

Meso–meso linked core modified 22π smaragdyrins with unusual absorption properties†

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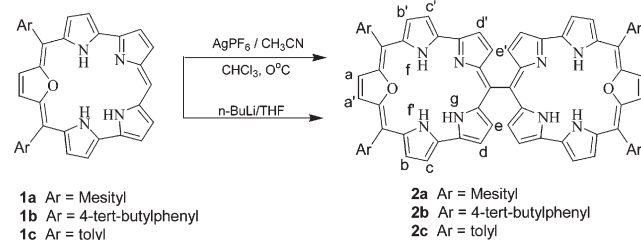
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The synthesis of the first meso–meso linked core modified smaragdyrins with unusual single photon properties is reported.

The electronic interactions between the conjugated π -electrons of large organic molecules are of current interest because of their potential applications in opto-electronic devices, sensors and as NLO materials.¹ Covalently linked multiporphyrinic arrays have attracted the attention of chemists for understanding electron and energy transfer^{2a} and as functional materials.^{2b} Meso–meso linked porphyrin arrays³ possess a unique position in that they are directly linked, favourable for rapid energy and electron transfer, and show enhanced nonlinear optical effects.⁴ Recently, linear porphyrin arrays which have large π -conjugated electrons have been shown to form molecular wires with strong electronic interactions due to an increased delocalization pathway;⁵ such interactions result in reduction in the HOMO–LUMO gap leading to tuning of the optical properties. Even though molecular arrays based on porphyrin systems are known in the literature, to the best of our knowledge there are no reports on meso–meso linked expanded porphyrins. In this communication we wish to report the synthesis of meso–meso linked core modified 22π smaragdyrins and their unique absorption properties.

The smaragdyrin dimers (**2a–2c**) were synthesized in moderate yields by treating the meso free smaragdyrin monomers (**1a–1c**) either with AgPF_6 or with $n\text{-BuLi}$ (Scheme 1)^{3b,3c} (see supporting information for synthesis). The isolated yields in both the methodologies depend on the nature of the meso substituents. The AgPF_6 method gave yields in the range of 3.7–19.3% while in the $n\text{-BuLi}$ method the yield was from 10–30%. The dimers were fully characterized by ^1H NMR and FAB mass spectrometry. The



Scheme 1 Synthesis of smaragdyrin dimers.

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formation of dimer **2b** was confirmed by the observation of an $[\text{M}^+]$ peak at m/z 1254 in the FAB mass spectra. The evidence for the meso–meso coupling came from the ^1H NMR (Fig. 1) characterization. The disappearance of the meso hydrogen signal at 9.8 ppm of the monomer readily confirms the formation of dimer connected through the meso position. Further, an upfield shift of $\Delta\delta = 0.54$ ppm is observed for the inner β -proton labelled as e, e' in Scheme 1, relative to that of smaragdyrin monomer. The signal of the remaining β proton (hydrogen atoms labelled as a–d and a'–d') appeared at nearly the same chemical shift as that of the monomer. At room temperature no NH signals were observed, while on lowering the temperature to -40 °C, the NH protons labelled as f, f' appeared at -3.14 ppm as a broad signal and the integration corresponds to four protons. The H-bonded proton labelled g could not be seen at -70 °C; a change of solvent from CDCl_3 to CD_2Cl_2 also did not give any signal. This may be due to the fast exchange of this hydrogen atom towards the azafulvene nitrogen atom. The cyclic voltammogram and differential pulse voltammogram (see supporting information) for the dimers were broad (for example, the peak width for monomer **1b** is 0.24 V and that for dimer **2b** is 0.36 V). In the dimers the two rings are oxidized in two separate one electron steps and the potentials were not very well separated. However, the first oxidation potential evaluated reveals easier first oxidation by 24 mV and the second oxidation is harder by 40 mV in the dimers relative to the monomer. These electrochemical features are supportive of perturbed π -electron conjugation in the dimer as compared to the monomer.

The absorption spectra of smaragdyrin dimer **2a** and monomer **1a** (in inset) are shown in Fig. 2. It is apparent that the direct C–C link at the meso carbon of smaragdyrin perturbs the electronic delocalization pathway of smaragdyrin dimer due to which the absorption spectrum becomes broader (FWHM 2465 cm^{-1}) and

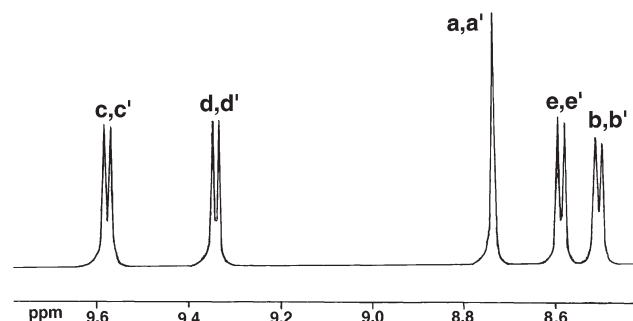


Fig. 1 ^1H NMR spectrum of **2a** at room temperature in CDCl_3 (labelling (a–e, a'–e') see Scheme 1).

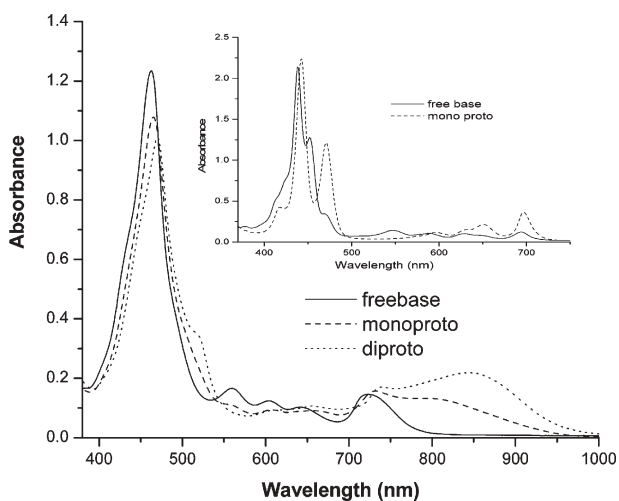


Fig. 2 UV-vis spectra of **2a** and its protonated derivatives (inset shows **1a** and its protonated derivative).

there is a red shift both in the Soret (25 nm) as well as the Q band (15 nm) as compared to the monomer. After protonation on each ring there is a steady red shift in both the Soret and the Q band; the Q band becomes much broader. The fluorescence emission spectra of smaragdyrin dimer exhibit slightly broadened emission as compared to monomer with peak maxima of 756 nm (see supporting information). The fluorescence quantum yields of monomer and dimer, determined in benzene relative to tetraphenylporphyrin, are 0.042 and 0.018 respectively.

It is well known that meso–meso linked systems exhibit a split Soret band due to excitonic coupling and as the number of porphyrin units in the meso–meso linked array increases,⁶ the splitting energy also increases. The splitting in the Soret band is explained by the point-dipole excitonic coupling theory developed by Kasha.⁷ However, to our surprise, the smaragdyrin dimer exhibits a Soret peak without any clear splitting. In order to probe this in detail we have resorted to theoretical calculation at the BLYP/6-31G* level of density functional theory (DFT)^{8,9} for geometry optimizations and the time dependent DFT method^{10,11} at the same level for the absorption spectra calculations.¹²

At first the geometry of the smaragdyrin monomer **1** is obtained (C_2 symmetry). This system is characterized by the presence of an intramolecular $N\cdots H-N$ hydrogen bond of length 1.887 Å (bond angle 133.3°), which suggests the possibility of the migration of hydrogen-bonded H to the interacting azafulvene nitrogen atom, leading to the new $N-H\cdots N$ interaction as in **1'**. A symmetric

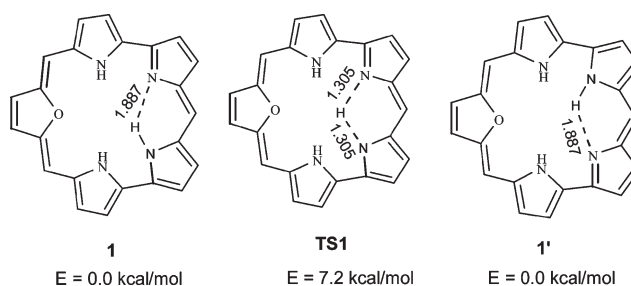


Fig. 3 Intramolecular H migration. The relative energy is also depicted.

transition state **TS1** (approximately C_{2v}) for the H migration reaction is also located (Fig. 3), and the activation energy required for **1** to **1'** conversion is found to be 7.2 kcal mol⁻¹, which is supportive of a very fast migration of the pyrrole H atom to the azafulvene nitrogen atom. Compared to the monomer **1**, the intramolecular $N\cdots H-N$ hydrogen bond is stronger in **2** (Fig. 4) as it showed a smaller H-bond distance of 1.844 Å (bond angle 133.8°), suggesting that the H-migration in this system could be faster than that in monomer **1**. The view of **2** through the X-axis (axis passing through the meso C–C bond) shows a twist angle of 71.2° between the plane of the two smaragdyrin units and a dipole moment of 1.048 D entirely in the Y-axis direction. However, compared to the dipole moment value of the dimer, monomer **1** showed a value of 2.311 D which was mainly in the X-direction as the X-, Y-, and Z-components were 2.123, 0.913, and 0.002, respectively. In the monomer, the direction of the dipole moment was from the azafulvene ring to the furan ring. It means that in the X-direction of the smaragdyrin dimer **2**, the dipole moment of the two smaragdyrin units will be in the opposite direction, leading to a net zero value for the X-component. This situation is entirely different from a normal porphyrin dimer because the X-component of the dipole moment will be enhanced in such systems.⁶ In fact, the excitonic coupling leading to a red shifted Soret peak in porphyrin arrays is usually explained in terms of the enhancement in the value of the X-component of the dipole moment. Therefore, the appearance of the single Soret peak in smaragdyrin dimer can be correlated with the presence of furan rings at the opposite ends of the X-axis direction of the molecule.

The calculated absorption spectrum of **2** showed a prominent peak at 466 nm and a small shoulder at 452 nm. The theoretical results are in good agreement with the experimental value of 460 nm obtained for the Soret band. Even a shoulder-like appearance is somewhat visible in the experimental spectrum at

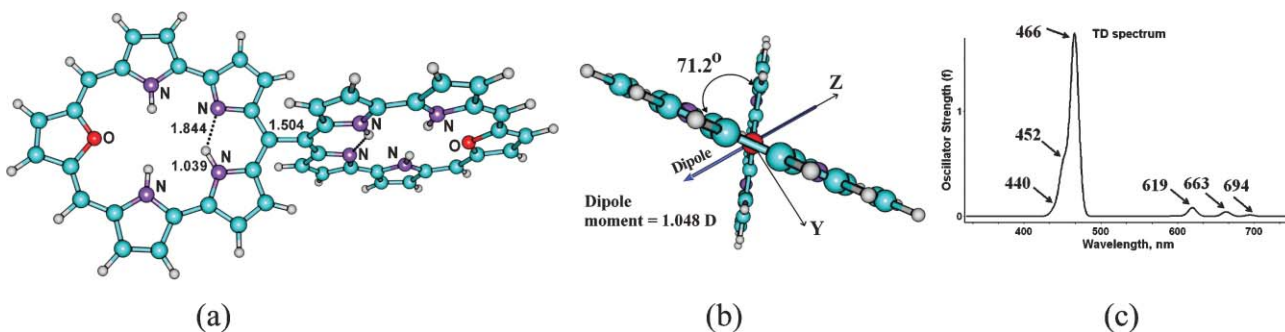


Fig. 4 (a) Optimized geometry of smaragdyrin dimer **2**. (b) View through X-axis direction. (c) Absorption spectrum calculated for **2** at the BLYP level.

around 450 nm, suggesting a small amount of excitonic coupling in the system.

The transition state model of monomer **1** (TS1) strongly suggests that the N \cdots H–N hydrogen bond interaction is responsible for a very fast oscillation of the bridging hydrogen atom between the pyrrole nitrogen and the azafulvene nitrogen in both **1** and **2** systems. It may be noted that in experiment, the NMR peak corresponding to H-bonded hydrogen atom (g) was not possible to locate even at a very low temperature of $-40\text{ }^{\circ}\text{C}$, which is also supportive of the oscillating hydrogen atom in the system. Therefore, in order to locate a structure similar to TS1, which would act as an extreme conformation for the H atom oscillation in **2**, we have optimized a structure **2'** wherein the migrating H atom is equidistant from both the pyrrole nitrogen atoms (see supporting information). The N \cdots H distance of 1.305 Å obtained for TS1 is used as the value for the N \cdots H distance in **2'**. The optimized structures of **2** and **2'** have approximately C_2 and D_2 symmetry, respectively. The higher symmetric **2'** showed a dipole moment value of zero. Moreover, a smaller twist angle of 63.6° is observed between the two smaragdyrin units in **2'** as compared to a value of 71.2° in **2**. A smaller twist angle in **2'** is expected to enhance the extended π -conjugation in the system.

The calculated absorption spectrum of **2'** showed only one prominent peak at 462 nm and a shoulder peak was not found. The peak position was in excellent agreement with the sharp Soret obtained in the experiment. The presence of only a single peak suggests the absence of excitonic coupling and this can be correlated with the zero dipole moment observed for this system. It is reasonable to assume that the meso–meso linked smaragdyrin is oscillating between two extreme conformations **2** and **2'**. Conformation **2** shows a Soret band which has negligible excitonic coupling, while **2'** has zero dipole moment and shows a sharp Soret with no excitonic coupling. In the case of singly and doubly protonated dimers, the system is expected to show more symmetry than the free base, giving rise to single Soret peak behaviour. In fact, in Fig. 2, the single Soret peak feature is more pronounced in the singly and doubly protonated systems than the free base.

In summary, this paper reports the synthesis of meso–meso linked core modified smaragdyrin systems. On the basis of theoretical calculations, a twist angle of 71 to 64° is expected between the smaragdyrin units. Therefore, enhanced π -conjugation

is possible in such systems, leading to a red shift of the absorption spectra by 25 nm compared to the monomer. All the systems are characterized by the presence of a sharp Soret with negligible excitonic coupling in their absorption spectra. Absence of excitonic coupling is explained in terms of the zero dipole moment component along the X-axis direction which is due to the presence of furan rings in the smaragdyrin units. The H atom oscillating between the two nitrogen atoms also enhances the single peak behaviour of the Soret band. A detailed investigation of the photonic properties of smaragdyrin dimers is in progress.

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