

Unsymmetrically Substituted Phthalocyanine Carboxylic Acids

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New unsymmetrically substituted phthalocyanine carboxylic acids were synthesized by mixed cyclotetramerization of substituted phthalonitriles. The UV-vis absorption and fluorescence spectra and quantum yields of fluorescence were studied in comparison to symmetrically substituted analogues. The distribution of phthalocyanine carboxylic acids on the surface of titanium dioxide was studied by UV-vis absorption spectroscopy.

Keywords: Unsymmetrically substituted phthalocyanines, photophysical properties, dye-sensitized solar cells.

Несимметрично замещенные фталоцианинкарбоновые кислоты

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Синтезированы новые несимметрично замещенные фталоцианинкарбоновые кислоты методом смешанной циклотетрамеризации замещенных фталонитрилов. Изучены электронные спектры поглощения и флуоресценции в УФ и видимой области и квантовые выходы флуоресценции в сравнении с симметрично замещенными аналогами. Методом электронной спектроскопии поглощения изучен характер распределения фталоцианинкарбоновых кислот на поверхности диоксида титана.

Ключевые слова: Несимметрично замещенные фталоцианины, фотофизические свойства, фотоэлектрохимические солнечные элементы.

Introduction

In recent years, phthalocyanines (Pcs) have attracted significant attention as photosensitizers in dye-sensitized solar cells (DSSCs)^[1-8] due to their high photochemical/electrochemical stability and intense absorption in the red-near infrared region. In DSSC, photosensitizer is usually attached to the titanium dioxide surface *via* one or two carboxylic groups which have to be π -conjugated with the chromophore for efficient photoinduced electron transfer to TiO₂. The highest power conversion efficiency (PCE) of 13 % of a DSSC was obtained for an unsymmetrical porphyrin derivative as photosensitizer.^[9] The advantage of phthalocyanines is their strong absorption in the red-near infrared (NIR) region. But they have very little absorption in the middle of the visible region, and highest PCE of Pc-based DSSC is only 6.4 %.^[6] Phthalocyanine-based DSSCs can be interesting as components of “smart windows” mostly transparent for visible light, or in combination with other photosensitizers^[8-12] to improve red-NIR response of the cells. First phthalocyanines for DSSCs were prepared in the group of Wöhrle in 1999^[13] but the efficiency did not exceed 1 %. Later, different structural modifications of the phthalocyanine molecule were made to improve the efficiency of DSSCs, such as:

- Modification of the central metal ion and extraligands. Mainly Zn^{II}, Ru^{II}, Si^{IV}, Ti^{IV} phthalocyanines were studied as photosensitizers. In most cases Zn^{II} showed the highest efficiency. The influence of the central metal ion is discussed in detail by Torres *et al.*^[8]

- Modification of the linker between the carboxylic group and the phthalocyanine core. It was shown^[1-8] that rigid conjugated linkers are essential for efficient charge transfer from the excited Pc molecule to TiO₂. The highest efficiencies were achieved when one carboxylic group was connected directly or *via* an ethynyl linker to one of the benzene rings of a phthalocyanine.^[1-8]

- Modification of substituents at other benzene rings. Unsymmetrically substituted phthalocyanines of the ABBB type containing one or two carboxylic groups at one benzene ring of A are preferable. The main disadvantage of phthalocyanines as photosensitizers is their strong aggregation on the surface which leads to excited states quenching and decreased charge separation efficiency. The PCE of 5.9–6.4 % was achieved with the help of very bulky substituents at three benzene rings B like 2,6-diphenylphenoxy-, 2,6-diisopropylphenoxy-, 4-methoxy-2,6-diphenylphenoxy-, 2,6-dibutoxyphenoxy-, *etc.*, whereas “traditional” *tert*-butyl groups were not bulky enough to suppress aggregation (the resulting PCE was only 3.5 %).^[8] The side effect of using too bulky substituents is the reduced light absorption due to decreased dye adsorption density, together with lower yields of the Pcs and expensive starting materials. Therefore it is important to find “minimal” substituents, just enough to suppress the Pc aggregation on the surface. One possible way is to use six smaller substituents, other possibility is to use three bulky substituents instead of six at the three benzene rings B.

Based on the before mentioned results described in the literature it was the aim in the present study, to prepare structurally optimized unsymmetrically substituted zinc(II) phtha-

locyanines with six 2,6-dimethylphenoxy substituents and with three 2,6-di-*tert*-butyl-4-methylphenoxy substituents at three benzene rings B. The fourth benzene ring A contains a directly connected carboxylic group. Their fluorescence properties and aggregation behaviour on TiO₂ surface was studied.

Experimental

Materials

Methyl 3,4-dicyanobenzoate **1**, 4,5-bis(2,6-dimethylphenoxy)-phthalonitrile **2**, 4-(2,6-di-*tert*-butyl-4-methylphenoxy)phthalonitrile **5**, zinc 2,3,9,10,16,17,23,24-octakis-(2,6-dimethylphenoxy)-phthalocyanine **8** and zinc 2,9,16,23-tetrakis-(2,6-di-*tert*-butyl-4-methylphenoxy)phthalocyanine **9** were prepared as previously described.^[7,14-16] Analytical reagent grade (Sigma-Aldrich) sodium hypochlorite solution (14 % active chlorine), nickel(II) chloride hexahydrate, 2,2'-bipyridyl, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and titanium dioxide nanoparticles (Degussa P25 grade, 21 nm primary particle size) were used as purchased. Zinc acetate dihydrate (analytical reagent grade, Sigma-Aldrich) was dried under vacuum at 120 °C for 4 h. The solvents used for the preparations (Sigma-Aldrich, VWR, reagent grade) were dried, distilled and stored under dry conditions. All syntheses were carried out under dry high purity nitrogen. Silica gel 60 (40–63 μ m; VWR) was used for chromatographic separations.

Measurements

¹H NMR spectra were recorded using a Bruker Avance DPX-200 (200 MHz) spectrometer, electrospray ionisation (ESI) MS spectra using a Bruker Esquire LC mass-spectrometer and IR spectra with a FSM 1201 spectrometer. The UV-vis absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 spectrophotometer. The adsorption of phthalocyanine carboxylic acids on TiO₂ was carried out as previously described,^[1] by immersion of TiO₂ powder in 0.1 mM Pc solution for 4 h followed by centrifugation and washing the precipitate with THF. The UV-vis spectra on the surface of titanium dioxide were recorded in KBr pellets prepared in the same way as for IR spectroscopy. The final spectra were obtained by subtracting the spectrum of pure TiO₂ in KBr which is essentially a spectrum of light dispersion by TiO₂ particles. The fluorescence spectra were obtained at room temperature using Perkin-Elmer LS55 with a standard 150W 50 Hz xenon flash lamp as a source. For all spectra quartz cuvettes 1×1 cm were used. The wavelength employed for the excitation was 610 nm, the slit width 2.5 nm for excitation and for emission. The optical density of the main Q-band maximum was in the range of 0.2 to 0.3 to minimize reabsorption. The compound **8** with $\Phi_F = 0.28$ measured earlier^[15] with higher precision was used as a reference for fluorescence quantum yield estimations.

Syntheses

Zinc(II) 2-pentoxycarbonyl-9,10,16,17,23,24-hexakis(2,6-dimethylphenoxy)phthalocyanine (3). A mixture of 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (0.74 g, 2 mmol) **2**, methyl 3,4-dicyanobenzoate **1** (93 mg, 0.5 mmol), zinc acetate (0.22 g, 1.2 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 mL) in *n*-pentanol (5 mL) was heated under reflux for 6 hours. After cooling the mixture was diluted with methanol (20 mL), the precipitate was collected by centrifugation, washed with methanol, dried under vacuum and dissolved in toluene. The resulting solu-

tion was separated by column chromatography on silica gel (60 Å, 40-63 μm) eluting with toluene-diethyl ether gradually increasing diethyl ether content from 0 to 6 vol. %. The second green fraction was collected. After solvent evaporation and reprecipitation from toluene with hexane, the precipitate was dried under vacuum at 60 °C. Dark green powder. Yield 130 mg (18 %). *m/z* (ESI, CH₂Cl₂/DMF 1:10): 1411 [(M+H)⁺], 1433 [(M+Na)⁺], 1449 [(M+K)⁺], 1445 [(M+Cl)⁺]. ¹H NMR (200 MHz, [D₆]DMSO + 0.01 M KCN) δ_H ppm: 9.55 s (1H), 9.15 d (8.1 Hz, 1H), 8.59 (d8.1 Hz, 1H), 8.16 s (1H), 8.14 s (1H), 7.90 br s (2H), 7.85 br s (2H), 7.30-7.67 br m (18 H), 4.43 t (6.6 Hz, 2H), 2.28-2.44 br m (36H), 1.88 br m (2H), 1.42-1.59 br m (4H), 1.00 br t (6.8 Hz, 3H). IR (mineral oil) ν_{max} cm⁻¹: 1720, 1698 sh.

Zinc(II) 2-carboxy-9,10,16,17,23,24-hexakis(2,6-dimethylphenoxy)phthalocyanine (4). To a solution containing **3** (70 mg, 0.05 mmol) in THF (10 mL) an aqueous 3 M sodium hydroxide solution (1 mL) was added. The mixture was stirred under reflux for 16 hours. After that, the solution was neutralized, concentrated to a small volume (approx. 2 mL), acidified with concentrated hydrochloric acid to pH 3 and diluted with water (10 mL). The precipitate was collected by centrifugation, washed with water and dried under vacuum at 60 °C. Dark green powder. Yield 61 mg (91 %). *m/z* (ESI, CH₂Cl₂/DMF 1:10): 1341 [M+H]⁺, 1363 [M+Na]⁺, 1379 [M+K]⁺, 1385 [M-H+2Na]⁺, 1401 [M-H+Na+K]⁺, 1375 [M+Cl]⁺. ¹H NMR (200 MHz, [D₆]DMSO + 0.01 M KCN) δ_H ppm: 9.48 s (1H), 8.88 d (8.1 Hz, 1H), 8.58 d (8.1 Hz, 1H), 8.15 s (1H), 8.14 s (1H), 7.89 m (2H), 7.85 br s (2H), 7.34-7.62 m (18H), 2.30-2.44 br m (36H). IR (mineral oil) ν_{max} cm⁻¹: 1692 br.

Phthalocyanines **6** and **7** were prepared by the same procedures as for compounds **3** and **4**, from phthalonitriles **1** (93 mg, 0.5 mmol) and **5** (0.69 g, 2 mmol).

Zinc(II) 2-pentoxycarbonyl-9,16,23-tris(2,6-di-tert-butyl-4-methylphenoxy)phthalocyanine (mixture of isomers) (6). Dark blue powder. Yield 109 mg (16 %). *m/z* (ESI, CH₂Cl₂/DMF 1:10): 1345 [M+H]⁺, 1367 [M+Na]⁺, 1379 [M+Cl]⁺. ¹H NMR (200 MHz, [D₆]DMSO + 0.01 M KCN) δ_H ppm: 9.73-9.89 br m (1H), 9.12-9.46 br m (7H), 8.64-8.78 br m (1H), 7.96-8.27 br m (3H), 7.08-7.30 br m (6H), 4.55 br t (6.3 Hz, 2H), 2.02-2.19 br s (9H), 1.88-2.02 br m (2H), 1.46-1.69 br m (4H), 1.26-1.46 br m (54H), 1.01 br t (7.1 Hz, 3H). IR (mineral oil) ν_{max} cm⁻¹: 1721, 1696 sh.

Zinc(II) 2-carboxy-9,16,23-tris(2,6-di-tert-butyl-4-methylphenoxy)phthalocyanine (mixture of isomers) (7). Dark blue powder. Yield 56 mg (88 %). *m/z* (ESI, CH₂Cl₂/DMF 1:10): 1275 [M+H]⁺, 1297 [M+Na]⁺, 1313 [M+K]⁺, 1319 [M-H+2Na]⁺, 1335 [M-H+Na+K]⁺, 1309 [M+Cl]⁺, 1331 [M-H+Na+Cl]⁺. ¹H NMR (200 MHz, [D₆]DMSO + 0.01 M KCN) δ_H ppm: 9.85 br s (1H), 9.14-9.55 br m (7H), 8.67-8.78 br m (1H), 7.90-8.27 br m (3H), 7.02-7.26 br m (6H), 2.03-2.18 br m (9H), 1.28-1.44 br m (54H). IR (mineral oil) ν_{max} cm⁻¹: 1719 br.

Results and Discussion

Synthesis

The preparation and spectral characterization of new unsymmetrically substituted zinc(II) phthalocyanines with one directly connected carboxylic group are described.

All phthalocyanines were synthesized by mixed cyclotetramerization of the corresponding substituted phthalonitriles. At first 2,6-dimethylphenoxy- and 2,6-di-tert-butyl-4-methylphenoxy substituted phthalonitriles **2** and **5** were obtained using conventional methods based on aromatic nucleophilic substitution.^[14,16] The carboxy substituted phthalonitrile **1** was prepared as described previously.^[7]

Then in a second step unsymmetrically substituted zinc phthalocyanines **3** and **6** were synthesized in good yields by the statistical mixed cyclotetramerization of the carboxy-substituted phthalonitrile **1** and the bulky phenoxy-substituted phthalonitriles **2** and **5** in the presence of the organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and zinc acetate in boiling pentanol (Figures 1 and 2). The obtained statistical mixtures of phthalocyanines was separated by column chromatography on silica gel using gradient elution with a toluene-diethyl ether mixture. The pentyl ester group is used as a "protecting group" necessary for a successful

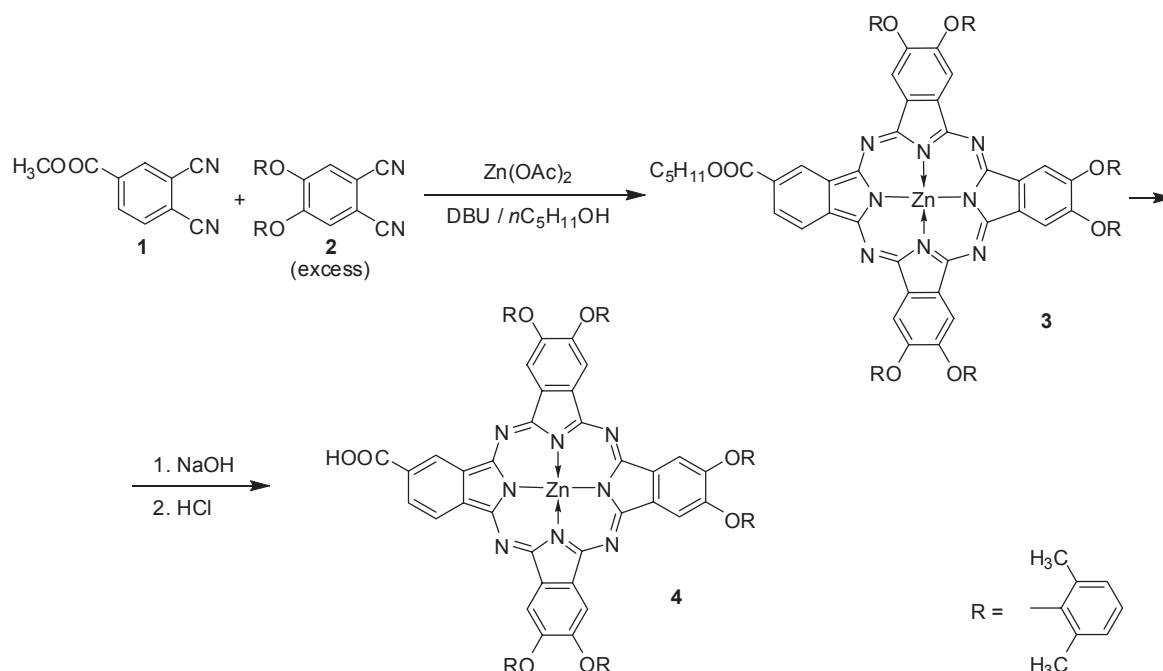


Figure 1. Synthesis of the unsymmetrically substituted phthalocyanines **3** and **4**.

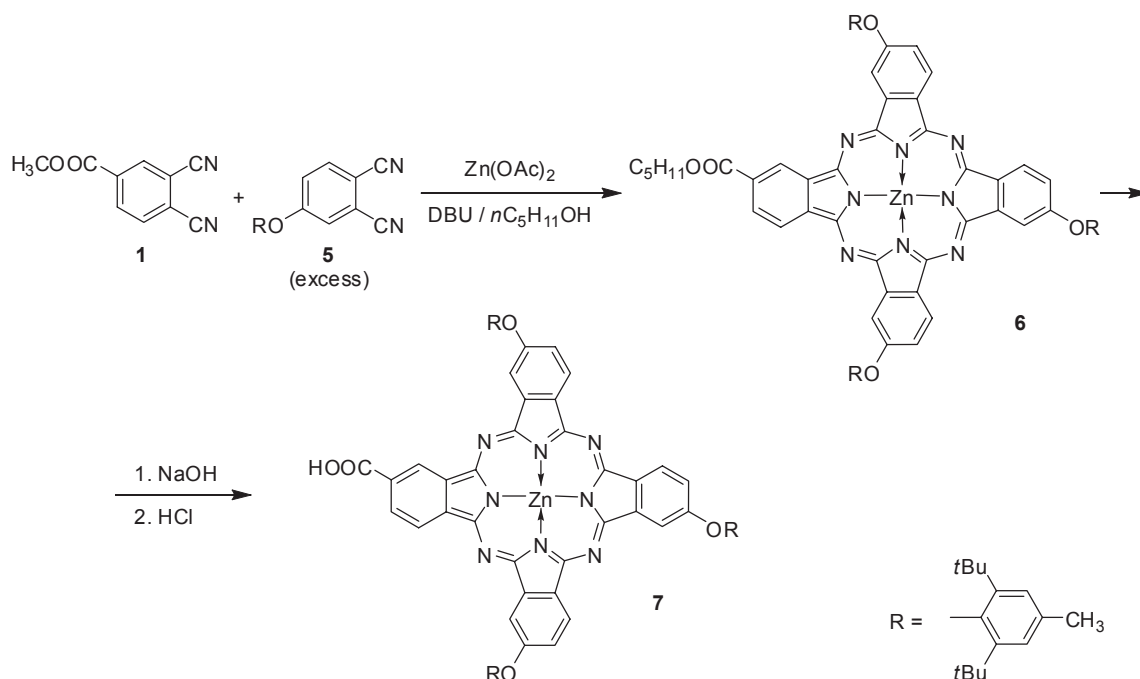


Figure 2. Synthesis of the unsymmetrically substituted phthalocyanines **6** and **7**.

separation of the phthalocyanine mixtures. Unwanted partial cleavage of the ester groups of the compounds **3** and **6** occurs if lithium or magnesium alkoxide is used as a basic catalyst, and therefore the DBU method^[17] is preferable.

In the final step the carboxylic ester groups of **3** and **6** were cleaved with sodium hydroxide in THF-water mixture to obtain the unsymmetrically substituted zinc phthalocyanine carboxylic acids **4** and **7** in nearly quantitative yields. All compounds were characterized by ¹H NMR, IR and ESI-MS spectra. It is necessary to point out that the compounds **6** and **7** are not single compounds but mixtures of positional isomers; the structural formula show only one of four possible isomers for each compound (same as in the case of symmetrically tetrasubstituted phthalocyanines^[18]).

Absorption and Fluorescence Spectra

UV-vis absorption and fluorescence spectra were recorded for the unsymmetrical Pcs **3**, **4**, **6** and **7** (esters and free carboxylic acids) and their symmetrical analogues **8** and **9**. An example of absorption and fluorescence spectra in tetrahydrofuran is shown in the Figure 3, the main spectral data are compared in the Table 1.

A small splitting of the Q-band is a result of the reduced symmetry. The change of the fluorescence band shape is minimal compared to symmetrical analogues, the Stokes shift is as small as it is usually observed for phthalocyanines (approx. 5–10 nm or 100–200 cm⁻¹).^[19] In contrast, the estimated fluorescence quantum yield is significantly reduced compared to symmetrical analogues, both for esters and free carboxylic acids. This could be a result of either self-quenching or intersystem crossing. The measurements of the triplet state quantum yield are in progress to understand the quenching mechanism of the excited singlet state. In the literature, unsymmetrically substituted zinc phthalocyanines

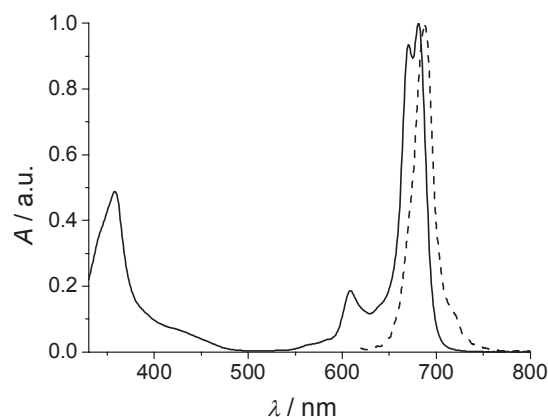
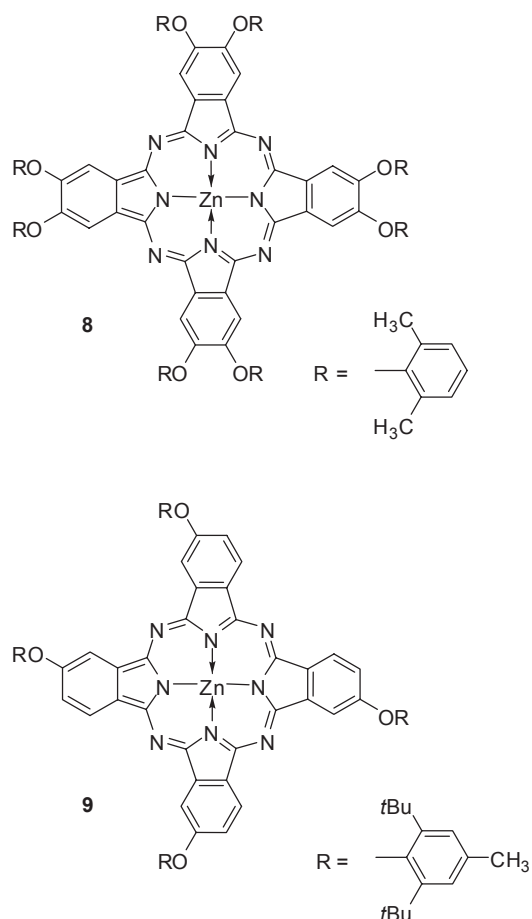


Figure 3. UV-vis absorption (solid line) and emission (dashed line) spectra of **4** in THF.

Table 1. Absorption and fluorescence maxima and estimated fluorescence quantum yields of ZnPcs.

Phthalocyanine	λ_{maxA} Q-band absorption maximum	λ_{maxF} Q-band fluorescence maximum	Fluorescence quantum yield Φ_F
3	683	689	0.14
4	681	687	0.16
6	676	687	0.12
7	674	685	0.14
8	674	679	0.28
9	673	678	0.27

often show reduced quantum yields of the fluorescence whereas the triplet state quantum yields remain relatively high (0.5–0.6).^[19–21]



The zinc(II) phthalocyanine carboxylic acids **4** and **7** were successfully adsorbed on titanium dioxide (Degussa P25, average particle size 21 nm) from THF solution. The UV-vis absorption spectra were recorded in KBr pellets, and the final spectra were obtained by subtracting the spectrum of titanium dioxide to (partially) eliminate contribution of light scattering by the particles. Although complete subtraction of the scattering was not possible (broad slope at shorter wavelengths) the Q-band quality is enough to compare with the solution spectra.

The UV-vis spectra of the compounds **4** and **7** on the surface of titanium dioxide are shown in the Figure 4A,B. The solution spectra are shown for comparison. The Q-bands are slightly broadened and red-shifted. The broad absorption band at 600–650 nm typical for aggregated Pcs^[22] is present in the spectrum of **7** with relatively low intensity. Such a band is not observed in the UV-vis spectrum of **4** which indicates mostly monomolecular distribution of the Pc on the surface. Therefore, relatively small 2,6-dimethylphenoxy groups are bulky enough to efficiently suppress aggregation of a phthalocyanine on the surface whereas a smaller number of much more sterically hindering substituents is less efficient. For comparison, zinc 2-carboxy-9,16,23-tris-*tert*-butylphthalocyanine (an ABBB phthalocyanine with one carboxy group in the benzene ring of A and one *tert*-butyl group in each of the three benzene rings B) shows even stronger aggregation on TiO₂ surface (Figure 4C).^[1] Thus, it had been shown that aggregation of zinc phthalocyanines on TiO₂ can be efficiently suppressed

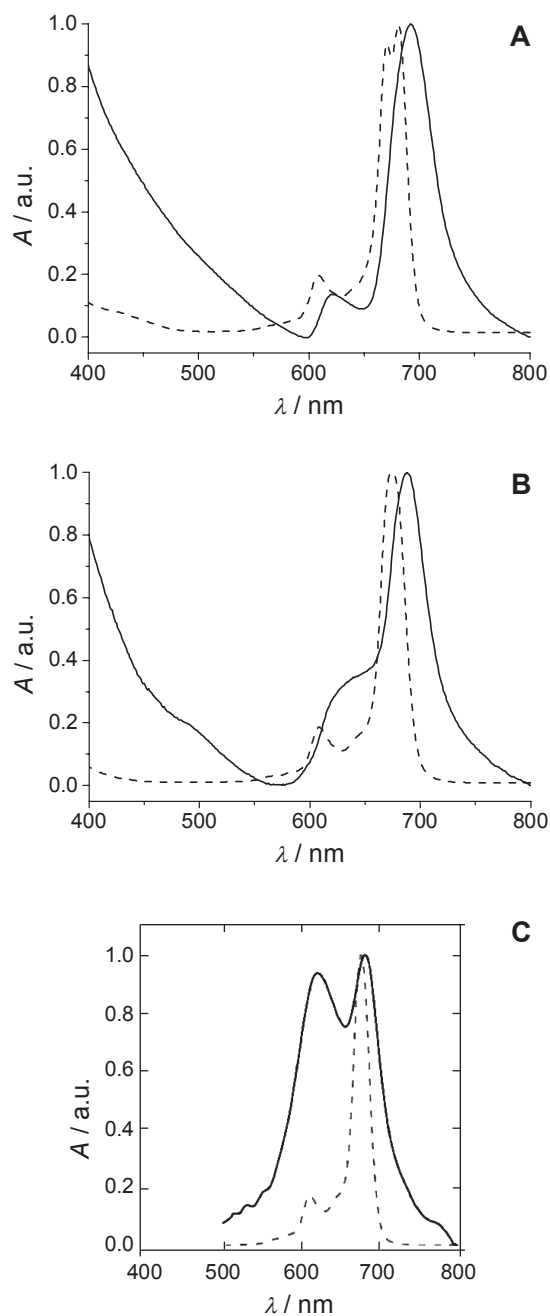


Figure 4. UV-vis absorption spectra of phthalocyanines **4** (A) and **7** (B) on TiO₂ (solid) and in THF (dashed). The corresponding spectra of zinc tri-*tert*-butylphthalocyaninecarboxylic acid (C)^[1] are shown for comparison.

by a proper choice of not too bulky substituents which will allow efficient photo-induced electron transfer to TiO₂. The photovoltaic performance of **4** and **7** in DSSC will be examined in the collaboration with another research groups.

Conclusions

New unsymmetrically substituted phthalocyanines of the ABBB type with a single directly attached carboxylic

groups at the benzene ring A and three or six bulky phenoxy substituents at the benzene rings B were prepared by mixed cyclotetramerization of substituted phthalonitriles.

The changes of UV-vis absorption and fluorescence spectra compared to symmetrically substituted analogues are minimal. The unsymmetrical electronic structure of the prepared phthalocyanines is indicated by significantly reduced fluorescence quantum yield compared to symmetrical analogues as known from the literature. More extended study of photophysical properties is necessary to understand the quenching mechanism of the excited singlet state.

Adsorbed on titanium dioxide, unsymmetrical phthalocyanine carboxylic acids **4** and **7** show little or no aggregation as indicated by their UV-vis absorption spectra. This makes them promising as photosensitizers in photocatalysis and dye-sensitized solar cells.

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