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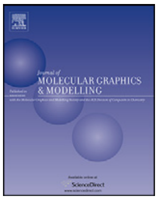

Toward panchromatic organic functional molecules: Density functional theory study on the nature of the broad UV–Vis–NIR spectra of substituted tetra(azulene)porphyrins

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ABSTRACT

To achieve full solar spectrum absorption of organic dyes for organic solar cells and organic solar antenna collectors, a series of tetra(azulene)porphyrin derivatives including H_2(TAzP), H_2(α-F_4TAzP), H_2(β-F_4TAzP), H_2(γ-F_4TAzP), H_2(δ-F_4TAzP), H_2(ε-F_4TAzP), H_2(ζ-F_4TAzP), H_2[α-$(NH_2)_4$TAzP], H_2[β-$(NH_2)_4$TAzP], H_2[γ-$(NH_2)_4$TAzP], H_2[δ-$(NH_2)_4$TAzP], H_2[ε-$(NH_2)_4$TAzP], and H_2[ζ-$(NH_2)_4$TAzP] were designed and their electronic absorption spectra were systematically studied on the basis of TDDFT calculations. The nature of the broad and intense electronic absorptions of H_2(TAzP) in the range of 500–1450 nm is clearly revealed. In addition, different types of $\pi \rightarrow \pi^*$ electronic transitions associated with different absorption bands are revealed to correspond to different electron density moving direction between peripherally-fused ten electron-π-conjugated azulene units and the central eighteen electron-π-conjugated porphyrin core. Introduction of electron-donating groups onto the periphery of H_2(TAzP) macrocycle is revealed to be able to lead to novel NIR dyes such as H_2[α-$(NH_2)_4$TAzP] and H_2[ε-$(NH_2)_4$TAzP] with regulated UV–Vis–NIR absorption bands covering the full solar spectrum in the range of 300–2500 nm. In addition, the basic designing rules for panchromatic organic functional molecules based on tetrapyrrole derivatives are proposed together with the suggestions in experiments, including low molecular symmetry and narrow gap between HOMO and LUMO/LUMO+1, which will be helpful toward the design and synthesis of new panchromatic organic functional molecules.

1. Introduction

Near infra-red (NIR) dyes have received considerable attentions in recent years due to their potential applications in solar cells [1–7], photodynamic therapy for cancer [8–11], NIR imaging [12–15], solar antenna collectors [16–18], and astronomical telescopes [19,20]. Tetrapyrrole derivatives, in particular porphyrins, phthalocyanines, and naphthalocyanines, are among the most important functional molecular materials with intense NIR absorption due to their high photo-chemical stability and intense absorption in the NIR region [21–28]. In recent years, a new skeleton of tetrapyrrole derivatives, tetra(azulene)porphyrins (TAzPs), with significantly intensified NIR absorption in the range of 900–1300 nm was synthesized [29,30]. Nevertheless, the very intense absorptions covering an astonishing broad UV, visible, and NIR range from 300 to 1400 nm revealed in their electronic absorption spectra suggest their great potentials in the fields of organic solar antenna collectors and organic solar cells [29–34].

Investigations in inorganic solar antenna collectors have made significant progress [35]. Actually multilayered inorganic solar antenna collector with absorption ability as high as nearly 90% of the full solar energy was reported [36]. In addition, solar cell fabricated from inorganic semiconductors can also reach high photo-electron transition efficiency of ~75% due to their intense absorptions over the full UV–Vis–NIR region of solar spectrum [37]. However, exploration in molecular functional materials with application in organic solar antenna collectors [38,39] and/or organic solar cells [35] appears to still be limited to those with absorptions in the UV–Vis region without extending into the NIR region. Taking account of the quite high ratio of NIR region emission over the total solar energy [26], 43%, easily synthesized and stable organic NIR dyes become highly desired towards high efficiency solar antenna collectors and solar cells [31–34].

Recently, an inorganic band-anticrossing full solar spectrum absorption material GaN_xAs_{1-x} was prepared by López and co-workers [40]. By inserting an intermediate energy band between the former valence band (VB) and conduction band (CB), the

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absorptions in the UV and visible range of the intrinsic material was extended into the NIR region due to the resulting narrow gaps [40]. In a similar manner, in the case that more extraneous orbitals are inserted into the original frontier orbitals of specific organic dyes with conjugated molecular structure, novel dyes with absorption extending into the NIR region are also expected to improve the efficiency of organic solar antenna collectors and solar cells [26].

Concerning the tetra(azulene)porphyrin (TAzP), significant interaction can be expected to exist between the central eighteen electron-π-conjugated porphyrin core and the four peripherally-fused ten electron-π-conjugated azulene units in the TAzP skeleton, leading to densely-distributed frontier orbitals and narrower gaps between these orbitals. This in turn will induce remarkably red-shifted broad Q bands into the NIR region, resulting in complicated electron absorption spectrum of tetra(azulene)porphyrins (TAzPs) relative to most general porphyrins (Pors) [41–43], tetraazaporphyrins (TAPs) [43], phthalocyanines (Pcs) [43–46], naphthalocyanines (Ncs) [47,48], and even many core-modified porphyrins [49–57]. In addition, the absorption spectra of some sandwich-type multi(tetarpyrrole) metal multiple-decker complexes can also cover such a broad NIR region [58–65]. However, their absorption intensity in this region is much weaker than TAzPs. Nevertheless, Osuka and co-workers synthesized a series of fully conjugated porphyrin tapes and porphyrin arrays also with broad and intense NIR electronic absorptions in their spectra, which significantly increases their light harvesting ability [1–3]. However, the great difficulty in their large scale of preparation precludes their wide range of applications in corresponding field. In good contrast, with a limited macrocylic tetrapyrrole molecular skeleton, the preparation of TAzPs is relatively easy in terms of large scale synthesis in comparison with either the sandwich-type multi(tetarpyrrole) metal multiple-decker complexes or the conjugated porphyrin tapes, therefore revealing their great potential as organic NIR dyes.

In the present paper, the electronic structures and electronic absorption spectra of a series of H_2(TAzP) have been theoretically investigated on the basis of density functional theory (DFT) and time dependent density functional theory (TDDFT) calculations. Introduction of electron-withdrawing or electron-donating groups onto the periphery of TAzP skeleton further tunes the HOMO–LUMO gap, inducing obvious red/blue-shift of the NIR electronic absorption bands of $H_2[\alpha\text{-}(NH_2)_4\text{TAzP}]/H_2[\varepsilon\text{-}(NH_2)_4\text{TAnP}]$ into the range of 1000–2500 nm. Moreover, in combination with the previous results [22,25–30,58–65], general rule regarding the design of panchromatic organic functional molecules is also proposed.

2. Computational summary and validity

Hybrid generalized gradient approximation (hGGA) method B3LYP [66,67] is proved suitable for the geometry optimization of porphyrins, phthalocyanines, as well as their various analogs [68–72]. As a consequence, in the present study B3LYP functional was employed for conducting the geometry optimization of the series of TAzP derivatives, Scheme 1. However, B3LYP always overestimates the transition energies for this type of large conjugated system, while generalized gradient approximation (GGA) method significantly improves the agreement between theoretical and experimental results [26,27,73–77]. As a result, GGA functional BP86 [78,79] with Becke88 exchange functional and Perdew86 correlation functional was used to simulate the photon-induced transition densities [26]. In order to further verify the reliability of our TDDFT computation results, the comparison between the calculated and experimental electronic absorption spectrum of tetra(azulene)porphyrins [H_2(TAzP)] was shown in Supporting Information.

In addition, Pople basis sets have been proved excellent for calculating the structure and properties of porphyrins and phthalocyanines as well as their analogs [80–83], leading to many applications in this field. Both DFT and TDDFT calculations were carried out using the basis set of 6-311++G(d,p). In addition, reduced density gradient (RDG) [84–86] and localized orbital locator (LOL) [85–90] were all calculated to explain corresponding properties. All the calculations are carried out using Gaussian 03 [91] and Multiwfn 2.1 [85,86]. Computational details are listed in Supporting Information.

3. Results and discussion

As shown in Scheme 1 and Table S1 (Supporting Information), direct fusion between the porphyrin (central core) and azulene (peripheral substituents) leads to tetra(azulene)porphyrins [H_2(TAzP)] with extended conjugated molecular skeleton. There are six types of substituent sites α, β, γ, δ, ε, and ζ in this porphyrin molecule. NH_2 and F are chosen as the representative electron-donating and -withdrawing groups, respectively [25,26,92–97], leading to a series of tetra(azulene)porphyrin derivatives including H_2(TAzP), $H_2(\alpha\text{-}F_4\text{TAzP})$, $H_2(\beta\text{-}F_4\text{TAzP})$, $H_2(\gamma\text{-}F_4\text{TAzP})$, $H_2(\delta\text{-}F_4\text{TAzP})$, $H_2(\varepsilon\text{-}F_4\text{TAzP})$, $H_2(\zeta\text{-}F_4\text{TAzP})$, $H_2[\alpha\text{-}(NH_2)_4\text{TAzP}]$, $H_2[\beta\text{-}(NH_2)_4\text{TAzP}]$, $H_2[\gamma\text{-}(NH_2)_4\text{TAzP}]$, $H_2[\delta\text{-}(NH_2)_4\text{TAzP}]$, $H_2[\varepsilon\text{-}(NH_2)_4\text{TAzP}]$, and $H_2[\zeta\text{-}(NH_2)_4\text{TAzP}]$.

3.1. Molecular structure and electronic structure

Fig. 1a and Table S1 (Supporting Information) show the optimized molecular structure of metal-free tetra(azulene)porphyrin [H_2(TAzP)] together with a scheme indicating that fusion between the four peripheral ten electron-π-conjugated azulene units ($\pi^{\text{Az}}_{10\text{e}}$ units) and a central eighteen electron-π-conjugated porphyrin core ($\pi^{\text{Por}}_{18\text{e}}$ core) forms the tetra(azulene)porphyrin skeleton. Fig. 1b shows the localized orbital locator (LOL) of all the π orbitals of the TAnP skeleton. In the LOL scheme, the π electron density is significantly localized between the anthracene and porphyrin units, confirming that fusing the central $\pi^{\text{Por}}_{18\text{e}}$ core with four $\pi^{\text{Az}}_{10\text{e}}$ units leads to the uniform non-coplanar conjugated system $\pi^{\text{TAzP}}_{58\text{e}}$ in the TAzP skeleton. In comparison with the azulene ten-electron conjugated system and porphyrin eighteen-electron conjugated system, this type of tetra(azulene)porphyrin with fifty-eight-electron conjugated system provides much more densely-distributed coupled frontier orbitals, which in turn results in many narrow gaps between frontier molecular orbitals [29,30]. This actually just resembles the inorganic full solar spectrum absorption material $\text{GaN}_x\text{As}_{1-x}$ reported recently as mentioned above [40]. Briefly summarizing above, bond interaction analysis for TAzP skeleton shows that fusion of the central $\pi^{\text{Por}}_{18\text{e}}$ core and four $\pi^{\text{Az}}_{10\text{e}}$ units forms the conjugated system in the TAzP skeleton and results in the densely-distributed TAnP frontier orbitals.

The non-bond interaction analysis of TAnP is shown in Fig. 2 and Fig. S1 (Supporting Information). Obviously, due to the steric hindrance of the peripheral azulene units as well as the α-H atoms, H_2(TAzP) employs a saddle structure instead of the planar one as for metal free porphyrin [H_2(Por)] and azulene (Az), therefore leading to a distorted $\pi^{\text{TAzP}}_{58\text{e}}$ system. It is worth pointing out that the balance between the repulsive force (between the α-H atoms of the peripheral azulene units) and the $\pi^{\text{TAzP}}_{58\text{e}}$ planar tendency induces the saddle H_2(TAzP) structure. As for TAzPs, the distorted TAzP skeleton is maintained since the peripheral substituents do have little influence on the molecular distorting degree, Table S1 (Supporting Information).