Synthesis and Self-Assembly of 2,9,16-Tri(*tert*-butyl)-23-(10-mercaptodecyloxy)phthalocyanine and the Application of Its Self-Assembled Monolayers in Organic Light-Emitting Diodes

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Abstract: 2,9,16-Tri(*tert*-butyl)-23-(10-mercaptodecyloxy)phthalocyanine (**8**) and its disulfide (**9**) have been synthesized and characterized, and their self-assembling behaviors on gold substrates have been studied. Characteristic Q-bands were observed at about 630 nm in the UV/visible spectra of the self-assembling monolayers (SAMs). They were broadened and blue-shifted relative to those observed in solution. Binding energies for S2p have the same values (161.70 eV) and are in accord with those for gold thiolates. The application of the SAMs in organic light-emitting diode was investigated. It shows that the SAM promotes the hole injection process from the anode.

Keywords: hole injection · organic light-emitting diode · phthalocyanines · self-assembly · synthesis design

Introduction

Phthalocyanines have attracted great interest due to their remarkable properties, which give them many possible applications. They have already been used in laser printers, photocopiers, and data storage systems, but still have many other potential applications.[1, 2] Phthalocyanine thin films are usually used in these devices.[2] Various methods have been used in fabricating such films, for example, the Langmuir–Blodgett technique, spin-coating, and self-assembly methods.[2–4] Among these, self-assembled monolayers (SAMs) are particularly attractive because they are simple to fabricate and have high stability and reproducibility.[5] Moreover, with the rapid growth of the promising research field of molecular-scale electronic devices, self-assemblies are receiving even more attention. Molecular field-effect transistors based on SAMs have been reported recently.[6] Ball described a bright future for commercially viable devices based on molecular self-assembly.[7] Though the self-assembly of small molecules, especially thiols, has been extensively studied,[5] only limited work has been done on the self-assembly of phthalocyanines. This probably comes from the synthetic difficulties of making functionalized phthalocyanines. Trichlorosilyl phthalocyanines assembled on glass or silicon substrates have been reported by Cook et al.[8] Russell et al. reported the self-assembly of mercapto- and disulfide-functionalized phthalocyanines on gold surfaces.[9] Phthalocyanine has been widely used in organic light-emitting diodes (OLEDs).[10, 11] It has been demonstrated that the phthalocyanine layer can enhance the hole injection from indium tin oxide (ITO) to the hole transport layer. In these devices, the phthalocyanine thin films were fabricated by thermal evaporation. No phthalocyanine SAM has been used in an OLED yet. In this paper, a more general method[12] was used for the synthesis of hydroxy phthalocyanine, which was then converted to the target phthalocyanines. *tert*-Butyl groups were introduced to enhance the phthalocyanines' solubility, and a long chain bearing a mercapto or disulfide group was used as functional group for self-assembly. Their assembled monolayers on gold-coated substrates were studied and characterized by UV/visible spectrometry and X-ray photoelectron spectrometry (XPS). The application of the SAM in OLEDs was investigated.

Results and Discussion

Synthesis: Condensation of phthalonitriles is a well-established method for the synthesis of pthalocyanines.[1] A lot of uniformly substituted phthalocyanines bearing various substituents have been synthesized by this method.[1] It has been used in the synthesis of nonuniformly substituted phthalocyanines as well.[13–19] Condensation of two (or more, theoretically) kinds of phthalonitriles bearing different substituents produces a mixture of phthalocyanines. From this mixture, a series of nonuniformly substituted phthalocyanines can be separated. Though the yield is rather low, this is the most used method and it seems to be the most convenient

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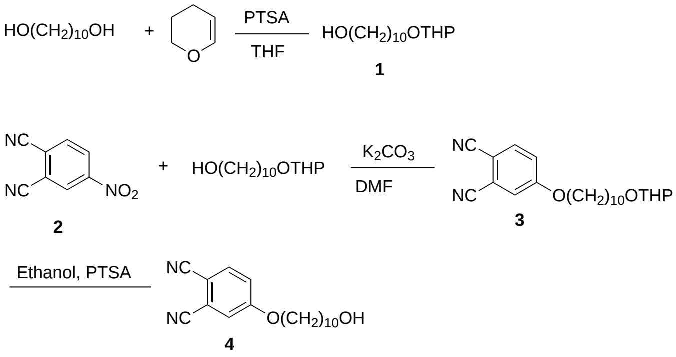
method at present, until a better method is developed. Phthalonitriles bearing an alkoxy group at the 4-position have been synthesized through the nucleophilic substitution of 4-nitrophthalonitrile (**2**), which is commercially available according to a literature method.[12] Using monohydroxy-protected decane-1,10-diol as nucleophile, we synthesized 4-(10-tetrahydropyranyldecyloxy)phthalonitrile (**3**). After deprotection of the hydroxy group, phthalonitrile **4** bearing a hydroxy group was obtained (Scheme 1). In phthalocyanine chemistry, solubility is a key factor that should be considered carefully. Here we chose 4-*tert*-butylphthalonitrile (**5**) as the other starting material, because the *tert*-butyl group can greatly enhance the solubility of the compound. The synthetic route to phthalocyanines is shown in Scheme 2. The reaction of phthalonitriles **4** and **5** (1:3) was carried out in *n*-pentanol in the presence of lithium pentoxide according to the literature method.[1] Due to the difference in polarity, the desired monohydroxy phthalocyanine was easily separated from the major product tetra-*tert*-butylphthalocyanine. The method developed by Cook[20] was used to convert the hydroxy phthalocyanine to the mercaptophthalocyanine. After mesylation of the hydroxy group, the methanesulfonyl group then reacted with thiourea to form the isothiouronium salt. Hydrolysis of the isothiouronium salt by base in situ afforded the mercaptophthalocyanine **8**. The disulfide **9** was separated as a byproduct.



Scheme 1. Synthesis route to phthalonitrile **4**.

Characterization: Phthalocyanines **8** and **9** were characterized by ^{1}H NMR spectroscopy, MALDI-TOF MS and UV/visible spectrometry. The ^{1}H NMR spectra of the mercaptophthalocyanine **8** and the corresponding disulfide **9** are similar. Protons on aliphatic carbons (δ from ca. 0.5 to 2.1 ppm) that indirectly link to O or S atoms appear as several overlapping multiple peaks, protons on carbons next to S atoms are observed at lower field ($\delta = 2.81$, 2.82 ppm for **8** and **9**, respectively), protons on carbons next to the more electronegative O atoms shift to about $\delta = 4$ ($\delta = 4.06$, 3.99 ppm for **8** and **9**, respectively), and aromatic protons appear at the lowest field as multiple peaks. But there is a difference. The signal for the NH protons at the center of the macrocycle of phthalocyanine **8** appears as a broad band centered at $\delta = -2.95$ ppm, while in the disulfide **9**, the corresponding signal is centered at $\delta = -3.14$ ppm. This means that there is a stronger shielding effect in the disulfide than in the mercaptophthalocyanine, and as a result the signal shifts to higher field. This probably comes from the intramolecular interaction of the two macrocycles of compound **9**. However, it is insufficient to allow the two compounds to be distinguished, because the SH proton could not be assigned. However, they can be clearly distinguished from each other by their MALDI-TOF mass spectra. Mercaptophthalocyanine **8** shows a parent ion peak at 870.8 [M^+], while disulfide **9** shows a parent plus one peak at 1740.0 [$M^+ + 1$]. The UV/visible spectra of **8** and **9** are almost the same except in intensity (Figure 1). This is reasonable when one considers the fact that the two macrocycles of the disulfide are linked by a long σ-bond chain consisting of two oxygen atoms, twenty carbon atoms, and two sulfur atoms. The distance between the two macrocycles is so great that the interaction between them is weak and has negligible influence on the electron structure. From the UV/visible spectra, we can also see that the aggregation tendency of the two compounds is very high. Even at low concentration (1.0×10^{-6} mol L^{-1} and 9.8×10^{-7} mol L^{-1} for **8** and **9**, respectively), they appear primarily as dimers[1] as shown in the Q-band of their UV/visible spectra; and the spectra have no significant difference from those measured at higher concentration (1.0×10^{-5} mol L^{-1} and 9.8×10^{-6} mol L^{-1} for **8** and **9**, respectively).

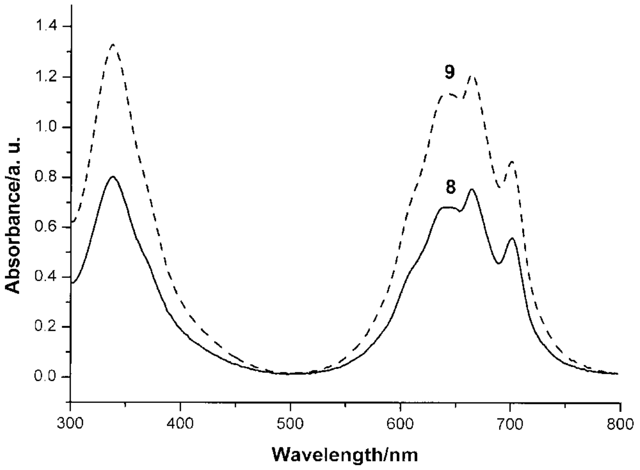
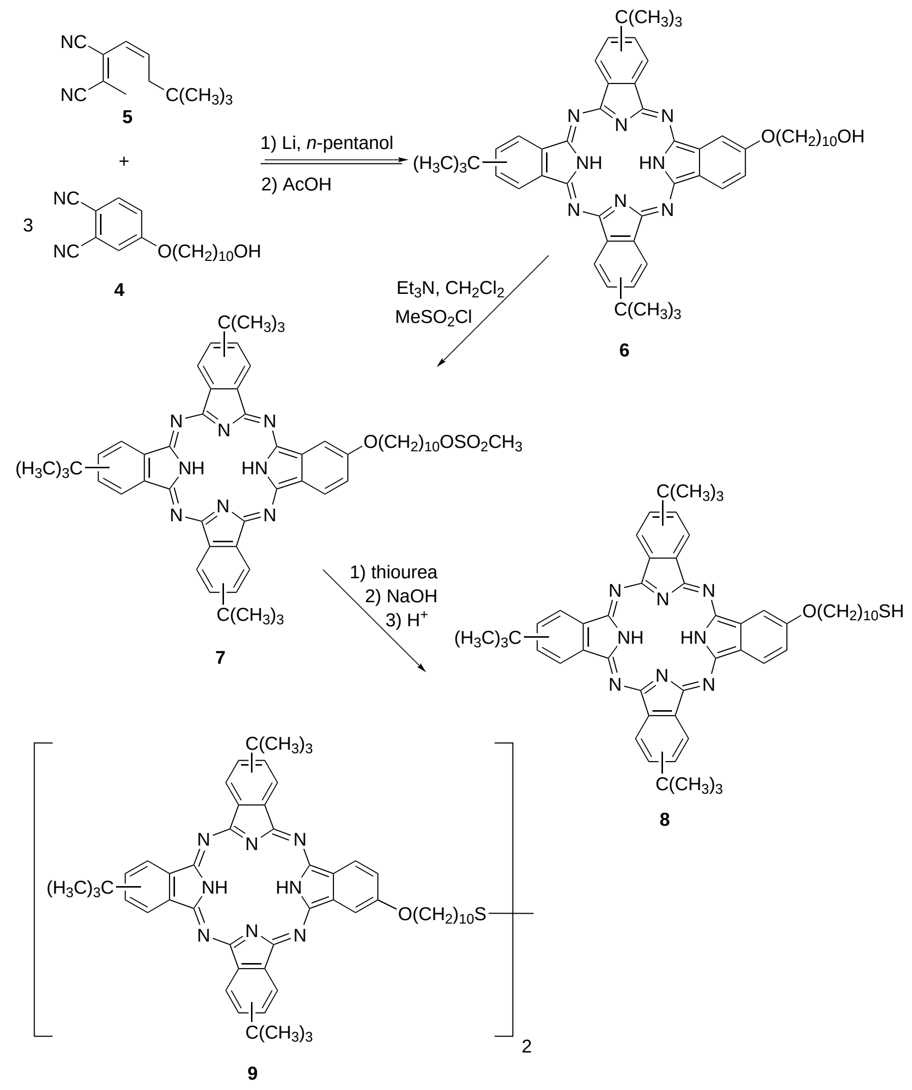


Figure 1. UV/visible spectra in $CHCl_3$ of **8** (1.0×10^{-5} mol L^{-1}; ——) and **9** (9.8×10^{-6} mol L^{-1}; - - - -).

Abstract in Chinese:

合成了 2，9，16－三特丁基－23－（10－巯基癸烷氧基）酞菁（8）和它的以硫－硫键结合的二联体（9）并进行了表征。研究了它们在金基底上的自组装行为。在它们的自组装单层膜的紫外－可见光谱中，可以观察到位于约 630 纳米处酞菁的典型的 Q－带吸收。与它们在溶液中的紫外－可见光谱相比，谱带变宽并且发生了蓝移。在 X－射线光电子能谱中，S2p 峰位于 161.70eV，这个值对应于自组装膜中生成的硫－金键。我们把自组装单层膜应用于有机发光二极管。结果表明酞菁的自组装单层膜对从阳极的空穴注入过程起到了促进作用。



Scheme 2. Synthesis route to phthalocyanines **8** and **9**.

Self-assembly: That thiols and disulfides can form self-assembled monolayers on gold substrates has long been established.[5] In this paper, we study the self-assembly behavior of phthalocyanine derivatives **8** and **9**. Both of them can form self-assembled monolayers on gold substrates. The gold substrates were immersed in solutions of compounds **8** and **9** in chloroform (6.7×10^{-5} mol L^{-1} and 2.9×10^{-5} mol L^{-1}, respectively) for 24 h. Then the substrates were washed thoroughly with chloroform to remove unbound phthalocyanine molecules. After that the substrates were dried in a stream of nitrogen.

UV/visible spectra of the self-assembled monolayers were obtained by using references prepared by immersing gold substrates in pure solvent. The UV/visible spectra of the self-assembled monolayers of **8** and **9** are shown in Figure 2. Both of them show the characteristic Q-band associated with phthalocyanine molecules in the spectra. The Q-bands are broadened and blue-shifted relative to those observed in solution (Figure 1). Such phenomena are also observed by other authors.[8, 9] XPS analysis shows direct evidence for the formation of the self-assembled monolayers. The C1s and S2p spectra of **8** and **9** SAMs on gold are presented in Figure 3. The S2p peaks clearly suggest that the major sulfur species present is a thiolate (RSAu). They appear at approximately the same position (161.70 eV). This value is nearly the same as those for gold thiolates reported by others.[21–24] No evidence of unbound thiols is observed.[21–24]

Primary results of SAMs in LEDs: Figure 4 illustrates the current–voltage ($I-V$) and luminance–voltage ($L-V$) characteristics of a ITO/Au/TPD/Alq$_3$/Al device with and without a SAM. It can be seen that both the $I-V$ and $L-V$ curves of the device with the SAM demonstrate remarkable improvements on the device without the SAM. The turn-on voltages are lowed from 17.4 V to 13.8 V for the current and from 12.9 V to 8.3 V for the luminance. Running at 10 mA, the brightness for ITO/Au-SAM/TPD/Alq$_3$/Al reaches 1250 cd m^{-2}, but only 40 cd m^{-2} for ITO/Au/TPD/Alq$_3$/Al. Since the same fabrication conditions were imposed, it seems that the SAMs play an important role in the charge injection process of the device. SAMs have been reported to influence the work function of metal substrates and charge injection at electrodes.[25] In the device with the SAM, the coated SAM might change the work

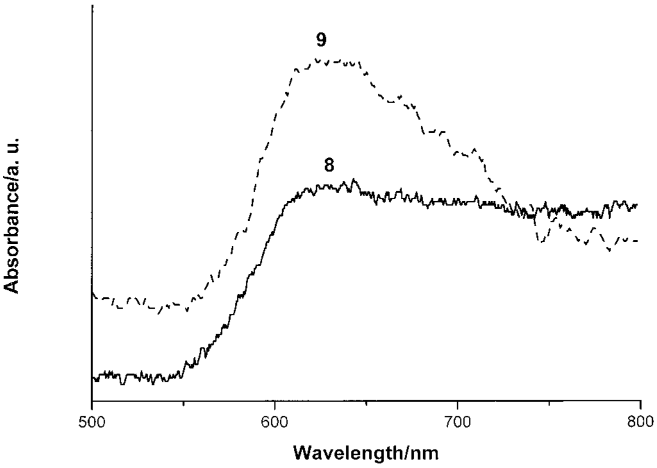


Figure 2. Visible absorption (Q-band) spectra of SAMs of **8** and **9**.

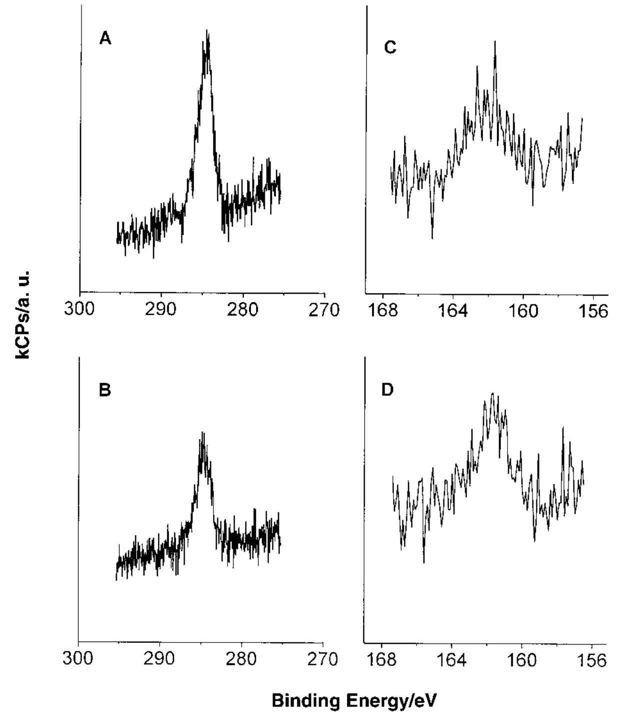


Figure 3. The XP spectra of SAMs of **8** and **9** on Au. A) C1s XP spectrum of **8**; B) C1s XP spectrum of **9**; C) S2p XP spectrum of **8**; D) S2p XP spectrum of **9**.

function of the Au substrate and promote the hole-injection process from the anode. Campbell and co-workers[25] studied the influence of SAMs of two conjugated thiols on the charge-injection process at electrodes, and found that the conjugated thiol ($HS(C_6H_4C_2)_2C_6H_4$-H) SAM retarded the hole injection from the anode. In contrast to their results, the SAMs of phthalocyanine promote hole injection from the anode because phthalocyanine is recognized as a p-type material, due to its richness in delocalized macrocyclic π-electrons, and has been used widely as a hole injection/transport layer in LEDs.[10–11, 26–28]

Conclusion

Mercaptophthalocyanine **8** and its disulfide **9** have been synthesized by converting the hydroxy group of hydroxyphthalocyanine **6** to a mercapto group. Hydroxyphthalocyanine **6** was synthesized by a general method, first nucleophilic substitution of the nitro group of phthalonitrile **2** by a protected alcohol and subsequent deprotection; then mixed condensation of phthalonitrile **4** and **5** in a ratio of 1:3. Because of the difference in polarity, the desired hydroxyphthalocyanine **6** was easily separated from the major product tetra-*tert*-butylphthalocyanine. The phthalocyanines were characterized by ^{1}H NMR, MALDI-TOF-MS and UV/visible spectrometry. Both the mercaptophthalocyanine **8** and its disulfide **9** can form self-assembled monolayers on gold substrates. Q-bands characteristic of phthalocyanines were observed in the UV/visible spectra of the self-assembled monolayers. XP spectra of the self-assembled monolayers were also obtained. S2p peaks were observed at a binding energy (BE) of 161.70 eV, which is in accord with those of thiolate (RSAu) S species. UV-visible spectra and XPS both proved the formation of the self-assembled monolayers. The SAM has been applied to LED device, lowered turn-on voltages and enhanced brightness were observed.

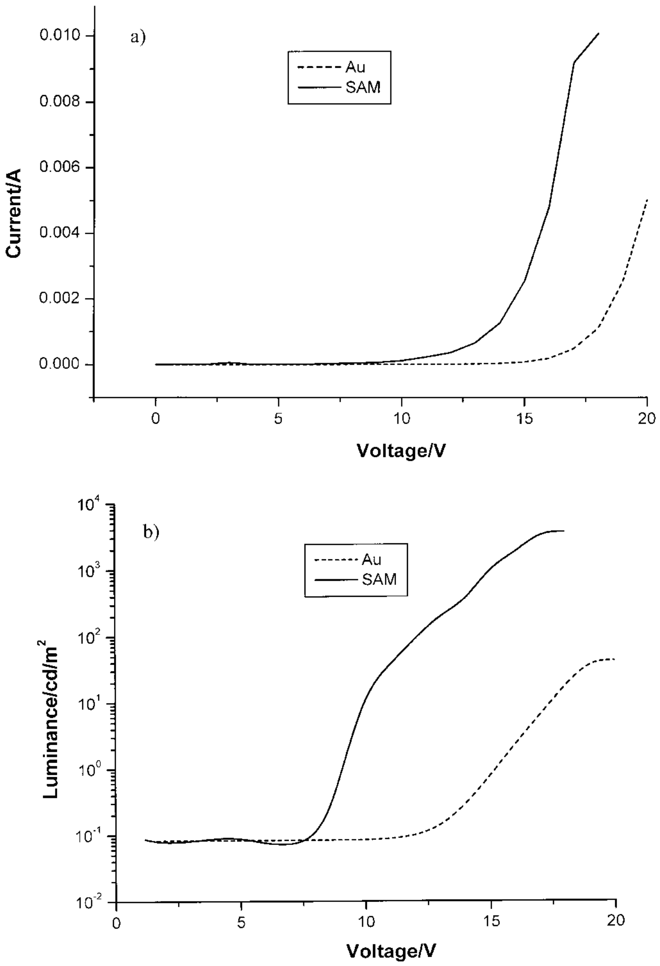


Figure 4. Current-voltage (a) and luminance-voltage (b) curves of the ITO/Au/TPD/Alq_3/Al LED with and without SAM.

Experimental Section

Materials: All reactions were carried out under an atmosphere of nitrogen. 4-Nitrophthalonitrile and 4-*tert*-butylphthalonitrile were purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. Tetrahydrofuran was distilled from Na benzophenone under nitrogen. Other solvents were dried over 4 Å molecular sieves and distilled prior to use.

Instrumentation: ^{1}H NMR spectra were obtained on a Varian Unity200 NMR Spectrometer or Bruker dmx300 NMR Spectrometer. UV/visible spectra were measured by using a Hitachi Model U-3010 spectrophotometer. MS spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEXIII Mass Spectrometer. The XPS measurements were performed on an EscaLab 220-IXL spectrometer with an $Al_{K\alpha}$ X-ray source monochromatized at 1486.6 eV. The radiation was generated at 20 mA and 15 kV under UHV at 2×10^{-7} Pa. High-resolution spectra were acquired with an analyzer pass energy of 40 eV. All spectra were recorded at a takeoff angle of 90° with response to the sample plane. EL spectra were recorded on a Hitachi F-4500 Fluorescence Spectrophotometer with the LED device forward biased. The power of EL emission was measured by using a Newport 2835-C multifunction optical meter. Current voltage characteristics were measured with a Hewlett Packard 4140B semiconductor parameter analyzer. All the measurements were performed under ambient atmosphere at room temperature.

Synthesis

*Synthesis of decane-1,10-diol monotetrahydropyranyl ether (**1**)*: A mixture of decane-1,10-diol (41.8 g, 240 mmol), *p*-toluene sulfuric acid monohydrate (0.8 g, 4 mmol), dihydropyran (2.0 g, 24 mmol) in THF (380 mL) was stirred at room temperature for 24 h. The resulting mixture was diluted with ether (500 mL), washed with saturated aqueous potassium carbonate solution and dried with anhydrous potassium carbonate. After the solvent had been removed, the remaining white solid was extracted with petroleum ether 60–90. Upon removal of the solvent, 6.0 g (97 % yield) of **1** was obtained as a light yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 1.30$ (m, 12 H), 1.56 (m, 6 H), 1.80 (m, 4 H), 3.32–3.56 (m, 2 H), 3.63 (t, 2 H), 3.71–3.93 (m, 2 H), 4.59 (t, 1 H).

*Synthesis of 4-[10-(tetrahydropyran-2-yloxy)-decyloxy]-phthalonitrile (**3**)*: A mixture of 4-nitrophthalonitrile (**2**) (4.0 g, 23 mmol), decane-1,10-diol monotetrahydropyranyl ether (**1**) (6.0 g, 23 mmol) and anhydrous potassium carbonate (10.0 g, 72 mmol) in DMF (120 mL) was stirred at 60 °C over night. The solvent was removed under reduced pressure. The residue was dissolved with dichloromethane, filtered and purified by column chromatography (silica gel) with dichloromethane as eluant. The product **3** was obtained (8.6 g, 97 % yield). ^{1}H NMR (200 MHz, [D$_6$]acetone) $\delta =$ 1.33–1.52 (m, 18 H), 1.82 (m, 4 H), 3.38 (m, 2 H), 3.70 (m, 2 H), 4.22 (t, 2 H), 4.55 (m, 1 H), 7.43 (dd, 1 H), 7.60 (d, 1 H), 7.94 (d, 1 H).

*Synthesis of 4-(10-hydroxydecyloxy)phthalonitrile (**4**)*: Phthalonitrile **3** (7.0 g, 18.2 mmol) and *p*-toluenesulfonic acid (PTSA) (0.35 g, 1.8 mmol) were dissolved in ethanol (140 mL). The resulting solution was stirred at 50 °C for 12 h. After removal of the solvent, the residue was purified by column chromatography (silica gel) with dichloromethane as eluant. Phthalonitrile **4** (3.2 g, 59 % yield) was obtained as a light yellow solid. ^{1}H NMR (300 MHz, [D$_6$]acetone) $\delta = 1.32$ (m, 10 H), 1.58 (m, 4 H), 1.86 (m, 2 H), 3.51 (t, 2 H), 4.22 (t, 2 H), 7.46 (dd, 1 H), 7.61 (d, 1 H), 7.96 (d, 1 H). EI-MS *m*/*z* (intensity): 300 [M^++1], 270 (3.6), 83 (26.5), 69 (56.3), 55 (100); elemental analysis calcd (%) for $C_{18}H_{24}N_2O_2$: C 71.97, H 8.05, N 9.33; found: C 72.19, H 8.11, N 9.39.

*Synthesis of 2,9,16-tri(*tert*-butyl)-23-(10-hydroxydecyloxy)phthalocyanine (**6**)*: 4-*tert*-butylphthalonitrile (**5**) (1.8 g, 10.0 mmol) and phthalonitrile **4** (1.0 g, 3.3 mmol) were added to *n*-pentanol (30 mL), and the mixture was brought to reflux. Then lithium metal (0.7 g, 0.1 mmol) was added in small portions. The reaction was continued for 6 h. After cooling, acetic acid (40 mL) was added, and the mixture was stirred for another 30 min. The solvents were removed under reduced pressure. The black residue was washed with methanol, and a black solid was obtained. The solid was further purified by column chromatography (silica gel) with chloroform as eluant. The first band proved to be tetra-*tert*-butyl phthalocyanine. Then the second band was collected. Upon removal of the solvents, the desiring product was obtained as a shining purple solid (230 mg, 8 % yield). ^{1}H NMR (300 MHz, C_6D_6) $\delta = 0.54$–2.03 (m, 43 H), 3.53 (m, 2 H), 4.03 (m, 2 H), 6.97–9.75 (m, 12 H); MALDI-TOF-MS: *m*/*z* calcd. for $C_{54}H_{62}N_8O_2$ 854.50, found 854.85 [M^+]; UV/visible (in chloroform): λ_{max} ($\log\varepsilon$) = 703 (2.534), 666 (2.171), 646 (0.909), 605 (0.515), 343 (1.355).

*Synthesis of 2,9,16-tri(*tert*-butyl)-23-(10-methanesulfonyloxydecyloxy) phthalocyanine (**7**)*: Triethylamine (20 drops) and methane sulfonyl chloride (10 drops) were added with stirring to an ice-cooled solution of **6** (40 mg, 46.8 µmol) in dichloromethane (20 mL). The mixture was allowed to warm to room temperature, and stirring was continued for 30 min. Then the resulting solution was washed with water and dried with anhydrous magnesium sulfate. The product was purified by column chromatography (silica gel) with chloroform as eluant. Compound **7** was obtained as a black blue solid (42 mg, 96 % yield).

*Synthesis of 2,9,16-tri(*tert*-butyl)-23-(10-mercaptodecyloxy)phthalocyanine (**8**) and its disulfide (**9**)*: A solution of phthalocyanine **7** (42 mg, 45 µmol) in THF (20 mL) and ethanol (6 mL) was brought to reflux. Then thiourea (20 mg, 0.26 mmol) was added. The reaction was monitored by TLC. After the all of the starting material was consumed, aqueous sodium hydroxide solution (20 %, 4 mL) was added. When the reaction was complete (TLC), the resulting mixture was poured into a mixture of dilute hydrochloride acid and ice and extracted with chloroform. The organic phase was separated and dried with anhydrous magnesium sulfate, then purified by column chromatography with chloroform/petroleum ether 30–60 (1:1) as eluant. The first band developed was mercaptophthalocyanine **8**, after removal of the solvents, a blue-black solid was obtained (26 mg, 66 % yield). The second band afforded disulfide phthalocyanine **9** (5 mg, 13 % yield) as a blue-black solid.

Data for **8**: ^{1}H NMR (300 MHz, C_6D_6) $\delta = -2.95$ (br, 2 H), 0.51–2.08 (m, 43 H), 2.81 (m, 2 H), 4.06 (m, 2 H), 6.99–9.27 (m, 12 H); MALDI-TOF-MS: *m*/*z* calcd. for $C_{54}H_{62}N_8OS$ 870.48, found 870.8 [M^+]; UV/vis (in chloroform): λ_{max} ($\log\varepsilon$) = 702 (0.558), 665 (0.754), 643 (0.682), 339 (0.804).

Data for **9**: ^{1}H NMR (300 MHz, C_6D_6) $\delta = -3.14$ (br, 4 H), 0.54–1.95 (m, 86 H), 2.82 (m, 4 H), 3.99(m, 4 H), 7.00–9.31 (m, 24 H); MALDI-TOF-MS: *m*/*z* calcd. for $C_{108}H_{122}N_{16}O_2S_2$ 1738.94, found 1740.0 [M^++1]; UV/vis (in chloroform): λ_{max} ($\log\varepsilon$) = 702 (0.859), 665 (1.214), 643 (1.135), 339 (1.328).

SAM preparation: Quartz slides were washed with chloroform and immersed in a solution of potassium hydroxide in deionized water (100 mL) and methanol (250 mL) for 12 h. Then the quartz slides were washed thoroughly with deionized water and dried in a steam of nitrogen. The gold substrates were prepared by thermal evaporation of a layer of gold onto freshly cleaned quartz slides that had been precoated with a chromium adhesion layer. For UV/visible characterization, 5 nm of chromium was deposited onto the cleaned quartz slides followed by an 8 nm gold layer. For XPS experiments, an ≈500 nm gold layer was deposited onto the cleaned quartz slides. Phthalocyanine SAMs were prepared by immersing gold substrates in phthalocyanine solutions in chloroform (6.7×10^{-5} mol L^{-1} and 2.9×10^{-5} mol L^{-1} for **8** and **9**, respectively) for 24 h. Reference for UV/visible measurements were prepared by immersing corresponding substrates in pure chloroform for 24 h. Then the substrates were washed thoroughly with chloroform and dried in a stream of nitrogen.

Fabrication of the LED: A double-layer light-emitting diode was fabricated by using Al as cathode, SAM-coated Au (which was prepared by thermal evaporation of < 50 nm Au onto ITO glass that had been precoated with a 5 nm Cr adhesion layer) as anode, tris(8-hydroxyquinolinato)aluminium (Alq$_3$) as emissive and electron-transporting layer and *N*,*N'*-diphenyl-*N*,*N'*-bis(3-methylphemyl)-1,1'-biphenyl-4,4'-diamine (TPD) as hole-transporting layer. Alq$_3$, TPD and the Al electrode were deposited at a pressure below 10^{-5} Torr. The active area of the device was about 7 mm^2.

Acknowledgements

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