annelation of the precursor heterocycles.

Recent years have witnessed an upsurge of interest in the development of multifunctional materials, giving rise to a variety of emerging applications. Organic compounds with chromophores having absorptions and emissions in the red or near-infrared (NIR) region are promising materials for a broad range of applications such as photodynamic therapy dyes,¹ microscopic imaging agents,² semiconductors in NIR light emitting diodes,³ dyes for NIR cut-filters⁴ and photo-sensitizers in NIR-utilizing solar cells.⁵ Most organic chromophores with NIR absorption/emission properties fit into one of the four categories: cyanines,⁶ phthalocyanines/porphyrins,⁷ squaraines⁸ or BODIPYs.⁹

Expanded porphyrins, *via* their remarkable new properties and multifunctional nature such as Möbius aromaticity, chirality, luminescence, two-photon absorption properties, multimodal coordination abilities and redox properties, offer prospects for many new applications in extremely diverse fields.¹⁰ These are structurally more sophisticated entities for achieving NIR absorption.^{10e,f} But, unfortunately, the chemistry of expanded porphyrins remains in its adolescence. Core annelation of macrocycles has been heralded as an important step in the drastic alteration of the UV-vis absorption in expanded porphyrins.¹¹ It is with this realization that, in this communication, we are interested in devising smaller congeners of

expanded porphyrins with physical properties comparable to higher analogues of expanded porphyrins. We have employed precursors, mainly pyrrole, phenanthrene and acenaphthylene annelated pyrrole,¹² and thieno[3,2-*b*]thiophene 1,¹³ to arrive at judiciously designed macrocycles with NIR absorption. Here, it is worth mentioning that these macrocycles are apparently the first [22] aromatic core modified expanded porphyrins with all the heterocycles fused/annelated to be reported in the literature.¹⁴

The methodology adopted here involves acid catalyzed Lindsey type condensation¹⁵ of thienothiophene diol **2** with pyrrole or annelated pyrrole 3/4 followed by oxidative ring closure to arrive at macrocycles **5**, **6** and **7**. Interestingly, no conceivable by-products were obtained under these reaction conditions. Column chromatographic separation over basic alumina followed by repeated silica gel (200–400 mesh) chromatographic separation yielded the macrocycles in 5%, 8% and 10% yields, respectively, as green lustrous solids.



The new macrocycles have been unequivocally characterized by MALDI-TOF, UV-vis, ¹H-NMR and single crystal X-ray crystallography. Macrocycles 5, 6 and 7 show parent ion peaks at m/z816.101, 1117.278 and 1065.321, respectively, under positive ionization conditions in HR MALDI-TOF mass spectrometry, thus confirming their compositions. The comparative UV-vis-NIR spectra for the free base forms of 5, 6 and 7 are shown in Fig. 1. The increased delocalization pathway upon annelation on pyrrolic β -carbons is evident from the marked red shift of about 56-57 nm of the Soret band and slight red shift of the Q-bands compared to macrocycle 5. For example, the electronic absorption spectrum of 5 shows an intense Soret band at 503 nm with a shoulder at 530 nm, followed by three distinct Q-bands at 725 nm, 868 nm and 957 nm. On the other hand, macrocycle 6 exhibits a Soret band at 559 nm with three distinct Q-bands at 656 nm, 719 nm and 973 nm, whereas 7 exhibits a Soret band at 560 nm along with four Q-bands at 659 nm, 725 nm,

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[†] Electronic supplementary information (ESI) available: Experimental details, spectroscopic characterization, electrochemical studies, theoretical studies. CCDC 990113 contains supplementary crystallographic data for macrocycle **6**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc02749c



Fig. 1 UV-vis absorption spectra of free bases 5, 6 and 7 in CH₂Cl₂.

840 nm and 942 nm, which is an indication of polypyrrolic/ heterocyclic aromatic macrocycles. Protonation of these macrocycles leads to the red shift of all bands, along with significantly greater molar extinction coefficients due to increased conjugation. Upon protonation, 6 exhibits a Soret band at 584 nm with Q-bands at 713 nm, 806 nm and 963 nm, whereas 7 exhibits a Soret band at 587 nm with Q-bands at 850 nm and 930 nm (see ESI⁺). This phenomenon can be explained by invoking the tilting of pyrrole rings slightly from the mean plane of the macrocycle, leading to the release of the repulsive interaction between ortho hydrogens of the tolyl rings and CHs of the adjacent phenanthrene moiety, increasing symmetry and leading to π conjugation. Contrary to these observations, upon protonation macrocycle 5 experiences only 6 nm red shift, with a Soret band at 509 nm and shoulder at 540 nm and only one very intense Q-band at 867 nm. This highly unusual nature may be due to the fact that, upon complete protonation, macrocycle 5 adopts a saddle like conformation owing to internal strain.¹⁶ For 5, 6 and 7, the absorption spectra changed gradually but distinctly on varying the temperature, in accordance with the fact that conformational flexibility and complexity is more apparent for expanded porphyrins. The Soret-like band experiences minor red shift with increasing intensity and the Q-bands are also slightly more intense upon lowering the temperature, whereas increasing the temperature has a reverse effect on the UV-vis spectral pattern. These spectral changes indicate that lowering the temperature caused an increase in aromatic character. Titration of all the macrocycles against TFA has been performed to isolate monoprotonated and diprotonated states (see ESI[†]).

Proton NMR spectroscopic analysis for all the macrocycles revealed a diatropic ring current effect ascribable to aromaticity in these macrocycles. These macrocycles were found to be conformationally flexible, despite the steric congestion at the β -positions of the heterocycles. Thus, room temperature NMR was found to give unresolved spectra and lowering the temperature upon complete protonation had a significant effect on the spectral resolution, making the assignment possible. The restriction imposed on the rapid rotation of the thienothiophene and *meso*-tolyl groups upon complete protonation at low temperature produced reasonably resolved spectra (see ESI†). For example, in the case of protonated **6** at 233 K, there are two different sets of signals in the regions 9.58–9.62 ppm, 8.02–8.57 ppm and 7.49–7.51 ppm, which have been assigned to *meso*-tolyl CH protons based on the ¹H–¹H correlation



(COSY) spectrum. These observations clearly substantiated the magnetically non-equivalent nature of the tolyl groups. Such a magnetic non-equivalent nature of the tolvl CH protons could be expected only if one of the meso-tolyl groups is adjacent to C of thienothiophene on one side and C of phenanthrene on the other side, which will force this particular tolyl group to be under the influence of the macrocyclic ring current to a greater extent, compared to the tolyl group which is adjacent to S of thienothiophene on one side and C of phenanthrene on the other side, making the latter tolyl group's CH protons resonate slightly downfield, due to the fact that the macrocyclic ring current effect on this tolyl substituent will be poor. For 6 (Fig. 2), the tolyl CH protons labelled N, L resonate as two sets of doublets in the range 9.58-9.62 ppm, those labelled O, M resonate as another two sets of doublets in the range 8.02-8.57 ppm and the tolyl CH protons labelled C, F and D, E resonate as two closely placed doublets at 7.48-7.53 ppm. The phenanthrene CH protons G, G' resonate as a multiplet in the region 7.43-7.48 ppm, H, H' resonate as a doublet at 8.63 ppm, I, I' resonate as a multiplet in the region 7.76-7.78 ppm and P, P' resonate as a doublet at 8.89 ppm. All these assignments are confirmed by ¹H-¹H COSY spectroscopy (see ESI[†]). We attribute the presence of a singlet at 8.57 ppm to the outer β -CH proton of thienothiophene, and the singlet near the TMS peak at 0.72 ppm to the inner β -CH proton of thienothiophene. The NH signal appears as a broad peak at -1.45 ppm, which has been confirmed by D_2O exchange experiment. The fact that all the protons present in the cavity of the macrocycle resonate in the upfield region, while signals for the peripheral protons are strongly deshielded, clearly indicates the strong diatropic ring current of the macrocycle. The aromatic nature of the macrocycles was further confirmed from the $\Delta\delta$ (the difference in the chemical shifts of the inner (NH/CH) and outer ring protons in the ¹H NMR spectrum) values of 11.377 ppm for 5, 11.165 ppm for 6 and 11.380 ppm for 7, which is a measure of the size of the ring current.¹⁷ As a quantitative probe of aromaticity, we have calculated the Nucleus-Independent Chemical Shift (NICS)18 values using quantum mechanical DFT calculations at the B3LYP/ 6-31G* level¹⁹ using the Gauge Independent Atomic Orbital (GIAO) method. The large negative NICS (0) values of -13.811 ppm for 5, -13.131 ppm for 6 and -13.730 ppm for 7 indicate a greater degree of aromaticity, reflecting the enhanced ring current effect of the planar geometry (see ESI[†]). The shapes of the plots of chemical shifts as functions of the distance of the NICS probe (Bq) from the molecular plane gave a clear indication of the occurrence of the diamagnetic ring current (see ESI⁺). Based on both X-ray crystal structure and theoretically optimized structure, we have estimated the Harmonic Oscillator Model of Aromaticity (HOMA) and bond

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length alternation (BLA) values.²⁰ The HOMA values of 0.772 Å from the X-ray crystal structure and 0.824 Å from the theoretically optimized geometry for **6** are well within the range of aromatic porphyrins. Maximum bond length alternations of 0.084 Å from the X-ray crystal structure and 0.086 Å from the theoretically optimized geometry also support the aromatic character of the macrocycle **6** (see ESI†).

Redox properties of the new macrocycles have been studied with the help of cyclic voltammetry and differential pulse voltammetry. **6** exhibits one irreversible and two reversible reduction peaks at -0.65 V, -1.15 V and -1.37 V with the HOMO-LUMO gap estimated as 1.17 V. For 7, a HOMO-LUMO gap of 1.18 V was observed (see ESI†), which is comparatively much smaller than those of *meso*-tetraphenyl porphyrin (2.26 V)²¹ and [26] tetrathia rubyrin (1.64 V).^{14a} Such a phenomenon may be due to the fusion of heterocycles into the core of the macrocycle, leading to HOMO-LUMO rearrangement, which is an offshoot of such core modifications that lead to a decrease in the $\Delta_{\rm redox}$ value. For macrocycle 5, a cyclic voltammogram has not been recorded due to very low solubility in any organic solvent.

Further support for the proposition that the macrocycles are aromatic came from solid state X-ray crystallographic analysis. A single crystal of 6 suitable for X-ray analysis was obtained by slow evaporation of a THF solution of the macrocycle. The steric demand of the phenanthrene moiety causes the ring skeleton of the macrocycle to deviate from planarity, albeit slightly. The observed conformation (Fig. 3) is due to the intrinsic structural constraints that arise from the requirement to form a cyclic structure and the steric bulk of the fused heterocycles. To minimize the steric interaction, thienothiophene, annelated pyrrole rings and the p-tolyl rings undergo deviation from the mean plane of the macrocycle defined by the four meso-carbons. The dihedral angles between the p-tolyl ring planes and the macrocycle plane are 49.319(22)° and 65.749(19)°. Similarly the dihedral angle between the fused thiophene ring plane and the macrocycle plane is 29.182(22)° (see ESI†). π -electron delocalization in the macrocyclic core is apparent from the observed bond lengths: 1.356(5) Å for the N-C_{α} bond and 1.418(6) Å for the C_{α} - C_{meso} bonds. The aromatic nature of 6 is evident from the fact that the C_{α} - C_{β} distances are greater than the C_{β} - C_{β} distances [1.432(6) Å vs. 1.394(5) Å for thiophene ring and 1.482(5) Å vs. 1.385(6) Å for pyrrole rings]. In short, these structural features are consistent with a 22 π -electron aromatic ring current extended over the nitrogen atoms, α -thiophene carbon atoms, α -pyrrolic carbon atoms, β -thiophene carbon atoms and the meso carbon atoms of the macrocycle.

In summary, simple molecular engineering and ingenious synthetic methodology have been synergistically coupled to develop



Fig. 3 X-ray crystal structures of 6; top view (left) and side view (right).

such NIR absorption in the smallest expanded porphyrin, which paves the way towards efficient devices. The design and synthesis of fused heteroannulenes that has become a competitive and mature selectivity offering intriguing aromaticity with NIR absorption that will be exploited in depth with much more to come from the author's laboratory very soon, since the authors feel that this area of research is still in its infancy and there is much room for further development.

The work at IACS was supported by DST-SERB (SR/S1/IC-37/ 2012), New Delhi, India, CSIR (02/(0120)/13/EMR-II), New Delhi, India and DST-SERB Ramanujan Fellowship (SR/S2/RJN-93/2011). AM thanks CSIR, New Delhi for junior research fellowship, TG thanks IACS for a junior research fellowship. We thank Prof. R. Murugavel for use of his single crystal X-ray diffraction facility established through DAE-SRC outstanding investigator award.

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