



Substituent effects on zinc phthalocyanine derivatives: A theoretical calculation and screening of sensitizer candidates for dye-sensitized solar cells

Linlin Yang^a, Lianshun Guo^a, Qianqian Chen^a, Huafei Sun^a, Hui Yan^a, Qinghua Zeng^a, Xianxi Zhang^{a,*}, Xu Pan^{b,*}, Songyuan Dai^b

^a Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China

^b Division of Solar Energy Materials and Engineering, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei, Anhui 230031, China

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ABSTRACT

A series of unsymmetrical phthalocyanine sensitizer candidates with different donor and acceptor substituents, namely ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂, were designed and calculated using density functional theory (DFT) and time-dependent DFT calculations. The molecular orbital energy levels, the molecular orbital spatial distributions and the electronic absorption spectra of the ZnPcB series molecules were compared with those of TT7 and TT8 to reveal the substituent effects of different donor and acceptor groups on the phthalocyanine compounds and select good sensitizer candidates. The results show that some of these compounds have considerably smaller orbital energy gaps, red-shifted absorption bands and better charge-separated states, causing them to absorb photons in the lower energy region. Several new absorption bands emerge in the 400–600 nm region, which makes it possible for them to become panchromatic sensitizers. This characteristic is superior to the phthalocyanine sensitizers reported previously, including the current record holder, PcS6. The sensitizer candidates screened in the current work are very promising for providing good performance and might even challenge the photon-to-electricity conversion efficiency record of 4.6% for phthalocyanine sensitizers.

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1. Introduction

Recently, dye-sensitized solar cells (DSSCs) [1–5] have been receiving significant attention as a low-cost alternative to the inorganic semiconductor-based photovoltaic devices for the conversion of sunlight into electricity. The light is absorbed by ruthenium-based dyes in most studied devices [6]; however, the main drawback of most ruthenium complex-based sensitizers is the lack of absorption or low absorption in the near-IR region of the solar spectrum [7]. Searching for novel sensitizers with an extended red response and a higher efficiency is thus very important.

Phthalocyanines are well known for their intense absorption in the red/near-IR (Q-band) regions; therefore, they are excellent alternatives for solar cell applications [8–10]. The molecular orbital energy levels and spectral properties of phthalocyanine compounds can be tuned by changing the size of their π -conjugated system or by introducing different types of substituents on their peripheral positions. Modification of the macrocycle periphery,

such as the introduction of donor or acceptor moieties, is the most common way of producing a red-shift in the Q-band absorption. Many types of unsymmetrical phthalocyanine sensitizer candidates have been designed and synthesized to obtain higher conversion efficiencies, including PCH003 with an energy conversion efficiency (η) of 1% [11], PCH001 with an η of 3.05% [12], TT1 with an η of 3.52% [13], TT15 with an η of 3.96% [14] and PcS6 with an η of 4.6% [15]. The modifications of the phthalocyanine sensitizers reported previously focus mainly on the acceptor section, which primarily alters the lowest unoccupied molecular orbital (LUMO) levels of the compounds. However, the donor sections, which mainly alter the highest occupied molecular orbital (HOMO) levels of the compounds, have been studied much less. Much more attention should be paid to optimizing the donor section from the viewpoint of tuning the absorption spectra of the phthalocyanine sensitizers.

Unfortunately, phthalocyanine chemistry is very limited because of the lack of solubility and synthetic methods that would allow selective functionalization of the unsubstituted macrocycle and because of the difficulty of preparing asymmetrically substituted derivatives from already functionalized precursors [16]. The trial-and-error methodology is not cost-efficient for the design and screening of the phthalocyanine sensitizer candidates.

* Corresponding authors. Tel.: +86 635 8230680; fax: +86 635 8239121.

E-mail addresses: zhangxianxi@lzu.edu.cn, xxzhang3@gmail.com (X. Zhang), mars.dark@hotmail.com (X. Pan).

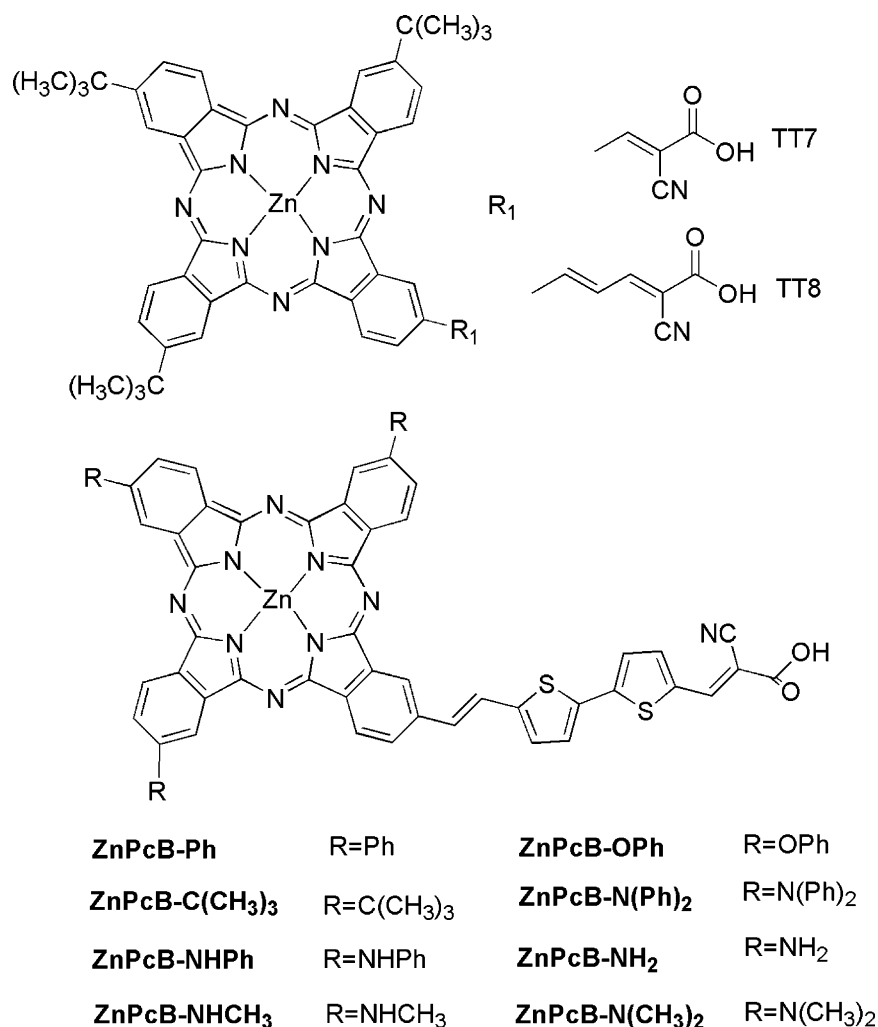


Fig. 1. The structures of TT7, TT8, and novel unsymmetrical ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂.

Quantum mechanical methodologies, however, can be of great help in the design and screening of new efficient dyes for DSSCs applications [17]. A fast and reliable theoretical method that involves calculating the molecular orbital energy levels and describing the spatial orientations as well as the electronic absorption spectra is highly desirable for screening sensitizer candidates. For ground state properties, density functional theory (DFT) is clearly the method of choice. Ground state properties are accurately described in DFT, and the scaling of the computational cost with the number of atoms is very favorable compared to high-level quantum chemistry approaches [18]. Concerning the calculation of the excited state properties, the time-dependent extension of density functional theory (TDDFT) [19] has been widely used in recent applications. DFT and TDDFT methods have been proven suitable for calculating the energy minimized structure, electronic distribution, molecular orbitals and electronic absorption spectra of a series of porphyrin and phthalocyanine derivatives [20–25]. Hence, DFT and TDDFT calculations are selected in this study.

Eight novel unsymmetrical phthalocyanine sensitizer candidates, namely ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂ as shown in Fig. 1, were designed and screened compared to TT7 and TT8 [14]. ZnPcB–tBu has the same donor groups with that of TT7 and TT8. Comparison among these three molecules

can show the substituent effect of the different bridging groups and the acceptors. The ZnPcB series complexes have the same bridging groups and acceptors while different electron-donating substituents, namely –Ph, –OPh, –C(CH₃)₃, –N(Ph)₂, –NHPh, –NH₂, –NHCH₃ and –N(CH₃)₂. Comparison among these ZnPcB series complexes can show the substituent effect of the different donor groups.

All of the compounds contain a relatively longer conjugation linker and a strong electron-withdrawing group, such as the cyanide group that is adjacent to the carboxylic acid group. The function of the carboxylic acid group is to graft the sensitizer onto the semiconductor surface and to provide intimate electronic coupling between its excited state and the conduction band of the semiconductor. The cyanide group adjacent to the carboxylic acid group is an electron-withdrawing group, which is helpful to lower the LUMO level and promote the electron transfer from the donor to the acceptor part. The electron-donating groups appear to minimize the aggregation and tune the HOMO level of the phthalocyanines. The molecular orbital energy gaps and the UV–vis absorption spectra of these compounds were found to be altered dramatically by connecting different substituents to their peripheral positions. Some phthalocyanine compounds that were screened were found to be very promising for providing good performance as sensitizers for dye-sensitized solar cells.

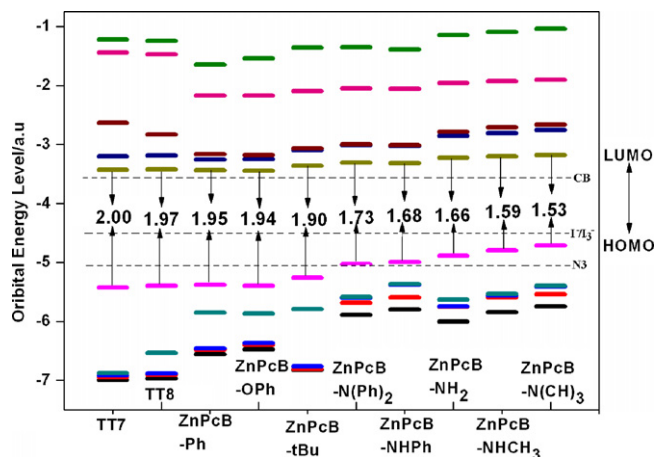


Fig. 2. Molecular orbital energy level graphs of TT7, TT8, ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂.

2. Computational method

DFT and TDDFT methods have been proven suitable for calculating the energy minimized structure, electronic distribution, molecular orbitals and electronic absorption spectra of a series of porphyrin and phthalocyanine derivatives [20–25]. DFT and TDDFT calculations are therefore selected in this study. The geometric optimizations and frequency calculations of the novel unsymmetrical ZnPcB sensitizers were calculated at the density functional B3LYP level with the LANL2DZ basis set because of the zinc atom included. The B3LYP exchange–correlation functional and LANL2DZ basis set may be not the precisest, but they are the most appropriate choice according to our requirement of screening large amount of huge molecules with relatively less cost at acceptable precision.

No imaginary frequency was found, which indicates that the optimized geometries are in the global energy minima. The optical properties of the above sensitizers were calculated with the time-dependent density functional theory (TDDFT) method using the LANL2DZ basis set at the density functional B3LYP level in ethanol. The TDDFT calculations were conducted using non-equilibrated solvent conditions with a PCM model. Forty states of each compound were considered in the TDDFT calculations. All of the calculations were performed using the Gaussian03 program [26] on the IBM P690 system in the Shandong Province High Performance Computer Center.

3. Results and discussion

3.1. Molecular orbital energy levels of the ZnPcB series molecules

The molecular orbital energy level graphs of these sensitizer candidates are shown in Fig. 2, which is arranged in descending order according to the energy gap between the LUMO and the HOMO. Ten energy levels of the molecular orbital, ranging from HOMO–4 to LUMO+4 of TT7, TT8 and the sensitizer candidates, are displayed in the figure. The data for the energy gaps are marked at the appropriate orbital energy levels. The relative positions of the conduction band of TiO₂, the redox potential of the I[–]/I₃[–], and the HOMO level of N3 are also shown in the figure.

The typical phthalocyanine sensitizers in DSSCs have the phthalocyanine moieties as the donors and the carboxyl-containing groups as the acceptors because the carboxylate groups have shown very good electronic coupling between the π* orbital of the electronically excited complex and the Ti 3d orbital of the TiO₂ film. The structures and physicochemical properties of the

Table 1

The LUMO and HOMO energy levels as well as the energy gaps of TT7, TT8, ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂ (eV).

Molecule	LUMO	LUMO–HOMO	HOMO
TT7	–3.43	2.00	–5.43
TT8	–3.43	1.97	–5.40
ZnPcB–Ph	–3.43	1.95	–5.38
ZnPcB–OPh	–3.45	1.94	–5.39
ZnPcB–C(CH ₃) ₃	–3.36	1.90	–5.36
ZnPcB–NHPh	–3.31	1.72	–5.03
ZnPcB–N(Ph) ₂	–3.31	1.68	–4.99
ZnPcB–NH ₂	–3.23	1.66	–4.89
ZnPcB–NHCH ₃	–3.20	1.59	–4.79
ZnPcB–N(CH ₃) ₂	–3.18	1.53	–4.71

phthalocyanine compounds can be easily tuned by modifying the donor and acceptor moieties. The photochemistry properties of the phthalocyanine sensitizers can thus be changed by varying the linker groups between the phthalocyanine rings and the anchoring group. The phthalocyanine compounds TT7, TT8 and ZnPcB–tBu all have tert-butyl groups as the electron-donating moieties. Their LUMO–HOMO energy gaps decrease along with the extended conjugation system. For the ZnPcB series molecules with the same acceptor, their energy gaps were also tuned gradually by introducing different donor substituents to the Pc rings.

The main orbital energy levels of TT7, TT8 and the ZnPcB series molecules, such as their LUMO, HOMO and energy gaps, are listed in Table 1 according to the descending type of energy gap. As shown in Table 1, there was a slight variation in the energy gaps of these sensitizer candidates when the carbon or oxygen served as the bridging atom that directly connects to the Pc rings. While the nitrogen atoms of the electron donor moieties were linked directly to the phthalocyanine rings, the sensitizer candidates possessed relatively low molecular orbital energy gaps. Compared with those of TT7 and TT8, the LUMO and HOMO levels of the compound ZnPcB–C(CH₃)₃ are both increased, mainly as a result of the π-extended thiophene-based linker. This extension efficiently connects the phthalocyanine to the cyanoacrylic acid binding group through one double bond. The variation of LUMO is also related to the types of donor moieties, as shown by ZnPcB–Ph to ZnPcB–N(CH₃)₂, which possess the same acceptor moieties. Hence, the theoretical screening of the ZnPcB series molecules showed that preparing phthalocyanine sensitizers in a suitable donor–acceptor structure might create a highly efficient phthalocyanine sensitizer.

The energy gaps between the HOMO and LUMO of these molecules are intimately related to the absorption band positions of the sensitizers. Smaller energy gaps can facilitate electron excitation. Consequently, more photons can be absorbed at the same time, which can contribute to obtaining a higher short circuit current density *J*_{sc} and a higher overall power conversion efficiency η.

The LUMO level of the dye must be sufficiently high for efficient charge injection into the conduction band of TiO₂, and the HOMO level should allow efficient regeneration of the oxidized dye by the electrolyte [27]. A higher LUMO level is helpful for providing a higher electron injection potential. As observed in Table 1, the novel sensitizer candidates, except for the ZnPcB–Ph and ZnPcB–OPh compounds, have higher LUMO energy levels than those of TT7 and TT8, which shows that these candidates are promising for providing higher electron injection efficiencies than those of TT7 and TT8. These observations imply that the LUMO level of the ZnPcB molecular system is sufficiently high for efficient charge injection into the conduction band of TiO₂ as shown in Fig. 2. In the case of the HOMO level, another reference is necessary for assessing the

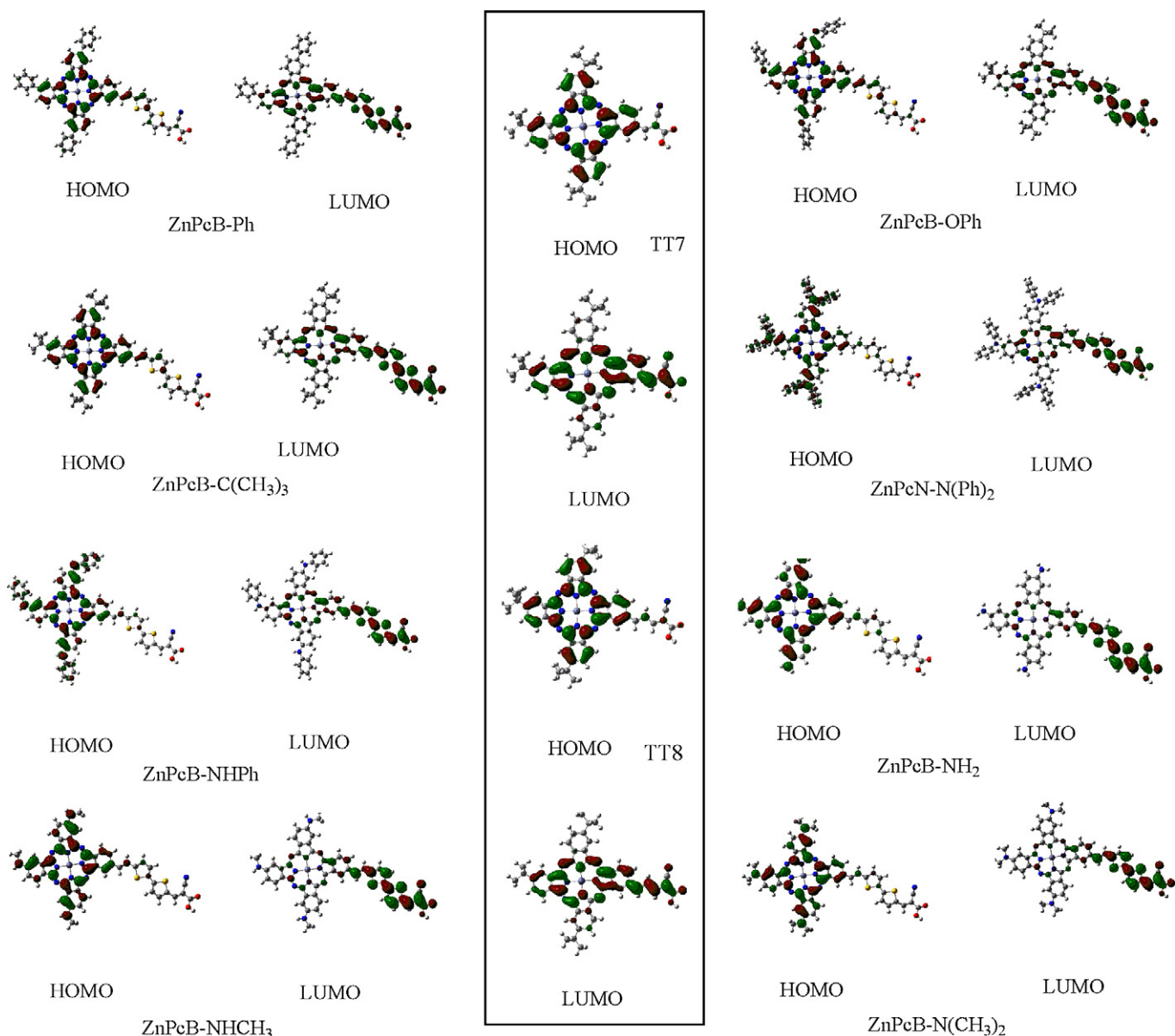


Fig. 3. Molecular orbital distributions for TT7, TT8, ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂.

sensitizer candidates because the theoretical redox potential of the electrolyte is difficult to obtain.

The driving force of the dye can indicate whether the sensitizers can be regenerated by the I_3^-/I^- couple or not. N3, the representative dye from the polypyridyl ruthenium sensitizer family, is a good choice for the reference. The sensitizer candidates with HOMO levels close to that of the N3 dye would be promising for the regeneration because the N3 dye can be regenerated very well. The highest HOMO level among the HOMOs of all of the ZnPcB molecules is -4.71 eV, while the HOMO of N3 is -5.08 eV when calculated with the same method, meaning that the highest HOMO level of ZnPcB is 0.37 eV higher than that of N3. The driving force for the regeneration of N3 is 0.75 eV [28], which indicates that the driving forces for the ZnPcB sensitizer candidates are still more than 0.38 eV. Wenger et al. [29] reported recently that sensitizers with a driving force as small as 0.15 eV can operate functionally in DSSCs and can eventually aid in reducing photovoltage losses that result from poor energetic alignment of the materials. In other words, if the HOMO energy level of dye sensitizer exceed -4.48 eV, the sensitizer would be regenerated by the I_3^-/I^- couple as shown in Fig. 2.

According to this study, the HOMO levels of the ZnPcB sensitizer candidates studied in the current work are still sufficiently low for the regeneration process.

3.2. The molecular orbital distribution of the ZnPcB series molecules

Mizuseki et al. [30] suggested that charge transport was also related to the spatial distribution and composition of the frontier orbital. To obtain more information about these sensitizer candidates, the spatial distribution and the composition of the HOMO and LUMO of the ZnPcB series molecules were calculated. The graphs are shown in Fig. 3, and the corresponding data are listed in Table 2.

The linker between the phthalocyanine ring and the anchoring group changes not only the energy level but also the spatial orientation of the molecular orbital, which further influences the efficiency of the charge-separated state. The charge transfer orientation is associated with the difference between the HOMO of the donor and the LUMO of the acceptor, which is a crucial factor that affects the electron injection efficiency. If the sensitizer

Table 2
Percent orbital composition of TT7, TT8, ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂.

Molecule	Group	HOMO	LUMO	Molecule	Group	HOMO	LUMO
TT7	C(CH ₃) ₃	0.53	0.27	ZnPcB–NHPh	NHPh	7.25	0.40
	COOH	0.38	3.10		COOH	0.10	3.73
	CN	0.39	1.59		CN	0.09	1.92
TT8	C(CH ₃) ₃	0.53	0.23	ZnPcB–N(Ph) ₂	N(Ph) ₂	11.6	0.40
	COOH	0.32	3.63		COOH	0.07	4.44
	CN	0.25	1.43		CN	0.06	2.21
ZnPcB–Ph	Ph	1.30	0.19	ZnPcB–NH ₂	NH ₂	3.48	0.09
	COOH	0.19	4.14		COOH	0.10	6.65
	CN	0.17	2.10		CN	0.08	3.19
ZnPcB–OPh	OPh	1.84	0.17	ZnPcB–NHCH ₃	NHCH ₃	4.83	0.17
	COOH	0.19	4.12		COOH	0.10	5.83
	CN	0.17	2.08		CN	0.09	2.82
ZnPcB–C(CH ₃) ₃	C(CH ₃) ₃	0.49	0.10	ZnPcB–N(CH ₃) ₂	N(CH ₃) ₂	6.34	0.12
	COOH	0.18	4.90		COOH	0.08	6.94
	CN	0.16	2.43		CN	0.06	3.30

candidates have better charge separation, then the donor should have higher HOMO and LUMO energy levels compared to those of the acceptor. This relationship means that the HOMO of the whole molecule will be dominated by the HOMO of the donor and that the LUMO will be dominated by the LUMO of the acceptor. When the donor absorbs light energy, it injects an electron into the LUMO of the acceptor, which then injects the electron into the conduction band of the TiO₂. The donor–acceptor pairs would provide realistic electronic and structural information on the sensitizer candidates.

The graphs of TT7 and TT8 were framed for the purpose of making a convenient comparison with the molecular orbital distributions of ZnPcB. As shown in Fig. 3, the HOMOs of TT7 and TT8 are mainly delocalized over the phthalocyanine skeleton, but the LUMOs of TT7 and TT8 are partly situated on the acceptor moieties. In contrast, the HOMOs of the sensitizer candidates distribute primarily on the central phthalocyanine rings, while the LUMOs locate much more at the acceptor section. The figure shows that most of the ZnPcB series molecules have better electron-separated states than those of TT7 and TT8. In other words, the photo-excited electrons can easily transfer from the phthalocyanine skeleton to the linker and the carboxylic acid group, which indicates that the photo-excitation of these sensitizers will result in migration of electrons toward the conduction band of the semiconductor.

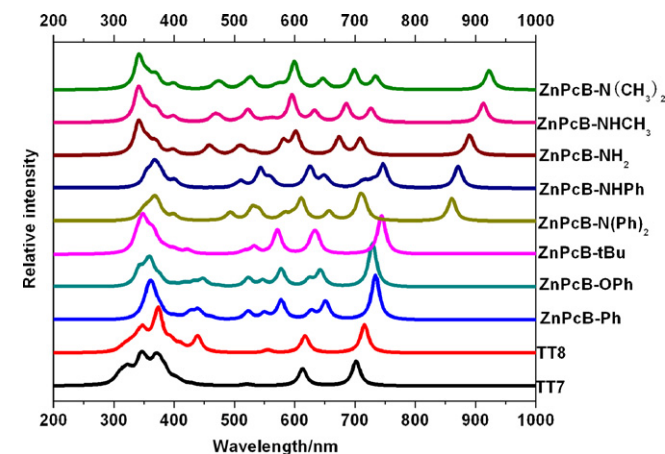


Fig. 4. Electronic absorption spectra of TT7, TT8, ZnPcB–Ph, ZnPcB–OPh, ZnPcB–tBu, ZnPcB–N(Ph)₂, ZnPcB–NHPh, ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂.

As shown in Table 2, the contributions of the carboxylic acid group to the LUMOs of these molecules are greater than those of the cyanide group to the LUMOs of all of the complexes. TT7, TT8 and ZnPcB–C(CH₃)₃ have the same donor moieties. In addition, TT7 and TT8 have similar acceptor moieties. The contribution of the cyanide group to the LUMO of TT8 is smaller than that of TT7, which may be relevant to the ratio of the cyanide group in the whole molecule. The portion of the cyanide group in ZnPcB–C(CH₃)₃ is smaller than in TT7 and TT8; however, the contribution of the cyanide group to

Table 3
Selected lowest-excited energies (ΔE), absorption wavelengths, oscillator strengths (f), and domination excitation characteristics for the low-lying singlet state of ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂.

State	Main configuration	$\Delta E/\text{eV}(\lambda/\text{nm})$	f
ZnPcB—NH ₂			
6	210 ^a → 214 ^b (0.61) 210 → 215 (0.14)	2.13(581)	0.439
11	209 → 214 (0.16) 210 → 215 (0.54) 210 → 216 (−0.20) 212 → 215 (−0.24) 212 → 216 (0.19)	2.41(515)	0.161
12	209 → 214 (0.62) 210 → 215 (−0.22) 211 → 216 (−0.12)	2.45(507)	0.186
15	207 → 216 (−0.13) 209 → 214 (−0.15) 209 → 215 (0.61) 213 → 217 (−0.23)	2.70(459)	0.153
17	208 → 214 (0.60) 210 → 217 (0.22) 212 → 217 (−0.18)	3.11(399)	0.156
ZnPcB—NHCH ₃			
6	222 ^a → 226 ^b (0.61) 222 → 227 (0.13)	2.08(596)	0.899
11	221 → 226 (0.66)	2.37(524)	0.312
14	221 → 227 (0.51) 225 → 229 (−0.44)	2.61(475)	0.153
17	220 → 226 (0.60) 222 → 229 (−0.29)	3.11(399)	0.167
ZnPcB—N(CH ₃) ₂			
6	234 ^a → 238 ^b (0.61) 234 → 239 (0.13) 235 → 240 (0.13)	2.07(600)	0.914
11	233 → 238 (0.66)	2.35(529)	0.310
14	233 → 239 (0.56) 237 → 241 (0.37)	2.59(478)	0.161
17	232 → 238 (0.60) 234 → 241 (−0.29)	3.10(400)	0.167

^a HOMO–3.

^b LUMO.

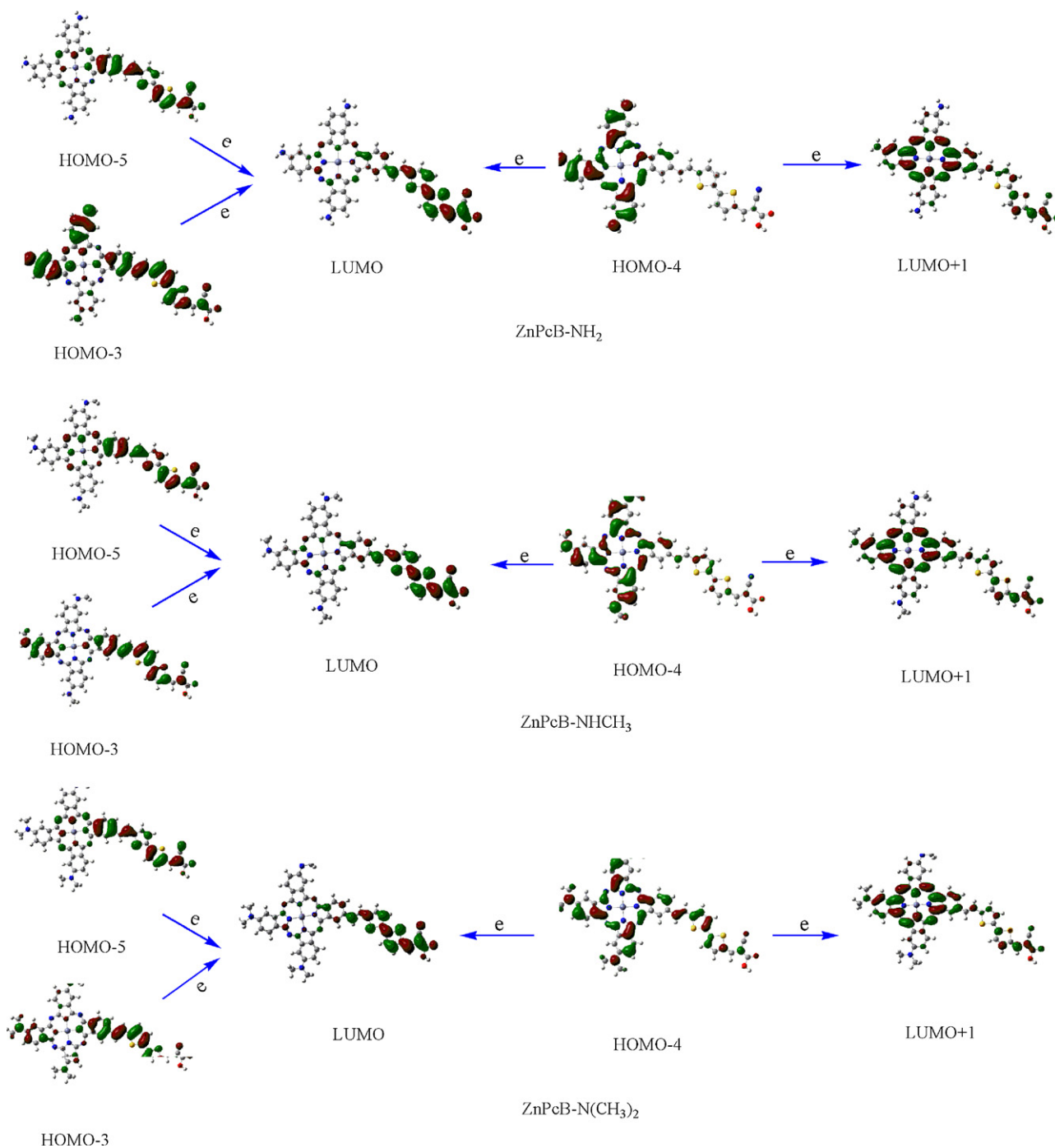


Fig. 5. Molecular orbital distribution for ZnPcB-NH_2 , ZnPcB-NHCH_3 and $\text{ZnPcB-N(CH}_3)_2$ (the blue arrow represents the direction of electron transfer).

the LUMO of the whole molecule is the largest. This relationship can be attributed to the thiophene groups of the acceptor moiety. The introduction of the thiophene group may facilitate the charge transfer from the donor moiety to the acceptor moiety.

Similar results are also observed for the other ZnPcB compounds. They have the same acceptor while different donor groups. The nitrogen bridged donors have much higher contribution to the HOMO than those of oxygen or carbon bridged donors.

In summary, the contributions of the carboxylic acid group and the cyanide group to the LUMO of these complexes correspond well with the molecular orbital distribution of these sensitizers. The donor group joined to the phthalocyanine by using nitrogen as a bridging atom has better properties than the group that employs

oxygen or carbon element as a bridge connecting it to the phthalocyanine ring.

3.3. Electronic absorption spectra

The calculated wavelengths, oscillator strengths, transition energies and molecular orbital excitation for the most relevant electron transitions of the electronic absorption bands of the zinc phthalocyanine derivatives in ethanol were obtained through TDDFT calculations. The electronic spectra are simulated by fitting to the Lorentzian line shape with a half-width at a half-maximum of 8 nm. The UV–vis spectra of these sensitizer candidates are shown

in Fig. 4 and are arranged according to the descending order of the energy gaps.

The first two curves of TT7 and TT8, as shown in the above figure, have very similar shapes and have identical numbers of absorption bands. The only difference is the position of all of the absorption bands of the TT8 red shift compared with TT7. The numbers of absorption bands of ZnPcB–Ph and ZnPcB–OPh are larger than the number of bands of ZnPcB–tBu, which could possibly result from the benzoic group's connection to the Pc rings. Similarly, the positions of the absorption bands of ZnPcB–N(Ph)₂ and ZnPcB–NHPH are situated in longer wavelength regions than for ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂, which could be attributed to the benzoic group attached to the nitrogen atom. It is also worthwhile to note that the compounds ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂ possess more decentralized absorption bands that are located at various wavelength regions compared to other complexes. This character is very helpful for the efficient absorption of the light.

An experimental maximum absorption band of TT7 emerges at 700 nm in THF [14], while a calculated maximum absorption peak of TT7 appears at 703 nm in THF and 702 nm in ethanol. This result indicates that the calculated data correspond well with the experimental data, and the solvents THF and ethanol have little influence on the position of the maximum band. ZnPcB–N(CH₃)₂ has a mostly red-shifted absorption band among these phthalocyanine sensitizer candidates, which corresponds well with its smallest HOMO–LUMO gap.

The absorption bands calculated for ZnPcB–N(Ph)₂ to ZnPcB–N(CH₃)₂ move significantly to the longer wavelength region with respect to that of TT7. They are located at 861, 871, 890, 913 and 923 nm, which are red-shifted by 159, 169, 188, 211 and 221 nm, respectively, compared to the peak of TT7 at 702 nm. Although several small absorption bands of the ZnPcB compounds all emerge in the 400–600 nm region, the numbers of those peaks of ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂ are larger, and their positions are more decentralized compared with the corresponding bands of the other compounds. These bands may complement the gap in the UV–vis spectra of the phthalocyanine compounds, which lack absorption or have low absorption in the region of 400–600 nm. The phthalocyanine dye candidates could become panchromatic sensitizers rather than the near infrared sensitizers if the new absorption bands theoretically predicted in this region could be confirmed.

Some significant excitations in this region for ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂ compounds are listed in Table 3, and the corresponding molecular orbital distributions are shown in Fig. 5. The reason why these new peaks emerge in the 400–600 nm region can be expounded as follows according to the data in the table and the molecular orbital distribution in the figure.

As shown in Table 3, the absorption bands that emerged in the 400–600 nm region are derived mainly from the electronic transitions from HOMO–3, HOMO–4 and HOMO–5 to LUMO as well as from HOMO–4 to LUMO+1. In addition, the orbital distributions of these energy levels and the corresponding channel of electron transfer are described in Fig. 5. In summary, the formation of these absorption bands can be interpreted well through the data listed in Table 3 and the orbital distribution shown in Fig. 5.

The spatial distributions of HOMO–5 and LUMO for these compounds are located mainly at the acceptor moiety, as exhibited in the figure, which means that the corresponding absorption bands are caused by the electron transfer from the π -system of the acceptors to the anchoring groups. However, the orbital distributions of HOMO–3 and HOMO–4 are not only localized at the acceptor substituents but also situated at the donor moieties, which means that both the donor and the acceptor substituents play a significant role in the formation of the other absorption bands in this region.

The phthalocyanine sensitizers TT7 and even the current record holder PcS6 have no absorption or a low absorption band in the 400–600 nm regions. Hence, the sensitizer candidates ZnPcB–NH₂, ZnPcB–NHCH₃ and ZnPcB–N(CH₃)₂ possess a certain superiority to the current record-holder PcS6, which is promising with respect to providing even higher efficiencies.

4. Conclusions

TT7, TT8 and eight novel unsymmetrical zinc phthalocyanine sensitizer candidates were calculated by means of the DFT/TDDFT method in ethanol. It is worthwhile to stress that all of the ZnPcB series dyes can provide driving forces for injecting an electron into the TiO₂ surface and for being regenerated by the I₃[–]/I[–] couple. The results show that the donor group joined to the phthalocyanine by using nitrogen as a bridging atom has better properties than the group that employs oxygen or carbon element as a bridge connecting it to the phthalocyanine ring. The thiophenes attached to the acceptor section of the phthalocyanine compound could increase the utilization rate of the sunlight. These complexes are very promising for providing better performance or developing into panchromatic sensitizers.

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