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

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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—NH_2, ZnPcB—$NHCH_3$ and ZnPcB—$N(CH_3)_2$, 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 sesitizer 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.

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.

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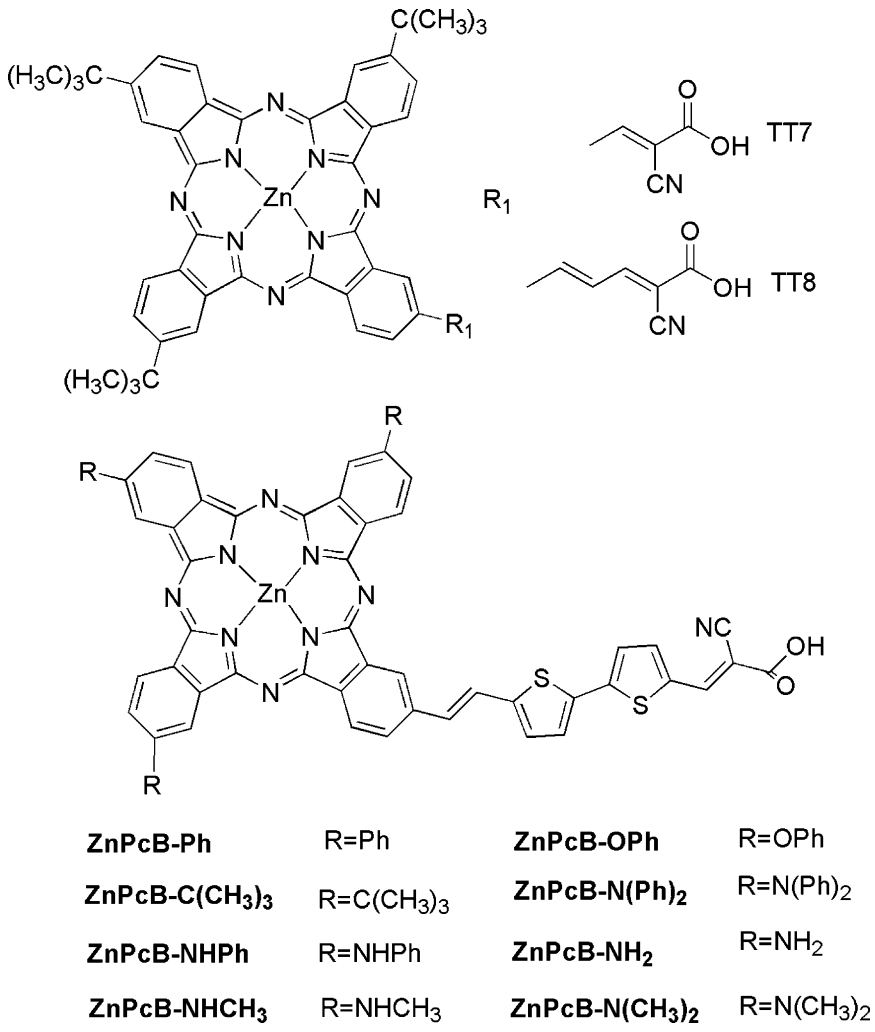

ZnPcB-Ph	R=Ph	**ZnPcB-OPh**	R=OPh
ZnPcB-C(CH$_3$)$_3$	R=C(CH$_3$)$_3$	**ZnPcB-N(Ph)$_2$**	R=N(Ph)$_2$
ZnPcB-NHPh	R=NHPh	**ZnPcB-NH$_2$**	R=NH$_2$
ZnPcB-NHCH$_3$	R=NHCH$_3$	**ZnPcB-N(CH$_3$)$_2$**	R=N(CH$_3$)$_2$

Fig. 1. The structures of TT7, TT8, and novel unsymmetrical ZnPcB—Ph, ZnPcB—OPh, ZnPcB—tBu, ZnPcB—N(Ph)$_2$, ZnPcB—NHPh, ZnPcB—NH$_2$, ZnPcB—NHCH$_3$ and ZnPcB—N(CH$_3$)$_2$.

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—NH$_2$, ZnPcB—NHCH$_3$ and ZnPcB—N(CH$_3$)$_2$ 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(CH$_3$)$_3$, —N(Ph)$_2$, —NHPh, —NH$_2$, —NHCH$_3$ and —N(CH$_3$)$_2$. 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.