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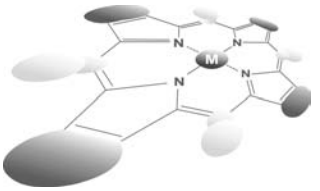

Mono-, bis- and tetrahydroxy phthalocyanines as building blocks for monomolecular layer assemblies

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ABSTRACT: We have developed three basic phthalocyanine structures, containing one, two, or four hydroxy groups, which are simple to synthesize and purify, as well as can be characterized well by NMR and MS. These building blocks can easily be further modified to have anchor groups, which make the molecules suitable for attachment to solid substrates. We have used thioacetate and pentafluorophenyl ester moieties, giving target phthalocyanines the ability to self-assemble on gold, metal oxides, and glass. Bonding densities calculated from the absorbances of the layers suggest mean molecular area to be in the range of 1–3 nm^2, which can be partially controlled by side substituents and the number of linkers.

KEYWORDS: self-assembly, pentafluorophenyl ester, thioacetate.

INTRODUCTION

Phthalocyanines (Pcs) have been the subject of much study over the years. These materials are important industrial dyes and pigments and commonly used as catalysts [1–4]. More recently, they have been employed for advanced applications such as sensors and organic solar cells. In these future devices, Pcs are present often as thin films [5–8]. Therefore, part of modern research has been devoted to developing chromophores containing anchors that could be attached to solid surfaces [9–13].

An evident advantage of covalent bonding is the stability of the formed layer [14]. The deposition of the molecules can be either one-step direct adsorption of the functional component that carries a surface-active group (*e.g.* thiol), or a two-step procedure where the functional components are bonded to preformed ω-functionalized (*e.g.* -COOH, $-NH_2$) tails, which are in turn covalently bonded to a solid surface [15]. The molecular assemblies thus formed are usually called self-assembled monolayers (SAMs). SAM is particularly attractive as a thin film preparation technique because it is simple to fabricate and has high stability and reproducibility [16].

There are many examples of porphyrin monomolecular layer assemblies used in solar cells, organic light-emitting diodes (OLEDs) and sensors [17–20]. Examples of phthalocyanine monomolecular layer assemblies are rare, though the chromophores themselves are widely used in solar cells as evaporated and spin-coated layers [21–24]. Problems arise due to difficulties with Pc functionalization (chiefly low solubility) and characterization (as they usually have a large number of regioisomers). However, compared to porphyrins, Pcs offer a much wider absorbance in the visible part of the solar spectrum, which makes them better candidates as light/energy harvesting materials. Porphyrins and phthalocyanines also have different photophysical and redox properties despite the structural similarities of the molecules [25].

In this paper we report the preparation of three basic phthalocyanine structures containing one, two, and four hydroxy groups, which are soluble in common organic solvents, are easy to synthesize and can be well-characterized by ^{1}H NMR, MS and UV-vis spectroscopies. The versatile building blocks are further used to add anchor groups, which gives Pcs the ability to self-assemble on various solid substrates. We have tested the attachment of our Pcs to gold, glass, and ITO, and we demonstrate that

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the bonding densities are similar for different substrates yielding mean molecular areas in the range of 1–3 nm^2.

RESULTS AND DISCUSSION

Synthesis

Preparation of hydroxy-substituted phthalocyanines. Mono-, bis-, and tetrahydroxy Pcs were synthesized using the well-known Li method. 3,6-dibutoxyphthalonitrile (**1**) and 4-[3-(hydroxymethyl)phenoxy]phthalonitrile (**2**) were used to prepare the monohydroxy phthalocyanine **3** (Scheme 1). A five-fold excess of the phthalonitrile **1** over compound **2** was loaded into the reaction to decrease the amount of other Pcs that form statistically as side products [26]. 1-butanol was chosen as solvent to keep the structure of phthalonitrile **1** intact because lithium alkoxide, which is formed in the reaction, can exchange the alkoxy substituent of phthalonitrile. The reaction mixture was heated at reflux for 4 h under a drying tube, and after chromatographic purification, the product **3** was obtained with a yield of 24%.

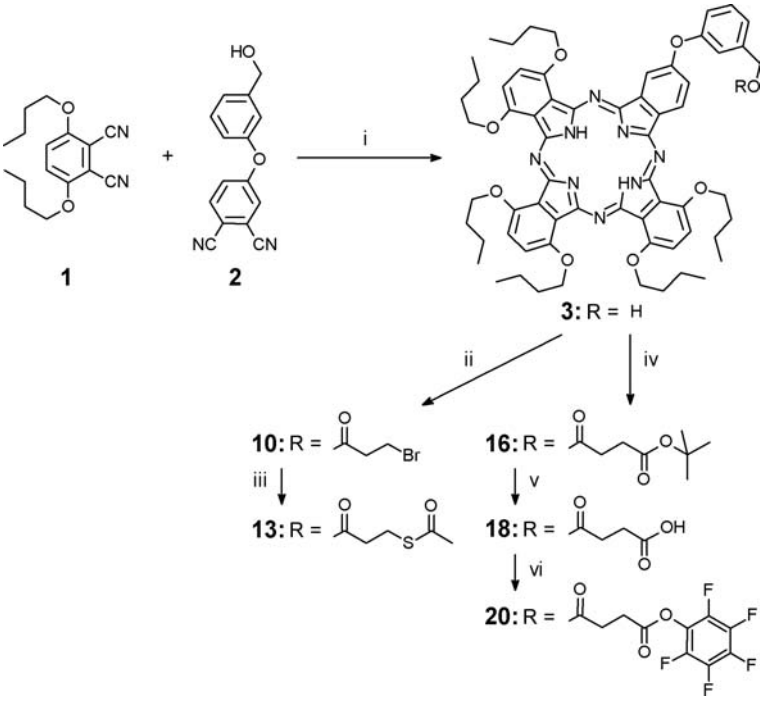
Synthesis of the bishydroxy phthalocyanine **6** was carried out using 3,6-di(hydroxypropyloxy)phthalonitrile (**4**) and 4-*tert*-butylphthalonitrile (**5**) (Scheme 2) [27]. The compound **5** was used in six-fold excess, thus improving the formation of A_3B type Pc. A 2.5 h reaction under argon atmosphere was most efficient, producing a 20% yield of Pc **6**. When the reaction time was prolonged or the reaction was done in ambient air, the yield of the product **6** decreased significantly.

3-[3-(hydroxymethyl)phenoxy]phthalonitrile (**7**) and lithium octoxide was used for the synthesis of tetrahydroxy phthalocyanine **8** (Scheme 3). The reaction mixture was stirred at 80 °C under argon atmosphere for 3 days. After work-up and purification the yield of tetrasubstituted Pc **8** was 78%. The starting materials **1** and **5** are commercially available, while the compounds **2**, **4** and **7** were prepared by known methods [27, 28]. Only one isomer is shown for clarity in Schemes 2 and 3.

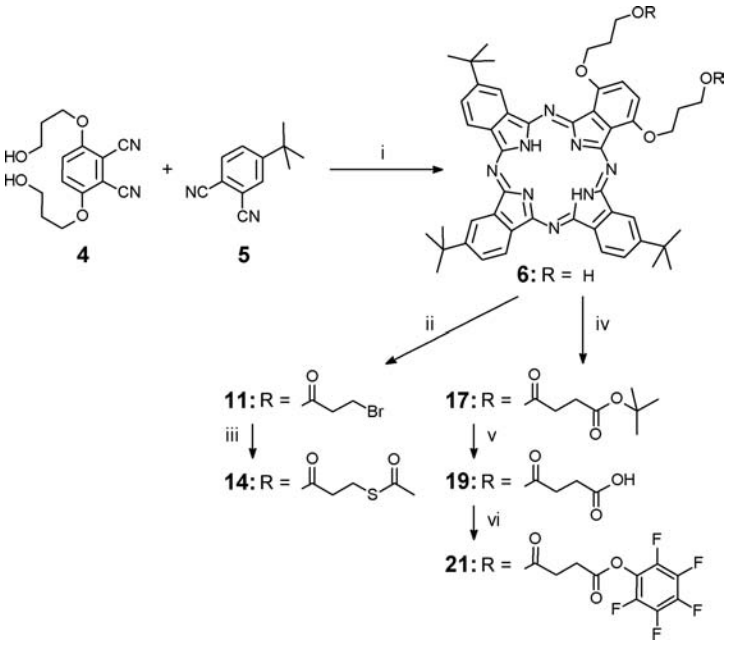
Preparation of thioacetyl-substituted phthalocyanines. Synthesis of thioacetyl-substituted phthalocyanine includes two steps. Bromopropionic acid was first attached to hydroxy Pc, and then the terminal bromine was exchanged to thioacetate group. 3-bromopropionyl chloride (**9**), which was used in acylation, was prepared by a known method just before use [29].

Hydroxy phthalocyanines **3** and **6** were dissolved in CH_2Cl_2 and a six-fold excess of bromopropionyl chloride per hydroxy group was added into the reaction. Tetrahydroxy Pc **8** should be first dissolved in THF/CH_2Cl_2 1:1 mixture and after that diluted with CH_2Cl_2. In this reaction the acid chloride **9** was used in 30-fold excess overall. Acylation of the bishydroxy Pc **6** and the tetrahydroxy Pc **8** requires stirring at room temperature for three days. For the monohydroxy phthalocyanine **3,** sufficient reaction time was one day at room temperature, and during this time the color of the solution changed from dark green to dark purple due to the protonation of the macrocycle. Acylation cannot be promoted by adding organic base (*e.g.* triethylamine), as it leads immediately to dehydrobromination and formation of acrylic esters. Yields of the products **10**, **11** and **12** after straightforward purification were 77%, 55% and 47%, respectively.

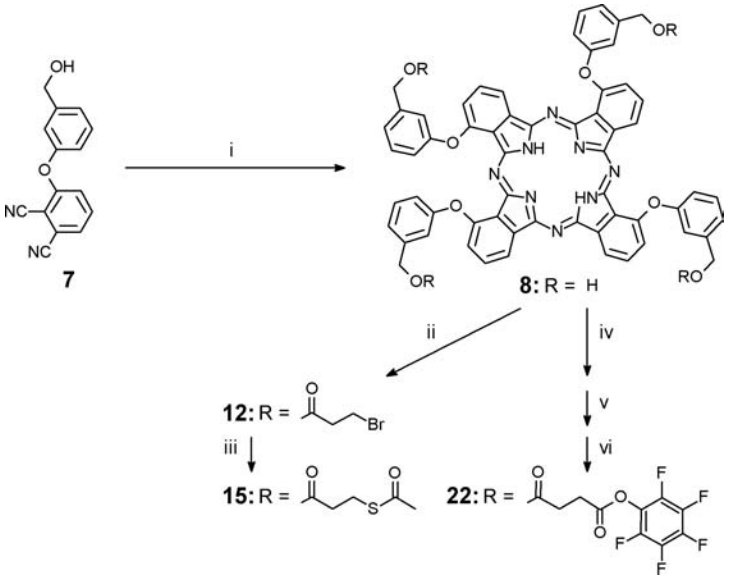
Exchange of terminal bromine to thioacetate was done in acetone using potassium thioacetate (KSAc). The monobromo Pc **10** was heated at reflux under a drying tube for three days in acetone with five-fold excess of KSAc. The monothioacetate product **13** was obtained as dark green solid with a 59% yield. Elevated temperature was required because of poor solubility of the product **10** in acetone, thus full conversion of starting material cannot be achieved at room temperature. Thioacetate exchange efficiency is strongly solvent dependent [30]. Similarly, in present case no reaction was observed in DMF at 60 °C or with refluxing THF.



Scheme 1. Synthetic route to monohydroxy phthalocyanine **3**, and its derivatives. *Reagents and conditions:* (i) Li, 1-butanol, reflux, 4 h; (ii) 3-bromopropionyl chloride, CH_2Cl_2, rt, 24 h; (iii) potassium thioacetate, acetone, reflux, 72 h; (iv) mono-*tert*-butyl succinate, DCC, DMAP, CH_2Cl_2, rt, 48 h; (v) TFA, dry CH_2Cl_2, rt, 3 h; (vi) pentafluorophenol, DCC, EtOAc, rt, 120 h



Scheme 2. Synthetic route to bishydroxy phthalocyanine **6**, and its derivatives. *Reagents and conditions:* (i) Li, 1-pentanol, reflux, Ar, 2.5 h; (ii) 3-bromopropionyl chloride, CH_2Cl_2, rt, 72 h; (iii) potassium thioacetate, acetone, rt, 96 h; (iv) mono-*tert*-butyl succinate, DCC, DMAP, CH_2Cl_2, rt, 48 h; (v) TFA, dry CH_2Cl_2, rt, 4.5 h; (vi) pentafluorophenol, DCC, EtOAc, rt, 96 h



Scheme 3. Synthetic route to tetrahydroxy phthalocyanine **8**, and its derivatives. *Reagents and conditions:* (i) lithium octoxide, THF, 80 °C, Ar, 72 h; (ii) 3-bromopropionyl chloride, THF/CH_2Cl_2, rt, 72 h; (iii) potassium thioacetate, acetone, rt 24 h, 60 °C 48 h; (iv) mono-*tert*-butyl succinate, DCC, DMAP, THF/CH_2Cl_2, rt, 168 h; (v) TFA, dry CH_2Cl_2, rt, 4.5 h; (vi) pentafluorophenol, DCC, EtOAc, 0 °C 48 h, rt 24 h

Preparation of bisthioacetyl Pc **14** is easier and can be done by stirring the Pc **11** and a four-fold excess of KSAc at room temperature for 4 days. Yield of the target product **14** was 70%. Besides the higher yield this reaction proceeds faster than monothioacetyl synthesis. In fact, after 16 h of stirring, the yield of bisthioacetate was as high as 67%.

Formation of tetrathioacetyl phthalocyanine **15** at room temperature is slower. Stirring the mixture of tetrabromo Pc **12** and a two-fold excess of KSAc in acetone for one day showed that the reaction was not complete, and heating for one day at 60 °C did not promote the reaction any further. However, when double excess of KSAc was added again and the solution was stirred at 60 °C for two days overall, the tetrathioacetate **15** was obtained with 70% yield after purification.

Preparation of pentafluorophenyl ester-substituted phthalocyanines. Synthesis of pentafluorophenyl ester phthalocyanines **20**–**22** includes three steps. At first succinic acid was attached to hydroxy-substituted Pc (**3**, **6** and **8**), and the *tert*-butyl succinate thus formed was deprotected. In the last step the pentafluorophenyl ester group was added [31].

Monohydroxy Pc **3** and bishydroxy Pc **6** were reacted with mono-*tert*-butyl succinate in CH_2Cl_2, using 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as a catalyst. Both reaction mixtures were stirred at room temperature for two days and after chromatographic purifications, the *tert*-butyl succinatoxy-substituted products **16** and **17** were obtained with quantitative yields. In the synthesis of tetra-*tert*-butyl succinatoxy-substituted Pc, tetrahydroxy phthalocyanine **8** was first dissolved in THF. Compared to others, the reaction was slow – the reaction mixture was stirred at room temperature for seven days. The long reaction time is due to the poor solubility of the Pc **8**. However, the intermediate product was obtained with quantitative yield.

The deprotection of phthalocyanines **16**, **17** and the intermediate product tetra-*tert*-butyl succinatoxy were carried out by treatment with trifluoroacetic acid (TFA) in dry CH_2Cl_2 for 3–4 h. After solvent evaporation the yield of monosuccinate **18** was 93%, and the yields of bissuccinate **19** and tetrasuccinate were quantitative. Pentafluorophenyl esters **20** and **21** were prepared by dissolving the compounds **18** and **19** in ethyl acetate and adding DCC and pentafluorophenol. Yield of the target monoester **20** was 55% after five days of stirring at room temperature and flash chromatography. The synthesis of bisester **21** was completed after 4 days of stirring at room temperature. Phthalocyanine **21** was obtained as a dark green solid with a yield of 41%. Tetra(pentafluorophenyl ester) **22** was prepared by dissolving the intermediate product

tetrasuccinate Pc in ethyl acetate on ultrasonic bath, and after that stirring the reaction mixture of phthalocyanine, DCC and pentafluorophenol in cold for three days. After purification by flash chromatography and preparative TLC plate, the product **22** was obtained as dark green solid with a 25% yield.

^{1}H NMR spectra. The structural characterization of phthalocyanines has always been difficult since Pcs have usually poor solubility and a number of regioisomers. We designed our particular chromophores to have good solubility, easy NMR analysis, and a reduced number of regioisomers.

The ^{1}H NMR spectra of the mono-functionalized compounds **3**, **13** and **20** are presented in Fig. 1. The spectra show clear aromatic regions where two doublets correspond to the phthalo-protons 25 (δ = 9.30 ppm) and 22 (δ = 8.90 ppm), and a doublet of doublets originates from the phthalo-proton 24 (δ = 7.83 ppm). The multiplet around 7.50 ppm consists of the signals of the rest of β-phthalo protons and the protons from the aryl ring. In the aliphatic region, the signals of alkoxy protons of the butoxy chains at the positions 1 and 18 are shifted upfield compared to other alkoxy protons due to the different environment. Eight alkoxy protons ($OCH_2C_3H_7$) of the butoxy chains, at the positions 4, 8, 11, and 15, are visible as multiplet (δ = 4.91–4.81 ppm) whereas the signals of alkoxy protons at the positions 1 and 18 appear as two triplets at 4.70 ppm and 4.61 ppm, respectively. The spectrum of the hydroxy Pc **3** shows a broad singlet at 4.78 ppm, which corresponds to methylene protons between the aryl ring and hydroxy group. In the other spectra this signal is shifted to lower field (δ = 5.21 ppm). The shift of this singlet is caused by the substitution with succinic residue, which deshields this CH_2 group. The signals of succinic protons $COCH_2CH_2Br$ and $COCH_2CH_2Br$ in the ^{1}H NMR spectrum of **10** appear as two multiplets at 3.01–2.83 ppm and 3.77–3.52 ppm, respectively (see Supporting information). The same signals for the thioacetate **13** are visible as triplets; for the protons $COCH_2CH_2S$, the triplet is observed at 2.70 ppm and for the protons $COCH_2CH_2S$, it is located at 3.11 ppm. The signal of methyl protons $SCOCH_3$ is found as a singlet (δ = 2.22 ppm) overlapping with a multiplet in the spectrum of **13**. The signals of the protons COC_2H_4CO appear as a multiplet in the spectra of the *tert*-butylsuccinate **16** and the succinate **18** (δ = 2.70–2.53 ppm) (see Supporting information). The shift of these signals to lower field occurs in the spectrum of the pentafluorophenyl ester **20**. For this the signals are divided into two multiplets at 2.97–2.91 ppm and 2.84–2.78 ppm. Characteristic signal of the *tert*-butyl group in the spectrum of **16** is observed at 1.40 ppm, and this singlet disappears from the spectrum of the deprotected compound **18**. The free-base Pcs include two protons in the central cavity and those NH-protons are observed as a singlet around 0.10 ppm in each spectrum.

In the ^{1}H NMR spectra of bishydroxy phthalocyanine **6** and its derivatives (see Supporting information), several multiplets are present due to constitutional isomers. In the aromatic region of the spectrum of **6**, three multiplets are visible. Signals of the phthalo-protons 2 and 3 are found as separate multiplets at 6.88–6.07 ppm. In the ^{1}H NMR spectra of bissucinate derivatives **17**, **19** and **21**, these signals are shifted to lower field. In the aliphatic region of the spectrum of the bishydroxy compound **6**, the signals of alkoxy protons $OCH_2CH_2CH_2OH$ of the

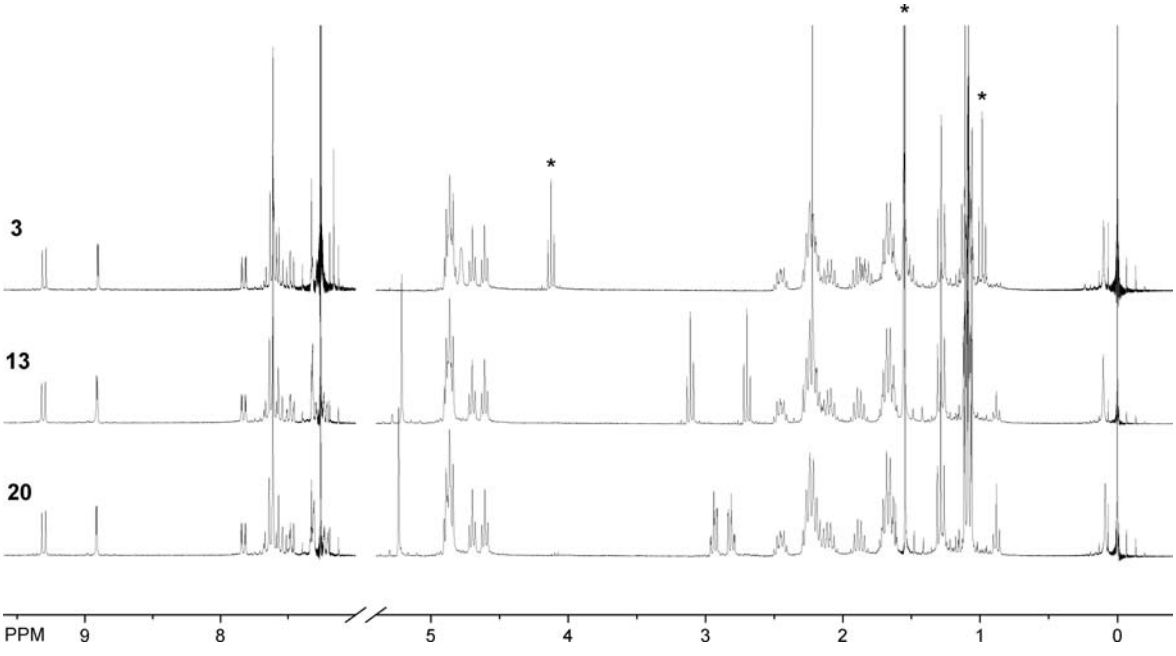


Fig. 1. ^{1}H NMR spectra of monohydroxy **3** (top), monothioacetate **13** (middle) and mono(pentafluorophenyl ester) **20** (bottom) phthalocyanines; signals of residual solvents are marked with asterisk

hydroxypropyloxy chains at the positions 1 and 4 are visible as broad multiplet (δ = 4.65–4.24 ppm). This multiplet is shifted to lower field in all other spectra. The same shift is visible when comparing the multiplet of methylene protons $OCH_2CH_2CH_2O$, for example, the spectrum of bromopropionate **11** shows the multiplet at 2.71–2.41 ppm, whereas the spectrum of **6** shows this multiplet at 2.51–2.23 ppm. The signals of the protons $COCH_2CH_2Br$ and $COCH_2CH_2Br$ of **11** appear both as multiplets at 3.03–2.76 ppm and 3.82–3.49 ppm, respectively. In the spectrum of thioacetate **14**, these multiplets are shifted to higher field. The multiplet at 2.76–2.54 ppm contains also the signals of protons $OCH_2CH_2CH_2O$, while the characteristic acetylic protons of **14** are visible as a group of singlets next to it (δ = 2.28–2.21 ppm). The signals of the three *tert*-butyl groups at the periphery of Pc are observed in the spectra of bishydroxy, bisbromopropionate, and bisthioacetate **6**, **11**, and **14** as a group of singlets at 1.91–1.68 ppm. Shifting of these signals is observed in ^{1}H NMR spectra of bissuccinates **17**, **19**, and **21** (δ = 1.89–1.76 ppm). The characteristic signal of *tert*-butyl ester protons in **17** appears as singlet at 1.44 ppm, and this peak vanishes in the spectrum of the deprotected **19**. NH-protons of bishydroxy Pc **6** appear as a multiplet at -2.40–2.97 ppm. For bispropionate derivatives these signals are shifted to lower field. Thus for the bisbromopropionate **11** the signals are found at -1.34–1.71 ppm, while for the Pc **14** this multiplet is visible at -1.03–1.34 ppm. NH-protons signals are visible as multiplet at -0.80–1.07 ppm, -1.81–2.54 ppm and -1.18–1.49 ppm in the spectra of the bissuccinic derivatives **17**, **19** and **21**, respectively.

In the aromatic region of the ^{1}H NMR spectrum of tetra-substituted phthalocyanine **8** (see Supporting information), the signals of 12 phthalo-protons on the Pc periphery are found as a multiplet (δ = 8.20–7.38 ppm). Another multiplet in higher field consists of the signals of aryl protons. Similar but broader multiplets are found also in the spectra of tetrabromopropionic and tetrathioacetate Pcs **12** and **15** (see Supporting information). The spectrum of tetra(pentafluorophenyl ester) phthalocyanine **22** shows the most clear signals in the aromatic region (see Supporting information). For example a triplet of β-phthalo-protons is located at 7.81 ppm. A broad triplet at 5.19 ppm with the coupling constant 5.6 Hz corresponds to four hydroxy protons in the spectrum of the compound **8**, and the signals of methylene protons are found as a multiplet at 4.57–4.39 ppm. The group of singlets from the methylene protons is found in much higher field in the spectra of **12**, **15** and **22** (around δ = 5.30–5.00 ppm). The signals of protons $COCH_2CH_2Br$ and $COCH_2CH_2Br$ are observed as multiplets at 3.04–2.68 ppm and 3.80–3.36 ppm in the spectrum of **12**, respectively. For tetrathioacetate Pc **15**, these multiplets are shifted to higher field; signals of protons $COCH_2CH_2S$ appear at 2.74–2.51 ppm and signals of protons $COCH_2CH_2S$ are found at 3.15–2.91 ppm. In the spectrum of **22**, signals of these protons (COC_2H_4CO) overlap and as a result a multiplet is found at 2.99–2.55 ppm. The signals of acetylic protons $SCOCH_3$ for the compound **15** are visible at 2.33–2.15 ppm as multiplet. Weak signals with negative chemical shift correspond to the NH-protons, and in the spectra of **12**, **15** and **22** these multiplets are found at -1.08–1.85 ppm, -1.40–2.31 ppm and -1.51–2.05 ppm, respectively. Shifting of these signals to lower field is evident when comparing the positions in the spectrum of the Pc **8** (δ = -2.03–2.62 ppm).

Mass spectra. The structures of the synthesized compounds were proved by high-resolution ESI-TOF mass spectrometry (see Supporting information). To obtain an accurate value of the mass, a solution of reference compound (Leucine Enkephaline) was infused simultaneously with analyte, and the experimental spectra were processed with peak centering and lock mass TOF correction. In the measurements the solvent was typically a mixture of $CHCl_3$/MeOH 1:1, and positive mode was used.

For monohydroxy-substituted Pc **3** the $[M + H]^+$ peak was observed at *m/z* 1069.5599 (accuracy 4 ppm), along with $[M + Na]^+$ peak at *m/z* 1091.5768. Also, aggregated $[2M + H]^+$ and $[2M + Na]^+$ peaks appeared at *m/z* 2138.6091 and 2160.1042, respectively, and the $[3M + 2H]^{2+}$ peak was observed at *m/z* 1603.8296. Molecular ion peak $[M + H]^+$ was observed at *m/z* 1203.4954 (accuracy 3 ppm) for the intermediate product **10**. The $[M + H]^+$ peak was found at *m/z* 1199.5671 (accuracy 2.6 ppm) for the compound **13** and the aggregated peaks $[2M + H]^+$ and $[3M + 2H]^{2+}$ were visible at *m/z* 2398.1262 and 1798.8522, respectively. For phthalocyanine **16**, the $[M + H]^+$, $[2M + H]^+$ and $[3M + 2H]^{2+}$ peaks were observed at *m/z* 1225.6375 (accuracy 3 ppm), 2450.2856 and 1837.9568, respectively. The $[M + H]^+$ peak for **18** was found at *m/z* 1169.5627 (accuracy 7 ppm), and aggregated $[2M + H]^+$ and $[3M + 2H]^{2+}$ peaks were visible at *m/z* 2338.0955 and 1753.8541, respectively. The $[M + H]^+$ peak for the compound **20** was observed at *m/z* 1335.5555 with high accuracy (0.075 ppm). Aggregated $[3M + 2H]^{2+}$ peak was also found at *m/z* 2002.8867 for Pc **20**.

The $[3M + 2H]^{2+}$ peak was visible at *m/z* 1246.6472 (accuracy 0.7 ppm) in the mass spectrum of bishydroxy phthalocyanine **6**, and the $[M + H]^+$ peak was observed at *m/z* 831.4359. Molecular ion peaks $[M]^+$ and $[M + Na]^+$ for the compound **11** were found at *m/z* 1098.3121 (accuracy 10 ppm) and 1121.3079, respectively. In mass spectrum of Pc **14**, the $[M]^+$ peak was observed at *m/z* 1090.4368 (accuracy 7 ppm). The $[M + Na]^+$ and aggregated $[2M + H]^+$, $[2M + Na]^+$ and $[3M + 2H]^{2+}$ peaks were also visible in the spectrum of **14** at *m/z* 1113.4219, 2181.8730, 2203.8757, and 1636.6528, respectively. The spectrum of the compound **17** was measured in positive mode, and aggregated molecular ion peak $[2M + H]^+$ was found at *m/z* 2286.1714 (accuracy 2 ppm). Also, the $[M + H]^+$ and $[3M + 2H]^{2+}$ peaks were observed at *m/z* 1143.5874 and 1714.8741, respectively. The mass

spectrum of **19** was measured in negative mode and the $[M - H]^-$ peak was visible at *m/z* 1029.4469 (accuracy 4 ppm), and the $[M + Cl]^-$ peak was found next to it (*m/z* 1065.4298). Aggregated $[2M - H]^-$ and $[3M - 2H]^{2-}$ peaks were observed at *m/z* 2059.9153 and 1544.6758, respectively. The $[M + Na]^+$ peak was visible at *m/z* 1385.4221 (accuracy 3.7 ppm) in the measurement of the compound **21**. This spectrum also showed the $[2M + Na]^+$ peak at *m/z* 2747.8450. When the mass measurement was carried out in negative mode for **21**, the $[M - H]^-$ and $[2M - H]^-$ peaks were observed at *m/z* 1361.4127 and 2723.8403, respectively.

The mass measurement of the tetrahydroxy-substituted Pc **8** was carried out in positive mode using MeOH as the solvent. The $[M + H]^+$ peak was observed at *m/z* 1003.3254 (accuracy 5 ppm), while aggregated or sodium adduct peaks were not visible. The $[M + H]^+$ peak was observed at *m/z* 1539.0872 (accuracy 13 ppm) for the compound **12**. The mass spectrum of phthalocyanine **15** showed the high accuracy $[M + H]^+$ peak at *m/z* 1523.3571 (accuracy 0.8 ppm). The structures of intermediate products of compound **22** were proved with mass spectrometry (see Supporting information). Tetra-*tert*-butylsuccinatoxy-substituted Pc was measured using negative mode, and the $[M - H]^-$ and $[2M - H]^-$ peaks were found at *m/z* 1625.6118 and 3252.2451 (accuracy 0.4 ppm), respectively. The $[M + H]^+$ peak was observed at *m/z* 1403.3928 (accuracy 6 ppm) for tetrasuccinate Pc. In the spectrum of the compound **22** the $[M + H]^+$ peak at *m/z* 2067.3279 (accuracy 3 ppm) was visible. Also, the $[3M + 2H]^{2+}$ peak was observed at *m/z* 3100.5364 in the spectrum of Pc **22**.

Absorption and emission spectra. In the absorption spectra of the monohydroxy phthalocyanine **3** (Fig. 2) and its derivatives, the Q and Soret bands are well visible. The Q band shows two maxima: one is located around 760 nm and the other between 734–739 nm, depending on the compound (Table 1, 2). The spectra also show a shoulder between 650–700 nm. The molar absorptivity

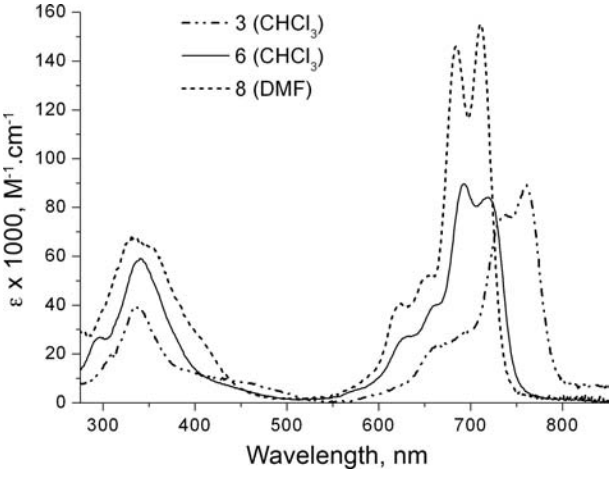


Fig. 2. Absorption spectra of monohydroxy **3**, bishydroxy **6** and tetrahydroxy **8** phthalocyanines

Table 1. Absorption and emission maxima of hydroxy-substituted phthalocyanines **3**, **6** and **8**

Compound	Absorption λ_{max}, nm	Emission λ_{max}, nm
3 ($CHCl_3$)	761, 739, 337	774
6 ($CHCl_3$)	719, 693, 340	730, 810
8 (DMF)	711, 685, 331	722, 810

Table 2. Absorption and emission maxima of thioacetyl-substituted phthalocyanines **13**–**15**, and pentafluorophenyl ester-substituted phthalocyanines **20**–**22**

Compound	Absorption λ_{max}, nm	Emission λ_{max}, nm
13 ($CHCl_3$)	761, 737, 339	774
14 ($CHCl_3$)	715, 688, 344	727, 810
15 (DMF)	713, 688, 332	722, 810
20 ($CHCl_3$)	760, 734, 335	772
21 ($CHCl_3$)	713, 689, 343	727, 810
22 ($CHCl_3$)	716, 684, 337	722, 810

(ε) of the compound **13** (99600 $M^{-1}.cm^{-1}$) (Fig. 3a) is a bit higher than that of the molecule **3** (89350 $M^{-1}.cm^{-1}$). The highest ε value (154900 $M^{-1}.cm^{-1}$) is found for the Pc **20** (Fig. 4a). The Soret band maximum is located between 335–339 nm, depending on the compound. These wavelengths were used as an excitation wavelength in fluorescence measurements. Emission maximum is situated at 774 nm for Pcs **3** and **13**, while for the compound **20** the maximum peak is shifted a little to shorter wavelength (see Supporting information). All these spectra were measured in $CHCl_3$.

The absorption spectra of the bishydroxy Pc **6** (Fig. 2) and its derivatives show Q band, which consists of two intense peaks around 700 nm and two lower shoulders between 600–660 nm. The peak around 688 nm is more intense than other maxima at higher wavelength. For the phthalocyanine **6**, these peaks are located at 693 nm and 719 nm, respectively (Table 1). The molar absorptivity of the bisthioacetate Pc **14** (130800 $M^{-1}.cm^{-1}$) is the highest of all of these compounds (Fig. 3a). In the Soret band, all absorptions show one intense broad band as well as one less intense one at roughly 300 nm. The Soret band maximum is located at 340 nm for the compound **6**, while for the molecules **14** and **21** (Fig. 4a) it is found at 343 nm (Table 2). These wavelengths were used as an excitation wavelength in emission measurements. Emission maximum is found at 730 nm for Pc **6** (see Supporting information). In other spectra the emission maximum is shifted by 3 nm to the red. Fluorescence spectra also show broad and weak emission around 810 nm for all the compounds.

Absorption spectra of the tetra-substituted Pcs **8** (Fig. 2), **15** (Fig. 3a) and **22** (Fig. 4a) show two maxima in the Q bands around 685 nm and 710 nm (Table 1, 2). In the spectra of the tetrahydroxy compound **8** and the

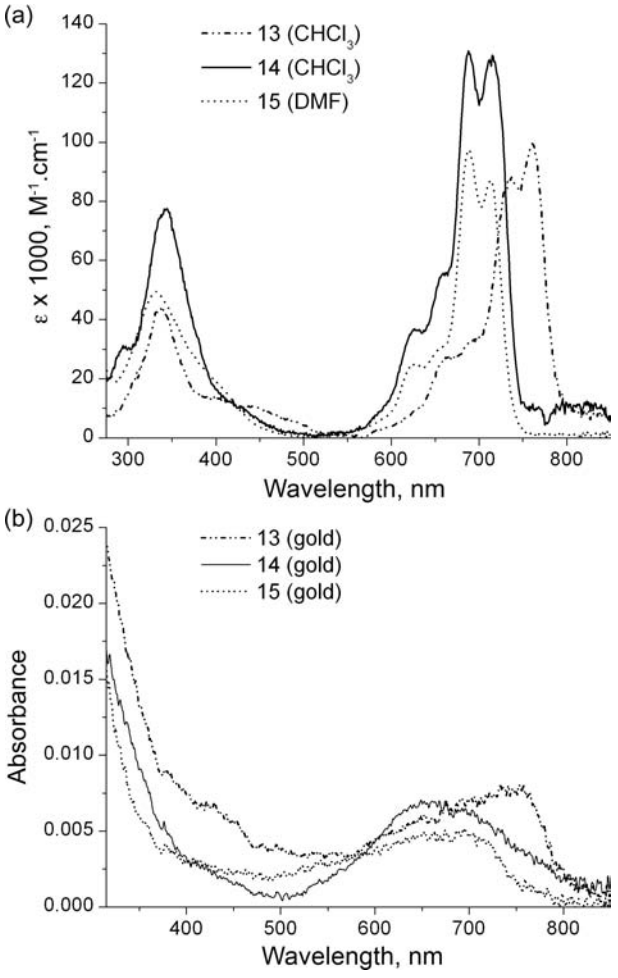


Fig. 3. (a) Absorption spectra of monothioacetate **13**, bisthioacetate **14** and tetrathioacetate **15** phthalocyanines, (b) absorption spectra of SAMs **13**–**15** on gold

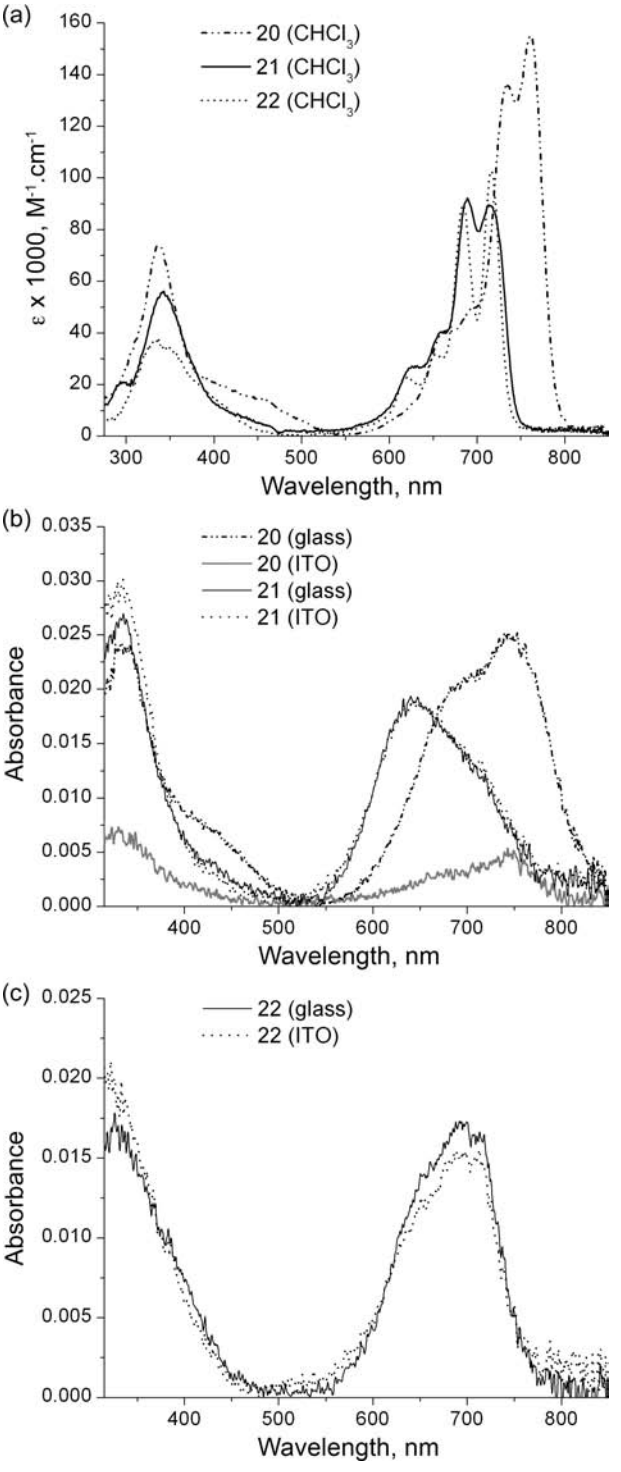


Fig. 4. (a) Absorption spectra of mono(pentafluorophenyl ester) **20**, bis(pentafluorophenyl ester) **21** and tetra(pentafluorophenyl ester) **22** phthalocyanines, (b) absorption spectra of SAMs **20** and **21** on glass and ITO, (c) absorption spectra of SAM **22** on glass and ITO

tetra(pentafluorophenyl ester) phthalocyanine **22** the intensity of the latter peak is higher, but in the spectrum of **15** this ratio is opposite. In Q bands a shoulder is found between 600–660 nm, which is also seen in the absorption spectra of bis-functionalized Pcs. Molar absorptivity (ε) of the compound **8** is 155200 $M^{-1}.cm^{-1}$ and for the tetrathioacetate molecule **15** the ε value has reduced a little bit to 97500 $M^{-1}.cm^{-1}$. For tetra(pentafluorophenyl ester) Pc **22** the value of ε is 102800 $M^{-1}.cm^{-1}$. The Soret band maximum is located around 330 nm in the spectra of the compounds **8**, **15** and **22**. The excitation wavelength of the emission measurements was the Soret band maximum for all compounds. The phthalocyanines **8**, **15** and **22** are emitting at roughly 722 nm; a weak emission band is visible at 810 nm (see Supporting information). The spectra of molecules **8** and **15** were measured in DMF, and measurements of Pc **22** were done in $CHCl_3$.

Immobilization on substrates

SAM on gold. It is well-known that organosulfur compounds can react with gold. In the case of thioacetyl, an oxidative addition of the S-Ac bond occurs on a gold surface, followed by a reductive elimination of acetyl group (Ac) [16]. For spectral measurements, a robust and optically transparent substrate is required, thus a titanium layer (2 nm) was thermally evaporated on cleaned glass plates first, and on top of this adhesion layer a 3 nm thick

Table 3. Absorption maxima and mean molecular areas (mma[a]) of SAMs **13**–**15** and **20**–**22** on different substrates

Compound	Absorption λ_{max}, nm	mma, nm^2
13 (gold)	750	2.07
20 (glass)	740, 330	2.06
14 (gold)	650	3.10
21 (glass/ITO)	640, 330	1.61
15 (gold)	695	3.24
22 (glass/ITO)	695, 330	1.90/2.13

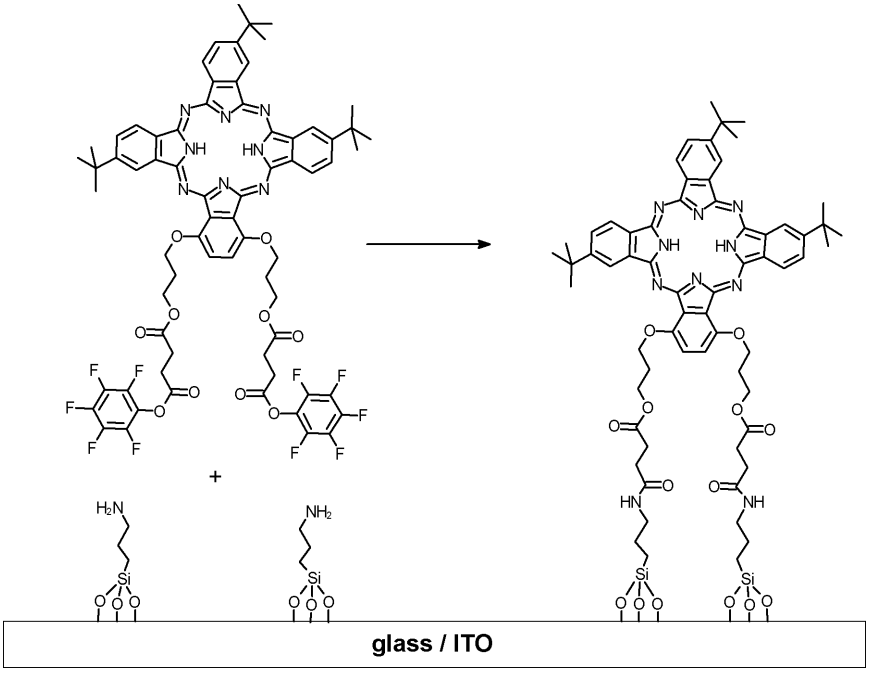
[a] mma = $\varepsilon/(N_A A)$, where ε is molar absorptivity, N_A is Avogadro constant and A is absorbance of the layer.

gold layer was evaporated. Absorption spectra of the substrates were recorded and used later to calculate the spectra of SAMs. Gold substrates were immersed into solutions of phthalocyanines **13**, **14** and **15** in CH_2Cl_2, where concentration of each solution was 3 mM [32]. The plates were kept at room temperature for 30 min, and after that SAMs on gold surface were rinsed several times with CH_2Cl_2 and $CHCl_3$ to remove unbound Pc molecules.

Absorption spectra of the SAMs **13**–**15** on gold surfaces show a band between 600–800 nm (Q band) (Fig. 3b). Compared to the spectra of solutions, the maxima of absorption spectra of SAM **13** and **14** are shifted to shorter wavelengths, even though defining the maxima of the spectra is difficult because of the low absorption of SAMs (Table 3). The shift of the band maxima of SAM **14** on gold is around 40 nm. The spectrum of SAM **15** is red-shifted by 10 nm compared to the spectrum of **15** in DMF. Besides shifting, the Q bands of the SAM spectra are also broader. No detectable emission of phthalocyanines SAMs was observed.

The absorption maxima of the Q bands provide a possibility to estimate the mean molecular areas (mma) of phthalocyanines in the SAMs. The mma values calculated assuming the same molar absorption of Pcs in solution and SAMs are presented in Table 3. Comparing the molecular areas of phthalocyanines **13**–**15,** the area increases towards larger chromophore as expected. However, differences in Pc bonding densities are small and the values are larger than what one could expect for tightly packed monolayers. This can be due to a gradual decrease of the molar absorption in SAMs compared to that in solution. Indeed, the Q bands are 2–3 times broader for films, indicating that the molar absorption can be 2–3 times lower for SAMs. The mean molecular area is better controlled when monolayers are prepared by Langmuir-Blodgett (LB) or Langmuir-Schäfer (LS) methods. It has been shown previously that one LS-monolayer of bis-hydroxy Pc **6** on quartz plate has an absorbance of *ca.* 0.005, which corresponds to the molecular area of 0.62 nm^2 and can be achieved in the case of vertical orientation of macrocycles in respect to the substrate [33]. In the present case, optical density of one layer on gold is 0.007, but the mma value calculated based on solution molar absorption is 3 nm^2. Therefore the mma values listed in Table 3 present the higher limits for actual mma values, but actual bonding densities of molecules are expected to be 2–3 times greater.

SAM on glass and ITO. Glass and ITO plates were cleaned by sonication in organic solvents before the preparation of SAMs (see Experimental section). SAMs were done with a two-step process: first, the plates were



Scheme 4. Covalent attachment of phthalocyanine **21** to activated surface

activated with 3-aminopropyltrimethoxysilane in dry toluene at 105 °C for 1 h. Phthalocyanines were then covalently attached to the aminopropylsilylated surface by immersing the plates into a solution of compound **20**, **21** or **22** in dry toluene. This was done through amide bond formation between pentafluorophenyl ester group on Pcs and amino group on silylated substrates (Scheme 4) [34]. This second step was completed in 2 h at 105 °C. Both steps were done under argon. To remove residual physisorbed Pc, the samples were sonicated in toluene and CH_2Cl_2 after the second step. After drying in argon, the UV-vis spectra of the plates with SAMs were measured.

In the absorption spectra of the monolayers on glass and ITO surfaces (Fig. 4b,c), one has to take into account that layers are formed on each side of the substrates. Therefore, comparing with absorbances of SAMs on gold surface (Fig. 3b), optical densities of SAMs on glass and ITO are roughly doubled. Absorption spectrum of the SAM **20** on glass substrate shows clear Q and Soret bands (Table 3). Both are shifted towards shorter wavelengths compared to absorption maxima of the Pc **20** in solution (Table 2). For unknown reasons, the absorption of SAM **20** on ITO is five times smaller than on glass. Results were also the same with an extended reaction time of both steps, so it seems that the molecules bond very weakly onto ITO. This kind of selectivity towards the substrate will be a subject of separate studies. However, the shapes of the absorption spectra of samples **20** on glass and on ITO are the same and very similar to the absorption in solution. In the absorption spectrum of SAM **21** on glass and ITO (Fig. 4b) the Q band is blue-shifted by almost 50 nm in comparison to the absorption spectrum of **21** in $CHCl_3$ (Table 2). This huge shift is also seen in the spectrum of same molecule on gold. The absorptions of SAM **21** on glass and on ITO are perfectly same on both substrates. The absorption spectra of SAM **22** on glass and ITO (Fig. 4c) are also the same; the absorbance of SAM on ITO is a little smaller than on glass. The spectra show Q band maxima around 695 nm, which is between the two maxima in the absorption spectrum of compound **22** in $CHCl_3$ (Table 2, 3). Emissions of SAMs **20**, **21** and **22** on glass/ITO substrates were not detectable.

Mean molecular areas (mma) of SAM **20** on glass, **21** and **22** on glass and ITO are very similar (Table 3). Sample **21** on both substrates gives a slightly smaller value than the mono-substituted Pc **20** on glass and the tetra-substituted Pc **22** on glass and on ITO. This difference could be because the molecule **20** has greater side substituents than the *tert*-butyl groups in molecule **21**, while molecule **22** should have preferably flat orientation on surface. Also, these results show high mma values and therefore presented results are the higher limits for actual mma values. Bonding density of the compound **20** on glass is the same as the value of SAM **13** on gold. On the other hand, comparing the molecular areas of SAM **14** on gold and SAMs **21** on glass and ITO, a difference of 1.5 nm^2 is noticed, which can be attributed to the different tilting angles of the molecules on different substrates. A smaller difference is observed when comparing the SAMs **15** (gold) and **22** (glass/ITO).

As can be seen, the arrangement of different Pcs on gold and on ITO/glass is similar and corresponds to the arrangement of chromophores in LB/LS films. However, the organization of the layer does not depend solely on the number of anchor groups, but is influenced as well by the side substituents and by the interaction of the macrocycle with the substrate surface.

EXPERIMENTAL

Materials and instrumentations

The solvents of HPLC grade were purchased from Aldrich Chemical Company, Merck, and VWR International. Chemicals were purchased from Acros Organics, Aldrich Chemical Company, or Fluka Chemie. All the materials were used as received without further purification. The monitoring of reactions was carried out by thin-layer chromatography (TLC), employing aluminum sheets precoated with Silica 60 F254 (Merck). The purification and isolation of the products was performed by column chromatography on Silica 60 (mesh size 40–63 μm) or Silica 100 (mesh size 63–200 μm).

The ^{1}H NMR spectra were measured on a Varian Mercury 300 MHz spectrometer (Varian Inc.). All chemical shifts are given in ppm relative to TMS as internal standard. Mass spectra were recorded on ESI-TOF LCT Permier XE mass spectrometer (Waters Corp.). The sample of the analyte was dissolved in an appropriate solvent at concentration *ca.* 0.01 $mg.mL^{-1}$ and infused at a rate of 15 $\mu L.min^{-1}$. The reference solution of Leucine Enkephaline (50 $pg.mL^{-1}$) was infused simultaneously. Original spectra were centered, and lock mass TOF correction was applied. Absorption spectra were measured using a Shimadzu UV-2501PC UV-vis recording spectrometer, and emission spectra were recorded on a Fluorolog Yobin Yvon-SPEX spectrofluorometer.

Synthesis

1,4,8,11,15,18-hexabutoxy-23-[3-(hydroxymethyl) phenoxy]phthalocyanine (3). 3,6-dibutoxyphthalonitrile (**1**) (408 mg, 1.5 mmol), 4-[3-(hydroxymethyl)phenoxy] phthalonitrile (**2**) (75 mg, 0.3 mmol) and lithium (40 mg, 5.8 mmol) were suspended in 1-butanol (12 mL). The reaction mixture was heated at reflux for 4 h under a drying tube. The dark green solution was cooled to room temperature and $CHCl_3$ (20 mL) was added. The organic phase was washed with water (4 × 100 mL) and the solvent was evaporated under reduced pressure (bath temperature 80 °C). The mixture of the reaction products was purified by column chromatography on Silica 100, eluting with $CHCl_3$. The product was obtained as the second fraction (R_f = 0.55 in $CHCl_3$/EtOH 18:1). The product

was crystallized on a watch glass and washed with acetonitrile. Second chromatographic purification was done on Silica 60, eluting with $CHCl_3$. The product **3** was obtained from the second fraction as a dark green solid (78 mg, 24%). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 337 (39167), 739 (77105), 761 (89351). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.30 (1H, d, J = 8.3 Hz, 25-phthalo-*H*), 8.90 (1H, d, J = 2.1 Hz, 22-phthalo-*H*), 7.83 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 24-phthalo-*H*), 7.68–7.12 (10H, m, phthalo-*H*, Ar-*H*), 4.91–4.81 (8H, m, 4,8,11,15-OCH_2C$_3$H$_7$), 4.78 (2H, br s, ArCH_2OH), 4.70 (2H, t, J = 6.4 Hz, 1-OCH_2C$_3$H$_7$), 4.61 (2H, t, J = 6.4 Hz, 18-OCH_2C$_3$H$_7$), 2.51–2.39 (2H, m, 1-OCH$_2$CH_2C$_2$H$_5$), 2.30–2.16 (10H, m, 4,8,11,15,18-OCH$_2$CH_2C$_2$H$_5$), 2.14–2.04 (2H, m, 1-OC$_2$H$_4$CH_2CH$_3$), 1.94–1.78 (2H, m, 18-OC$_2$H$_4$CH_2CH$_3$), 1.72–1.61 (8H, m, 4,8,11,15-OC$_2$H$_4$CH_2CH$_3$), 1.28 (3H, t, J = 7.4 Hz, 1-OC$_3$H$_6$CH_3), 1.14–1.05 (15H, m, 4,8,11,15,18-OC$_3$H$_6$CH_3), 0.10 (2H, s, N*H*), ArCH$_2$O*H* was not resolved. MS (ESI-TOF; CH_2Cl_2/MeOH 1:1): *m/z* 1069.5599 $[M + H]^+$ (calcd. for $C_{63}H_{72}N_8O_8$ 1069.5552).

3-bromopropionyl chloride (9). Oxalyl chloride (0.36 mL, 4.25 mmol) and DMF (5 μL) were added to a solution of 3-bromopropionic acid (500 mg, 3.27 mmol) in CH_2Cl_2 (5 mL). The solution was stirred at room temperature for 16 h. The solvent was evaporated under reduced pressure (bath temperature 40 °C) to yield quantitatively the compound **9**. The residue was redissolved in CH_2Cl_2 (2 mL). Concentration: 1.64 M.

1,4,8,11,15,18-hexabutoxy-23-[3-(3-bromopropanoatemethyl)phenoxy]phthalocyanine (10). Phthalocyanine **3** (20 mg, 18.7 μmol) was dissolved in CH_2Cl_2 (5 mL) and 3-bromopropionyl chloride (**9**) (1.64 M solution in CH_2Cl_2, 68 μL, 112.2 μmol) was added to the solution. The reaction mixture was stirred at room temperature for 1 day. A few milliliters of $CHCl_3$ were added and the organic layer was washed with saturated $NaHCO_3$ (aq) (13 × 50 mL) and water (2 × 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified three times by column chromatography on Silica 60, eluting with $CHCl_3$. The product was collected as first green fraction (R_f = 0.83 in $CHCl_3$/EtOH 18:1) and was crystallized on a watch glass and washed with *n*-pentane. The compound **10** was obtained as a dark green solid (17 mg, 77%). UV-vis ($CHCl_3$): λ_{max}, nm (abs.) 339 (0.04963), 735 (0.09788), 761 (0.11309). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.31 (1H, d, J = 8.3 Hz, 25-phthalo-*H*), 8.91 (1H, d, J = 2.0 Hz, 22-phthalo-*H*), 7.83 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 24-phthalo-*H*), 7.69–7.12 (10H, m, phthalo-*H*, Ar-*H*), 5.24 (2H, s, ArCH_2O), 4.91–4.82 (8H, m, 4,8,11,15-OCH_2C$_3$H$_7$), 4.70 (2H, t, J = 6.4 Hz, 1-OCH_2C$_3$H$_7$), 4.61 (2H, t, J = 6.4 Hz, 18-OCH_2C$_3$H$_7$), 3.77–3.52 (2H, m, COCH$_2$CH_2Br), 3.01–2.83 (2H, m, COCH_2CH$_2$Br), 2.51–2.39 (2H, m, 1-OCH$_2$CH_2C$_2$H$_5$), 2.30–2.16 (10H, m, 4,8,11,15,18-OCH$_2$CH_2C$_2$H$_5$), 2.14–2.03 (2H, m, 1-OC$_2$H$_4$CH_2CH$_3$), 1.95–1.82 (2H, m, 18-OC$_2$H$_4$CH_2CH$_3$), 1.73–1.60 (8H, m, 4,8,11,15-OC$_2$H$_4$-CH_2CH$_3$), 1.28 (3H, t, J = 7.4 Hz, 1-OC$_3$H$_6$CH_3), 1.13–1.05 (15H, m, 4,8,11,15,18-OC$_3$H$_6$CH_3), 0.10 (2H, s, N*H*). MS (ESI-TOF; CH_2Cl_2/MeOH 1:1): *m/z* 1203.4954 $[M + H]^+$ (calcd. for $C_{66}H_{75}N_8O_9Br$ 1203.4918).

1,4,8,11,15,18-hexabutoxy-23-[3-(3-acetylsulfonylpropanoatemethyl)phenoxy]phthalocyanine (13). The product **10** (17 mg, 14.1 μmol) was dissolved in acetone (25 mL) and KSAc (3.2 mg, 28.2 μmol) was added. The mixture was heated at reflux under a drying tube for 3 days. After 24 h and 48 h of refluxing, more KSAc (2 mg) and acetone were added. Finally the green solution was cooled down to room temperature and the solvent was evaporated under reduced pressure. The crude product was dissolved in $CHCl_3$, the organic phase was washed with water (5 × 50 mL), and evaporated to dryness under reduced pressure. The product was purified twice by column chromatography on Silica 60, eluting with toluene/EtOAc 5:1, and the compound **13** was collected as second green fraction (R_f = 0.50 in toluene/EtOAc 5:1). The product **13** was obtained as a dark green solid (10 mg, 59%) after crystallizing on a watch glass and washing with *n*-pentane. UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 339 (44056), 737 (88228), 761 (99622). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.30 (1H, d, J = 8.3 Hz, 25-phthalo-*H*), 8.91 (1H, d, J = 2.1 Hz, 22-phthalo-*H*), 7.83 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 24-phthalo-*H*), 7.69–7.12 (10H, m, phthalo-*H*, Ar-*H*), 5.21 (2H, s, ArCH_2O), 4.91–4.82 (8H, m, 4,8,11,15-OCH_2C$_3$H$_7$), 4.70 (2H, t, J = 6.4 Hz, 1-OCH_2C$_3$H$_7$), 4.61 (2H, t, J = 6.4 Hz, 18-OCH_2C$_3$H$_7$), 3.11 (2H, t, J = 7.0 Hz, COCH$_2$CH_2S), 2.70 (2H, t, J = 7.0 Hz, COCH_2CH$_2$S), 2.51–2.39 (2H, m, 1-OCH$_2$CH_2C$_2$H$_5$), 2.30–2.23 (5H, m, OCH$_2$CH_2C$_2$H$_5$), 2.22 (3H, s, SCOCH_3), 2.21–2.16 (5H, m, OCH$_2$CH_2C$_2$H$_5$), 2.14–2.03 (2H, m, 1-OC$_2$H$_4$-CH_2CH$_3$), 1.95–1.81 (2H, m, 18-OC$_2$H$_4$CH_2CH$_3$), 1.74–1.60 (8H, m, 4,8,11,15-OC$_2$H$_4$CH_2CH$_3$), 1.28 (3H, t, J = 7.4 Hz, 1-OC$_3$H$_6$CH_3), 1.13–1.05 (15H, m, 4,8,11,15,18-OC$_3$H$_6$CH_3), 0.10 (2H, s, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1199.5671 $[M + H]^+$ (calcd. for $C_{68}H_{78}N_8O_{10}S$ 1199.5640).

1,4,8,11,15,18-hexabutoxy-23-[3-(*tert*-butylsuccinatoxymethyl)phenoxy]phthalocyanine (16). The compound **3** (50 mg, 46.8 μmol) was dissolved in CH_2Cl_2 (20 mL) and DCC (14 mg, 70.2 μmol), DMAP (2 mg, 14.0 μmol) and mono-*tert*-butyl succinate (12 mg, 70.2 μmol) were added. The reaction mixture was stirred at room temperature for two days. DCC (14 mg) and mono-*tert*-butyl succinate (12 mg) were added more after one day of stirring. The solvent was evaporated under reduced pressure, the product was redissolved in a few milliliters of CH_2Cl_2, and the solution was filtered twice through a cotton plug. Column chromatography was used for purification of the product (Silica 60, eluting with $CHCl_3$). The product was collected as first green fraction (R_f = 0.85 in $CHCl_3$/EtOH 18:1), crystallized on a watch glass, and washed with 2 mL of acetonitrile.

The product **16** was obtained as a dark green solid with quantitative yield (57 mg). ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.30 (1H, d, *J* = 8.3 Hz, 25-phthalo-*H*), 8.91 (1H, d, *J* = 2.1 Hz, 22-phthalo-*H*), 7.82 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 24-phthalo-*H*), 7.69–7.12 (10H, m, phthalo-*H*, Ar-*H*), 5.22 (2H, s, ArCH_2O), 4.91–4.82 (8H, m, 4,8,11,15-OCH_2C$_3$H$_7$), 4.70 (2H, t, *J* = 6.4 Hz, 1-OCH_2C$_3$H$_7$), 4.61 (2H, t, *J* = 6.4 Hz, 18-OCH_2C$_3$H$_7$), 2.70–2.53 (4H, m, COC$_2H_4$CO), 2.51–2.40 (2H, m, 1-OCH$_2$CH_2C$_2$H$_5$), 2.30–2.17 (10H, m, 4,8,11,15,18-OCH$_2$CH_2C$_2$H$_5$), 2.15–2.03 (2H, m, 1-OC$_2$H$_4$CH_2CH$_3$), 1.99–1.76 (2H, m, 18-OC$_2$H$_4$CH_2CH$_3$), 1.74–1.60 (8H, m, 4,8,11,15-OC$_2$H$_4$CH_2CH$_3$), 1.40 (9H, s, OC(CH_3)$_3$), 1.28 (3H, t, *J* = 7.4 Hz, 1-OC$_3$H$_6$CH_3), 1.14–1.05 (15H, m, 4,8,11,15,18-OC$_3$H$_6$CH_3), 0.10 (2H, s, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1225.6375 $[M + H]^+$ (calcd. for $C_{71}H_{84}N_8O_{11}$ 1225.6338).

1,4,8,11,15,18-hexabutoxy-23-[3-(succinatoxymethyl)phenoxy]phthalocyanine (18). The product **16** (57 mg, 46.5 μmol) was dissolved in dry CH_2Cl_2 (2 mL), TFA (2 mL) was added, and the solution was stirred at room temperature for 3 h. More CH_2Cl_2 was added and the organic phase was washed with water (3 × 50 mL). After evaporating the solvent under reduced pressure, the product was crystallized on a watch glass and washed with *n*-pentane. The product **18** (R_f = 0.30 in $CHCl_3$/EtOH 9:1) was obtained as dark green solid (50 mg, 93%). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 335 (43472), 734 (85217), 761 (98005). ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.30 (1H, d, *J* = 8.3 Hz, 25-phthalo-*H*), 8.85 (1H, d, *J* = 2.0 Hz, 22-phthalo-*H*), 7.84 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 24-phthalo-*H*), 7.69–7.12 (10H, m, phthalo-*H*, Ar-*H*), 5.21 (2H, s, ArCH_2O), 4.90–4.81 (8H, m, 4,8,11,15-OCH_2C$_3$H$_7$), 4.69 (2H, t, *J* = 6.4 Hz, 1-OCH_2C$_3$H$_7$), 4.59 (2H, t, *J* = 6.4 Hz, 18-OCH_2C$_3$H$_7$), 2.67–2.52 (4H, m, COC$_2H_4$CO), 2.50–2.39 (2H, m, 1-OCH$_2$CH_2C$_2$H$_5$), 2.30–2.18 (10H, m, 4,8,11,15,18-OCH$_2$CH_2C$_2$H$_5$), 2.16–2.03 (2H, m, 1-OC$_2$H$_4$CH_2CH$_3$), 1.97–1.77 (2H, m, 18-OC$_2$H$_4$CH_2CH$_3$), 1.74–1.59 (8H, m, 4,8,11,15-OC$_2$H$_4$CH_2CH$_3$), 1.28 (3H, t, *J* = 7.4 Hz, 1-OC$_3$H$_6$CH_3), 1.12–1.05 (15H, m, 4,8,11,15,18-OC$_3$H$_6$CH_3), 0.09 (2H, s, N*H*), COO*H* was not resolved. MS (ESI-TOF; MeOH/$CHCl_3$ 10:1): *m/z* 1169.5627 $[M + H]^+$ (calcd. for $C_{67}H_{76}N_8O_{11}$ 1169.5712).

1,4,8,11,15,18-hexabutoxy-23-[3-((pentafluorophenoxy)succinatoxymethyl)phenoxy]phthalocyanine (20). DCC (14 mg, 68.4 μmol) and pentafluorophenol (13 mg, 68.4 μmol) were added to a solution of the compound **18** (40 mg, 34.2 μmol) in EtOAc (10 mL). The mixture of compounds was stirred at room temperature. After one day of stirring, DCC (14 mg) and pentafluorophenol (13 mg) were added more. After five days the solvent was evaporated under reduced pressure and the product was dissolved in a few milliliters of CH_2Cl_2 and filtered through a cotton plug. Purification was carried out twice by column chromatography on Silica 100 and on Silica 60, eluting both times with $CHCl_3$. The product **20** was collected as first green fraction (R_f = 0.85 in $CHCl_3$/EtOH 18:1) and crystallized on a watch glass. After washing with *n*-pentane, the compound **20** was obtained as a dark green solid (25 mg, 55%). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 335 (73731), 734 (136634), 760 (154889). ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.30 (1H, d, *J* = 8.3 Hz, 25-phthalo-*H*), 8.91 (1H, d, *J* = 2.1 Hz, 22-phthalo-*H*), 7.83 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 24-phthalo-*H*), 7.69–7.12 (10H, m, phthalo-*H*, Ar-*H*), 5.23 (2H, s, ArCH_2O), 4.91–4.82 (8H, m, 4,8,11,15-OCH_2C$_3$H$_7$), 4.70 (2H, t, *J* = 6.4 Hz, 1-OCH_2C$_3$H$_7$), 4.61 (2H, t, *J* = 6.4 Hz, 18-OCH_2C$_3$H$_7$), 2.97–2.91 (2H, m, COC$_2H_4$CO), 2.84–2.78 (2H, m, COC$_2H_4$CO), 2.51–2.40 (2H, m, 1-OCH$_2$CH_2C$_2$H$_5$), 2.30–2.18 (10H, m, 4,8,11,15,18-OCH$_2$CH_2C$_2$H$_5$), 2.15–2.03 (2H, m, 1-OC$_2$H$_4$CH_2CH$_3$), 1.95–1.81 (2H, m, 18-OC$_2$H$_4$-CH_2CH$_3$), 1.74–1.60 (8H, m, 4,8,11,15-OC$_2$H$_4$CH_2CH$_3$), 1.29 (3H, t, *J* = 7.4 Hz, 1-OC$_3$H$_6$CH_3), 1.12–1.05 (15H, m, 4,8,11,15,18-OC$_3$H$_6$CH_3), 0.09 (2H, s, N*H*). MS (ESI-TOF; MeOH/$CHCl_3$ 10:1): *m/z* 1335.5555 $[M + H]^+$ (calcd. for $C_{73}H_{75}N_8O_{11}F_5$ 1335.5554).

1,4-di[hydroxypropyloxy]-9(10),16(17),23(24)-tri[*tert*-butyl]phthalocyanine (6). Lithium (80 mg, 12 mmol) was dissolved in 1-pentanol (40 mL) under argon atmosphere. 3,6-di(hydroxypropyloxy)phthalonitrile (**4**) (160 mg, 0.58 mmol) and 4-*tert*-butylphthalonitrile (**5**) (641 mg, 3.48 mmol) were added and the reaction mixture was heated at reflux for 2.5 h under argon atmosphere. The solution was cooled to room temperature and the solvent was evaporated under reduced pressure (bath temperature 80 °C). The product was dissolved in $CHCl_3$, the organic layer was washed with water (2 × 100 mL) and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on Silica 100, eluting the first fraction with $CHCl_3$ and the second fraction with $CHCl_3$/EtOH 20:1. The product **6** was obtained from the second fraction (R_f = 0.40 in $CHCl_3$/EtOH 18:1). Second fraction was repurified on Silica 60, eluting as before. The collected product **6** was crystallized on a watch glass, washed with acetonitrile, and obtained as a dark green powder (99 mg, 20%) after drying. UV-vis ($CHCl_3$/EtOH 1:1): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 340 (59122), 693 (89631), 719 (84165). ^{1}H NMR (300 MHz; $CDCl_3$/CD_3OD 10:1; Me_4Si): δ_H, ppm 9.50–8.45 (6H, m, phthalo-*H*), 8.28–8.07 (3H, m, phthalo-*H*), 6.88–6.07 (2H, m, 2,3-phthalo-*H*), 4.65–4.24 (8H, m, OCH_2CH$_2$CH_2OH), 2.51–2.23 (4H, m, OCH$_2$-CH_2CH$_2$OH), 1.91–1.68 (27H, m, C(CH_3)$_3$), -2.40–2.97 (2H, m, N*H*), CH$_2$O*H* were not resolved. MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 831.4359 $[M + H]^+$ (calcd. for $C_{50}H_{54}N_8O_4$ 831.4346).

1,4-di[(3-bromopropanoate)propyloxy]-9(10),-16(17),23(24)-tri[*tert*-butyl]phthalocyanine (11). Phthalocyanine **6** (20 mg, 24 μmol) was dissolved in CH_2Cl_2 (5 mL) and 3-bromopropionyl chloride (**9**) (1.64 M solution in CH_2Cl_2, 0.176 mL, 288 μmol) was added to the sealed vial. The reaction mixture was stirred at room

temperature for three days. A little amount of $CHCl_3$ was added, the organic phase was washed with saturated $NaHCO_3$ (aq) (9 × 50 mL) and water (1 × 50 mL), and the solvent was evaporated under reduced pressure. Column chromatography was used for purification of the product (Silica 100, eluting with $CHCl_3$). The target product was collected as first green fraction (R_f = 0.94 in $CHCl_3$/EtOH 18:1). The product **11** was crystallized on a watch glass, washed with *n*-pentane and was obtained as a dark green solid (14 mg, 55%). UV-vis ($CHCl_3$/EtOH 1:1): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 340 (62352), 689 (94878), 717 (91875). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.49–8.63 (6H, m, phthalo-*H*), 8.35–8.10 (3H, m, phthalo-*H*), 7.15–6.69 (2H, m, 2,3-phthalo-*H*), 4.91–4.33 (8H, m, $OCH_2CH_2CH_2O$), 3.82–3.49 (4H, m, $COCH_2CH_2Br$), 3.03–2.76 (4H, m, $COCH_2CH_2Br$), 2.71–2.41 (4H, m, $OCH_2CH_2CH_2O$), 1.90–1.76 (27H, m, $C(CH_3)_3$), -1.34–1.71 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1098.3121 $[M]^+$ (calcd. for $C_{56}H_{60}N_8O_6Br_2$ 1098.3003).

1,4-di[(3-acetylsulfonylpropanoate)propyloxy]-9-(10),16(17),23(24)-tri[*tert*-butyl]phthalocyanine (14). The product **11** (19 mg, 17.3 μmol) was dissolved in acetone (7 mL). KSAc (7.9 mg, 69.2 μmol) was added and the reaction mixture was stirred at room temperature for four days. The solvent was evaporated under reduced pressure and the dry product was dissolved in $CHCl_3$. The organic phase was washed with water (5 × 50 mL) and then evaporated to dryness under reduced pressure. Purification of the crude product was performed by column chromatography on Silica 100, eluting with toluene/EtOAc 5:1. The target product **14** was collected as second fraction (R_f = 0.27 in toluene/EtOAc 5:1), crystallized on a watch glass, and washed with *n*-pentane. The compound **14** was obtained as a dark blue-green powder (13 mg, 70%). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 344 (77457), 688 (130813), 715 (129384). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.50–8.80 (6H, m, phthalo-*H*), 8.34–8.16 (3H, m, phthalo-*H*), 7.17–6.91 (2H, m, 2,3-phthalo-*H*), 4.91–4.46 (8H, m, $OCH_2CH_2CH_2O$), 3.18–3.04 (4H, m, $COCH_2CH_2S$), 2.76–2.54 (8H, m, $COCH_2CH_2S$, $OCH_2CH_2CH_2O$), 2.28–2.21 (6H, m, $SCOCH_3$), 1.88–1.76 (27H, m, $C(CH_3)_3$), -1.03–1.34 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1090.4368 $[M]^+$ (calcd. for $C_{60}H_{66}N_8O_8S_2$ 1090.4445).

1,4-di[*tert*-butylsuccinatoxypropyloxy]-9(10),-16(17),23(24)-tri[*tert*-butyl]phthalocyanine (17). The compound **6** (50 mg, 60.2 μmol) was dissolved in CH_2Cl_2 (20 mL). DCC (50 mg, 240.8 μmol), DMAP (6 mg, 48.2 μmol) and mono-*tert*-butyl succinate (42 mg, 240.8 μmol) were added to the solution and the mixture was stirred at room temperature for two days. After one day, more DCC (25 mg) and mono-*tert*-butyl succinate (21 mg) were added. The solvent was evaporated under reduced pressure. The crude product was dissolved in a few milliliters of CH_2Cl_2 and then filtered through a cotton plug. The product was purified twice by column chromatography on Silica 60, eluting with $CHCl_3$. The compound **17** was collected as first fraction (R_f = 0.88 in $CHCl_3$/EtOH 18:1). The product **17** was obtained as a dark green solid with quantitative yield (68 mg). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.51–8.93 (6H, m, phthalo-*H*), 8.33–8.21 (3H, m, phthalo-*H*), 7.40–7.10 (2H, m, 2,3-phthalo-*H*), 4.92–4.54 (8H, m, $OCH_2CH_2CH_2O$), 2.81–2.49 (12H, m, $OCH_2CH_2CH_2O$, COC_2H_4CO), 1.87–1.76 (27H, m, $C(CH_3)_3$), 1.44 (18H, s, $OC(CH_3)_3$), -0.80–1.07 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 2286.1714 $[2M + H]^+$ (calcd. for $C_{132}H_{156}N_{16}O_{20}$ 2286.1760).

1,4-di[succinatoxypropyloxy]-9(10),16(17),23(24)-tri[*tert*-butyl]phthalocyanine (19). TFA (2 mL) was added to a solution of the product **17** (68 mg, 59.5 μmol) in dry CH_2Cl_2 (2 mL), and the reaction mixture was stirred at room temperature for 4.5 h. More CH_2Cl_2 was added, and the organic phase was washed with water (4 × 50 mL). The solvent was evaporated under reduced pressure and the compound **19** was crystallized on a watch glass and washed with *n*-pentane. The product **19** (R_f = 0.44 in $CHCl_3$/EtOH 9:1) was obtained as dark green solid with quantitative yield (61 mg). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 343 (45530), 688 (66999), 717 (70093). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.46–7.85 (9H, m, phthalo-*H*), 7.21–6.80 (2H, m, 2,3-phthalo-*H*), 4.91–4.15 (8H, m, $OCH_2CH_2CH_2O$), 2.80–2.42 (12H, m, $OCH_2CH_2CH_2O$, COC_2H_4CO), 1.89–1.74 (27H, m, $C(CH_3)_3$), -1.81–2.54 (2H, m, N*H*), COO*H* were not resolved. MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1029.4469 $[M - H]^-$ (calcd. for $C_{58}H_{62}N_8O_{10}$ 1029.4510).

1,4-di[(pentafluorophenoxy)succinatoxypropyloxy]-9(10),16(17),23(24)-tri[*tert*-butyl]phthalocyanine (21). The product **19** (50 mg, 48.5 μmol) was dissolved in EtOAc (10 mL), and DCC (20 mg, 97.0 μmol) and pentafluorophenol (18 mg, 97.0 μmol) were added. The solution was stirred at room temperature for four days. DCC (40 mg) and pentafluorophenol (36 mg) were added more after one day of stirring. The solvent was evaporated under reduced pressure and the dry product was dissolved in a few milliliters of CH_2Cl_2 and filtered through a cotton plug. Purification of the crude product was performed twice by column chromatography; first on Silica 100 and second on Silica 60, eluting both times with $CHCl_3$. The product **21** was obtained from the first green fraction (R_f = 0.90 in $CHCl_3$/EtOAc 10:1) and crystallized on a watch glass. After washing with *n*-pentane, the product **21** was obtained as a dark green solid (27 mg, 41%). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 343 (56115), 689 (92162), 713 (89484). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.50–8.75 (6H, m, phthalo-*H*), 8.34–8.14 (3H, m, phthalo-*H*), 7.22–6.80 (2H, m, 2,3-phthalo-*H*), 4.93–4.40 (8H, m, $OCH_2CH_2CH_2O$), 2.97–2.48 (12H, m, $OCH_2CH_2CH_2O$, COC_2H_4CO), 1.89–1.76 (27H, m, $C(CH_3)_3$), -1.18–1.49 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1385.4221 $[M + Na]^+$ (calcd. for $C_{70}H_{60}N_8O_{10}F_{10}Na$ 1385.4170).

1(4),8(11),15(18),22(25)-tetrakis[3-(hydroxymethyl)phenoxy]phthalocyanine (8). Lithium (200 mg, 29 mmol) was dissolved in 1-octanol (20 mL) under argon atmosphere by heating the solution for 45 min. The lithium octoxide (20 mL) formed was added in the solution of 3-[3-(hydroxymethyl)phenoxy]phthalonitrile (**7**) (300 mg, 1.2 mmol) in THF (2 mL). The reaction mixture was stirred at 80 °C under argon atmosphere for three days. The dark green solution was cooled to room temperature, and MeOH/water 1:1 (100 mL) was added. The organic phase was separated and washed two times with water. First obtained water phase was washed with $CHCl_3$, and organic layers were combined and solvents were evaporated. The crude product was poured into hexane (120 mL) and left to precipitate for one day. The precipitation was filtered and washed with hexane (2 × 40 mL) and diethyl ether (4 × 40 mL). The product was dissolved in toluene/DMF 2:1 from the filter, and most of the solvent was evaporated under reduced pressure. The dark green product was purified by column chromatography on Silica 100, eluting with toluene/DMF 2:1. The target product was obtained from the first blue-green fraction (R_f = 0.29 in toluene/DMF 4:1). The product was evaporated to dryness under reduced pressure (bath temperature 70 °C), dissolved in MeOH and crystallized on a watch glass. After drying and washing twice with diethyl ether, the compound **8** was obtained as a dark green solid (235 mg, 78%). UV-vis (DMF): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 331 (69011), 685 (146151), 711 (155172). ^1H NMR (300 MHz; $(CD_3)_2SO$; Me_4Si): δ_H, ppm 8.20–7.38 (12H, m, phthalo-*H*), 7.35–6.91 (16H, m, Ar-*H*), 5.19 (4H, br t, *J* = 5.6 Hz, $ArCH_2O$*H*), 4.57–4.39 (8H, m, $ArCH_2OH$), -2.03–2.62 (2H, m, N*H*). MS (ESI-TOF; MeOH): *m/z* 1003.3254 $[M + H]^+$ (calcd. for $C_{60}H_{42}N_8O_8$ 1003.3204).

1(4),8(11),15(18),22(25)-tetrakis[3-(3-bromopropanoatemethyl)phenoxy]phthalocyanine (12). The compound **8** (100 mg, 0.1 mmol) was dissolved in THF/CH_2Cl_2 1:1 (10 mL) and 3-bromopropionyl chloride (**9**) (1.64 M solution in CH_2Cl_2, 0.6 mL, 1.0 mmol) was added to the vial. The solution was diluted with CH_2Cl_2 (20 mL) and the reaction mixture was stirred at room temperature for three days. After 24 h and 48 h of stirring additionally 0.6 mL of **9** was added. Water (3 mL) was added to the reaction mixture and stirring was continued for one day. The organic phase was separated, washed with water (6 × 50 mL), and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on Silica 60, eluting with $CHCl_3$. The product **12** was collected as first fraction (R_f = 0.90 in $CHCl_3$/EtOH 18:1) and crystallized on a watch glass. After washing with *n*-pentane, the compound **12** was obtained as a dark green tar (73 mg, 47%). UV-vis (DMF): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 330 (54185), 688 (104861), 714 (101833). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.90–7.75 (12H, br, phthalo-*H*), 7.69–7.03 (16H, m, Ar-*H*), 5.34–5.06 (8H, m, $ArCH_2O$), 3.80–3.36 (8H, m, $COCH_2CH_2Br$), 3.04–2.68 (8H, m, $COCH_2CH_2Br$), -1.08–1.85 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1539.0872 $[M + H]^+$ (calcd. for $C_{72}H_{54}N_8O_{12}Br_4$ 1539.0673).

1(4),8(11),15(18),22(25)-tetrakis[3-(3-acetylsulfonylpropanoatemethyl)phenoxy]phthalocyanine (15). The product **12** (50 mg, 32.4 μmol) and KSAc (30 mg, 0.26 mmol) were dissolved in acetone (32 mL). The reaction mixture was stirred at room temperature for one day and, after that, at 60 °C for one day more. More of KSAc (30 mg) was added, and stirring was continued at 60 °C of one day more. The solution was cooled and the solvent was evaporated under reduced pressure. The crude product was taken into $CHCl_3$ and the organic layer was washed with water (5 × 100 mL). The solvent was evaporated to dryness under reduced pressure. Purification was performed by column chromatography on Silica 60, eluting with $CHCl_3$. The product was collected as first fraction (R_f = 0.73 in $CHCl_3$/EtOH 18:1), crystallized on a watch glass, and washed with *n*-pentane. The product **15** was obtained as a dark green tar (35 mg, 70%). UV-vis (DMF): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 332 (49416), 688 (97500), 713 (87202). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.83–7.73 (12H, br, phthalo-*H*), 7.67–7.03 (16H, m, Ar-*H*), 5.30–4.99 (8H, m, $ArCH_2O$), 3.15–2.91 (8H, m, $COCH_2CH_2S$), 2.74–2.51 (8H, m, $COCH_2CH_2S$), 2.33–2.15 (12H, m, $SCOCH_3$), -1.40–2.31 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 1523.3571 $[M + H]^+$ (calcd. for $C_{80}H_{66}N_8O_{16}S_4$ 1523.3558).

1(4),8(11),15(18),22(25)-tetrakis[3-((pentafluorophenoxy)succinatoxymethyl)phenoxy]phthalocyanine (22). The compound **8** (30 mg, 30 μmol) was dissolved in THF (5 mL). CH_2Cl_2 (10 mL), mono-*tert*-butyl succinate (26 mg, 0.15 mmol), DCC (31 mg, 0.15 mmol) and DMAP (catalytic amount) were added to the solution. The reaction mixture was stirred at room temperature overall for seven days. More DCC (30 mg) and mono-*tert*-butyl succinate (26 mg) were added after one, four and six days. The solvent was evaporated under reduced pressure, and the residue was dissolved in EtOAc (3 mL), filtered through a cotton plug and evaporated again. The crude product was purified by column chromatography on Silica 60, eluting first with $CHCl_3$. The intermediate product, 1(4),8(11),15(18),22(25)-tetrakis-[3-(*tert*-butylsuccinatoxymethyl)phenoxy]phthalocyanine, was collected after changing the eluent to $CHCl_3$/EtOH 20:1 (R_f = 0.87 in $CHCl_3$/EtOH 18:1). After crystallizing the product on a watch glass, washing it with *n*-pentane and drying it in exsiccator for few days, the compound was obtained as green solid with quantitative yield (48 mg). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 3252.2451 $[2M - H]^-$ (calcd. for $C_{92}H_{90}N_8O_{20}$ 3252.2463).

The whole amount of 1(4),8(11),15(18),22(25)-tetrakis[3-(*tert*-butylsuccinatoxymethyl)phenoxy]phthalocyanine was dissolved in dry CH_2Cl_2 (2 mL), and TFA (2 mL) was added. The solution was stirred at room temperature for 4.5 h, and after that evaporated under reduced pressure. The residue was dried in exsiccator overnight.

The intermediate product, 1(4),8(11),15(18),22(25)-tetrakis[3-(succinatoxymethyl)phenoxy]phthalocyanine, (R_f = 0.05 in $CHCl_3$/EtOH 9:1) was obtained as dark green solid with quantitative yield (41 mg). MS (ESI-TOF; MeOH): *m/z* 1403.3928 $[M + H]^+$ (calcd. for $C_{76}H_{58}N_8O_{20}$ 1403.3845).

The product 1(4),8(11),15(18),22(25)-tetrakis[3-(succinatoxymethyl)phenoxy]phthalocyanine (41 mg, 30 μmol) was dissolved in EtOAc (15 mL) on ultrasonic bath. Pentafluorophenol (44 mg, 0.24 mmol) and DCC (49 mg, 0.24 mmol) were added. The reaction mixture was stirred in ice bath for two days and at room temperature for one day. After one day of stirring in cold, more DCC (49 mg) and pentafluorophenol (44 mg) were added. The solvent was evaporated under reduced pressure and the dry product was dissolved in CH_2Cl_2 (3 mL) and filtered through a cotton plug. The crude product was purified by column chromatography on Silica 60, eluting with $CHCl_3$. The product **22** was obtained from the first green fraction (R_f = 0.94 in $CHCl_3$/EtOAc 18:1) and crystallized on a watch glass. The compound **22** was repurified first by flash chromatography (Silica 60, eluent $CHCl_3$) and finally on preparative TLC plate (Silica gel 60 F_{254}), eluent $CHCl_3$. After solvent removal, the product **22** was crystallized on a watch glass, washed with *n*-pentane and obtained as a dark green solid (15 mg, 25%). UV-vis ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}.cm^{-1}$) 337 (37420), 684 (89705), 716 (102761). ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.79–8.21 (4H, m, α-phthalo-*H*), 7.81 (4H, t, *J* = 7.6 Hz, β-phthalo-*H*), 7.57–7.38 (4H, m, β-phthalo-*H*), 7.38–7.02 (16H, m, Ar-*H*), 5.20–5.01 (8H, m, ArCH_2O), 2.99–2.55 (16H, m, COC_2H_4CO), -1.51–2.05 (2H, m, N*H*). MS (ESI-TOF; $CHCl_3$/MeOH 1:1): *m/z* 2067.3279 $[M + H]^+$ (calcd. for $C_{100}H_{54}N_8O_{20}F_{20}$ 2067.3213).

Immobilization

Glass plates were cleaned first manually with a cotton stick and $CHCl_3$, and then by sonication in $CHCl_3$, acetone, chromosulfuric acid and NaOH (aq) (0.001 M), 30 min in each solvent. After sonication in acetone, acid and NaOH, the plates were washed several times with MilliQ water. The cleaned glass plates were dried in oven at 150 °C. Glass plates with ITO layer on one side were cleaned by sonication in acetone/water 1:1, 2-propanol and CH_2Cl_2, 5 min in each solvent, and dried in oven at 150 °C.

The gold substrates were prepared by thermal evaporation under vacuum of a layer of gold onto cleaned glass plates that had been precoated with a titanium adhesion layer. Titanium and gold layers were 2 nm and 3 nm thick, respectively. Phthalocyanine SAMs were prepared by immersing the gold-coated glass plates in the Pc **13**, **14** and **15** solutions in CH_2Cl_2 (3 mM) for 30 min at room temperature [32]. After that, the plates were rinsed with CH_2Cl_2 and $CHCl_3$, altogether ten times, and dried in air.

A reaction vessel, which was cooled after being in oven (150 °C), was charged with dry toluene (20 mL), isopropyl amine (0.4 mL) and 3-aminopropyltrimethoxysilane (2 mL) under argon flow [34]. The plates (glass and ITO) were immersed in the solution, the reaction vessel was filled with argon and heated at 105 °C for 1 h. The activated plates were cleaned right from the reactor by 15 s sonication in toluene and toluene/acetone 1:1 mixture. The plates were dried in argon flow (30 min), and used for further Pc immobilization immediately. Phthalocyanine (2 mg) was dissolved in dry toluene (20 mL) and loaded in the reaction vessel with argon. Concentration of **20** was 75 μM, concentration of **21** was 73 μM, and concentration of **22** was 48 μM. The dried activated plates were immersed in the solution, and reaction vessel was filled again with argon and heated at 105 °C. After 2 h the plates were sonicated twice in toluene and once in CH_2Cl_2, 15 s in each solvent, and the samples were dried in argon flow (30 min).

CONCLUSION

We have developed a set of basic phthalocyanine structures, which can be easily fuctionalized to produce the monomolecular layers on gold, glass and ITO. We have demonstrated that the organization of the layer does not depend on the number of anchor groups only, but is influenced as well by the interaction of the macrocycle and the side substituents with the substrate surface. Research on the application of the synthesized Pcs in optical fiber sensors, organic solar cells, and chromophore-functionalized gold nanoparticles and SPR-sensors are under way and will be published in due time.

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Supporting information

Mass spectra of all synthesized Pcs (**3**, **6**, **8** and **10**–**22**), NMR spectra of the Pcs **6**, **8**, **10**–**12**, **14**–**19**, **21** and **22**, and emission spectra of Pcs **3**, **6**, **8**, **13**–**15** and **20**–**22** are given in the supplementary material. This material is available free-of-charge at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

1. Herbst W and Hunger K. *Industrial Organic Pigments: Production, Properties, Applications* (3rd edn.), Wiley-VCH: Weinheim, 2004; pp 422–452.
2. Gregory P. *J. Porphyrins Phthalocyanines* 2000; **4**: 432–437.

3. Thomas AL. *Phthalocyanine Research and Applications*, CRC Press: Boca Raton, 1990; pp 43–52.
4. De la Torre G, Claessens CG and Torres T. *Chem. Commun.* 2007; **20**: 2000–2015.
5. Cook MJ. *Pure Appl. Chem.* 1999; **71**: 2145–2151.
6. Armstrong NR, Wang W, Alloway DM, Placencia D, Ratcliff E and Brumbach M. *Macromol. Rapid Commun.* 2009; **30**: 717–731.
7. Nyokong T and Bedioui F. *J. Porphyrins Phthalocyanines* 2006; **10**: 1101–1115.
8. Muzikante I, Parra V, Dobulans R, Fonavs E, Latvels J and Bouvet M. *Sensors* 2007; **7**: 2984–2996.
9. Gryko DT, Clausen C and Lindsey JS. *J. Org. Chem.* 1999; **64**: 8635–8647.
10. Ohyama J, Hitomi Y, Higuchi Y, Shinagawa M, Mukai H, Kodera M, Teramura K, Shishido T and Tanaka T. *Chem. Commun.* 2008; **47**: 6300–6302.
11. Huang X, Liu Y, Wang S, Zhou S and Zhu D. *Chem. Eur. J.* 2002; **8**: 4179–4184.
12. DiBenedetto SA, Facchetti A, Ratner MA and Marks TJ. *Adv. Mater.* 2009; **21**: 1407–1433.
13. Cid J-J, García-Iglesias M, Yum J-H, Forneli A, Albero J, Martínez-Ferrero E, Vázquez P, Grätzel M, Nazeeruddin MK, Palomares E and Torres T. *Chem. Eur. J.* 2009; **15**: 5130–5137.
14. Metzger RM. *Chem. Rev.* 2003; **103**: 3803–3834.
15. Würthner F. *Supramolecular Dye Chemistry,* Springer: Berlin, 2005; pp 257–313.
16. Ulman A. *Chem. Rev.* 1996; **96**: 1533–1554.
17. Imahori H, Norieda H, Yamada H, Nishimura Y, Yamazaki I, Sakata Y and Fukuzumi S. *J. Am. Chem. Soc.* 2001; **123**: 100–110.
18. Guo C-C, Ren T-G, Song J-X, Liu Q, Luo K, Lin W-Y and Jiang G-F. *J. Porphyrins Phthalocyanines* 2005; **9**: 830–834.
19. Andersson M, Holmberg M, Lundström I, Lloyd-Spetz A, Mårtensson P, Paolesse R, Falconi C, Proietti E, Di Natale C and D'Amico A. *Sens. Actuators, B* 2001; **77**: 567–571.
20. Amao Y, Asai K, Miyakawa K and Okura I. *J. Porphyrins Phthalocyanines* 2000; **4**: 19–22.
21. Hoppe H and Sariciftci NS. *J. Mater. Res.* 2004; **19**: 1924–1945.
22. Uchida S, Xue J, Rand BP and Forrest SR. *Appl. Phys. Lett.* 2004; **84**: 4218–4220.
23. Loi MA, Denk P, Hoppe H, Neugebauer H, Winder C, Meissner D, Brabec C, Sariciftci NS, Gouloumis A, Vázquez P and Torres T. *J. Mater. Chem.* 2003; **13**: 700–704.
24. Vivo P, Ojala M, Chukharev V, Efimov A and Lemmetyinen H. *J. Photochem. Photobiol., A* 2009; **203**: 125–130.
25. El-Khouly ME, Ito O, Smith PM and D'Souza F. *J. Photochem. Photobiol., C* 2004; **5**: 79–104.
26. De la Torre G, Claessens CG and Torres T. *Eur. J. Org. Chem.* 2000; **2000**: 2821–2830.
27. Isosomppi M, Tkachenko NV, Efimov A, Vahasalo H, Jukola J, Vainiotalo P and Lemmetyinen H. *Chem. Phys. Lett.* 2006; **430**: 36–40.
28. Cook MJ, Dunn AJ, Howe SD, Thomson AJ and Harrison KJ. *J. Chem. Soc., Perkin Trans. 1* 1988; 2453–2458.
29. Tercel M, Stribbling SM, Sheppard H, Siim BG, Wu K, Pullen SM, Botting KJ, Wilson WR and Denny WA. *J. Med. Chem.* 2003; **46**: 2132–2151.
30. Zheng T-C, Burkart M and Richardson DE. *Tetrahedron Lett.* 1999; **40**: 603–606.
31. Isosomppi M, Tkachenko NV, Efimov A, Kaunisto K, Hosomizu K, Imahori H and Lemmetyinen H. *J. Mater. Chem.* 2005; **15**: 4546–4554.
32. Yasseri AA, Syomin D, Malinovskii VL, Loewe RS, Lindsey JS, Zaera F and Bocian DF. *J. Am. Chem. Soc.* 2004; **126**: 11944–11953.
33. Lehtivuori H, Kumpulainen T, Hietala M, Efimov A, Lemmetyinen H, Kira A, Imahori H and Tkachenko NV. *J. Phys. Chem. C* 2009; **113**: 1984–1992.
34. McCallien DWJ, Burn PL and Anderson HL. *J. Chem. Soc., Perkin Trans. 1* 1997; 2581–2586.