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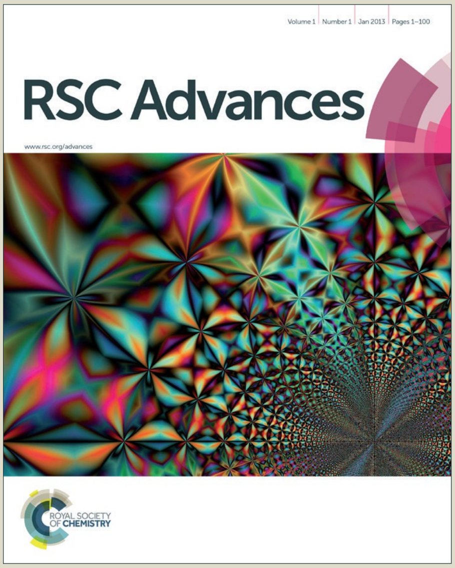

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Shifting UV-vis absorption spectrum through rational structural modifications of zinc porphyrin photoactive compounds

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Metalloporphyrin assemblies such as Zn-porphyrins are significant photoactive compounds with a number of applications including molecular device and dye-sensitized solar cell (DSSC). Recent Zn-porphyrin based DSSC, which achieves significant efficiency as high as 13%, stimulates rational molecular design through computer aided chemical and structural modifications. In the present study, time-dependant density functional theory (TD-DFT) is employed to simulate the ultraviolet-visible (UV-vis) spectra of the new photoactive compounds through chemical modification of the donor (D) and π-bridge of a high performing reference Zn-porphyrin (Pzn-EDOT) dye in DSSC. It is found that substitutions with the electron donating groups such as $-NH_2$, $-OCH_3$ and $-N(CH_3)_2$ at the *meso* positions of the D of the dye reduce the highest occopied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gap by lifting up the occupied frontier orbitals; whereas chemical modification of the π-bridge with dyad monomers such as pyrimidine (Py), thiophene (THn) and EDOT reduces the HOMO-LUMO energy gap by lowering the frontier virtual orbitals. The new dye compounds exhibit the predicted changes to the UV-vis spectra, by a splitting of the Soret band and a distinct red-shift of the Q-bands. The study demonstrates that modification of the π-bridge is an attractive approach for tuning Zn-porphyrin assemblies for DSSC applications. The present study provides a rational to design new architectures of molecular devices and for the improvement of metalloporphyrin assemblies.

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Introduction

Metalloporphyrin plays an important role in analytical and bioinorganic chemistry. A large number of metals can be inserted in the centre of the planar tetrapyrrolicmacrocycle forming metalloporphyrins. Indeed chromophores of this class play an important role in numerous other non-biological applications. O'Regan and Grätzel in 1991 reported a mesoscopic solar cell based on a light absorbing chromophore or dye with very low cost,[1] widely known as the Grätzel cell or organic dye-sensitised solar cells (DSSC).[1, 2] The substantial issue of the organic DSSC is its very low efficiency, relative to other non-chromophore based photovoltaic devices, and has been a focus of this research area since these early reports.[1] Since then, meaningful work in this direction has been carried out to improve the light-harvesting efficiency and one important direction is the organic dye in the DSSC and certainly computer based rational design for a high performance dye is very attractive.[4] The Grätzel group recently reported a molecularly engineered metalloporphyrin (Zn-porphyrin) based dye, coded SM315[4] which features the prototypical structure of a donor (D)–π-bridge–acceptor (A) where both D and A maximizes electrolyte compatibility and improves light-harvesting properties with a reported 13% power conversion efficiency (PCE).

Structurally analogous to the parent metalloporphyrin, porphyrin-based D–π-bridge–A dyes provide a highly flexible platform for the development of panchromatic sensitizers.[4-7] Porphyrin is a naturally occurring chromophore playing a central part in photosynthesis and haemoglobin structure biological oxidation and reduction and oxygen transport.[8] They have seen applications in photocatalysis[9] and energy conversion devices.[10, 11] The porphyrin chromophore has intrinsically strong light absorption in the Soret (UV) at ca 400 nm and Q-bands (Vis) at ca 550 nm, but there is a lack of significant absorption in the spectral region between these two features.[4, 6, 7]A major number of studies regarding porphyrin assemblies are reported for various applications. For example, a report in 2010 by Luo *et al.* demonstrated the porphyrin macrocycle as a superior class of organic dyes using a co-sensitisation method (YD2-o-C8)[12, 13] in a DSSC with cobalt based electrolyte achieving comparable 11% PCE to the Ruthenium-based N719 dye.[14]

Further structural modification of the parent porphyrin macrocycle in 2011 was able to suppress aggregation by inclusion of long alkoxy chains, effectively partitioning the porphyrin core and achieving record PCE of 12.3%.[15, 16] This macrocyclic structure and co-sensitisation method in porphyrin chromophore provided panchromatic absorption extending to 700 nm. Most recently, the Zn-porphyrin based SM315 D–π-bridge–A sensitizer,[4] exhibiting a vivid green colour, with limited absorption between 500–600 nm[4, 7, 17-21, 23] was reported with 13% PCE.

In designing new chromophore structure, an ideal dye for DSSC applications must absorb in the visible and extend into the near infrared region. The recent high efficiency Zn-porphyrin based SM315 D–π-bridge–A sensitizer[4] motivated the present study to explore rational for chemical and structural modifications of a Zn-porphyrin photoactive compound to improve the spectral absorption of the resultant new dyes.

Computational details

The model geometries utilised Becke's three-parameter-hybrid (B3LYP) and a 6-31G* basis set. This B3LYP/6-31G* model is able to reproduce good agreement with experimental data.[7, 17, 18] Tirado-Rives reports that the results obtained with this model are of comparable quality to the larger Dunning-type basis sets up to aug-cc-pVTZ.[19] Time dependant density functional theory (TD-DFT)[7] is employed to calculate the UV-vis spectra using the polarizable continuum model (PCM) in chloroform solution. All calculations performed using Gaussian 09 computational chemistry package.[18]

Absorption UV-vis spectra are calculated in gas phase and in the chloroform solutions, respectively, for the lowest 30 excited states with singlet–singlet transitions in the TD-DFT calculations. Absorption spectral profiles were simulated using a full-width half maximum (FWHM) of 2000 cm^{-1}.

Results and Discussion

Strategy for improvement of zinc-porphyrin photoactive compounds

Zn-tetraphenylporphyrin (the donor, D, of the reference PZn-EDOT dye in Figure 1) is a widely utilized supramolecular chromophore building block.[22] Zinc-porphyrin derivatives displays strong visible light absorption bands due to the π–π* electronic transitions from the closely spaced highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) frontier orbital manifold.[20, 21] These transitions are found to produce a high energy S_2 excited state or Soret band around 420 nm with large oscillator strength and a lower energy S_1 excited state or Q band with diminished oscillator strength between 500 nm and 650 nm.[20, 21] Emission from both the S_2 and S_1 excited states[24-27,] of a compound display dual fluorescence[28] and can be quite stable electrochemically.[29] As an important Zn porphyrin derivative, 2-Cyano-3-(3,4-ethylenedioxy-5-(4-(10,15,20-tris(4-methylphenyl)) porphyrina-tozinc(II)yl)phenyl)thienyl acrylic acid (Pzn-EDOT) see Figure 1) has been synthesised recently by Xiang *et al.*[30] The relative positions of the S_1/S_2 excited bands can be tuned through structural modifications at *meso* positions as indicated on the structure of the reference Pzn-EDOT (Figure 1) or the π-bridge moieties, in order to provide rationale for molecular design to improve absorption of incident photon flux.[32]

In the reference Pzn-EDOT photoactive compound, a Zn porphyrin macrocycle acts as an electron D moiety, a cyanoacrylic acid group as an electron A moiety and 3,4-ethylenedioxythiophene (EDOT) as a π-bridge, forming a D-π-A structure. The reference Pzn-EDOT photoactive compound in a DSSC exhibited performance characteristics of 6.47%, j_{sc} (short circuit current density) = 15.59 mA cm^{-2} , V_{oc} (open circuit voltage) = 0.64 V and *FF* (fill factor) = 0.65.[30] The recent SM315 dye exhibited broadening of the Soret and Q-band absorbance features, demonstrated an enhancement in green light adsorption, resulting in an improved j_{sc} (18.1 mA cm^{-2}) when used in the DSSC.[4] In the present study, Pzn-EDOT is employed as the reference photoactive compounds to rationalise the improvement of the UV-vis spectrum through chemical modifications.

The improvement is required to redshift (bathochromic shift) the absorption spectrum, that is, to reduce the HOMO-LUMO energy gap (ΔE) of the new dyes.[3] The strategies are to chemically modify the D moiety, the π-bridge and the A moiety of the D-π-A structure, respectively. In an earlier study of rational design of the TA-St-CA dyes,[3] the chemical modifications were concentrated on the π-bridge based on Dewar's rules,[31] using electron donation (ED) and electron withdrawing (EW) groups. It was found that chemical modifications to the reference TA-St-CA dye using ED substitutions on certain positions of the π-bridge exhibit advantages over the EW substitutes to reduce the HOMO-LUMO energy gap of the new dyes.[3] The HOMOs of the new dyes are energetically lifted more apparently than the energetic lowering of the LUMOs.[3] In the present study, we explore rational to chemically modify the moiety (metalloporphyrin) using electron donation groups (which produce Group I dyes) and to modify the π-bridge (which produce Group II dyes) from the reference Pzn-EDOT dye photoactive compound.

Geometrical and other molecular properties of the dyes

The chemical structure of the reference photoactive compound Pzn-EDOT is shown in Figure 1a. The electron rich Zn-porphyrin macrocycle is an electron contributing D, the (benzyl-) EDOT is considered as a π-bridge and cyanoacrylic acid acts as A, as marked in the figure. To produce Group I photoactive compounds, the reference Pzn-EDOT dye[30] is chemically substituted by the methyl groups of three aromatic toluene groups (at the *meso*-positions of the Zn-porphyrin) using ED groups[3] such as $-NH_2$, $-OCH_3$, $-N(CH_3)_2$, respectively. The new dyes are called, Zn-P-NH_2, Zn-P-OCH_3 and Zn-P-$N(CH_3)_2$, accordingly. An alternative way to design new dyes is to modify the π-bridge of the reference dye using photoactive monomers. In this respect, monomers such as pyrimidine (Py), thiophene (THn) and EDOT[33] presented in Figure 1b, are employed to construct the dyad π-bridges of the new dyes. For example, Py-EDOT, EDOT-Py, Py-THn, and THn-Py as the new π-bridges of two pairs of the new dyes of Zn-P_ π_1, dyes Zn-P_ π_3 (Pair A) and Zn-P_ π_2 and dyes Zn-P_ π_4 (Pair B) for Group II new dyes, respectively. The optimized structures of the dyes are given in Figure S1 in the Supplementary Data. More detailed geometric properties of the new dyes are given in Table S1 in the Supplementary Data.

Selected geometrical and other molecular properties of the reference dye as well as the new dyes in vacuum and in chloroform solution are calculated and given in Table 1. As indicated by Hirao and co-workers,[34] Zn insertion to porphyrin has little effect on the geometrical changes of the latter. It is well established that solvents have an apparent effect on molecular properties such as the molecular dipole moment and energy levels.[1, 22, 35-40] It is seen from this table, while only small changes in the HOMO-LUMO energy gap from vacuum to chloroform solution (using polarizable continuum model (PCM)), other properties such as dipole moment of the new dyes are indeed enhanced in solution. Molecular dipole moment results due to charge separation and is dependent on intramolecular distances between charges which influence the magnitude of the resultant dipole.

Porphyrin assemblies are effective in DSSC applications due to their large dipole moments affording the photostablility as well as influencing charge injection and recombination of the dye.[34, 36, 38, 42] It is observed that the dipole moments of all new dyes in the table are larger in the chloroform solutions than the dipole moments of the dyes in vacuum. For example, the reference Pzn-EDOT dye possesses a dipole moment of 6.18 D in vacuum; it increases to 7.88 D in chloroform solution. The dipole moments of Group I dyes, Zn-P-NH_2, Zn-P-OCH_3 and Zn-P-$N(CH_3)_2$, respectively, which are given by 7.69 D, 7.49 D and 9.42 D in vacuum, increase to 9.54 D, 9.46 D and 11.57 D, respectively. Similarly, the dipole moments of Group II dyes also increase in the chloroform solution. For example, the dipole moment of Zn-P-π_1 increases from 3.83 D in vacuum to 5.13 D in the chloroform solution. However, it is interesting to see that unlike the Group I dyes which all enlarge the dipole moment of the reference dye, modifications of the π-bridge of the reference dye result in reduction of the dipole moments of the new dyes, except the Zn-P_π_3 dye. This dye exhibits an increase in dipole moment to 8.15 D in solution, from 6.18 D in vacuum.

The Py monomer positions forming the Group II dyads also affect properties of new dyes. It is found that the new Group II dyes can be enhanced when electron rich monomer is connected. The connection is with the electron D, such as D-EDOT and electron poor monomer with the electron A, such as Py-A than the alternative arrangement, that is, the D-Py and EDOT-A dyes. For example, Pair A dyes (i.e., Zn-P_π_1 and Zn-P_π_3) seem to exhibit smaller HOMO-LUMO gaps and larger dipole moment when being connected as D-EDOT-Py-A (Zn-P_π_3) than as D-Py-EDOT-A (Zn-P_π_1). The similar trend is observed in Pair B new dyes in which D-Thn-Py-A seems preferred over D-Py-Thn-A. It is a known phenomenon that chemical interactions are influenced by solvent properties, which include dipole moment refractive index, polarity, polarizability, dielectric constant, and nature of solute solvent interaction. Molecular dipole moment, as a result of charge separation and intramolecular distances between charge centres and ultimately influences the magnitude of the resultant dipole. Porphyrin dyes are effective in DSSC application due to their large dipole moments affording them photostablility as well as influence charge injection and recombination of the dye. In the chloroform phase the higher values indicate the strong influence of solvent interaction with the charges centres of the dye molecule and effectively the molecular dipole moment.

The electronic spatial extent (<R^2>) can be used as a measure of the solvent influence on the charge centres of the molecular structures, and is defined as summing over all electrons as shown below.[34]

$$<R^2> = \langle \sum R_i^2 \rangle$$

Therefore, the electronic spatial extent (<R^2>),[43] is an indicator of the relative electronic boundary of the dyes, is expanded in the new dyes except for Zn-P-NH_2 (as $-NH_2$ is smaller than $-CH_3$). Chloroform as a solvating medium, as a general observation, enlarges the electronic spatial extent of all dyes in Table 1. The trend remained alike to other geometrical parameters which increased in the chloroform solution. Conversely, the (<R^2>) decreased in case of Group II dyes.

UV-vis spectra and splitting of Soret bands of new dyes

The UV-vis spectra of metalloporphyrins, such as Zn-porphyrin, contain essentially a sharp intense Soret band (B band) around 400 nm in the near UV region and two weak Q bands responsible for the red to purple colour in the visible region between 500 to 700 nm.[44] Figure 3 compares the calculated UV-vis spectra of the reference dye (PZn-EDOT) in a chloroform ($CHCl_3$) dielectric medium with the measured spectra[30] in the same physical solution. The UV-vis absorption spectrum of PZn-EDOT exhibits a typical strong Soret band at 423 nm ($S_0 \rightarrow S_2$) and moderate Q band at 550 nm.[30] The simulated spectrum shows two major bands with the strong Soret band at 432 nm and the less intensive Q band at 585 nm, respectively. Note that the measured porphyrin UV-vis spectra are dependent on the temperature of the dye solution. For example, Yatskuo et al[45] revealed that the spectral band shift of metalloporphyrin assemblies can be as large as 15 nm when the temperature changes from 50°C to 10°C. The simulation is performed at 0 K (-273.15 °C). As the experiment measurements are available in solution, all discussions will concentrate on dyes in chloroform solutions.

One of the most important purposes of the design of photoactive compounds is to expand the UV-vis spectra, in order to improve the light absorption. Figure 4 compares the simulated UV-vis spectra of the new dyes with respect to the references in chloroform solution for Group I dyes (a) and Group II dyes (b). Both Group I and Group II dyes in this study exhibit the Q-band bathochromic shift (red shifted) and more interestingly, the strong Soret bands of all new dyes are apparently broader than the reference dye. As pointed by Hirao and co-workers[25] that the intensity and colour of the Q band as well as the macrocyclic porphyrin skeleton are perturbed to a greater or lesser extent by various chemical modifications. Insertion of aza groups in meso positions leads to the contraction of the spatial dimensions of the porphyrin centre and substitution of nitrogen atoms for meso carbon atoms significantly intensifies the oscillator strength of the higher energy side transition of the Q band with the peak position unchanged.

The intense Soret band and weaker Q band and their corresponding oscillator strength information of the new dyes are summarised in Table 2. All new dyes exhibit split Soret bands in the spectra, which is well known for Zn-porphyrin assemblies (tetramers)[36] and SM315 dye.[4] The Soret band at near 400 nm split into two major excitations with one blue shift band under 430 nm region and the other red shifted band above 430 nm. The splitting ranges from 9 nm to 42 nm for the new dyes. For example, the Soret band of the Pzn-EDOT–NH_2 dye splits to 438 (1.84) nm and 429 (0.94) nm in chloroform solution. Such Soret band slitting is also seen in the recent high performance metalloporphyrin SM315 which splits into 440 nm and 454 nm.[4] Similarly, the Group II dyes such as the Zn-P-π_3 dye show the same band splitting at 451(1.56) nm and 409(1.39) nm. Inspecting the Soret-band positions, it is revealed that the Zn-P_π_1 and Zn-P_π_3 dyes in Group II are 427 (2.36) nm and 407 (1.40) nm, and 451 (1.56) nm and 409 (1.39) nm are red shifted, making the EDOT and Py monomers, i.e., Pair A dyes are more attractive for solar cell applications amongst other Group II dyes. Moreover, the fragment positions also make an apparent difference. For example, Zn-P_π_3 (Pair A) dye, the π-bridge formed by EDOT-Py has shown a larger red shift in the region of Soret at 451 nm, than the Soret band at 427 nm of Zn-P_π_1 dye with the π-bridge of Py-EDOT. As a result, Zn-P_π_3 is a more attractive dye to solar cells than the Zn-P_π_1 dye, in agreement with the previous findings of HOMO-LUMO gap and dipole moment.

The weaker Q-Band regions of the new dyes have been significantly red shifted to beyond 600 nm with respect to the reference PZn-EDOT dye of 585 nm (calculated). For example, the Q-band of the Group II dyes locate at as 629 nm (0.43), 666 nm (0.39), 650 nm (0.24) and 686 nm (0.29), for the Zn-P_π_n (where n=1, 2, 3, 4) dyes respectively, which are a remarkably red-shifted compared to the calculated reference dyes.

Orbital energies of the dyes

Depicted in Figure 5 are the frontier orbital energy levels for the reference and new dyes in chloroform solution. The frontier orbitals of the reference Pzn-EDOTdye are well predicted using the porphyrin four orbitals (4Orb) model of Gouterman.[46, 47] That is, the orbital energy levels of the frontier orbitals of the reference dye, two occupied MOs, i.e., the HOMO and HOMO-1 and two virtual (unoccupied) MOs, i.e., the LUMO and LUMO+1 are closely located. Thus, these four orbitals are closely located and the energy gaps between HOMO-1 and HOMO-2, and LUMO+1 and LUMO+2 are sufficiently large so that the transitions are dominated by the transitions among the close four orbitals, HOMO, HOMO-1, LUMO and LUMO+1 in Pzn-EDOT, and therefore, dominate the UV-vis spectra of the reference metalloporphyrin. The frontier orbitals of the new dyes, apparently changes the four orbital pattern of porphyrin by either increasing the HOMO orbitals or lowering the LUMO virtual orbitals as shown in Figure 5. As a result, the lower frontier orbitals are accessible in the new dyes so that the UV-vis spectra of the dyes become broadened accordingly.

To broaden the spectral absorption of chromophores for DSSC applications, the new dyes need to exhibit a smaller HOMO-LUMO energy gap. This can be achieved when the energies of higher virtual orbitals are lower in energy with respect to the LUMO or alternatively, the energies of the lower occupied orbitals increases in energy toward the HOMO. As indicated in Figure 5, all the new dyes, either Group I dyes or Group II dyes achieve the goal of reduction of the HOMO-LUMO energy gap of 2.43 eV for the reference dye. For example, the energy gap of Zn-P-NH_2, a Group I dye is 2.21 eV and the Zn-P-π_3, a Group II dye is 2.21 eV.

Next, the new dyes should be tuned to absorb across the spectral range which includes extending into the visible light region (that is, a red shifted absorption relative to the reference dye structure). In order to achieve this, the chemical structure of the reference dye needs to be modified so that the frontier orbitals, either virtual or occupied orbitals of the new dyes are localised in the HOMO-LUMO region. This means that the new dyes can either lower the frontier virtual orbitals or lift up the occupied frontier orbitals. As shown in Figure 5, if the electron D moiety is modified at the meso positions of the Zn-porphyrin macrocycle such as the Group I dyes, the frontier occupied orbitals are indeed increased in population in the HOMO vicinity, resulting in broadening of the UV-vis spectra in Figure 4(a). For example, the Zn-P-$N(CH_3)_2$ dye in Group I increased a number of occupied frontier orbitals, which contributes to expansion of the Soret band at 449 nm and 422 nm (See Fig. 4(a)). Alternatively, this can also be achieved with reduction of the virtual orbital energies to populate the frontier virtual orbital vicinity.

Group II dyes which are designed with chemical modification to the π-bridge of the reference dye show apparent decreased in energy of virtual orbitals. For example, the new Zn-P-π_4 dye is able to broaden the UV-vis spectrum of the reference to above 680 nm (Q-band) as indicated in Figure 4(c). For the DSSC application perspective, there limited potential for the HOMOs of metalloporphyrin assemblies to increase further as the HOMO energies are already very close to the reduction potential of I^-/I_3, implying very limited increase in performance would be expected in this direction for the meso-substitution metalloporphyrin dyes (i.e., Group I). Rather, significant improvement can be achieved by lowering the LUMO of such dyes as all the LUMOs of the dyes are well above the energy of TiO_2.

Finally, solvent induced effects affected some occupied frontier orbitals of the Group I dyes down shifted in energy (more negative)[1, 22, 35-41] yet only minor impact to the virtual orbitals with respect to their vacuum counterparts. On the other hand, as shown in Figure S2, the solvent effects do not change the occupied frontier orbitals of the Group II dyes but some small changes to the frontier virtual orbitals of the Group II dyes are observed. A comparison of the molecular orbitals of the dyes in vacuum and in chloroform ($CHCl_3$) solution is given in Figure S2 for Group I dyes and Figure S3 for Group II dyes.

Conclusions

Metalloporphyrin assemblies such as Zn-porphyrins are important photoactive compounds and the ability to tune the spectral absorption of these chromophores by molecular structure changes has been shown through a rationale for computer aided molecular design (click-chemistry). The current study provided a rational to improve the properties such as UV-vis spectra of the photoactive compounds through chemical modification of the metolloporphyrin donation group and the π-bridge of the high performing reference Zn-porphyrin. It has been demonstrated that chemical modifications of the metalloporphyrin D and the conjugate π-bridge can effectively reduce the HOMO-LUMO energy gap and broaden the spectral absorption providing a route to design of enhanced light-harvesting compounds. Using this approach, new metalloporphyrin dyes have been presented that show modification of the LUMO can be tuned without impacting the electron charge transfer between the frontier orbitals. Importantly, there was a distinct improvement in excitations for the Q-Band of these new structures compared to the parent structure. It further reveals that substitutions with the electron donating groups $-NH_2$, $-OCH_3$ and $-N(CH_3)_2$ at the *meso* positions of the metalloporphyrin D, i.e., Group I dyes systematically increase the occupied frontier orbitals of the new metalloporphyrin dyes. Further, modification of the π-bridge with dyad monomers such as (Py), (THn) and EDOT significantly reduced the energies of the frontier virtual orbitals, which is effective for DSSC applications as the TiO_2 energy level remains well below the LUMOs of the Group II dyes. The rationale for molecular design presented in this study will find useful application in designing co-sensitised dye structures and the development of tandem based solar cells.

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Table 1: Molecular parameters of the Group 1 and 2 new zinc porphyrin dyes in vacuum and chloroform solution using B3LYP/6-31G (d) model

Molecule Name	$\Delta\varepsilon^{a}$ (eV)	$\langle R^2\rangle^{b}$(a.u.)	μ ^{c}(Debye)	Total Energy (E_h)	$\Delta\varepsilon$ (eV)	$\langle R^2\rangle$ (a.u.)	μ (Debye)	Total Energy (E_h)
			Vacuum				**$CHCl_3$**	
				Group I				
Pzn-EDOT (Ref)	2.47	97501.78	6.18	-4946.892477	2.43	97704.42	7.88	-4946.916695
Zn-P-NH_2	2.26	97169.08	7.69	-4995.027943	2.21	97375.84	9.54	-4995.061476
Zn-P-OCH_3	2.41	108153.57	7.49	-5172.492484	2.37	110187.98	9.46	-5144.734510
Zn-P-$N(CH_3)_2$	2.14	119221.12	9.42	-5230.712057	2.07	119434.89	11.57	-5230.740926
				Group II				
Zn-P_π_1	2.20	96252.11	3.83	-4978.989450	2.27	96406.21	5.13	-4979.015795
Zn-P_π_2	2.06	87333.89	4.37	-4751.193828	2.15	87383.32	4.83	-4751.217682
Zn-P_π_3	2.24	86516.14	6.82	-4978.995193	2.21	86365.29	8.15	-4979.019621
Zn-P_π_4	2.10	83210.97	4.81	-4751.198412	2.10	83273.67	5.38	-4751.219239

* The B3LYP/6-31G (d) model in gas phase and $CHCl_3$.

[a] $\Delta\varepsilon$ = HOMO-LUMO gap.

[b] $\langle R^2\rangle$ = Electronic spatial extent.

[c] μ = Dipole moment.

Table 2: Soret and Q - band comparison of experimental and theoretical frequencies in vacuum and chloroform phases (nm).*

Zn-porphyrin	VACUUM	CHLOROFORM
	Soret band, Q-band	**Soret band, Q-band**
Pzn-EDOT(exp)		423(2.55), 550(0.17)
Pzn-EDOT(theo)	415(1.98), 570(0.22)	432(2.26), 585(0.32)
	Group I	
Zn-P-NH_2	420 (1.72), 409 (0.77), 622(0.21)	438(1.84), 429(0.94), 642(0.28)
Zn-P-OCH_3	393(1.11), 372(1.00), 585(0.23)	433(2.33), 411(1.46), 601(0.33)
Zn-P-$N(CH_3)_2$	429(0.97), 405(0.87), 658(0.19)	449(1.04), 422(1.01), 685(0.25)
	Group II	
Zn-P_π_1	413(2.07), 392(0.90), 643(0.34)	427(2.36), 407(1.40), 629(0.43)
Zn-P_π_2	416(1.03), 401(1.03), 687(0.31)	422(2.29), 410(1.38), 666(0.38)
Zn-P_π_3	437(1.11), 392(0.77), 637(0.18)	451(1.56), 409(1.39), 650(0.24)
Zn-P_π_4	419(1.97), 390(1.05), 680(0.20)	432(2.22), 409(1.28), 686(0.30)

*Oscillator strength (which is summed over all absorption bands in a molecule) is in the parentheses.

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Figure Legends

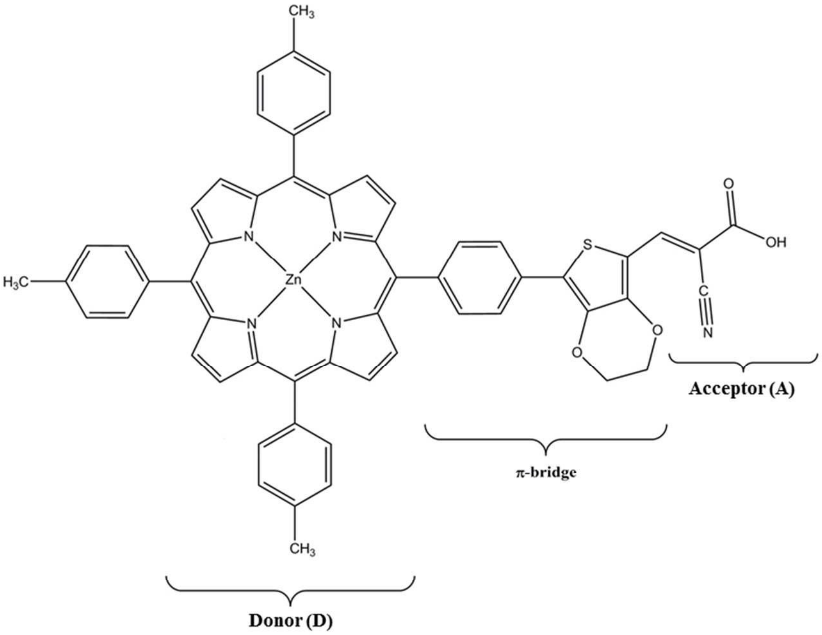
Fig.1 Chemical structure of the reference photoactive compound Pzn-EDOT. The positions of substitutions are indicated on the structure.

Fig.2 Chemical structures of new dyes designed in the present study with substitutions at (a) Group I (meso positions) and (b) Group II (π positions) dyes.

Fig.3 Comparison of the measured (black) and the simulated (red) UV-vis absorption spectra of Pzn- EDOT in $CHCl_3$ solution.

Fig.4 Calculated absorption UV-vis absorption spectra in $CHCl_3$ solution of (a) Group I dyes and (b) Group II dyes. An FWHM of 2000 cm^{-1} is employed.

Fig.5 Comparison of calculated frontier molecular orbitals of the new (Group I and II) and reference dyes (Pzn-EDOT) in chloroform solution using the B3LYP/6-31G* model.



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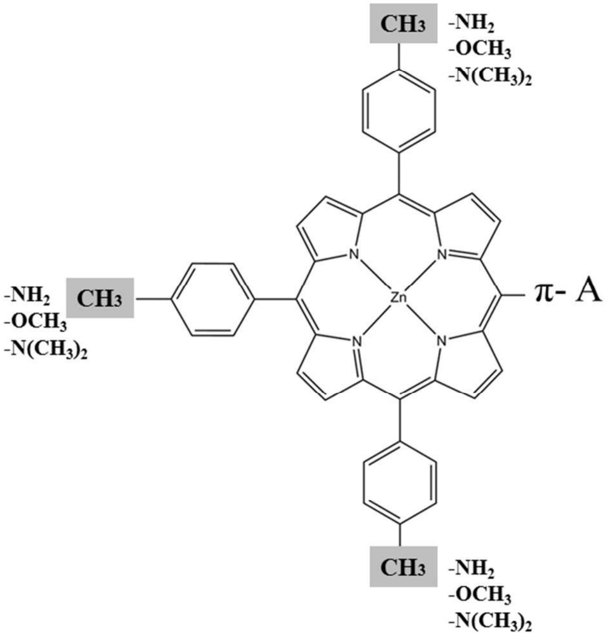

Group I

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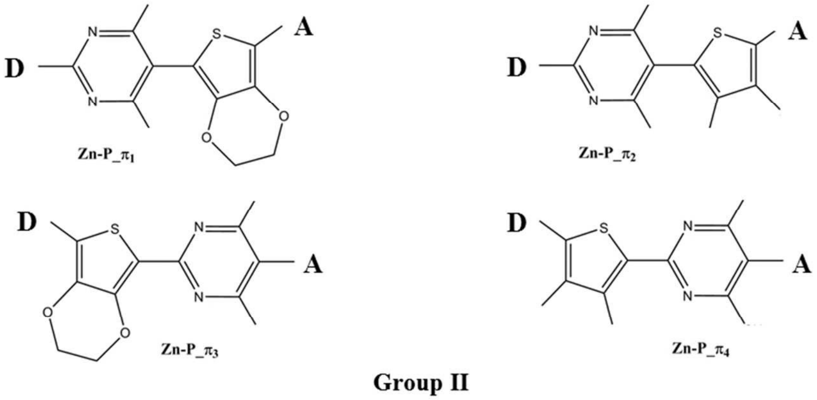

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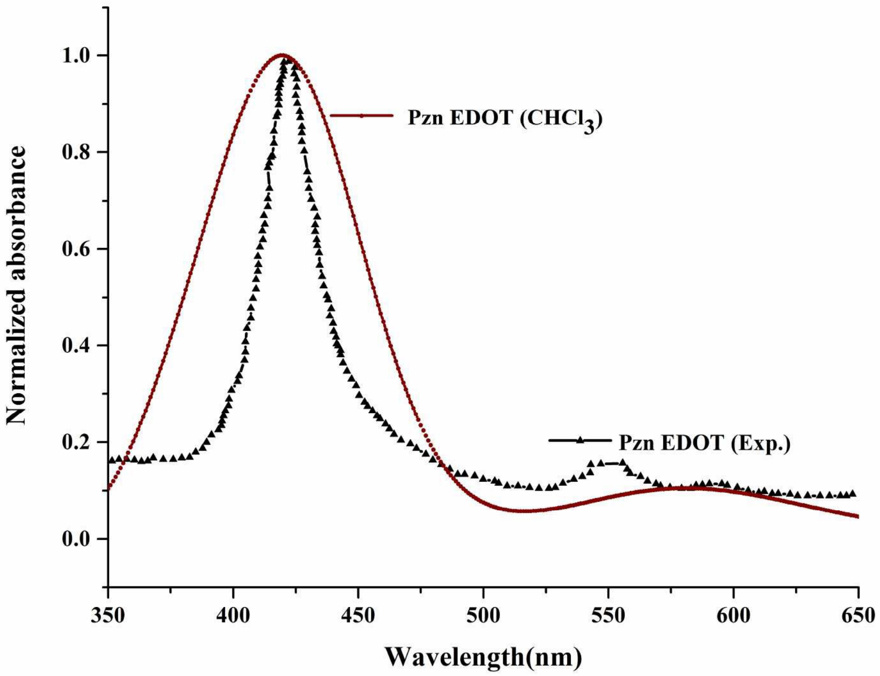

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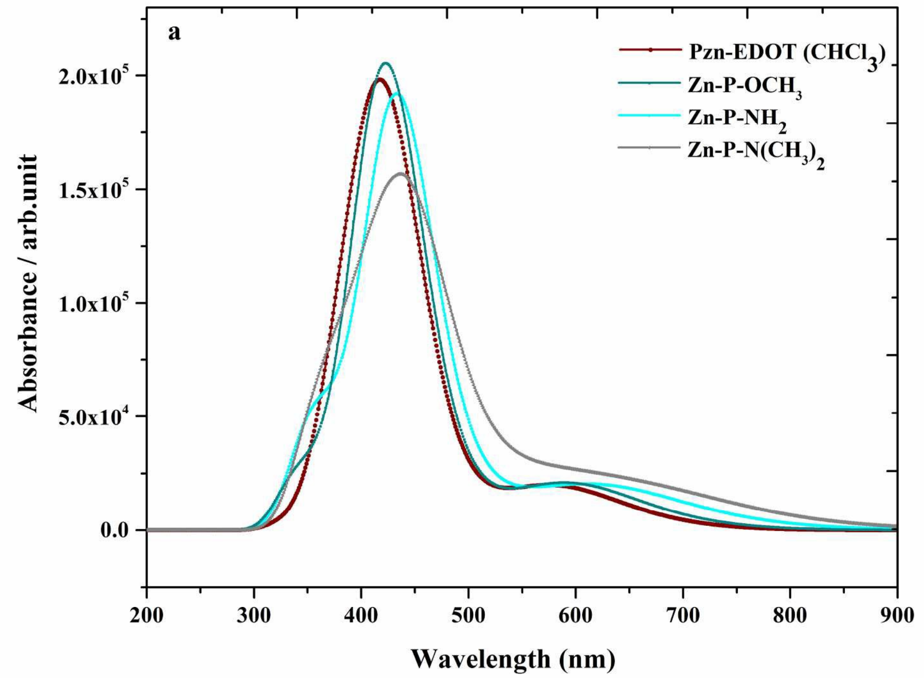

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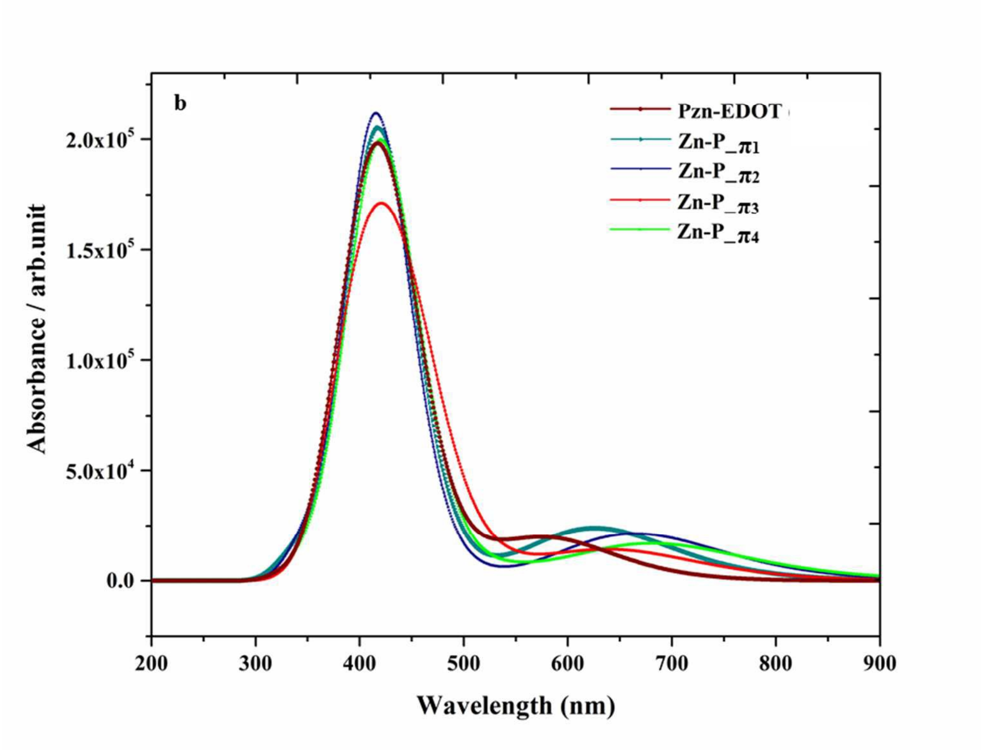

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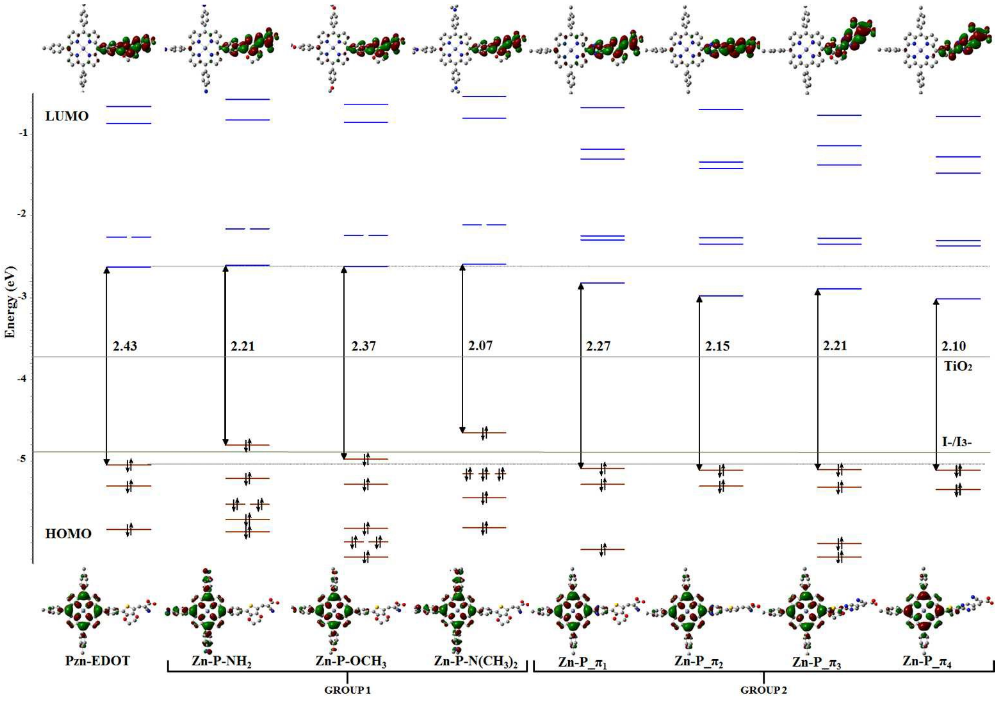

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