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Near-infrared absorption of fused core-modified expanded porphyrins for dye-sensitized solar cells ⊘

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ABSTRACT

Photophysical, photovoltaic, and charge transport properties of fused core-modified expanded porphyrins containing two pyrroles, one dithienothiophene (DTT) unit, and 1–4 thiophenes (1–4) were inspected by using density functional theory (DFT) and time-dependent DFT. Compounds 1–3 have been investigated experimentally before, but 4 is a theoretical proposal whose photophysical features match those extrapolated from 1 to 3. They exhibit absorption in the range of 700–970 nm for their Q bands and 500–645 nm for their Soret bands. The rise of thiophene rings placed in front of the DTT unit in the expanded porphyrin ring causes a bathochromic shift of the longest absorption wavelength, leading to near-infrared absorptions, which represent 49% of the solar energy. All the systems show a thermodynamically favorable process for the electron injection from the dye to TiO₂ and adsorption on a finite TiO₂ model. The electron regeneration of the dye is only thermodynamically feasible for the smallest expanded porphyrins 1 and 2 when Γ/I_3^- electrolyte is used. The charge transport study shows that for voltages lower than 0.4 V, junctions featuring pentaphyrin 1 and octaphyrin 4 are more conductive than those containing hexaphyrin 2 or heptaphyrin 3. The results showed that the four fused core-modified expanded porphyrins investigated are potential dyes for applications in dye-sensitized solar cells, mainly pentaphyrin 1 and hexaphyrin 2. Moreover, increasing the number of thiophene rings in the macrocycle proved fruitful in favoring absorption in the near-infrared region, which is highly desired for dye-sensitized solar cells.

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I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are one of the sunlight-based energy sources that continue to attract great interest with a view to reducing our dependence on fossil fuels. The functioning of a DSSC can be explained in four steps: (1) light absorption and dye excitation; (2) injection of the excited electrons of the dye into the conduction band of the semiconductor; (3) circulation of the electrons through the external circuit; (4) arrival of the electrons to the cathode and reduction of a redox system intently added to the medium, which has to regenerate the dye by donating it an electron (Scheme 1).^{1,2} Since the photosensitizing dye participates in three of these photocurrent generation steps, selecting suitable dyes is undoubtedly essential for the proper functioning of the cell.^{3–6} As minimum requirements, they must be able to absorb in the range of wavelengths of solar radiation, especially between 400 and 900 nm, which is the most intense solar radiation; they must also have virtual orbitals with energy higher than that of the conduction band of the semiconductor (at least 0.2 eV higher)^{7.8} to facilitate the injection stage. The oxidized form of the dye must have semi-occupied orbitals with energy lower than that of the redox mediator to regenerate the dye quickly.^{3–6}

Among the numerous dyes investigated for their use in DSSCs, porphyrins, which consist of four pyrrole rings interconnected at their α carbon atoms by methine bridges denoted as meso positions, continue to attract much attention due to their highly delocalized π -conjugated macrocyclic structure, easy synthetic fabrication, and strong absorption in the 400–450 nm region (Soret band) as well as moderate absorption in the 500–700 nm region (Q bands).^{9–14} Expanded porphyrins containing more than four

call the Soret band the most intense one located in the UV–Vis spectrum and Q bands the rest of the bands that appear in the Vis region.

Although there is no x-ray structural determination of heptaphyrin



SCHEME 1. Schematic view of the working principles in DSSCs: **1** light absorption and dye excitation; **2** electron injection into the semiconductor conduction band (CB); **3** electron flux through the external circuit; and **3** dye regeneration by a reducing agent of the electrolyte.

pyrrolic/heterocyclic rings also exhibit red-shifted absorption bands and are, therefore, excellent candidates for near-infrared (NIR) dyes.^{15–19} Despite this, their application in DSSCs has been little explored.^{20–24} We want to partially cover the lack of studies focused on expanded porphyrins by investigating whether increasing the number of rings in a given porphyrinoid macrocycle results in DSSC dyes with enhanced photosensitizing properties. We particularly consider expanded porphyrins with at least one dithienothiophene (DTT) unit consisting of two thiophene rings fused by a bridging sulfur atom. DTT is an electron-rich rigid moiety that has been incorporated into expanded porphyrins in an attempt to stiffen them and generate planar macrocycles, thus allowing strong π -electronic conjugation, which is essential for electronic and optoelectronic applications.^{25–31}

Several expanded porphyrins with one or two DTT units have been synthesized and characterized (see Scheme 2).^{25–31} These fused compounds differ in the number of DTT units, non-fused thiophene rings, pyrrole rings, and meso-aryl bridges. The presence of non-fused thiophene rings instead of the original pyrrole ones in porphyrinic-type macrocycles increases the electron richness of their π -conjugated system. The fused expanded porphyrins in Scheme 2 are grouped based on the planarity of the macrocycle core. Considering that each DTT contributes two rings to the macrocycle, they are named according to the total number of rings involved in the macrocycle. Therefore, we have porphyrinoids with five (pentaphyrin P1), six (hexaphyrins HX1 and HX2), seven (heptaphyrins HP1-3), eight (octaphyrins O1 and O2), and nine (nonaphyrin N1) rings. The macrocycle core of the hexaphyrins HX1 and HX2 (also known as rubyrins) and the octaphyrin O1 is almost flat and without inverted heterocycles. Their UV-Vis spectra show an intense Soret-type band ranging from 513 to 584 nm and weak-moderate Q-like bands in the region 606-1131 nm, consistent with their aromatic character as evidenced by ¹H nuclear magnetic resonance (NMR) experiments.^{25,31} By the nomenclature followed by experimentalists^{25,31} and to facilitate comparison of previous results with ours, we will henceforth

HP1, the ¹H NMR results indicate that its structure is nearly planar, with no inverted heterocycles and an aromatic nature, which coincides with the presence of well-defined UV-Vis absorption peaks, such as a split Soret band at 553 and 579 nm and a distinct Q band at 797 nm.²⁵ According to x-ray structural analysis, the remaining porphyrin derivatives (P1, HP2, HP3, O2, and N1 in Scheme 2) have been characterized as non-planar. Pentaphyrin P1, also known as sapphyrin, shows the inversion of the thiophene ring opposite to the DTT moiety, has an aromatic character, and its UV-Vis spectrum exhibits a sharp Soret band at 495 nm and four weak Q bands between 500 and 900 nm, of which the most significant one appears at 662 nm.²⁷ Heptaphyrins HP2 and HP3 present different structural and aromatic features. The DTT unit and the pyrrole ring between the two thiophenes in HP2 are inverted, whereas there is no inversion in HP3. In addition, macrocycle HP2 is antiaromatic; consequently, its UV-Vis absorption spectrum exhibits a slightly moderate Soret band at 502 nm and a weak shoulder at 597 nm. In contrast, macrocycle HP3 has a Mobius aromatic character, which is in consonance with well-defined peaks in its UV-Vis spectrum, an intense Soret band at 604 nm, and a distinct Q band at 868 nm.²⁸ The octaphyrin O2 and nonaphyrin N1 adopt a twisted figure-eight conformation with no inverted rings.^{30,31} Their UV–Vis spectra have in common the presence of broad and ill-defined peaks with three major bands (348, 528, and 680 nm for O2 and 390, 519, and 722 nm for N1), without any distinct Q bands, which is typical of their nonaromatic character evidenced by ¹H NMR. Based on the spectral data just described, compounds P1, HX1, HX2, HP1, HP3, and O1 show well-defined absorptions in the red and NIR regions, making them good candidates to be explored as dyes for DSSCs. Among them, we decided to conduct a theoretical study of four porphyrin derivatives that have in common a DTT unit flanked by two pyrrole rings and four meso-mesityl bridges but differ in the number of non-fused thiophene rings opposite to the DTT unit. The selected compounds are an isomer of pentaphyrin P1 with the non-fused thiophene ring in a normal position rather than in the inverted one, hexaphyrin HX1, heptaphyrin HP1, and a hypothetical octaphyrin with four non-fused thiophene rings pointing inward to the macrocycle core, hereafter referred to as 1, 2, 3, and 4, respectively (see Scheme 3). The choice of 1 is based on the theoretical fact that this conformer is 2.2 kcal/mol more stable than its inverted isomer P1,³² and this conformation facilitates a better comparison with 2 and 3. Analogous pentaphyrins with selenophene instead of thiophene have shown a balance between the inverted and noninverted conformers, the latter being 2.2 kcal/mol more stable than the former. The hypothetical octaphyrin 4 has been included as the logical expansion to test the trends in the photosensitizing properties that could be found when moving from 1 to 3. The addition of another thiophene ring in the macrocycle skeleton of octaphyrin 4 to yield a nonaphyrin is not expected to provoke a higher redshift or NIR shift, as greater conformational flexibility tends to generate less planar structures, which does not favor the further extension of the π -conjugated system. Therefore, for porphyrinoids 1–4, we aim to analyze their geometrical and electronic structure and their photophysical and photovoltaic properties to assess their quality as photosensitizers in DSSC. In other words, we want to understand

the effect of the extent of π -conjugation and the degree of distortion from the planarity of the macrocycle on these relevant properties. We also investigate its adsorption on a TiO₂ cluster as a model of the semiconductor and assess how the π -conjugation represented by the non-fused thiophene rings plays a role in the charge transport properties.

II. COMPUTATIONAL METHODS

molecular structures of porphyrinoids 1-4 in The Scheme 3 were fully optimized in their ground state using the hybrid density functional $B3LYP^{33-35}$ and the $6-31+G(d)^{36}$ Pople basis set in the gas phase. B3LYP was chosen for the geometry optimization based on previous results obtained for porphyrins and expanded porphyrins.^{22,37} The inclusion of diffuse (+) and polarization (d) functions was considered necessary to properly model the high number of electrons present in these structures. In the case of the porphyrinoids displaying a non-planar conformation, we also located the transition state (TS) connecting this conformer to its enantiomer. Given the large size of these macrocycles and the computational cost of finding TSs, we had to resort to the B3LYP/LANL2DZ level of theory, with LANL2DZ being a basis set describing the valence electrons with double-zeta quality functions and the core electrons with the Los Alamos effective core potential (ECP).^{38,39} Although this computational level is lower than the B3LYP/6-31+G(d) one, the comparison of the optimized geometries of the non-planar macrocycles at both levels of theory does not reflect significant discrepancies, thus confirming the reliability of the B3LYP/LANL2DZ computations. In addition, this level of theory has been successful in similar studies.⁴⁰ Intrinsic reaction coordinate (IRC) calculations with the second-order Gonzalez-Schlegel integration method^{41,42} were performed to connect each TS to the two associated enantiomers. The nature of the stable species and TSs found was confirmed using harmonic vibrational frequency calculations at the B3LYP/6-31+G(d) and B3LYP/LANL2DZ levels, respectively.

A statistical thermodynamic treatment has been performed within the ideal gas, rigid rotor, and harmonic oscillator approximations at a pressure of 1 atm and a temperature of 298.15 K^{43} to calculate the Gibbs energy for some relevant species.

B3LYP/6-31+G(d) optimized geometries were used to calculate the electronic absorption spectra with the time-dependent density functional theory (TD-DFT)^{44,45} approach in the solution phase at the M05/6-31+G(d) level of theory, with M05 being a hybrid-meta density functional having 28% Hartree-Fock exchange energy.⁴⁶ It is known that dispersion interactions must be included in the density functional used to calculate accurate TD-DFT excitations, even more so in the case of large systems such as those investigated in this work. Among others, M05 is a functional that does not contain an explicit dispersion term but has been parameterized for systems governed by dispersion interactions. Therefore, considering this and previous functional calibrations,^{47,48} we selected M05 as an adequate functional for our electronic absorption calculations. Besides, the TD-DFT computational protocol mentioned earlier has proven to be successful in similar investigations on porphyrin-based systems. The electronic excitations were calculated as singlet-singlet vertical transitions following the Franck-Condon principle. A total of ten excited states for each molecular system were required to obtain the characteristic Soret and Q bands typical of porphyrins and their derivatives. Bulk solvent effects in TD-DFT computations were simulated using the conductor-like polarizable continuum model (CPCM)^{49,50} and atomic radii obtained with the United Atom Topological Model.⁵¹ The solvent of choice is CH₂Cl₂ ($\varepsilon = 8.93$), since it was the solvent used both for the synthesis and for obtaining the electronic absorption spectra of the DTT-containing porphyrinoids, three of which are investigated in this work.^{25,27} To investigate new factors that could contribute to increase the NIR absorption, we also analyzed the constant dielectric effect on the electronic absorption spectra of porphyrinoids **1**–4 by considering the solvents chloroform ($\varepsilon = 4.71$), 2-butanol ($\varepsilon = 15.94$), and *N*,*N*-dimethylformamide ($\varepsilon = 37.22$).

All the calculations mentioned so far were performed using the Gaussian 09 package.⁵² To better understand the absorption bands, the most relevant molecular orbitals involved in the electronic transitions were analyzed at the same level of theory as that used in calculating the electronic absorption spectra.

Aromaticity analysis of the fused porphyrinoids has been performed using magnetic and geometric criteria according to previous recommendations⁵³⁻⁵⁵ at the M05/6-31+G(d) level of theory. Regarding the magnetic criterion, nucleus-independent chemical shift (NICS) indices were computed at the ring critical points (RCP),^{56,57} obtained from an electron density topology analysis in conjunction with the Gauge Independent Atomic Orbital (GIAO) method.58 Specifically, NICS values were calculated at the geometric ring center, i.e., at the RCP, and at 1 Å above the RCP (NICS_{zz}), considering only the out-of-plane component for the latter. The topological analysis of the electron density performed is based on the Atoms-in-Molecules (AIM) theory of Bader⁵⁹ ⁻⁶¹ using the AIMAll program.⁶² In addition, vectorial maps of magnetically induced current density (MICD)⁶³ have been plotted 1 a.u. above the molecular plane using the AIMAll program. Clockwise circulation indicates a diatropic (aromatic) character, and anticlockwise shows an antiaromatic (paratropic) behavior. For the geometrical criterion, the Harmonic Oscillator Model of Aromaticity (HOMA)⁶⁴ has been computed for thiophene and pyrrole rings to understand the local aromaticity of these rings by using the Multiwfn package.⁶⁵ Values close to 1.0 indicate bond equalization related to aromaticity. In contrast, values close to zero indicate non-aromatic behavior.

In the DSSCs working mechanism, high values of the efficiency of electron injection from the photo-induced excited state of the dye into the conduction band of the semiconductor and regeneration of the oxidized dye by the reduced part of the redox mediator in the electrolyte are required to obtain excellent solar-to-electrical conversion.⁹ The efficiencies for electron injection (ϕ_{inj}) and dye regeneration (ϕ_{reg}) are directly proportional to the corresponding driving forces (ΔG_{inj} and ΔG_{reg}) as $\phi_{inj} \propto f(-\Delta G_{inj})$ and $\phi_{reo} \propto f(-\Delta G_{reg})$, respectively. ΔG_{inj} can be defined as^{8,66–68}

$$\Delta G_{inj} = E_{CB} - ESOP = E_{CB} - (GSOP + E_{0-0}), \qquad (1)$$

in which E_{CB} is the energy level of the semiconductor conduction band, which has a value of -4.2 eV for the TiO₂ semiconductor considered in this study.^{69,70} ESOP and GSOP refer to the oxidation potential energy of dye in the excited state and ground state, respectively. E_{0-0} represents the electronic singlet-singlet vertical transition energy at the maximum absorption wavelength obtained from the

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core-modified expanded porphyrins containing at least one DTT unit and five (pentaphyrin P1), six (hexaphyrins HX1 and HX2), seven (heptaphyrins HP1-3), eight (octaphyrins O1 and O2), and nine (nonaphyrin N1) rings in the macrocycle core that have been previously synthesized.

SCHEME 2. Molecular structure of fused

TD-DFT computations.^{7,44,45} GSOP values were calculated according to Eq. (2) as the difference between the neutral (G^0) and oxidized (G^+) Gibbs energies of the dye in its ground state,⁷¹

$$GSOP = \left(G^0 - G^+\right)_{GS}.$$
 (2)

 ΔG_{reg} can be written as^{2,67}

$$\Delta G_{reg} = GSOP - E_{mediator},\tag{3}$$

where E_{mediator} is the redox potential of the mediator, which has a value of -4.8 eV for the electrolyte I⁻/I₃⁻.⁷²

Since efficient electron injection is directly related to an electronic coupling between the dye and the semiconductor, it is essential to simulate the adsorption of porphyrinoids 1-4 on the semiconductor. For this purpose, we used a finite model of the TiO₂ semiconductor based on the crystallographic structure of anatase (101) with a stoichiometry of H₄O₈₂Ti₄₀ that is passivated with hydrogen atoms at the edges. From this model, we selected one layer with titanium atoms with fourfold and fivefold coordination (Ti_{4C} and Ti_{5C}, respectively) and oxygen atoms with three-fold and twofold coordination (O_{3C} and O_{2C}, respectively).^{73–75} To bond the expanded porphyrin to TiO₂, one of the methyl groups of the meso-aryl was replaced by a carboxylic group. We have



SCHEME 3. Sketch structures of the fused core-modified expanded porphyrins investigated in this work.

checked that this replacement does not affect the photophysical properties of 1 (Fig. S1). Optimization of the molecular structure of the porphyrinoid-TiO₂ complexes in the gas phase was carried out with the generalized gradient approximation exchangecorrelation functional Perdew–Burke–Ernzerhof (PBE)⁷⁶ and the double- ζ -polarized (DZP) basis set, along with the PseudoDojo norm-conserving pseudopotential.⁷⁷ To avoid the deformation of the anatase structure, a constraint was added that implied the use of frozen TiO₂. These calculations were performed with the QuantumATK package.⁷⁸ Due to the large size of the interacting systems, van der Waals interactions were also computed using Grimme's D3 dispersion.⁷⁹

To probe the transport properties of each of the studied macrocycles, we prepared a series of theoretical molecular junctions featuring each complex as the active molecular elements in the scattering region, coupled through thiol anchors to two gold electrodes, represented by semi-infinite Au(111) wires. We started with the geometry optimization of each compound through DFT methodology, substituting two hydrogen terminal groups with S-Au groups, then placing the Au atoms of each optimized structure in the hollow sites of the Au(111) electrodes terminal surfaces. To determine the transport properties, such as the transmission probabilities and current-voltage profiles, we adopted a combination of the Keldysh nonequilibrium Green's function formalism with the DFT (DFT-NEGF).⁸⁰⁻⁸² Both the geometry optimizations of the substituted complexes with the thiol anchors as well as the transport properties of each of the proposed junctions were computed utilizing the QuantumATK software package, employing the PBE functional and the DZP basis set together with PseudoDojo norm-conserving pseudopotentials to represent all atoms. For all calculations, the mesh cutoff energy for both the reciprocal and real space grids was 250 Ry, with a threshold value of 10^{-4} eV as the convergence criteria for the changes in the norm of the Hamiltonian matrix and the total energy. In the case of the geometry optimization calculations, the threshold value for the changes in the interatomic forces was set to 0.04 eV/Å to consider the structure converged.

III. RESULTS AND DISCUSSION A. Conformational study

Figure 1 collects the optimized geometries of porphyrinoids 1–4 in Scheme 3 (more details are given in the supplementary material). It has been suggested that including a planar DTT unit in a porphyrin macrocycle would lead to a flat cycle.²⁷ This has been previously confirmed for fused core-modified hexaphyrins and heptaphyrins.²⁵ Our calculations agree with this observation for this kind of molecule since 2 and 3 are planar (see Fig. 1). However, our smallest (1) and largest (4) porphyrinoids, although having a DTT unit, are not planar. In pentaphyrin 1, the two pyrrole rings and the isolated thiophene one are nearly co-planar, but the DTT unit is distorted into a dome shape. Similar conclusions have been reached in a recent theoretical study on the stability of the same fused thio-modified pentaphyrins.³² In contrast, in octaphyrin 4, DTT is the moiety closest to planarity, with the chain of four thiophene non-fused rings curved and pulling the lateral pyrrole rings.

The non-planarity of the macrocycle skeletons of 1 and 4 makes possible the existence of their corresponding enantiomers. Therefore, to fully characterize these systems, we intended to look for the TSs, TS-1 and TS-4, connecting a corresponding couple of enantiomers. As indicated in Sec. II, we could only find them using the B3LYP/LANL2DZ level. Therefore, we could locate TS-1' and TS-4', where the prime symbol (') is used for the structures with the lowest computational level (see Fig. 1). IRC calculations link TS-1' and TS-4' with a couple of non-planar enantiomers of 1' and 4', respectively, whose bond angles and distances are very similar to those of 1 and 4 found at the B3LYP/6-31+G(d) level (except for C-S bond distances, which are significantly longer at the lower level) (see Fig. S2). The TSs present a flat macrocycle, and the Gibbs energy barriers from the non-flat stable structures 1' and 4' amount to 11.3 kcal/mol for TS-1' and 4.4 kcal/mol for TS-4'. The planar configuration of TS-1' forces the bonds involving all meso C atoms to elongate compared to those in 1', and the bond angles involving the meso C atoms closer to the single thiophene ring must reach values larger



FIG. 1. B3LYP/6-31+G(d) molecular structures of the fused core-modified expanded porphyrins studied in this work and the TSs connecting a couple of geometrical enantiomers, when existing, at the B3LYP/LANL2DZ level. Front and side views of each species are given. Some relevant distances (in Å) and bond angles (in degrees) are also shown in black and red, respectively. Significant dihedral angles (in degrees) are also given (atom numbering is shown for 1 but is easily extrapolated for the rest of the molecules).

than 130° . That is, the macrocycle of **TS-1'** expands its perimeter to allow the fitting of the DTT unit in the same plane as the rest of the penta-heterocycles, but this produces an extra angular strain responsible for the observed Gibbs energy barrier. Similarly, some ring tension develops at **TS-4'**, but now the bond angles involving the meso C atoms close to DTT are the ones that need to open to values larger than 130° to fit the large chain made of four thiophene rings opposite to DTT.

As previously said, the medium size porphyrinoids (hexaphyrin 2 and heptaphyrin 3) are stable, highly symmetric planar molecules (see Fig. 1). At 2, both DTT and the chain of two thiophene rings have a similar length between their ending C atoms [distance (a' - b') = 6.446 Å; distance (a - b) = 6.356 Å; see Fig. 1]; at 3, these non-bonding C–C lengths differ by as much as 3.388 Å [distance (a' - b') = 6.488 Å; distance (a - b) = 9.876 Å], but both fragments (DTT and the chain of three thiophenes) still manage to fit in the same plane without an unaffordable strain.

Obviously, as the size of the porphyrin macroring increases, the two meso angles close to DTT tend to enlarge (from 121.6° at 1 to 129.3° at 4) to provide room for the chain of thiophene rings. In contrast, those angles close to the chain of thiophene rings tend to reduce (from 129.6° at 1 to 125.1° at 4).

B. Topological analyses of the electron density and aromaticity

Figure 2 shows the position of the ring critical points (RCPs) of the electron density for planar porphyrinoids (2 and 3), which can be divided into three types: those located inside the macroring (RCPs numbered from 1 to 7), those placed at the thiophene units (RCPs numbered from 8 to 13), and those in the pyrrole rings (RCPs denoted as 14 and 15). Besides, in hexaphyrin 2, there is an external RCP (12') between the two non-fused thiophene rings. RCPs for non-planar porphyrinoids (1 and 4) are shown in Fig. S3. No analogous to RCP 12' has been found for 3 and 4 due to the larger distance between neighbor thiophene rings in these molecules. The NICS and NICS_{zz} values calculated at the RCPs of 2 and 3 are collected in Table I and suggest very similar large aromatic behavior for the macro and thiophene rings in both porphyrinoids. For the case

of the thiophene rings, except for RCP 9 in the DTT unit, the NICS and NICS_{zz} values (ranging from -14.1/-13.6 to -21.1/-23.3 ppm and from -28.3/-31.1 to -45.2/-48.5 ppm for 2/3, respectively) are much more negative than in the free ring (-13.3 and -9.5 ppm), respectively), indicating a coupling between macrocyclic and local aromaticity.83 The results also show that NICS_{zz} values are more sensitive to the electronic structure than the respective NICS values. RCP 9 is an expected exception in the thiophene trend⁸⁴ since it presents positive NICS_{zz} values (32.7 and 34.4 ppm for 2 and 3, respectively) and small negative NICS values (-1.7 and -1.4 ppm for 2 and 3, respectively). Although this could indicate an antiaromatic character, it may also be a consequence of the induced ring current of the fused thiophene being opposite to the induced macrocyclic ring current. As displayed in Fig. S4, the diatropic macrocyclic ring current and the local paratropic thiophene ring current vectors are opposite at the bridging S atom but in the same direction at the fused thiophene double bond region,⁸⁴ which causes this central ring to present a weak aromatic character (see Fig. S4). Concerning the pyrrole rings, RCPs 14 and 15 show NICS and NICSzz values close to zero (1.3/2.0 and 1.3/2.1 for 2/3, respectively) and very positive (24.3/26.3 and 24.4/26.4 ppm for 2/3, respectively), suggesting an antiaromatic behavior in contrast to free pyrrole. This can be ascribed to a situation similar to that previously described for the fused thiophene ring since the diatropic macrocyclic and paratropic pyrrolic ring currents accumulate at the pyrrolic N atoms but offset each other at the pyrrolic double bond regions.⁸⁵ In 2, the RCP 12' presents a small positive NICS value and a large positive NICS_{zz} value in agreement with its external position between the two non-fused thiophene rings.

Additionally, when counting electrons according to the main conjugation pathway from the [N]annulene model,⁸⁶ it is possible to observe 26π and 30π electron conjugation for **2** and **3**, respectively, based on the MICD vector maps collected in Fig. S4, in apparent agreement with Hückel's rule.⁸⁷

The aromatic behavior of the fused thiophene ring in 2 and 3 is confirmed by the results obtained from the HOMA indicator, which show that the central ring presents a favorable bond equalization. Based on the NICS and NICS_{zz} values for the latter ring, a HOMA value close to zero is expected. The high values obtained for



FIG. 2. Ring critical points (RCPs) of the electron density located for porphyrinoids 2 and 3. For 2, the RCP situated between the two non-fused thiophenes is referred to as 12' to differentiate it from the RCP 12 in 3.

TABLE I. NICS, NICS_{zz}, and HOMA values for porphyrinoids 2 and 3 at the M05/6-31+G(d) level of theory. The corresponding values obtained for free thiophene and pyrrole rings are also included for comparison purposes.

| | | | 2 | | | 3 | | |
|-----------------------------|--------|-------|--------------------|-------|-------|--------------------|-------|--|
| Ring | NRCP | NICS | NICS _{zz} | НОМА | NICS | NICS _{zz} | HOMA | |
| | 1 | -14.1 | -33.6 | | -13.6 | -33.6 | | |
| | 2 | -15.8 | -35.7 | | -14.4 | -34.4 | | |
| | 3 | -15.7 | -35.6 | | -14.4 | -34.5 | | |
| Inner part of the macroring | 4 | -20.8 | -44.1 | | -20.7 | -46.4 | | |
| | 5 | -20.8 | -44.2 | | -20.7 | -46.4 | | |
| | 6 | -20.4 | -45.2 | | -21.5 | -48.4 | | |
| | 7 | -20.3 | -45.1 | | -21.5 | -48.5 | | |
| | 8 | -21.1 | -29.7 | 0.636 | -21.9 | -31.1 | 0.459 | |
| | 9 | -1.7 | 32.7 | 0.543 | -1.1 | 34.4 | 0.601 | |
| Thiophone | 10 | -21.1 | -29.7 | 0.636 | -21.9 | -31.1 | 0.460 | |
| Thiophene | 11 | -20.4 | -28.3 | 0.577 | -22.8 | -36.3 | 0.670 | |
| | 12'/12 | 9.1 | 40.6 | | -23.3 | -35.0 | 0.721 | |
| | 13 | -20.4 | -28.4 | 0.578 | -22.8 | -36.2 | 0.670 | |
| Drawala | 14 | 1.3 | 24.3 | 0.368 | 2.0 | 26.3 | 0.338 | |
| Pyrrole | 15 | 1.3 | 24.4 | 0.369 | 2.1 | 26.4 | 0.338 | |
| Free thiophene | | -13.3 | -9.5 | 0.832 | -13.3 | -9.5 | 0.832 | |
| Free pyrrole ^a | | -13.6 | -31.0 | 0.870 | -13.6 | -31.0 | 0.870 | |

^aReference 85.

2 and **3** (0.543 and 0.601, respectively) could be explained in terms of possible contamination with the bonds belonging to rings 8 and 10, which are part of the main aromatic pathway (Fig. S4). The non-fused thiophene rings also show values consistent with an aromatic nature compared to the free thiophene ring. HOMA values for the pyrrole rings indicate a less aromatic behavior than free pyrrole, in agreement with the trend obtained for the NICS and NICS_{zz} values.

Concerning 1 and 4, the aromaticity of the macrocycle is significantly reduced due to the loss of planarity according to the magnetic and geometrical criteria (see Fig. S4 and Table S1). For the case of octaphyrin, the large geometry distortion makes that only 3 RCPs exist inside the macrocycle. Additionally, the fused thiophene rings also have a reduced aromatic character, while the non-fused ones show aromaticity similar to that of the free ring. Finally, the pyrrole rings retain their low aromatic nature.

C. PHOTOPHYSICAL PROPERTIES

Table II collects the main features of the electronic absorption spectra obtained for porphyrinoids 1-4 at the CPCM-M05/6-31+G(d) level of theory. We select hexaphyrin 2 as a model to compare our theoretically predicted spectrum with the experimental one reported for this molecule.^{25,31} As collected in Table II, our computational methodology perfectly matches the experimental UV–Vis spectrum for 2 (wavelength differences smaller than 7 nm), except for the Q band at the highest energy that is described with a longer wavelength (781 nm) than the experimental one (711 nm).

All four compounds present two low-intensity bands (Q bands) at wavelengths in the range of 700–970 nm, that is, in the NIR zone,

and two very intense Soret bands varying between 500 and 645 nm, that is, in the visible region where the emission of solar photons is large, which is a very favorable feature for their use as dyes. As the size of the molecules increases, most of the bands shift to longer wavelengths (with bigger variation for the Q ones), as is expected from the extent of the π -delocalization. The largest shifts in the Q bands happen when going from 1 to 2 (that is, from the smallest non-planar structure to a larger planar one) and, mainly, from 2 to 3 (the size of the macrocycle increases while maintaining planarity). For Soret bands, the largest wavelength increase occurs in the evolution from 2 to 3. Derivative 4 is geometrically far from planar and more irregular, as previously seen, but their Soret bands still shift to wavelengths longer than those of 3, with a new small absorption appearing at 502 nm (2.47 eV, f = 0.359) (see Fig. S5). For 4, only the most intense Q band is shifted to a longer wavelength. It is also interesting to note that increasing the size of the macrocycle increases the intensity of the most intense bands in the Q and Soret sets.

So far, we have confirmed a strategy to obtain absorption in the NIR region for this kind of molecule, i.e., the increase of the number of non-fused thiophene rings. This result is relevant since the dye has to strongly absorb in the zone of the electromagnetic spectrum where the solar radiation is intense (NIR). Moreover, the theoretically proposed compound, **4**, keeps the trend found for its smaller counterparts and presents improved photophysical features.

As solvents could affect the NIR absorption, we explored the bulk solvent effects on the electronic spectrum of each expanded porphyrin. The UV–Vis spectra of 1-4 were calculated with the following solvents of increasing dielectric constant: chloroform

| | Q | | Q | Q | | Soret | | | |
|---|---|------------------|--|------------------|---|------------------|---|------------------|--|
| | λ (nm) | E (eV) | λ (nm) | E (eV) | λ (nm) | E (eV) | λ (nm) | E (eV) | |
| | 741 | 1.68 | 702 | 1.77 | 522 $H - 2 \rightarrow L$ $-0.141 \ 17$ | 2.38 | 512 | 2.42 | |
| 1 | $H - 1 \rightarrow L + 1$ -0.368 41 $H \rightarrow L$ 0.602 21 | <i>f</i> = 0.048 | $H - 1 \rightarrow L$ 0.435 06 $H \rightarrow L + 1$ 0.554 91 | <i>f</i> = 0.064 | $\begin{array}{c} H-1 \rightarrow L+1 \\ 0.58823 \\ H \rightarrow L \\ 0.36344 \end{array}$ | <i>f</i> = 0.999 | $H - 2 \rightarrow L$ 0.548 28 $H \rightarrow L + 2$ -0.430 52 | <i>f</i> = 1.616 | |
| | 829 (822) | 1.49 | 781 (711) | 1.59 | 538 (536) | 2.30 | 514 (517) | 2.41 | |
| 2 | $H - 1 \rightarrow L$ -0.431 31 $H \rightarrow L + 1$ 0.560 82 | <i>f</i> = 0.029 | $H - I \rightarrow L + I$ 0.35352 $H \rightarrow L$ 0.61332 | <i>f</i> = 0.293 | $H - I \rightarrow L$ $0.566 \ 69$ $H \rightarrow L + 1$ $0.439 \ 30$ | <i>f</i> = 1.409 | $H - I \rightarrow L + I$ $0.615 \ 30$ $H \rightarrow L$ $-0.365 \ 14$ | <i>f</i> = 2.702 | |
| | 946 | 1.31 | 916 | 1.35 | 596 | 2.08 | 557 | 2.23 | |
| 3 | $H - 1 \to L$ -0.439 05 $H \to L + 1$ 0.555 24 | <i>f</i> = 0.020 | $H - 1 \rightarrow L + 1$ 0.313 98 $H \rightarrow L$ 0.636 50 | <i>f</i> = 0.500 | $H - 1 \rightarrow L$ 0.563 54 $H \rightarrow L + 1$ 0.449 95 | <i>f</i> = 1.539 | $H - 1 \rightarrow L + 1$ $0.636 \ 01$ $H \rightarrow L$ $-0.330 \ 42$ | <i>f</i> = 3.024 | |
| | 968 | 1.28 | 849 | 1.46 | 645 | 1.92 | 586 | 2.12 | |
| 4 | $H - I \rightarrow L + 1$ -0.254 73 $H \rightarrow L$ 0.659 89 | <i>f</i> = 0.678 | $H - 1 \rightarrow L$ 0.420 68 $H \rightarrow L + 1$ 0.564 45 | <i>f</i> = 0.021 | $H - 1 \rightarrow L$ 0.571 14 $H \rightarrow L + 1$ -0.428 56 | <i>f</i> = 1.293 | $H - 1 \rightarrow L + 1$ 0.644 11 $H \rightarrow L$ 0.263 14 | f = 2.043 | |

TABLE II. Most relevant results^a for the electron excitations of porphyrinoids 1–4 obtained at the TD-CPCM-M05/6-31+G(d) level of theory in CH₂Cl₂ solution. For comparison purposes, experimental wavelength values are included in parenthesis. Italic is used to establish a difference between the parameters.

^a λ : wavelength (in parenthesis, experimental values), E: energy, *f*: oscillator strength,^{25,31} and the most significant molecular orbital contributions to the corresponding electronic transitions.

($\varepsilon = 4.71$), 2-butanol ($\varepsilon = 15.94$), and *N*,*N*-dimethylformamide ($\varepsilon = 37.22$), which were compared with those previously obtained with CH₂Cl₂ ($\varepsilon = 8.93$). The results obtained are collected in Table III and allow us to confirm that, for the molecules here considered, the solvent dielectric constant has little impact on the spectra, which means that the photophysical properties of this set of expanded porphyrins remain unchanged in a wide range of solvents, the only concern being the solubility of the compounds.

Figure S6 collects the natural transition orbitals (NTOs) involved in each of the electronic transitions of porphyrinoids 1-4. It can be seen that, for every porphyrinoid, the Q and Soret bands involve the same kind of NTOs but with different electron excitations among them. Therefore, Fig. 3 shows the common NTOs for each compound. The first two columns are occupied NTOs, whereas the last two correspond to unoccupied ones. For each molecule, one of the occupied orbitals presents lobes involving the adjacent a and β C atoms of the thiophene and pyrrole rings, excluding the heteroatoms (α_0 type NTO). The lobes of the other occupied NTO extend over the ring heteroatoms, the β C atoms of the thiophene rings, and the meso C bonds (β_0 type NTO), with no participation of the β C atoms of the pyrrole units. The β_0 occupied orbital of 4 does not fully match the previous β_0 NTO description, since the intermediate thiophene rings in the chain of non-fused thiophenes hardly participate and those at the end of the chain contribute with

TABLE III. Excitation wavelength (nm) of the Q and Soret absorption bands calculated at the TD-CPCM-M05/6-31+G(d) level of theory in the solvents chloroform (CHCl₃), 2-butanol (2-ButOH), and *N*,*N*-dimethylformamide (DMF) for porphyrinoids **1–4**. For comparison purposes, spectral data obtained for dichloromethane (CH₂Cl₂) are also included.

| Solvent | Band | 1 | 2 | 3 | 4 |
|-------------------|-------|-----|-----|-----|-----|
| | Q | 744 | 832 | 947 | 966 |
| CHCl ₃ | Q | 704 | 781 | 916 | 848 |
| | Soret | 511 | 511 | 554 | 582 |
| | Q | 742 | 831 | 947 | 961 |
| 2-ButOH | Q | 702 | 779 | 912 | 848 |
| | Soret | 508 | 508 | 550 | 581 |
| | Q | 742 | 831 | 947 | 964 |
| DMF | Q | 702 | 779 | 913 | 849 |
| | Soret | 509 | 510 | 553 | 584 |
| | Q | 741 | 829 | 946 | 968 |
| CH_2Cl_2 | Q | 702 | 781 | 916 | 849 |
| | Soret | 512 | 514 | 557 | 586 |

 $\alpha\beta$ lobes. The empty NTOs of all of the molecules could also be classified as α and β , although they differ from the corresponding filled ones in the participation of the pyrrole rings. Therefore, α_u NTO hardly includes the β C atoms of the pyrrole rings but does

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FIG. 3. CPCM-M05/6-31+G(d) NTOs involved in the electronic absorption spectra of porphyrinoids 1-4 in CH₂Cl₂ solution.

their N ones, and the β_u NTO mixes lobes placed at the β C atoms of the thiophene rings with those extended over the α and β C atoms of the pyrrole moieties.

As just said, we have checked that each transition (Q and Soret) involves the same NTOs for all the porphyrinoids. The shape of these NTOs indicates that all bands correspond to $\pi - \pi^*$ electronic transitions only involving the macrocycle of each molecule. Therefore, the first Q (with the least intensity in the Q set of bands) is mainly described by the transition $\beta_0 \rightarrow \beta_u$ and, with less weight, by $\alpha_o \rightarrow \alpha_u$; the second Q is described by $\beta_0 \rightarrow \alpha_u$ and $\alpha_o \rightarrow \beta_u$; the first Soret by $\alpha_o \rightarrow \alpha_u$ and $\beta_o \rightarrow \beta_u$; and the second Soret by $\alpha_o \rightarrow \beta_u$ and $\beta_o \rightarrow \alpha_u$.

Table IV collects the energies of the frontier Kohn–Sham (KS) orbitals and the HOMO-LUMO gap for porphyrinoids 1–4. As the size of the system increases, the energy of the occupied orbitals goes up, that of the LUMO goes down, and the energy of LUMO+1 keeps nearly constant. Consequently, the HOMO-LUMO energy gap reduces, in agreement with the red-shift observed in the UV–Vis spectra. For a favorable injection of electrons from the dye into a typical semiconductor such as TiO₂, the energy of the LUMO of

TABLE IV. Frontier Kohn–Sham orbital energies and HOMO–LUMO energy gaps (eV) of porphyrinoids 1–4 calculated at the CPCM-M05/6-31+G(d) level of theory in CH_2Cl_2 solution.

| Porphyrinoid | HOMO-1 | НОМО | LUMO | LUMO+1 | $\Delta E_{LUMO-HOMO}$ |
|--------------|--------|-------|-------|--------|------------------------|
| 1 | -5.80 | -5.50 | -3.01 | -2.98 | 2.49 |
| 2 | -5.62 | -5.19 | -3.07 | -2.89 | 2.12 |
| 3 | -5.48 | -4.99 | -3.21 | -2.91 | 1.77 |
| 4 | -5.43 | -4.94 | -3.21 | -2.83 | 1.73 |

the dye must be larger than that of the conduction band of TiO_2 (-4.2 eV).⁷³⁻⁷⁵ All the porphyrinoids here are considered to fulfill this requirement.

D. Electron injection and dye regeneration

As two of the relevant parameters affecting the solar-toelectrical conversion efficiency of DSSC devices, the thermodynamic

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FIG. 4. Energetic diagram of ESOP and GSOP values for the fused core-modified expanded porphyrins investigated. Vertical lines represent E_{0-0} energies (blue), $\Delta G_{\textit{inj}}$ (violet), and ΔG_{reg} (green), and dotted lines point out the experimental TiO₂ CB edge and the potential energy of the I-/I3- redox mediator.

plausibility of the electron injection and regeneration processes of porphyrinoids 1-4 were checked by calculating ΔG_{ini} and ΔG_{reg} using Eqs. (1) and (3), respectively. Figure 4 collects the obtained ESOP, GSOP, ΔG_{inj} , and ΔG_{reg} values. All four porphyrinoids investigated show ESOP values between -3.43 and -3.60 eV, and thus more than 0.2 eV7 above the conduction band of the semiconductor TiO₂ (-4.2 eV),^{73–75} resulting in negative ΔG_{inj} values between -0.60 and -0.77 eV that ensure more than a sufficient driving force for electron injection.

Concerning the regeneration process of the oxidized dye species, Fig. 4 shows that the GSOP values for 3 and 4 are 0.03 and 0.09 eV above the potential of the I^{-}/I_{3}^{-} redox pair (-4.8 eV),⁷² whereas those of 1 and 2 are 0.46 and 0.16 eV below it. Therefore, the dye regeneration is thermodynamically favorable for the smallest porphyrinoids, pentaphyrin 1 ($\Delta G_{reg} = -0.46 \text{ eV}$) and hexaphyrin 2 ($\Delta G_{reg} = -0.16$ eV), but not for the largest porphyrinoids, heptaphyrin 3 ($\Delta G_{reg} = 0.03 \text{ eV}$) and octaphyrin 4 ($\Delta G_{reg} = 0.09 \text{ eV}$). For the latter, employing a mediator with a higher (more positive) reduction potential would be necessary. Although the more common redox couple is I⁻/I₃, excellent results have been obtained with other cobalt- and copper-based mediators.^{88,89} The linkage of porphyrin derivatives with other structures to form a dyad could be a strategy to vary the GSOP value and keep the porphyrins' good absorption properties.90

E. Adsorption of porphyrinoids 1-4 on TiO₂

So far, we have investigated the interaction between porphyrinoids 1-4 and TiO₂ from an energetic point of view using electron injection-free energy without considering their electronic coupling. Nonetheless, as efficient electron injection is directly related to such coupling, we studied the adsorption of 1-4 on a TiO₂ cluster model, previously used in related processes and described in Sec. II.

All the optimized complexes (see Fig. 5 and Table S2) show a nearly covalent interaction between one oxygen atom of a carboxylic

3 (-25.75 kcal/mol).

group linked to the dye and one octahedral titanium of TiO₂. The hydrogen atom of the OH group approaches one oxygen in TiO₂. The O(dye)-Ti(TiO₂) distances are 2.08 Å (1), 2.10 Å (2), 2.07 Å (3), and 2.09 Å (4), wherein the number in parenthesis indicates the dye. These distances are similar to the O-Ti bond lengths in TiO₂ (1.93 and 1.98 Å), indicating strong adsorption of the dye on TiO_2 . The size of the porphyrin does not show an effect on this interaction distance. Figure 5 displays the frontier KS orbitals of the combined systems and shows in all cases that HOMO and LUMO are localized on the dye and TiO₂, respectively. This means that an electron transfer can be easily produced from the donor species (porphyrinoid) to the acceptor one (TiO₂). Interestingly, in the octaphyrin-TiO₂ complex, the LUMO involves TiO₂ units close to the dye, whereas the largest contribution to the LUMO of the rest of the complexes comes from TiO₂ units distant from the dye.

The adsorption energies between porphyrinoids 1-4 (por) and the TiO₂ cluster are calculated in the gas phase,

$$E_{ad} = E_{por-\mathrm{TiO}_2} - (E_{por} + E_{\mathrm{TiO}_2}),$$

where $E_{por-TiO_2}$ and E_{por} are the energies of the dye-TiO₂ complex and isolated dye, respectively, and E_{TiO_2} is the energy of TiO₂ cluster. All the E_{ad} values obtained are notably negative, thus indicating favorable adsorption of porphyrinoids on TiO₂. There is not a trend with the size of the porphyrinoid, but non-planar structures such as 1 (-27.81 kcal/mol) and 4 (-29.70 kcal/mol) present more negative values for E_{ad} than planar ones 2 (-26.04 kcal/mol) and

The projected density of states (PDOSs) (Fig. S7) was also calculated for the complexes dye-TiO₂ using the optimized molecular geometry (Table S2) at the same level of calculation a the adsorption energies. In all the cases, a couple of peaks of the dyes in the (-1:0) eV range appear closer to the Fermi level, indicating that the dyes dominate this valence band region. On the contrary, TiO₂ has a significant impact in the conduction band region in the (0:3) eV



FIG. 5. Frontier Kohn–Sham orbitals (HOMO and LUMO) calculated on the optimized molecular structure for the adsorption of porphyrinoids 1-4 on a TiO₂ anatase model.

range with several strongly intense peaks. These results are coherent with the frontier Kohn–Sham orbitals, confirming the behavior of each fragment in the complexes: electron donor for the dyes and electron acceptor for TiO_2 .

F. Charge transport in molecular junction model

The charge transport properties of porphyrinoids 1–4 were theoretically studied by attaching each molecule, through its meso substituents, to two Au(111) nanowires through bridges of sulfur atoms. The thiol groups of each complex are bonded to gold atoms corresponding to adatoms in the hollow position of the Au(111) surface. This contact mode was previously utilized in several works devoted to the transport properties of molecules employing gold nanowires.^{22,91–97} The calculated energy-resolved transmission coefficients [T(E)], zero-bias conductance, as well as the corresponding projected density of states (PDOSs) on the molecular kernel, are reported in Table V and Fig. 6.

As can be seen in Table V, two of the studied junctions, the ones featuring pentaphyrin 1 and octaphyrin 4 as active molecular elements, present conductance values three/two orders of magnitude greater than the systems employing hexaphyrin 2 and heptaphyrin 3, with the pentaphyrin 1 bridged setup showing the highest conductance. The marked differences observed in the conductance values stem from the transmission profiles of each system (see Fig. 6), where only the pentaphyrin and octaphyrin junctions exhibit considerable signals, along with the corresponding bands in the PDOS at the

TABLE V. Zero-bias conductance values for porphyrinoids pentaphyrin 1, hexaphyrin2, heptaphyrin 3, and octaphyrin 4 in G_0 units.

| Porphyrinoid | Conductance (G ₀) | | |
|--------------|-------------------------------|--|--|
| 1 | 3.81×10^{-5} | | |
| 2 | $8.42 	imes 10^{-8}$ | | |
| 3 | $7.18 	imes 10^{-8}$ | | |
| 4 | 4.77×10^{-6} | | |



FIG. 6. Transmission spectra and PDOS of the molecular junctions featuring each of the studied porphyrinoids 1–4 as active molecular elements.

same energy positions. It is worth mentioning that the pentaphyrincontaining junction transmission peaks are remarkably more broadened than in their octaphyrin counterparts, reflecting a stronger hybridization of the complex molecular orbitals with the electrodes and, therefore, enhancing the electronic transport of the former.

To identify which of the complexes' frontier molecular orbitals resonances with electrode Bloch states originates the peaks in the transmission spectrum, the transmission eigenfunctions at the peak of each signal were computed, as well as the complexes' frontier orbitals under the influence of the electrodes through the molecular projected self-consistent Hamiltonian (MPSH) states in the pentaphyrin and octaphyrin junctions. The MPSH states are obtained by diagonalizing the molecular part of the full self-consistent Hamiltonian of the open molecular junction device.

In the case of the pentaphyrin junction, the strongest signal below the Fermi level at -0.67 eV is due to the resonance with the complex HOMO [see Fig. 7(a)]. The highest peak above the Fermi level, at 0.76 eV, is due to the resonance with the LUMO [see Fig. 7(b)]. For the junction featuring the octaphyrin as an active element, the same trend is observed, but with a weak signal below the Fermi level (-0.35 eV) and a sharp peak above the Fermi level (0.42 eV), products of the resonance of the complexes HOMO and LUMO, respectively [see Figs. 7(c) and 7(d)].

Finally, the current passing through each studied molecular junction was calculated, and their I–V profiles are reported in Fig. 8. From this last figure, it can be observed that at a low bias regime

(0 to around 0.3 V, see Fig. 8), the current behaves as expected according to the zero-bias conductance values obtained before, i.e., with the pentaphyrin junction exhibiting the highest current values, followed by the one containing octaphyrin as a molecular bridge, and the two remaining ones showing values around three orders of magnitude lower. Nevertheless, increasing the applied voltage to values higher than 0.3 V and more remarkably above 0.7 V, a dramatic increase in the octaphyrin junction current values is observed, being almost one order of magnitude greater than in the system that follows it (the pentaphyrin) at 1 V. This behavior is due to the broad transmission signals present in the pentaphyrin junction, which contribute to a higher transmission value at the Fermi level than the high but narrow spikes in the octaphyrin system. As the applied voltage Vb increases, the octaphyrin signals produced by the resonance with complex HOMO and LUMO enter the current integration window (-Vb/2, Vb/2) at around 0.8 V, whereas to have the main signals in



FIG. 7. Transmission channels on each of the studied junctions at energy values corresponding to the observed peaks in the transmission spectra, along with the corresponding resonant expanded porphyrins molecular orbitals obtained through the MPSH methodology. For simplicity, two mesityl substituents were replaced by hydrogen atoms.



FIG. 8. Calculated current vs applied bias voltage on each of the studied molecular junctions. In the inset, a detail of the current from 0 to 0.5 V is shown.

the pentaphyrin case contribute to the calculated current, an applied bias of about 1.2 V would be needed.

VI. CONCLUSIONS

Fused core-modified expanded porphyrins containing two pyrroles, a dithienothiophene (DTT) unit, and 1-4 thiophene rings on the opposite side of DTT (pentaphyrin 1, hexaphyrin 2, heptaphyrin 3, and octaphyrin 4, respectively) have been investigated by using density functional theory (DFT), timedependent DFT (TD-DFT), and the Keldysh nonequilibrium Green's function for obtaining their photophysical, photovoltaic, and charge transport properties to assess their capability as dyes for DSSC.

The computed electronic absorption spectra of all four compounds present two low-intense Q bands in the range of 700–970 nm and two very intense Soret bands varying between 500 and 645 nm. The increase in the number of thiophene rings facing DTT provokes a bathochromic shift of the longest absorption wavelengths, leading to absorptions in the near-infrared (NIR) regions, which represent 49% of the solar energy. These results are highly desired for the photosensitizers for DSSC solar cells. The solvent effect on the electronic absorption spectra was investigated, considering dielectric constants varying from 4.71 to 37.22, finding a little impact with changes in the absorption wavelengths up to 4 nm.

Two other important photovoltaic parameters related to the efficiency of DSSCs have also been investigated: the electron injection from the dye into the conduction band of TiO_2 and the dye electron regeneration. All the compounds investigated show Gibbs free energies of electron injection greater than 0.2 eV, specifically between 0.60 and 0.77 eV, which suggests efficient electron injection processes. However, dye regeneration using an I^-/I_3^- mediator is only feasible for pentaphyrin **1** and hexaphyrin **2** with Gibbs free energies of electron regeneration of 0.46 and 0.16 eV, respectively. For the remaining compounds, these values are very close to zero. On the other hand, the adsorption of **1–4** on a finite TiO₂ model was found to be very favorable, with adsorption energies between –25.75 and –29.70 kcal/mol.

Aromaticity analysis according to magnetic and geometrical criteria shows that planar porphyrinoids (2 and 3) exhibit strong macrocyclic and local aromaticity in their thiophene rings. The diatropic currents are coupled in the case of thiophenes. The fused thiophene rings present an aromatic behavior where the outer rings are more aromatic than the central one, showing coupling of the local currents. The geometrical criterion indicates higher values than in free thiophene. On the other hand, the pyrrole rings show behavior characteristics of low aromatic systems. Concerning 1 and 4, they show a remarkable reduction in aromaticity due to the loss of planarity. The fused rings also present a large decrease in aromaticity, while the non-fused ones behave similarly to the free ring according to the geometrical criterion.

The charge transport studies show that in a low bias regime (0 to ~0.4 V), the junctions featuring pentaphyrin 1 and octaphyrin 4 are correspondingly nearly three and two orders of magnitude more conductive than the ones containing hexaphyrin 2 or heptaphyrin 3, in concomitance with the corresponding calculated current values. However, for applied voltages greater than 0.4 V, the current through the octaphyrin-junction increases exponentially, increasing from nano to microamperes at 1 V, while the remaining three systems stay in nano ampere-range current values. This last behavior is because the pentaphyrin-containing junction transmission peaks are much broader than the ones observed for the octaphyrin, enhancing the zero-bias conductance, in contrast to the narrow but closer to Fermi level (due to the complex lower HOMO-LUMO energy gap) resonances observed in the octaphyrin case, chiefly the one produced by the complex LUMO, entering entirely in the energy window contributing to the current (-V/2 to V/2) at high voltage.

SUPPLEMENTARY MATERIAL

See the supplementary material for the results of the UV–Vis is spectra, molecular structures, RCP, magnetically induced current density map, NICS and HOMA values, NTOs orbitals, optimized molecular geometry, and projected density of states of the dye–TiO₂ complexes.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

María Isabel Menéndez: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Validation (equal); Writing - original draft (equal); Writing review & editing (equal). Nicolas Montenegro-Pohlhammer: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing - original draft (equal); Writing - review & editing (equal). Ricardo Pino-Rios: Investigation (equal); Writing – original draft (equal). Rodrigo Urzúa-Leiva: Investigation (equal); Writing - original draft (equal). Simone Morales-Lovera: Investigation (equal). Merlys Borges-Martínez: Investigation (equal). Kevin Granados-Tavera: Investigation (equal). Ramón López: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing - original draft (equal); Writing - review & editing (equal). Gloria Cárdenas-Jirón: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Validation (equal); Writing - original draft (equal); Writing - review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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