

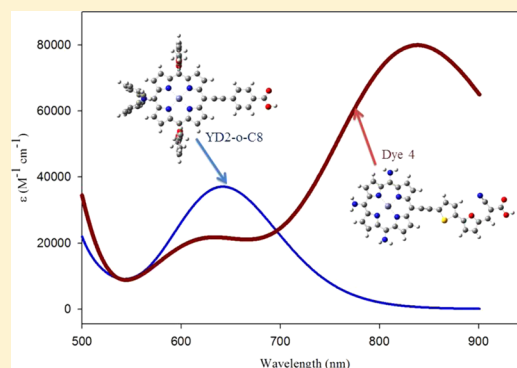
Molecular Design of Porphyrins for Dye-Sensitized Solar Cells: A DFT/TDDFT Study

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Supporting Information

ABSTRACT: To design efficient sensitizers for dye-sensitized solar cells (DSSCs), a series of porphyrin sensitizers with different electron-donating and withdrawing substituents are investigated using the density functional theory (DFT) and time-dependent DFT approach. We found that the designed dyes have smaller highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO–LUMO) energy gap values, and the absorption bands are broadened and shifted to longer wavelengths compared to the so far best sensitizer (YD2-o-C8). Importantly, our designed dyes have larger contributions of the anchoring group to the LUMOs, which enhance the electron injection process. Our calculation results indicated that the new systems should have better performance than the existing efficient dyes due to their improved optical properties.

**SECTION:** Energy Conversion and Storage; Energy and Charge Transport

In the current scenario, to utilize solar energy for practical applications, dye-sensitized solar cells (DSSCs) are the most promising alternative to conventional silicon-based solar cells owing to their potential application for photovoltaic devices.^{1–4} In recent years, many attempts were made to develop new and efficient sensitizers that are suitable for real-world use. Sensitizers based on ruthenium complexes,^{5–7} zinc porphyrin,^{8–11} and metal-free organic dyes^{12,13} were developed and used as efficient light harvesters for DSSCs. Among them, the ruthenium complexes^{5,6,14,15} and porphyrin sensitizers¹⁶ have reached power conversion efficiencies of more than 11%. However, the abundant nature and the environmental complications of ruthenium make it necessary to search for the best alternative dyes.

Nowadays, π aromatic molecules such as porphyrins are considered to be an alternative to the expensive Ru complexes in the fabrication of DSSCs because of their good electron donating/accepting nature and their strong and intense absorption at 400–450 nm (Soret or B band) and moderately intense absorption band at 500–650 nm (Q-band). Moreover, they have many reaction sites, in which different substitutions can be easily attached to further increase the photoelectric conversion efficiency. In the literature, a lot of attempts have been made to increase the efficiency of the DSSCs based on porphyrin dyes. Recently, Yella et al.¹⁷ synthesized a D- π -A-based zinc porphyrin dye (YD2-o-C8) and achieved a power conversion efficiency of 12.3%, which so far is the best reported porphyrin dye other than the Ru based complexes. However, the major issue of these efficient sensitizers is that they show relatively less absorption intensity in the long-wavelength region, which greatly decreases the light-harvesting abilities.

In this Letter, we made a systematic search for sensitizers based on porphyrin to obtain improved light absorption properties at Soret and Q bands. For this, different ancillary ligands and π -bridge moieties were substituted with basic porphyrin structure and thereby we constructed different structures of porphyrin-based sensitizers and studied their intrinsic optical properties using the density functional theory (DFT) and time dependent density functional theory (TDDFT) methods. The constructed structures are illustrated in Scheme S1 of the Supporting Information. All the electron donors and π -bridge systems are substituted in the *ortho* and *meso* positions of the basic porphyrin dye, since it has been shown that substitutions in this positions help not only enhance the photovoltaic properties but also reduce the degree of dye aggregation for a higher electron injection.^{18,19} Generally, dye aggregation is considered an undesired process leading to decreased efficiency of DSSCs, which occurs when the dyes are packed so tightly that their wave function overlap is large enough to change their electronic character. It is well known that suitable molecular design can prevent dye aggregation on the TiO_2 surface.^{20,21} Moreover, the electron dynamics in the dye and semiconductor surface are also important in the DSSC, and it involves a variety of processes. Previously Prezhdo et al.^{22–24} described nonadiabatic effects in the electron transfer (ET) dynamics by TDDFT within the Kohn–Sham approach to characterize the interfacial ET. They performed a series of time domain simulations over the DSSCs and quantum dots in

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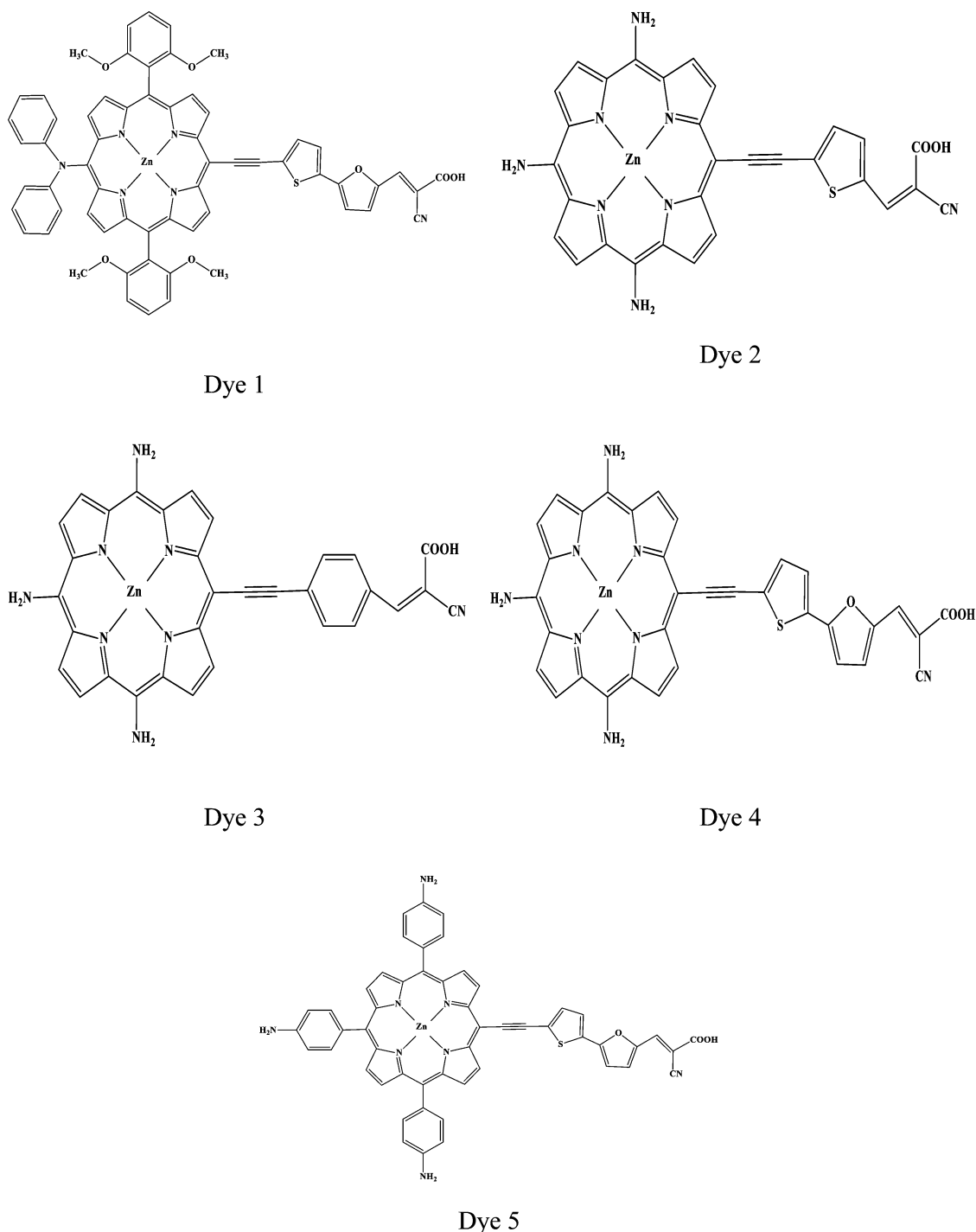


Figure 1. Molecular structures of the investigated porphyrin sensitizers.

which they considered the chemical structure of the system and determined the role of the vibrational motion and nonadiabatic coupling.^{25–27} Their results suggest improvement of the electronic properties of the DSSCs and control of the ET between the dye and surfaces. The designed different structures of porphyrin sensitizers are compared with the available efficient sensitizers, namely, YD2-o-C8 of porphyrin¹⁷ and N3 of ruthenium,²⁸ among which we selected only five dyes that have optical properties better than the reference dyes.

The structures of different functional group-substituted porphyrin derivatives (Dyes 1–5) considered in this study are illustrated in Figure 1. In the basic porphyrin structure, the

central two H^+ ions were replaced by Zn^{2+} for all the structures used. The ground-state geometries and electronic properties such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and the gap between the HOMO and LUMO of all the structures have been calculated using the long-range corrected functional CAM-B3LYP.²⁹ A mixed basis set was used in these calculations (LANL2DZ basis set for Zn atom and 6-31G (d) basis set for C, H, N, O and S atoms). The vibrational frequency analyses were performed at the same level of theory, which confirms that the selected porphyrin structures are true minima (no imaginary frequencies) on the potential energy surfaces. The

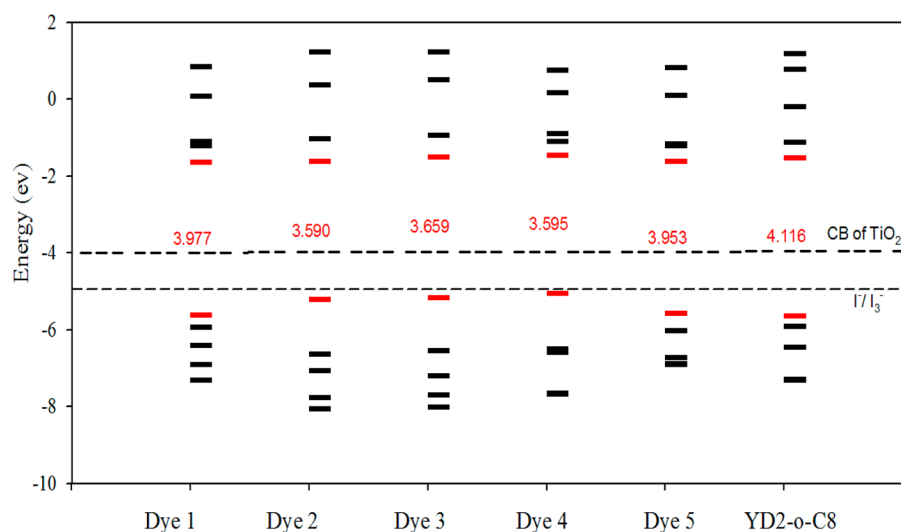


Figure 2. Molecular orbital energy levels of selected porphyrin sensitizers and the reference dye YD2-o-C8.

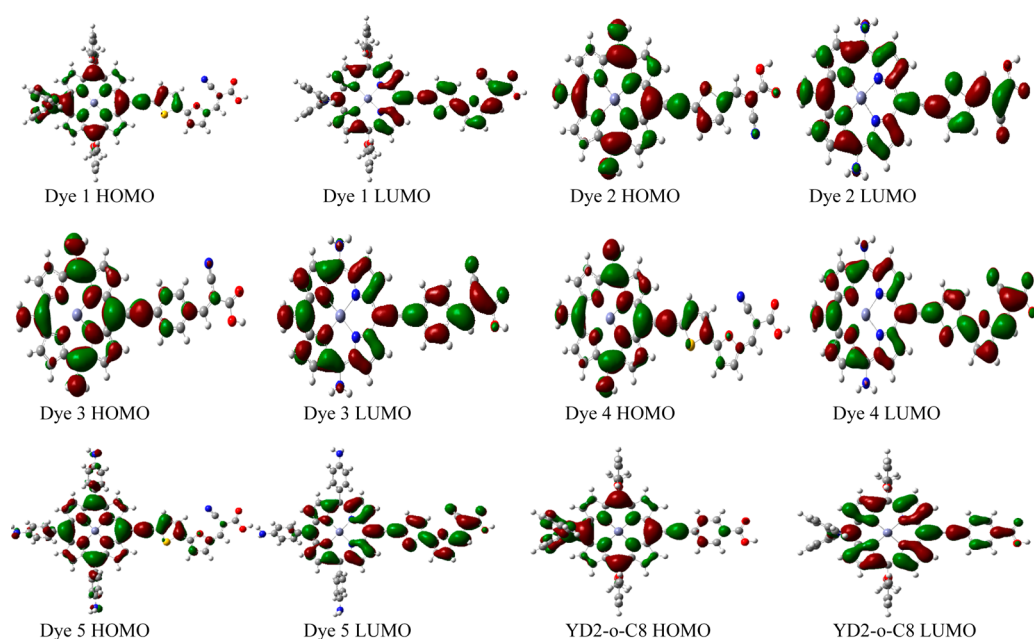


Figure 3. The frontier molecular orbital distributions for the selected porphyrin sensitizers and the reference dye YD2-o-C8.

calculated data for the HOMO, LUMO, and HOMO–LUMO gap for selected porphyrin sensitizers are listed in Table S1 (Supporting Information), and the molecular orbital graphs from HOMO–4 to LUMO+4 are shown in Figure 2. From Table S1 and Figure 2, it can be observed that the minimal energy gaps between the HOMO and LUMO is 3.590 and 3.595 eV for Dyes 2 and 4, respectively, and the energy gap values of all the dyes (1–5) are smaller than the reference dye YD2-o-C8. The HOMO–LUMO gaps of the selected porphyrin dyes are as follows: Dye 2 (3.590 eV) < Dye 4 (3.595 eV) < Dye 3 (3.659 eV) < Dye 5 (3.953 eV) < Dye 1 (3.977 eV). It is expected from previous studies that^{10,30} the sensitizers that have smaller energy gap values show higher efficiency in the DSSCs, therefore our designed dyes (1–5) may have better light harvesting ability than the reference dye. It has been noticed that the decrease in energy gap values is mainly due to the increase of HOMO energy levels (~ 0.01 – 0.58 eV) of the designed dyes. This result confirms that the

energy levels of the dye sensitizers can be tuned by means of substituting the suitable electron donating and withdrawing groups. From Table S1 it can be noted that the value of the LUMO for Dye 4 is greater than that of the reference dye and others studied here, which indicates that this may be more efficient than the others, and it can form a good charge-separated state between the donor and acceptor.³¹

The molecular orbital contribution plays a vital role in determining the charge-separated states of porphyrin analogues. In order to create an efficient charge-separated state, HOMOs must be localized on the donor subunit, and LUMOs must be localized on the acceptor and anchoring groups. Figure 3 illustrates the electron density distributions of the frontier molecular orbitals (HOMO and LUMO) for all the selected porphyrin sensitizers that are built using the CAM-B3LYP level of theory. From Figure 3, it can be seen that the electron densities of HOMOs of these sensitizers are mainly localized on the porphyrin unit, and the LUMOs are delocalized through

the cyanoacrylic acid fragments, which indicates a good charge-separated state. As we know, for a good sensitizer, the HOMO and LUMO of the whole system is dominated by the HOMO of the donor part and the LUMO of the acceptor, respectively. Comparison of the frontier molecular orbitals of the selected porphyrin dyes shows that the shapes of the HOMOs of all five porphyrins are very similar. However, the LUMO shapes of all the porphyrins are different. This difference in LUMO is due to the different strengths of the electron-withdrawing groups that are substituted in the basic porphyrin structure.

The compositions of the HOMO and LUMO for selected porphyrin sensitizers are listed in Table 1, which shows that the

Table 1. Molecular Orbital Composition (in %) of the Highest Occupied and Two Lowest Unoccupied Molecular Orbitals of Selected Porphyrin Sensitizers and Reference Dyes (YD2-o-C8 and N3)

system	orbital	anchoring ligand	π -linker	porphyrin	ancillary ligand
DYE 1	HOMO	1	18	55	26
	LUMO	22	34	38	6
	LUMO+1	32	23	37	7
DYE 2	HOMO	3	16	68	13
	LUMO	18	22	55	5
	LUMO+1	33	24	39	3
DYE 3	HOMO	2	15	70	13
	LUMO	20	21	54	5
	LUMO+1	27	15	53	5
DYE 4	HOMO	1	19	67	12
	LUMO	24	31	41	4
	LUMO+1	30	21	45	4
DYE 5	HOMO	1	19	68	12
	LUMO	20	32	46	2
	LUMO+1	34	24	40	2
YD2-o-C8	HOMO	0	6	70	23
	LUMO	2	11	80	7
	LUMO+1	0	0	96	4
	orbital	anchoring ligand	π -linker	Ru	ancillary ligand
N3	HOMO	0	4	19	77
	LUMO	13	82	4	0
	LUMO+1	12	80	7	1

HOMO is mainly contributed from the porphyrin ring, whereas the contributions of different acceptors to the LUMO of the dyes are apparently different. We know that the contributions from the anchoring group to the LUMO strongly influence the electronic coupling between the excited adsorbed dye and the 3d orbital of TiO₂.³² Our results show that the contributions from the anchoring group of the selected dyes to the LUMOs (LUMO, LUMO+1) are comparatively larger than the so far best dyes YD2-o-C8 and N3. The contribution of anchoring groups of YD2-o-C8 and N3 dyes to LUMO is only 2 and 13% respectively, whereas our selected dyes contributed more than 20%. Therefore we may anticipate that our designed dyes have more electronic coupling with the semiconductor surface and would be more favorable for electron injection into the surface than the reference dyes.

The 25 lowest-energy electronic transitions of all the selected porphyrin-sensitizers were computed with TDDFT on the basis of the optimized ground-state geometries. These were transformed, using the SWizard program,³³ into simulated spectra as

described before,³⁴ using Gaussian functions with half-widths of 3000 cm⁻¹, as shown in following equation:

$$\varepsilon(\omega) = c_1 \sum_I \frac{f_I}{\Delta_{1/2,I}} \exp\left(-2.773 \frac{(\omega - \omega_1)^2}{\Delta_{1/2,I}^2}\right) \quad (1)$$

where ε is the molar extinction coefficient, given in units of M⁻¹·cm⁻¹; the energy ω of all allowed transitions included in eq 1 is expressed in cm⁻¹; f_I and $\Delta_{1/2}$ represent the oscillator strength and the half-bandwidths (3000 cm⁻¹), respectively. All the calculations were performed using the Gaussian 09 program package.³⁵

In order to choose a relatively reliable method to calculate the absorption spectra of the porphyrin sensitizers that we considered here, we performed benchmark calculations for the reference dye (YD2-o-C8), which have recently been studied experimentally¹⁷ and considered to be an efficient dye. In order to save computational cost, we replaced C₆H₁₃ and C₈H₁₇ in the ancillary ligands by hydrogen and methyl groups, respectively. Here we used different time-dependent density functional methods such as, B3LYP,^{36,37} CAM-B3LYP,²⁹ BHandHLYP,³⁸ M06-2X,³⁹ and M06-HF^{40,41} with different basis set combinations. We have also included the solvent effects on the benchmark calculations since the effect of solvent in the calculation of the excited states is required in depicting the real environment of the system, which can give a much better agreement with the experimental values. The previous theoretical studies confirm that inclusion of the solvent effects is essential to describe the absorption spectra of the sensitizers.^{11,42,43} Here, we included tetrahydrofuran (THF) as a solvent medium, and these solvent effects were considered in the framework of the self-consistent reaction field polarizable continuum model (PCM).⁴⁴ The calculated absorption energies by different DFT methods along with experimental value of YD2-o-C8 are summarized in Table S2 (Supporting Information). By comparing the absorption energy values at B and Q bands with available experimental values, it turns out that the TD-B3LYP combined with 6-31G(d) in the THF medium provides better agreement with the experimental values. The calculated absorption energies of the B and Q bands are 437 and 642 nm, respectively, by the TD-B3LYP level of theory, whereas the experimental absorption energies of the B and Q bands are 448 and 650 nm, respectively. Therefore we choose the TD-B3LYP/6-31G(d) method in the THF environment for further calculations.

The simulated UV-vis spectra in THF along with the reference dye (YD2-o-C8) are shown in Figure 4, and the calculated transition energies, oscillator strength, and molecular orbital excitations for the most relevant transitions of the electronic absorption bands of porphyrin sensitizers (Dyes 1–5) are given in Table S3 (Supporting Information). From Figure 4, it has been clearly observed that the absorption spectra at the B and Q bands for all the selected dyes (1–5) are broadened and red-shifted significantly compared to those of YD2-o-C8. The UV-visible spectrum of YD2-o-C8 shows a Q-band at 650 nm, whereas dyes 1–5 show them at 680, 783, 772, 839, 684 nm, respectively. In particular, the Q bands of dyes 2 and 4 are the most red-shifted absorption bands among the others, which agrees well with them having the smallest HOMO–LUMO gaps, and this covers a broad range in the visible/near-infrared (vis/NIR) region, in which conventional sensitizers (N3 and others) do not have this. From Table S3 and Figure 3 it can be observed that the Q bands of all the dyes

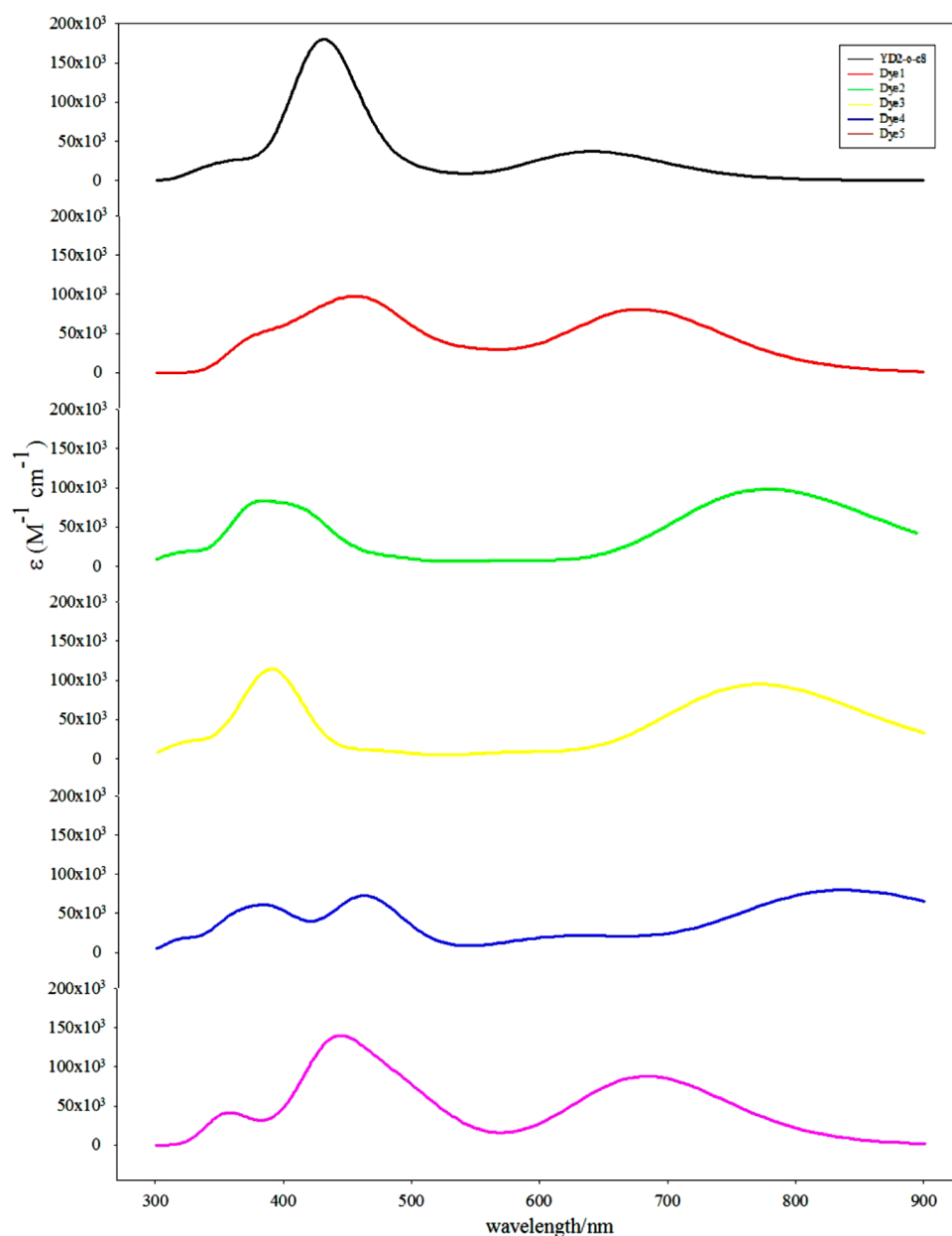


Figure 4. The simulated absorption spectra for selected porphyrin sensitizers and the reference dye YD2-o-C8.

correspond to a $\pi \rightarrow \pi^*$ transition with a strong HOMO-to-LUMO transition (more than 90%). More importantly, the oscillator strengths (which is the measure of the intensity of the absorption peaks) of the Q bands are increased dramatically compared to that of the existing dyes such as YD2-o-C8 and N3. This indicates that the introduction of thiophene in the acceptor doubled the oscillator strength of the Q-band. The broadening and red-shift of the absorption bands together with an increase in the intensity of the Q bands compared to that of the Soret band are promising strategies to solve the inadequate light-harvesting properties of the ruthenium complexes. Hence, this behavior may assist in the design of new porphyrin dyes that give increased light harvest ability.

In this work, we present the theoretical study of newly designed porphyrin dyes (1–5) for DSSC applications. We have found that Dyes 2 and 4 exhibit smaller HOMO–LUMO energy gaps and much stronger absorption in the Q band than the others. The calculated results show that the contributions

from the anchoring group of the designed dyes to the LUMOs are comparatively larger, which indicates that the designed dyes have more electronic coupling with the semiconductor surface and would be more favorable for electron injection into the surface than the so far best dyes YD2-o-C8 and N3. Our present results confirm that the $-\text{NH}_2$ -substituted porphyrin donors combined with thiophene acceptor are found to be the best sensitizers. All these features make Dyes 1–5 attractive sensitizers for the application of DSSCs in a range covering the entire visible region. Even though the designed dyes have improved optical properties, the formation of dye aggregation on the semiconductor surface will play an important role in the conversion efficiencies; hence, further studies are needed to rationalize these issues.

■ ASSOCIATED CONTENT

■ Supporting Information

Supporting results (Scheme S1 and Tables S1, S2, S3 and S4) are shown. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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