

Phthalocyanines

Low-Symmetry Ω -Shaped Zinc Phthalocyanine Sensitizers having Panchromatic Light-Harvesting Property for Dye-Sensitized Solar Cells

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Abstract: Two low-symmetry phthalocyanines (Pcs) substituted with thiophene units at the non-peripheral (α) and peripheral (β) positions were synthesized and their optical, electronic-structure, and electrochemical properties were investigated. The substitution of thiophene units at the α positions of the phthalocyanine skeleton resulted in a red shift of the Q band and significantly modified the molecular-orbital electronic distributions just below the HOMO and just above the LUMO, with distortion of the typical Gouterman four-orbital arrangement of MOs. Two amphiphilic Ω -shaped ZnPcs (α PcS1 and α PcS2) bearing a π -conjugated side chain with an adsorption site at an α position of the Pc macrocy-

cle were synthesized as sensitizers for dye-sensitized solar cells (DSSCs). The absorption spectra of α PcS1 and α PcS2 showed red shifted Q bands and a broad band from 350 to 550 nm assignable to the intramolecular charge-transfer transition from the ZnPc core to the side chains. Time-dependent DFT calculations provided a clear interpretation of the effect of the thiophene conjugation on the typical phthalocyanine core π MOs. Compound α PcS1 was used as a light-harvesting dye on a TiO₂ electrode for a DSSC, which showed a panchromatic response in the range 400–800 nm with a power conversion efficiency of 5.5% under one-sun conditions.

Introduction

Phthalocyanines (Pcs) and their metal complexes (MPcs) are synthetic analogues of porphyrins and have attracted special attention as sensitizers in solar-energy conversion applications because of their intense absorption bands in the red/near-infrared (NIR) region (Q bands), high molar extinction coefficients, and excellent stabilities.^[1] The molecular engineering of MPc-based sensitizers has been widely explored to improve photon-to-electron power conversion efficiency (PCE) in organic-based solar cells.^[2] The PCE values for MPc-based dye-sensitized solar cells (DSSCs) have been enhanced significantly by applying molecular-design rules such as a low-symmetry structure, steric isolation, intramolecular push-pull structure, and optimization of the adsorption site.^[3] The expansion of the light-harvesting wavelength range in the NIR region is one of the key issues to be solved in order to enhance the solar-cell performance. To date, several attempts have been made to expand the light-harvesting wavelength range of MPc-based DSSCs by extension of the π -conjugated system and substitution of peripheral positions.^[4] We recently reported the lightharvesting property in the NIR region of ring-expanded sensitizer NcS1, and a DSSC sensitized with NcS1 showed a photoresponse at wavelengths in the 600-850 nm region.[4c] However, these MPc-based solar cells exhibited little sensitization in the region between the B and the Q bands due to the absence of transitions in this area. Co-sensitization with different dyes that have complementary absorption properties in the visible region has been applied to cover whole region from visible to NIR.^[3d, 5] The fabrication of co-sensitized DSSCs requires careful control of the adsorption process to optimize the ratio of the

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two dyes on the TiO₂ surface. Ince et al. reported the panchromatic response of hybrid MPc-based sensitizers having peripheral $\pi\text{-conjugated}$ bis-thiophene substituents. $^{\text{\tiny [6]}}$ However, the reported PCEs of DSSCs sensitized with the hybrid sensitizers were less than 3% due to their strong tendency for intermolecular aggregation. In this work, we investigated the optical effects of substitution of thiophene at the α or β position of ZnPcs 1 and 2. Since α -substituted ZnPc 1 showed a larger red shift of the Q band, we chose it for the design of two new hybrid chromophoric systems, $\alpha PcS1$ and $\alpha PcS2$, in which a π conjugated side chain with an adsorption site was introduced at an α position of the MPc to act as the photosensitizer for DSSCs. A photoresponsive cell sensitized with $\alpha PcS1$ provided a PCE of 5.5% under a simulated air mass with AM1.5 global sunlight; $\alpha PcS1$ could convert photon energy to electronic energy over a wide wavelength range from the visible to the NIR regions of the solar spectrum to electronic energy.

Results and Discussion

Effect of thiophene substitution positions on the optical and electrochemical properties

The effect of substituents on the position and intensity of the Q bands has been systematically investigated.^[7] Peripheral substitution with electron-donating groups such as alkoxyl and alkylthio groups at the α positions of the MPc skeleton shifts the Q band to longer wavelength compared to β -substituted counterparts, and these effects can be reasonably explained by considering the magnitude of the atomic orbital coefficients of the carbon atoms derived from molecular orbital calculations.^[7b] However, the effect of the introduction of thiophene units at the α and β positions of the MPc skeleton on the optical and electrochemical properties has not been examined. We synthesized two structural isomers **1** and **2** having two thiophene units at the α or β positions on one side of the macrocycle (Figure 1) and investigated their optical, electronic structure and electrochemical differences.

Phthalonitriles **3** and **4** bearing two thiophene rings at different positions were synthesized by palladium-catalyzed coupling reactions of 3,6-dihydroxyphthalonitrile and 4,5-dichlo-

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Figure 1. Substitution patterns in the $ZnPc(tBu)_4$ core of compounds 1 and 2.

rophthalonitrile, respectively (Scheme 1). The phthalonitrile having thiophene rings at the 3- and 6-positions was synthesized by Migita-Kosugi-Stille cross-coupling between 3,6-bis-(trifluoromethanesulfonyloxy)phthalonitrile and 2-(tributylstannyl)thiophene in 81% yield.^[8,9] The 4,5-dithiophenephthalonitrile was synthesized by Suzuki-Miyaura cross-coupling of 4,5dichlorophthalonitrile with 2-thiopheneboronic acid by using 2-dicyclohexylphosphino-2',6'-methoxybiphenyl (SPhos) as ligand in 88% yield.^[10] After treatment with N-bromosuccinimide (NBS), the resulting bromides were treated with 4-tert-butylphenylboronic acid in the presence of [Pd(PPh₃)₄] to produce 3 and 4 in 90 and 86% yield, respectively. The peripherally substituted, low-symmetry ZnPcs 1 and 2 were prepared by mixed condensation reaction between 4-tert-butylphthalonitrile and 3 or 4 in 3:1 molar ratio in N,N-dimethylaminoethanol (DMAE) in the presence of Zn(AcO)₂, and were isolated by column chromatography and preparative HPLC.^[11]

Figure 2 a shows absorption spectra of α -substituted **1** and β -substituted **2** in THF. While the absorption spectrum of ZnPc(*t*Bu)₄ lacking thiophene rings showed the expected sharp and strong Q band at 672 nm (Supporting Information, Figure S2), the low-symmetry **1** and **2** displayed broader, split Q bands red shifted by about 20 nm relative to that of



 $\begin{array}{l} \textbf{Scheme 1. a) $ 2-(Tributylstannyl) thiophene, $ [Pd(PPh_3)_{a}], LiCl, dioxane; b) $ NBS, DMF; c) $ [Pd(PPh_3)_{a}], $ 1 \ M $ K_2CO_3 $ aq., DME; d) $ 2-Thiopheneboronic acid, $ Pd(AcO)_{7}, $ SPhos, $ K_3PO_4, toluene. $ \end{array} }$

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ZnPc(tBu)₄. Furthermore, the molar extinction ε at the Q band for 1 was significantly lower than that of 2 (Table 1). Splitting of the Q band was not observed in the previously reported zinc α -octaphenylphthalocyanine complexes.^[13] Thus, the introduction of the thiophene units at both the α and β positions of the MPc skeleton strongly affects the electronic properties of the MPc core π system. The emission maximum of 1 is red shifted by 14 nm relative to that of 2, and this suggests that 1 has a narrower bandgap than 2 (Figure 2a). The magnetic circular dichroism (MCD) spectrum of 1 showed a Faraday Aterm-like curve with a peak at 672 nm and trough at 697 nm (Figure 2b). This is assignable as a pseudo-Faraday A term produced by superimposition of close lying Faraday B terms of opposite sign because of the approximate C_{2v} symmetry.^[14] This suggests splitting of the LUMO and LUMO+1 energy levels of the low-symmetry complexes. The HOMO energy levels of 1 and 2 were also determined by using a differential pulse voltammetric (DPV) technique (Supporting Information, Figure S3). The first oxidation potentials of 1 (+0.02 V vs. Fc $^+$ /Fc) and **2** (+0.04 V vs. Fc⁺/Fc) are negatively shifted compared to that of $ZnPc(tBu)_4$ (+0.09 V vs. Fc⁺/Fc). The increased energy of the HOMO level of 1 compared with that of 2 indicates the effective destabilization of the HOMO levels by substitution at α positions.



Figure 2. a) Absorption and emission spectra of 1 (solid and dotted lines) and 2 (dashed and dashed-dotted line) in THF. b) MCD spectra of 1 (solid line) and 2 (dashed line) in THF.

DFT calculations at the CAM-B3LYP/6-31G* level of theory (6-31G* is also termed 6-31G(d))^[15] (Gaussian 09) were carried out for ZnPc, **1**, and **2** to enhance our understanding of the spectroscopic and electrochemical data. Figure 3 shows energy-level diagrams of **1**, **2**, and the core ZnPc, and calculated electronic absorption spectra of **1** and **2**. Whereas the estimated LUMO and LUMO+1 levels of unsubstituted ZnPc are degenerate, the degeneracy of LUMO and LUMO+1 levels for **1** and **2** is broken by substitution with thiophene units. The appearance of thiophene-related orbitals between the HOMO and the

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band gap.

Table 1. Optical and electrochemical data for 1 and 2.							
Dye	Absorption ^[a]	Emission ^[b]	E _{HOMO} ^[d]	E ₀₋₀ ^[e]	E _{LUMO} ^[f]		
	[nm] (10 ⁻⁵ ε [m^{-1} cm ⁻¹]	[nm] $(\phi_{\rm f})^{\rm [c]}$	[V vs. Fc ⁺ /Fc]	[eV]	[V vs. Fc ⁺ /Fc]		
1	694 (0.68), 678 (0.69), 347 (0.72)	713 (0.1)	+ 0.02	1.76	-1.74		
2	690 (1.56), 675 (1.1), 350 (0.82)	698 (0.2)	+ 0.04	1.79	-1.75		
[a] In THF. [b] In THF by exciting at the peak position of the B band. [c] Fluorescence quantum yield ϕ_t was determined with ZnPc(tBu) ₄ as standard in THF ($\phi_t = 0.3^{[1/2]}$). [d] E_{HOMO} was determined from the first oxidation potential of the dye in <i>o</i> -DCB solution; [e] Optical bandgap E_{0-0} was determined from the intercept of the normalized absorption and emission spectra. [f] E_{HIMO} was calculated from the HOMO and the							

typical Gouterman HOMO-1,^[16] which are identified by the nodal patterns for the +/-4 angular momentum of the core porphyrazine ring, is an important aspect of the use of the thiophene units. Whereas HOMO-1 for Pcs is always lower in energy by a significant amount (here >2 eV) for peripheral substituents that do not interact with the conjugation, no orbitals are usually introduced between the HOMO and its paired four-node orbitals HOMO-1 nominally the 2nd of the e_u pair in symmetry. The energy splitting correlates well with the Qband intensity.^[17] Time-dependent (TD) DFT calculations reproduced the spectral differences between 1 and 2 (Figure 3 b and Table S1 of the Supporting Information) very well. The split Q bands can be assigned to the HOMO \rightarrow LUMO and $HOMO\!\rightarrow\!LUMO\!+\!1$ transitions of the Pc ligand. The lowestlying electronic transition of 1 was red shifted by 13 nm compared with that of 2 due to the narrowing of the HOMO-LUMO bandgap through destabilization of the HOMO level and stabilization of the LUMO level. For isolated MOs like those in ZnPc, the HOMO-LUMO gap can closely predict the Q-band energy.^[17] These results reveal that substitution of thiophene units at the α positions of the Pc skeleton leads to expansion of the light-harvesting region in the NIR region by red shifting of Q bands as well as tuning of the HOMO and LUMO energy levels to optimize the photoinduced electron-transfer reaction for the DSSC system. Thus, the α -substituted ZnPc sensitizers were used to prepare α PcS1 and α PcS2 by adding an adsorption site that was designed and synthesized to improve the enhancement of DSSC performance.

Low-symmetry ZnPc sensitizers for DSSCs

We designed and synthesized two ZnPc-based dyes based on 1, α PcS1 and α PcS2, in which a cyanocarboxyl group was attached at one terminal of the conjugated thiophene side chain on the Pc ring (Figure 4). Since the ring expansion of Pc leads to more red shifting of the Q band,^[18] the ring-expanded dye α PcS2 was synthesized from 1,4-dihydroxy-2,3-dicyanonaphthalene, with the expectation of further enhancement of the light-harvesting region for DSSCs. For both dyes, six bulky 2,6diisopropylphenoxyl substituents were added to the peripheral positions of the ZnPc core to prevent the formation of intermolecular aggregates.^[3f,19] Phthalonitriles **7** and **12** bearing a protected terminal aldehyde group were synthesized by stepwise coupling reactions, as shown in Scheme 2 (Supporting Information, Scheme S1). Low-symmetry AB₃-type ZnPcs were synthesized by statistical tetramerization of the bulky 4,5-bis(2,6-diisopropyl)phenoxyphthalonitrile **8** and **7** or **12**. After deprotection of the pinacol-protected aldehyde group, the aldehyde terminal group was allowed to react with an excess of cyanoacetic acid in the presence of piperidine to afford **aPcS1** and **aPcS2**. We also synthesized symmetrical ZnPc **5** as a reference compound using phthalonitrile **8**.^[19]



Figure 3. a) Calculated energy levels of 1 (left), ZnPc (middle), and 2 (right); b) Calculated absorption spectra of 1 (red) and 2 (blue) derived from CAM-B3LYP/6-31G(d) DFT calculations. LUMO and LUMO + 1 at about -2 eV are degenerate for ZnPc, and slightly split for 1 and 2.

Optical data for $\alpha PcS1$ and $\alpha PcS2$

Figure 5 shows the absorption and MCD spectra of $\alpha PcS1$ and $\alpha PcS2$ in THF. The attachment of thiophene side chains at the α positions on one side of the Pc macrocycle resulted in a red shift and splitting of the Q band compared to symmetrical ZnPc 5. The Q MCD bands of $\alpha PcS1$ and $\alpha PcS2$ appeared at longer wavelengths and their bandwidths were larger than that of 5 (particularly the Q band for $\alpha PcS1$), and hence the Q-band MCD can be interpreted as a pseudo-Faraday A terms. The ring-expanded $\alpha PcS2$ shows a sharp Q band at 708 nm, which is slightly red shifted compared with that of $\alpha PcS1$. The splitting width of the Q band for $\alpha PcS2$ predicted by the TDDFT calculation (15.0 nm) was narrower than that of $\alpha PcS1$

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Figure 4. Structures of αPcS1, αPcS2, and 5.^[19]



Scheme 2. a) 4,4,5,5-Tetramethyl-2-[5-(4,4,5,5-tetrametyl-1,3-dioxolan-2-yl)thien-2-yl]-1,3,2-dioxaborolane, [Pd(PPh₃)₄], DME, 1 \bowtie K₂CO₃ aq.; b) 4-*tert*-Butylphenylboronic acid, DME, 1 \bowtie K₂CO₃ aq.; c) Zn(AcO)₂, DMEA, *o*-DCB; d) 10% CHI aq., THF; e) Piperidine, cyanoacetic acid, CHCI₃.

(29.2 nm). This narrow splitting width of **\alphaPcS2** results in increased sharpness of the Q MCD pseudo-Faraday *A* term and larger absorption coefficient of the Q band. The first oxidation potential of α PcS2, measured by DPV in *ortho*-dichlorobenzene (*o*-DCB), was +0.02 V versus Fc⁺/Fc, which is more negative than that of α PcS1 by 50 mV (Supporting Information, Figure S5). The TDDFT calculation also suggested destabilization of the HOMO energy level for α PcS2 by annulation with a benzene unit. Therefore, we can conclude that the HOMO-LUMO gap of α PcS2 decreased because of destabilization of the HOMO level through annulation with a benzene ring.



Figure 5. a) Absorption and b) MCD spectra of $\alpha PcS1$ (solid line), $\alpha PcS2$ (dashed line) and 5 (dashed-dotted line) in THF solution.

Identification of a thiophene-specific charge-transfer band from the MCD spectra and TDDFT calculations

A new broad band appeared in the 380-480 nm region in the absorption spectrum of $\alpha PcS1$ and $\alpha PcS2$ that is not seen for 3, 4, or 5. The MCD spectra in the 380-480 nm regions are surprisingly very similar for aPcS1, aPcS2, and 5. The lack of significant MCD intensity under the broad absorption band in the 380-480 nm region implies that negligible angular momentum is involved in these electronic transitions.^[20] This is consistent with the TDDFT calculations for $\alpha PcS1$ and $\alpha PcS2$, that is, the transition identified between the B and Q bands for $\alpha PcS1$ at 467 nm (f=0.69) is assigned to the HOMO \rightarrow LUMO+2 transition (Figure 6, Table 3, Supporting Information, Figure S6), where the LUMO+2 (#549) MO is not a core π ring MO. The transition for $\alpha PcS1$ showed negative solvatochromism with increasing solvent polarity, which indicates a change of the energy level in this excited state following the interaction between the dye and solvent molecules (Supporting Information,

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Table 2. Optical and electrochemical data for αPcS1 and αPcS2.							
Dye	Absorption ^(a)	Emission	Absorption ^[c]	E _{HOMO}	E ₀₋ ^{0[f]}	E _{LUMO} ^[g]	
	[nm] (10 ⁻⁵ ε [M^{-1} cm ⁻¹]	[nm] ($\phi_{ m f}$) ^[b]	[nm]	[V vs. NHE]	[eV]	[V vs. NHE]	
αPcS1	702 (1.0), 687 (1.1), 359 (0.83)	713 (0.1)	692	$+ 0.70^{[d]} (+ 0.88)^{[e]} + 0.65^{[d]} (+ 0.80)^{[e]}$	1.76	-1.06 (-0.88)	
αPcS2	708 (2.2), 357(0.97)	715 (0.02)	708		1.74	-1.09 (-0.94)	
[a] In THF. [b] Fluorescence quantum yields ϕ_i were determined with ZnPc(tBu) ₄ as standard in THF (Supporting Information, Figure S6). [c] On TiO ₂ elec-							

[a] in THE. [b] Fluorescence quantum yields ϕ_f were determined with ZhPC(Bu)₄ as standard in THE (Supporting Information, Figure S6). [c] On TiO₂ electrode. [d] E_{HOMO} was determined from the first oxidation potential of the dye in *o*-DCB solution. [e] E_{HOMO} was determined from the first oxidation potential of the dye in *o*-DCB solution. [e] E_{HOMO} was determined from the first oxidation potential of dye-stained TiO₂ electrode. [f] Optical bandgap E_{0-0} was estimated from the crossing point of the normalized absorption and emission spectra. [g] E_{LUMO} was calculated as $E_{HOMO} - E_{0-0}$.

Figure S7).^[16b,21] The introduction of the electron-accepting cyanocarboxyl group on one end of the conjugated side chain is considered to create this intramolecular charge-transfer (ICT) transition from the electron-rich Pc core to the side chain. Because of the close connection to the Pc core, this broad absorption band will contribute to improving the light-harvesting efficiency in the wavelength region between the Q and the B bands in DSSCs.

Performance of α PcS1- and α PcS2-based DSSCs

Mesoporous TiO₂ electrodes were immersed in THF solutions of **\alphaPcS1** and **\alphaPcS2** (5×10⁻⁵ M) at room temperature to give dye-stained TiO₂ electrodes by formation of an ester linkage between the anchoring carboxyl groups of the dyes and the TiO₂ surface. In general, the adsorption of dyes on the TiO₂ surface results in absorption-spectral and electrochemical changes because of deprotonation of the anchoring group^[22] or electronic interaction between the dye LUMO and the conduction band of TiO₂.^[23] Whereas the Q-band positions of **aPcS1** and **aPcS2** were almost the same as those in solution, red shifts of the Q-band onsets and positive shifts of the HOMO levels from the electrochemical measurements were observed (Supporting Information, Figure S8, Table 2). The adsorption densities of **aPcS1** and **aPcS2** on the TiO₂ surface were determined from the absorbance of the ZnPcs released from the dye-stained TiO₂ electrodes. The adsorption densities of **aPcS1** and **aPcS2** are lower than that previously reported for **PcS18** (1.4× 10^{-4} mol cm⁻³).^[4c] The occupied areas of **aPcS1** and **aPcS2** on the TiO₂ surface were estimated to be 3.0 nm² by using their



Figure 6. DFT-calculated energy level diagrams and molecular orbital surfaces of α PcS1 (left) and α PcS2 (right) (The HOMO is #546 in α PcS1 and #571 in α PcS2).

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Table 3. Calculated transition energies, oscillator strengths f, and configurations.						
Dye	Energy [eV (nm)]	f	Configurations (main contributions)			
αPcS1	1.87 (661.50)	0.69	546 (H)→547 (L) (90%)			
	1.96 (632.22)	0.62	546→547 (3%), 546→548 (89%)			
	2.65 (467.27)	0.69	545→549 (9%), 546→549 (62%), 546→550 (8%)			
	3.04 (408.40)	0.19	545→547 (73 %)			
	3.14 (395.40)	0.08	545→548 (37%), 545→549 (20%)			
	3.25 (382.10)	0.52	542→548 (21 %), 545→548 (26 %), 545→549 (17 %)			
	3.27 (379.10)	0.19	541→547 (73 %)			
	3.29 (376.47)	0.04	542→548 (50%), 545→548 (19%)			
	3.34 (371.17)	0.08	543->548 (66 %)			
	3.44 (360.45)	0.11	546→550 (65%)			
αPcS2	1.84 (672.50)	0.66	571 (H)→572 (L) (82%), 571→573 (4%), 571→574 (8%)			
	1.89 (657.54)	0.67	571→573 (84%), 571→574 (9%)			
	2.59 (477.96)	0.18	571→572 (9%), 571→574 (66%), 571→575 (12%)			
	3.07 (403.38)	0.82	565→574 (2%), 569→572 (11%), 569→574 (15%), 570→572 (19%), 570→574 (9%), 571→574 (11%), 571→575 (13%)			
	3.12 (397.76)	0.27	569→574 (7%), 571→575 (65%)			
	3.23 (383.90)	0.01	557			
	3.30 (376.28)	0.12	568→572 (60%)			
	3.36 (368.73)	0.05	566→572 (11%), 566→573 (47%), 566→574 (14%)			
	3.37 (367.42)	0.06	566→573 (14%), 570→573 (40%)			
	3.46 (358.47)	0.04	570→572 (41%), 570→574 (15%)			

optimized molecular models (Supporting Information, Figure S9). These estimated areas are about 1.6 times of that of **PcS18**. The enlargement of the molecular size by the attachment of the conjugated side chain to the ZnPc core reduced the packing density of the dyes in the self-assembled monolayer on the TiO_2 surface.

The photovoltaic performances of the **\alphaPcS1** and **\alphaPcS2** cells were evaluated with a liquid electrolyte containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M Lil, 0.05 M l₂, and 0.5 M *tert*-butylpyridine in acetonitrile. Figure 7 a shows the *J*–*V* curves measured under AM 1.5G simulated full-sunlight il-



Figure 7. a) *J–V* curves for DSSCs based on α **PcS1+CDCA** (\odot) and α **PcS2+CDCA** (\triangle) under AM 1.5G simulated solar light. b) IPCE spectra of DSSCs based on α **PcS1+CDCA** (\odot) and α **PcS2+CDCA** (\triangle).

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 α PcS1 cell showed a short-current density J_{sc} of 10.1 mA cm⁻², an open-circuit voltage V_{oc} of 0.61 V, and a fill factor (FF) of 0.73, giving an overall PCE of 4.5% (Supporting Information, Figure S10 and Table 4). In contrast, the α PcS2-based cell showed a lower J_{scr} leading to a lower PCE value of 3.2%. Chenodeoxycholic acid (CDCA) was used as a co-adsorbent in the DSSCs to prevent dye aggregation on the TiO₂ surface.^[24] The half-width of the Q band of $\alpha PcS1$ decreased from 63 to 56 nm following the addition of CDCA (Supporting Information, Figure S8), which suggests that the aggregates on the TiO₂ surface were dissociated by co-adsorption with CDCA. The α PcS1-based cell with co-adsorbed CDCA provided a higher PCE of 5.5% compared with the cell without CDCA (Supporting Information, Figure S11). The onset voltage in dark current-voltage measurements was improved by co-adsorption with CDCA, and this implies an enhanced blocking effect of $I_3^{\,-}.^{\mbox{\scriptsize [24b]}}$ Since the enlarged dyes make space within the dye layer on the TiO₂ surface, electrons in the TiO₂ are lost by contact with I₃⁻ in the electrolyte passing through the loose packing layer of dye molecules. The dissociation of aggregates and the enhancement of the blocking of I_3^- by co-adsorption with CDCA could improve the performance of aPcS1 and aPcS2 cells. The incident photon-to-current (IPCE) spectrum of the $\alpha PcS1$ -based cell followed the absorption feature of $\alpha PcS1$ adsorbed on the TiO₂ electrode, and showed a panchromatic response from the visible to the NIR regions. The α PcS1 cell showed a photoresponse in the wavelength range of 400-600 nm corresponding to the broad ICT band. The substitution with oligothiophene units bearing an adsorption site at the α positions of the Pc skeleton results in absorption in the typical ZnPc window at 500 nm and expansion of the light-harvesting range by 50 nm compared to that of PcS18. However, the maximum IPCE value at the Q band of α PcS1 was 47%, which is lower than that of PcS18 (ca. 80%). This implies

lumination (100 mW cm²) for cells based on the two ZnPcs. The

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a lower electron-injection efficiency from the excited ZnPc to the conduction band of the TiO₂ electrode compared to **PcS18**. This is probably caused by poor electronic coupling between the ZnPc core and the adsorption site at the LUMO and LUMO + 1 levels, as shown in Figure 6. Further improvement of the IPCE values can be achieved by structural optimization of the π -conjugated linker between the ZnPc core and the adsorption site.

Table 4. Performance of ZnPc-sensitized DSSCs.						
Dye ^[a]	[CDCA] [mм]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF	PCE [%]	Absorption density [10 ⁵ mol cm ⁻³]
a DeC 1	0	0.61	10.1	0.73	4.5	6.8
urcs i	0.5	0.62	11.9	0.75	5.5	4.1
aBesa	0	0.60	7.1	0.74	3.2	5.2
urc52	0.5	0.63	7.8	0.77	3.8	2.8
[a] [Dye] = 0.05 mм in THF.						

Conclusions

We have demonstrated expansion of the light-harvesting wavelength range of ZnPc-based DSSCs by hybridization with π -conjugated side chains. The effect of substitution at the α position of low-symmetry ZnPcs on the optical and electrochemical properties was investigated. We found that substitution with thiophene units at the α positions resulted in red shifting of the Q band into the NIR region as well as tuning of the HOMO and LUMO energy levels. Two ZnPc-based photosensitizers $\alpha PcS1$ and $\alpha PcS2$, in which the π -conjugated side chain bearing an adsorption site was attached at the α positions of the Pc ring, were synthesized by stepwise coupling reactions. The presence of the nonperipheral thiophene groups resulted in insertion of thiophene-based MOs between the HOMO and the typical four-node a_{2u} HOMO-1 of the Gouterman model. Similarly, there were new thiophene-related MOs just above the LUMO and LUMO + 1. The absorption spectra of $\alpha PcS1$ and $\alpha PcS2$ showed a broad band from about 380 to 480 nm, which was assigned to an ICT transition from the ZnPc core to the side chain on the basis of the lack of significant MCD signal intensity and the predicted spectral bands from TDDFT calculations. Whereas the previously reported ZnPc-based sensitizers for DSSCs did not harvest in the green region, the $\alpha PcS1$ showed a panchromatic response in the range 400-800 nm with a PCE of 5.5% when used as a lightharvesting dye on a TiO₂ electrode for DSSCs under one-sun conditions. The hybridization of chromophores is one way to design panchromatic ZnPc-based sensitizers with high energyconversion efficiencies.

Experimental Section

General

NMR spectra were recorded for ¹H and ¹³C in $CDCI_3$ solution with a Bruker AVANCE 400 FT NMR. Chemical shifts are reported relative

to internal TMS. UV/Vis spectra and fluorescence spectra were measured with a JASCO V-650 and a JASCO FP-750. MALDI-TOF mass spectra were obtained with a Bruker autoflex spectrometer with dithranol as matrix. High-resolution mass spectra with electrospray ionization were obtained with a Bruker Daltonics micrOTOF II. DPV data were recorded with an ALS 720C potentiostat, and electrochemical experiments were performed under purified nitrogen gas. Nanoporous TiO₂ working electrodes (thickness: 6 µm) were prepared by applying pastes of TiO₂ nanoparticles having 15-20 nm diameter onto transparent conducting glass substrates (SnO2:F on 1.8 mm-thick glass substrate, Asahi Glass). The TiO₂ electrodes were immersed in 0.05 mm THF solutions of α PcS1 and α PcS2 for 3 h, and the dye-stained electrodes were used as working electrodes. The reference electrode was Ag/AgCl, corrected for junction potentials by referencing to the ferrocenium/ferrocene (Fc⁺/Fc) couple. DFT and TDDFT calculations were performed with the Coulomb-attenuating B3LYP (CAM-B3LYP) functional and 6-31G* basis set as implemented in the Gaussian 09 software suite. $\ensuremath{^{[25]}}$ The fabrication of DSSCs and the evaluation of solar-cell performance was conducted according to the methods reported by us.^[3d]

All chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed with activated alumina (Wako, 200 mesh). Recycling preparative gel permeation chromatography was carried out with a JAI recycling preparative HPLC with CHCl₃ as eluent. Analytical TLC was performed with commercial Merck plates coated with aluminum oxide 60 F_{254} .

Synthesis of α PcS1

A mixture of 7 (34 mg, 0.54 µmol), 8 (78 mg, 0.16 mmol), and Zn(CH₃COO)₂ (9.8 mg, 0.54 µmol) in 6 mL of DMAE and 3 mL of o-DCB was heated at 160°C with stirring overnight. After the reaction mixture was cooled, it was diluted with MeOH. A precipitate formed, which was collected by filtration and washed with MeOH several times to remove excess Zn ion. The residue was purified by column chromatography on activated alumina by eluting with CH₂Cl₂, followed by recycling preparative HPLC to give 9 (27 mg, 24%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 8.93$ (d, J = 4.0 Hz, 1 H, thiophene H), 8.78 (d, J=4.0 Hz, 1 H, thiophene H), 8.34 (s, 1 H, PcH), 8.32 (s, 1H, PcH), 8.21 (s, 1H, PcH), 8.12 (s, 1H, PcH), 8.15 (s, 2H, PcH), 8.14 (s, 2H, PcH), 7.64-7.54 (m, 10H, ArH), 7.49-7.42 (m, 12H, ArH), 7.19 (d, J=3.6 Hz, 1 H, thiophene H), 7.15 (d, J=3.6 Hz, 1 H, thiophene H), 6.41 (d, J=4.0 Hz, 1H, thiophene H), 6.34 (d, J=4.0 Hz, 1 H, thiophene H), 6.28 (s, 1 H, CH), 3.49-3.34 (m, 12 H, CH), 1.47 (s, 9H, C(CH₃)₃), 1.44 (s, 6H, CH₃), 1.36 (s, 6H, CH₃), 1.22 ppm (brs, 72 H, CH₃); MALDI-TOF MS (dithranol): m/z 2140.35 [M] (100%); calcd for C₁₃₃H₁₄₂N₈O₈S₃Zn: *m/z* 2139.94.

Complex **9** (27 mg, 0.13 µmol) was dissolved in a 1.2 molL⁻¹ aqueous solution of HCl (3 mL) and THF (6 mL). The mixture was heated at 50 °C for 3 h and then poured into water. Ethyl acetate was added, and the organic layer was washed with water until neural pH, dried over anhydrous Na₂SO₄, and the solvent was evaporated. The residue was purified by column chromatography on activated alumina with CH₂Cl₂ to give **10** (20 mg, yield 78%). ¹H NMR (400.13 MHz, CDCl₃): δ = 9.71 (s, 1H, CHO), 8.84 (d, *J*=4.0 Hz, 2H, thiophene H), 8.34 (s, 1 H, PcH), 8.27 (s, 1 H, PcH), 8.21 (s, 2 H, PcH), 8.15 (s, 4 H, PcH), 7.74 (d, *J*=4.0 Hz, 1 H, thiophene H), 7.49–7.44 (m, 8H, ArH), 7.38 (s, 4H, ArH), 7.33 (d, *J*= 4.0 Hz, 1 H, thiophene H), 6.54 (d, *J*=4.0 Hz, 1 H, thiophene H), 6.42 (d, *J*=4.0 Hz, 1 H, thiophene H), 3.48–3.34 (m, 12 H, CH), 1.47 (s, 9 H, C(CH₃)₃), 1.26 ppm (s, 72 H, CH₃); MALDI-TOF MS (dithranol):

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m/z 2037.9 [*M*] (100%); calcd for C₁₂₇H₁₃₀N₈O₇S₃Zn: m/z 2038.9; IR (ATR): $\tilde{\nu} = 1666.50 \text{ cm}^{-1}$ (CHO).

Cyanoacetic acid (8.3 mg, 9.8 µmol) and a catalytic amount of piperidine were added to a solution of **10** (20 mg, 9.8 µmol) in CHCl₃ (3 mL). After stirred for overnight at 65 °C, water (50 mL) was poured into the reaction mixture. The mixture was stirred till precipitate formed. Isolation of the precipitate by vacuum filtration afforded the pure product, **αPcS1**, as a dark green solid (18 mg, 90%). ¹H NMR (400.13 MHz, CDCl₃): δ = 8.82 (brs, 1H, CH=), 8.35-8.30 (m, 4H, thiophene H), 8.23–8.05 (m, 8H, PcH), 7.60–7.54 (m, 10H, ArH), 7.49–7.45 (m, 12H, ArH), 6.51–6.49 (m, 2H, thiophene H), 3.47–3.36 (m, 12H, CH), 1.60 (s, 18H, C(CH₃)₃), 1.25 (brs, 72H, CH₃); MALDI-TOF MS (dithranol): *m/z* 2105.2 [*M*+H] (100%); calcd for C₁₃₀H₁₃₁N₉O₈S₃Zn: *m/z* 2105.9; UV/Vis (THF): λ_{max} (log ε) = 702 (5.05), 687 (5.05), 359 nm (4.92).

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- [1] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 2010, 110, 6595-6663.
- [2] a) M. V. Martínez-Díaz, G. de La Torre, T. Torres, *Chem. Commun.* 2010, 46, 7090-7108; b) L. Martín-Gomis, F. Fernández-Lázaro, Á. Sastre-Santos, *J. Mater. Chem. A* 2014, *2*, 15672-15682.
- [3] a) J.-J. Cid, J.-H. Yum, S.-R. Jang, M. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, M. Grätzel, T. Torres, Angew. Chem. Int. Ed. 2007, 46, 8358-8362; Angew. Chem. 2007, 119, 8510-8514; b) P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikantam, J.-H. Yum, K. Kalyanasundaram, M. Grätzel, M. K. Nazeeruddin, Angew. Chem. Int. Ed. 2007, 46, 373-376; Angew. Chem. 2007, 119, 377-380; c) S. Mori, M. Nagata, Y. Nakahata, K. Yasuta, R. Goto, M. Kimura, M. Taya, J. Am. Chem. Soc. 2010, 132, 4054-4055; d) M. Kimura, H. Nomoto, N. Masaki, S. Mori, Angew. Chem. Int. Ed. 2012, 51, 4371-4374; Angew. Chem. 2012, 124, 4447-4450; e) M.-E. Ragoussi, J.-J. Cid, J.-H. Yum, G. de La Torre, D. D. Censo, M. Grätzel, M. K. Nazeeruddin, T. Torres, Angew. Chem. Int. Ed. 2012, 51, 4375-4378; Angew. Chem. 2012, 124, 4451-4454; f) M. Kimura, H. Nomoto, H. Suzuki, T. Ikeuchi, H. Matsuzaki, T. N. Murakami, A. Furube, N. Masaki, M. J. Griffith, S. Mori, Chem. Eur. J. 2013, 19, 7496-7502; g) T. Ikeuchi, H. Nomoto, N. Masaki, M. J. Griffith, S. Mori, M. Kimura, Chem. Commun. 2014, 50, 1941 - 1943.
- [4] a) L. Yu, X. Zhou, Y. Yin, Y. Liu, R. Li, T. Peng, *ChemPlusChem* 2012, *77*, 1022–1027; b) B. Lim, G. Y. Margulis, J.-H. Yum, E. L. Unger, B. E. Hardin, M. Grätzel, M. D. McGehee, A. Sellinger, *Org. Lett.* 2013, *15*, 784–787; c) T. Ikeuchi, S. Mori, N. Kobayashi, M. Kimura, *Inorg. Chem.* 2016, *55*, 5014–5018.
- [5] a) C. Qin, Y. Numata, S. Zhang, A. Islam, X. Yang, K. Sodeyama, Y. Tateyama, L. Han, Adv. Funct. Mater. 2013, 23, 3782–3789; b) J.-H. Yum, S.-R.

Jang, P. Walter, T. Geiger, F. Nüesch, S. Kim, J. Ko, M. Grätzel, M. K. Nazeeruddin, *Chem. Commun.* **2007**, *44*, 4680–4682.

- [6] M. Ince, F. Cardinali, J.-H. Yum, M. V. Martínez-Díaz, M. K. Nazeeruddin, M. Grätzel, T. Torres, Chem. Eur. J. 2012, 18, 6343 – 6348.
- [7] a) N. Kobayashi, N. Sasaki, Y. Higashi, T. Osa, *Inorg. Chem.* 1995, 34, 1636–1637; b) N. Kobayashi, H. Ogata, N. Nonaka, E. A. Luk'yanets, *Chem. Eur. J.* 2003, 9, 5123–5134.
- [8] K. Sakamoto, E. Ohno-Okumura, T. Kato, H. Soga, J. Porphyrins Phthalocyanines 2010, 14, 47–54.
- [9] S. Y. Al-Raqa, J. Porphyrins Phthalocyanines 2006, 10, 55-62.
- [10] S. Eu, T. Katoh, T. Umeyama, Y. Matano, H. Imahori, *Dalton Trans.* 2008, 40, 5476-5483.
- [11] J. Mack, N. Kobayashi, Chem. Rev. 2011, 111, 281-321.
- [12] D. M. Guldi, I. Zilbermann, A. Gouloumis, P. Vázquez, T. Torres, J. Phys. Chem. B 2004, 108, 18485–18494.
- [13] T. Fukuda, S. Homma, N. Kobayashi, Chem. Eur. J. 2005, 11, 5205-5216.
- [14] J. Mack, M. J. Stillman, N. Kobayashi, Coord. Chem. Rev. 2007, 251, 429– 453.
- [15] a) J. Mack, J. Stone, T. Nyokong, J. Porphyrins Phthalocyanines 2014, 18, 630–641; b) S.-H. Chou, C.-H. Tsai, C.-C. Wu, D. Kumar, K.-T. Wong, Chem. Eur. J. 2014, 20, 16574–16582.
- [16] J. Mack and M. J. Stillman, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2002**, Chapter 103, pp. 43–116.
- [17] J. Mack, Y. Asano, N. Kobayashi, M. J. Stillman, J. Am. Chem. Soc. 2005, 127, 17697–17711.
- [18] N. Kobayashi, J. Mack, K. Ishii, M. J. Stillman, Inorg. Chem. 2002, 41, 5350.
- [19] N. B. McKeown, S. Makhseed, K. J. Msayib, L.-L. Ooi, M. Helliwell, J. E. Warren, Angew. Chem. Int. Ed. 2005, 44, 7546–7549; Angew. Chem. 2005, 117, 7718–7721.
- [20] S. Omomo, Y. Maruyama, K. Furukawa, T. Furuyama, H. Nakano, N. Kobayashi, Y. Matano, *Chem. Eur. J.* **2015**, *21*, 2003 – 2010.
- [21] J. T. Lin, P.-C. Chen, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, M.-C. P. Yeh, Org. Lett. 2009, 11, 97–100.
- [22] a) Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, J. Phys. Chem. C 2007, 111, 7224–7230; b) X.-H. Zhang, Z.-S. Wang, Y. Cui, N. Koumura, A. Furube, K. Hara, J. Phys. Chem. C 2009, 113, 13409–13415.
- [23] C. Kim, H. Choi, S. Kim, C. Baik, K. Song, M.-S. Kang, S. O. Kang, J. Ko, J. Org. Chem. 2008, 73, 7072–7079.
- [24] a) S. Zhang, X. Yang, C. Qin, Y. Numata, L. Han, J. Mater. Chem. A 2014, 2, 5167–5177; b) J. Li, W. Wu, J. Yang, J. Tang, Y. Long, J. Hua, Sci. China Chem. 2011, 54, 699–706.
- [25] Gaussian 09, Revision A.1 ed., M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

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FULL PAPER

Phthalocyanines

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Low-Symmetry Ω-Shaped Zinc Phthalocyanine Sensitizers having Panchromatic Light-Harvesting Property for Dye-Sensitized Solar Cells

Hybrid Chromophore System



Omega sensitizers: Two amphiphilic Ω shaped zinc phthalocyanines, denoted α **PcS1** and α **PcS2**, bearing a π -conjugated side chain with an adsorption site (see figure), were synthesized as sensitizers for dye-sensitized solar cells (DSSCs). Compound α **PcS1** was used as a light-harvesting dye on a TiO₂ electrode for DSSCs, which showed a panchromatic response in the range 400– 800 nm with a power conversion efficiency of 5.5% under one-sun conditions.

Panchromatic Phthalocyanine Sensitizer



A π -conjugation side chain with an adsorption site was introduced at an α position of a zinc phthalocyanine (ZnPc) macrocycle. The compound (α PcS1) shows a red shifted Q band and a broad absorption band from 350 to 550 nm, which is assigned to the intramolecular charge–transfer transition from the ZnPc core to the side chains. TD-DFT calculations provide a clear interpretation of the effect of the thiophene conjugation on the typical π molecular orbitals of the Pc core. The α PcS1 cell showed a panchromatic response in the range 400–800 nm with a power conversion efficiency of 5.5% when used as a lightharvesting dye on a TiO₂ electrode for the dye-sensitized solar cell under one-sun conditions. For more information, see the Full Paper by M. Kimura et al. on page

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