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Synthesis and optical properties of axially bromo-substituted subphthalocyanines☆

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Abstract

Subphthalocyanines (SubPc) are composed of three iso-indole units containing boron inside, which defines a molecular axis and forms a cone-shaped structure. Despite being non-planar, they show a delocalized 14π-electron system similar to that present in phthalocyanines. The attractive characteristics of SubPc are their chemical stability and thermal stability. In this paper, we report here the synthesis of five SubPc compounds, in which the axial substituent is a bromide. The peripheral substituent in the compounds leads to an improved solubility in common organic solvents such as ethanol and chloroform etc. The spectral and optical properties of these compounds were studied. The spectra and optical constants (refractive index, extinction coefficient) of the sublimed films of these SubPcs were measured by a spectrophotometer and an ellipsometer respectively. We also measured the static optical recording performance of these films with a thin Al (or Ag) reflective layer on them. These results demonstrated that SubPc showed a strong and broad absorption region near 600 nm and it will be a promising candidate for short-wavelength optical recording (such as DVD-R), if high-quality films can be got. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Subphthalocyanine; Optical storage; DVD-R; Absorption spectra

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1. Introduction

In the last few years, there has been increasing interest in different metallo-phthalocyanines. Arising from the considerable scientific and technological interest in the unusual electrical and optical characterizations of the organic materials, a variety of technological applications of phthalocyanines (Pc) have been investigated based on the nature of the peripheral substituents and the central metal ion, such as xerography, photovoltaics, electro-chromism, optical disc, laser dyes, liquid crystals, molecular catalysis, chemical sensors and photodynamic cancer therapy [1]. These attractive features prompted people to study different types of phthalocyanine analogues: macrocyclic compounds with modifications in the basic structure of the tetraazatetrabenzoporphyrin ligand. Interesting examples of Pc-related compounds are the so-called subphthalocyanines (SubPc) [2]. These

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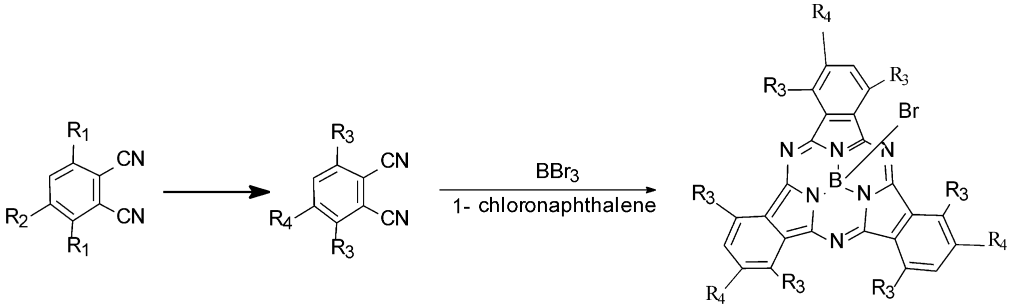
macrocyclic complexes are composed of three iso-indole units containing boron inside (Pc consists of four iso-indole units). A boron atom (or other atom) remains on the center, defining a molecular axis and forming a cone-shape structure [3]. Despite being non-planar, they show a delocalized 14π-electron system similar to that presented in Pc. They exhibit aromatic behavior [4]. Other attractive characteristics of SubPc are their chemical (they support inorganic acids) and thermal (they can be sublimated at 10^{-4} mmHg at 350 °C) stability [5].

The applications of SubPc are limited mainly because of the problems of dealing with their purification [6,7]. In addition, the described procedures to synthesize SubPc sometimes are not easy to reproduce. Moreover, unsubstituted SubPcs are practically limited soluble in common organic solvents. Up to now the use of these compounds has been restricted to the applications as intermediate materials for the synthesis of nonsymmetrical phthalocyanines [8], and more recently to optical recording media [9], electroluminescent [10] and charge generation [11]. We thought subphthalocyanine (SubPc) is a novel kind of potential optical recording dyes [12]. It shares many of the excellent properties of Pc and its absorption spectra is similar to that of metallophthalocyanines (MPc) but shifted toward the blue out of its fewer number of coordinated organic rings. All these properties are advantageous for the applications in DVD-R (Digital Versatile Disc-Recordable), whose recording laser wavelength is 650 nm. Therefore, we prepared some SubPcs, in which the axial substituent is a bromide. The synthetic procedure is shown in Scheme 1. The peripheral alkoxyl substituent in SubPc leads to an improved solubility in common organic solvents, such as chloroform, dichloromethane and especially in alcohol. The alcohol solvents are promise solvents of spin-coating for practical application of DVD-R. Moreover, the optical properties of SubPcs are detected and the results indicated that SubPc should be a promising candidate for short-wavelength optical recording.

2. Experimental

Unless otherwise stated, all reactions were performed under dry, oxygen-free argon. The chemical structures of SubPcs were confirmed by ^{1}H NMR



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$a{:}R_1=R_3=H,\ R_2=R_4=NO_2$
$b{:}R_1=R_3=H,\ R_2=NO_2,\ R_4=OCH_2C(CH_3)_3$
$c{:}R_1=R_3=H,\ R_2=NO_2,\ R_4=OCH(CH_3)_2$
$d{:}\ R_2=R_4=H,\ R_1=OH,\ R_3=OCH(CH_3)_2$
$e{:}\ R_2=R_4=H,\ R_1=OH,\ R_3=O(CH_2)_4\ CH_3$

Scheme 1. The synthetic routes of peripheral substituted SubPcs.

(Brucker AM-500), UV-vis absorption (Shimadzu UV-260 and Varian Cary 500), MS (VG QUATTRO) and IR (Nicolet Magna-IR550). Chemical shifts are given in ppm (δ) relative to tetramethylsilane (TMS). All solvents were distilled prior to use.

2.1. *Compound **2b** [13]*

Three and a half grams of **1a** (0.02 mol) was added to a stirred solution of 6.4 g of neopentyl alcohol (0.072 mol) dissolved in DMSO (60 ml, dried prior to use), then 3.6 g anhydrous K_2CO_3 (0.026 mol) was added in three portions for the first 3 h. Subsequently the reaction mixture was stirred for 27 h at 60 °C.The crude reaction mixture was poured into water (300 ml). After vigorous stirring, the precipitate was collected by filtration, washed thoroughly with water, then dried by vacuum. The crude product was purified by silica gel column chromatography using ethyl acetate–petroleum ether (1:10) as the eluting solvent, followed by recrystallization from a mixture of ether–petroleum ether to give 2.7 g of white crystal of **2c**, m.p. 51–52 °C (lit. [13] 53 °C), in 63% yield.

2.2. *Compound **2c** [13]*

A DMSO (30 ml, dried prior to use) solution of 1.73 g of 1a (0.01mol), isopropanol (2.0 ml, 0.026 mol) and 3.6 g anhydrous K_2CO_3 (0.026 mol) was stirred at 60 °C as described for the preparation of **2b**, column chromatography of the reaction product on silica gel using ether–petroleum ether(1:2). It was then recrystallized from a mixture of ether–hexanes ether–petroleum ether to yield 1.18 g of slightly yellow crystals of **2b**, m.p. 55 °C (lit. [13] m.p. 56–57 °C) in 64% yield.

2.3. *Compound **2d** [14]*

To a well stirred slurry of 3,6-dihydroxy-1,2-benzenedinitrile (2.5 g, 0.0156 mol) and K_2CO_3 (4.8 g, 0.0343 mol) in DMF (60 ml, dried prior to use) was added 2-bromopropane (4 ml), and the solution was heated at 60 °C for 48 h. At this time an additional portion of 2-bromopropane (1 ml) was added, and the solution was heated at the same temperature for 12 h. The reaction mixture was poured into water (300 ml), and the solution was vigorously stirred. The resulting white solid was filtered and then recrystallized from MeOH to give a 3.3 g of white crystal of **2d**, m.p. 190 °C (lit. [14] 191–193 °C), in 91% yield.

2.4. *Compound **2e** [14]*

A stirred DMF (60 ml, dried prior to use) solution of 3,6-dihydroxy-1,2-benzenedinitrile (1.6 g, 10 mmol) and K_2CO_3 (3.6 g, 26 mmol) was added 1-bromopentane (4 ml), and the solution was heated at 60 °C for 48 h. At this time an additional portion of 1-bromopentane (4 ml) was added, then the solution was performed as described for the preparation of **2d**, 2.7 g white crystal of **2e** was yielded by recrystallization from MeOH, m.p. 178 °C (lit. [14] 179–180 °C), in 90% yield.

2.5. *Compound **3a***

Dried 4-nitrophthalonitrile (0.87 g, 5 mmol) was suspended in 1-chloronaphthalene (2 ml) at 0 °C. Then BBr_3 (0.47 ml, 5 mmol) was added. The mixture was heated at 120 °C for 1.5 h with vigorous stirring. After cooling the blue-colored precipitate was washed with abundant hexane using a Soxhlet extractor for 24 h to yield 0.78 g (77%) of a deep blue powder: m.p.$>$300 °C. ^1H NMR ($CDCl_3$) δ = 8.84–8.88 (d×d, 3H), 9.06–9.08 (d×d, 3H), 9.78–9.79 (d×d, 3H). IR/cm^{-1} (KBr) ν = 1614 (C=N), 1529, 1495 (C=C), 857 (B–Br). λ_{max}/nm (log ϵ): 695 (3.5), 659 (3.5), 585 (4.4), 575 (4.4), 300 (4.5). MS (ESI): 609 (M^+, 23%). Element anal. calcd. for $C_{24}H_9BBrN_9O_6$: C, 47.23; H, 1.48; N, 20.66. Found: C, 47.14; H, 1.47; N, 20.61%.

2.6. *Compound **3b***

To a vigorously stirred suspension of 4-neopentoxy phthalonitrile (1.28 g, 6 mmol) in 1-chloronaphthalene (4 ml) at 0 °C, and BBr_3 (0.57 ml, 6 mmol) were added. The mixture was heated at 120 °C and stirred for 2 h. Subsequently the solvent was eliminated by vacuum distillation. The crude product was purified by column chromatography, using a mixture of ethyl acetate/petroleum ether (1:5) as eluent to give 0.33 g (23%) of violet colored powder. m. p. >300 °C. ^{1}H NMR ($CDCl_3$): 1.12 (m, 27H), 4.0 (m, 6H), 7.52–7.55 (d×d, 3H), 8.22–8.24 (d×d, 3H), 8.62×8.65 (d×d, 3H). IR/cm^{-1} (KBr) 2950, 2850, 1605, 1458, 1397, 1365, 1258, 1050, 800, 700. Absorption (in CH_3CH_2OH) λ_{max}/nm (log ϵ): 572.8(4.6), 334.6 (4.3). MS (ESI): 732 (M^+, 30%). Element anal. calcd. for $C_{39}H_{42}BBrN_6O_3$: C, 63.87; H, 5.73; N, 11.46. Found; C, 63.75; H, 5.70; N, 11.42%.

2.7. Compound **3c**

A suspension of **2c** (1.12 g, 6 mmol) and of BBr_3 (0.57 ml, 6 mmol), in 1-chloronaphthalene (4 ml) was stirred at 0 °Cas described the preparation of compound **3b**. The crude product was purified by column chromatography on silica gel using hexane/acetic ester as eluent to yield 0.26 g (19%) of violet colored powder. m.p.>300 °C. ^{1}H NMR ($CDCl_3$): 1.37–1.40 (d, 18H), 4.65 (m, 3H), 7.13–7.16 (m, 3H), 7.22–7.24 (m,3H), 7.67–7.70 (m, 3H). Absorption (in CH_3CH_2OH) λ_{max}/nm (log ϵ): 574.0(4.2), 302(4.5).

2.8. Compound **3d**

To a stirring suspension of **2d** (1.47 g, 6 mmol) in 1-chloronaphthalene (4 ml) at 0 °C was quickly added BBr_3 (0.57 ml, 6 mmol). Then the reaction mixture was slowly heated to 260 °C for refluxing 20 min. The solvent was removed by column chromatography on silica gel using hexane/acetic ester as eluent. After removing the solvent, brownish-red colored powder, in a yield of 0.21 g (13%) were obtained. m.p.>300 °C. ^{1}H NMR ($CDCl_3$): 1.31–1.52 (m, 36H), 4.48–4.66 (m, 6H), 7.06–7.25 (m, 6H). Absorption (in CH_3CH_2OH) λ_{max}/nm (log ϵ): 546.8(3.3), 312(3.4).

2.9. Compound **3e**

A suspension of **2e** (1.8 g, 6 mmol) and of BBr_3 (0.57 ml, 6 mmol) in 1-chloronaphthalene (4 ml) was stirred at 0 °C as described the preparation of compound **3d**. The eluent for purification by column chromatography is ethyl acetate/petroleum ether (1:2). A brownish-red colored powder, in a yield of 0.37 g (19%) were obtained. m.p.>300 °C. ^{1}H NMR ($CDCl_3$): 0.98 (t, J=7.3 Hz, 18H), 1.25–1.44 (m, 24H), 1.81–2.04 (m, 12H), 4.08 (m, 12H), 7.54 (m, 6H). IR/cm^{-1} (KBr): 2910, 1650, 1618, 1498, 1470, 1365, 1300, 1260, 1240, 1050, 950, 820, 800, 710. λ_{max}/nm (log epsi;): 548.8 (3.4), 332.6 (3.5). MS (ESI): 990 (M^+, 28%). Element anal. calcd. for $C_{54}H_{72}BBrN_6O_6$: C, 65.40; H, 7.27; N, 8.48. Found: C, 65.24; H, 7.23; N, 8.44%.

2.10. Preparation of SubPc films

In this paper, SubPcs **3a** and **3b** were studied emphasizely for their representativeness (the rest will be reported in elsewhere). SubPc **3b** was prepared by spin coating from a chloroform solution of SubPcs in PMMA (available) because of its good solubility in common organic solvents. The solution, filtered with 0.5 μm millipore to remove particle impurities, was spin coated onto a leveled K9 glass substrate under normal laboratory conditions. SubPc **3a** evaporated film was also prepared by vacuum sublimation in a vacuum chamber at 2.7×10^{-3} Pa onto a single-crystal silicon substrate and a K9 glass substrate for different measurement uses. The substrate was kept in room temperature throughout the deposition processes.

2.11. Measurements

The absorption, reflection and transmission spectra of thin films were measured in Perkin-Elmer Lamda 9 UV/vis/NIR spectrophotometer at room temperature. The complex refractive index was measured in air with an improved rotating analyser-polarizer (RAP) type of scanning ellipsometer [15]. The optical recording characterization of SubPcs thin films was measured by a static optical recording tester. The reflectivity contrast C is defined as $C = 2|R_f - R_i|/(R_f + R_i)$, where R_i and R_f denotes the film's reflectivity before and after writing. A He–Ne laser was used as light source, whose wavelength (632.8 nm) is very close to the wavelength (630 or 650 nm) of the semiconductor lasers used in commercial DVD drivers.

2.12. Results and discussion

2.12.1. Absorption spectra

The absorption spectra of these SubPcs in solution are shown in Fig. 1. As seen in Fig. 1, SubPcs all have the narrow absorption band with the maximum peaks at around 550 nm, especially the very sharp tail in the longer wavelength region. SubPc with substituents at its α-positions such as compound **3d** or **3e** has a broad absorption band with blue shift of the maximum peak for sake of its molecular inherent characteristics resulting from large steric obstruction. The SubPc does not exist in aggregate formation in solution because of its cone structure. Fig. 2 supported the conclusion.

The absorption spectra of SubPc thin films are shown in Fig. 3, in which sharp tails in the longer wavelength region are also observed. The dominant absorption Q bands arise from the $\pi \rightarrow \pi^*$ transitions of the macrocyclic π-system consisting of C and aza-N atoms. In the thin films, similar absorption with broadening are observed. The broadening effect originates from extensive excitation coupling between adjacent conjugated macrocycles, and the extent of the broadening strongly correlates with the degree of coupling, which depends on several factors, such as the closeness of adjacent macrocycles, the tilting angle, the overlap position, the substituted groups, and the extinction coefficients of the transition bands involved [16]. The considerable red-shift can be attributed to the absence of solvent effect and strengthening of interactions among molecules.

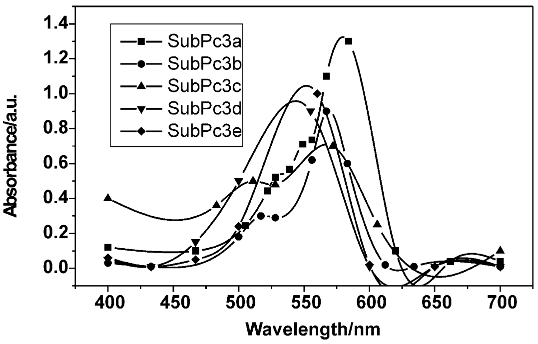

Fig. 1. UV-vis absorption spectra of SubPcs in $CHCl_3$.

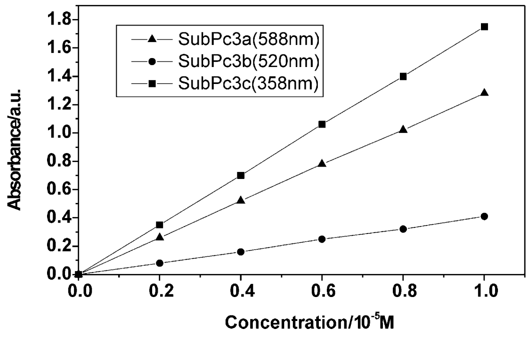

Fig. 2. Relationship of the absorbance and the concentration.

2.12.2. Optical constants of evaporated/coated SubPc thin film

Figs. 4 and 5 show the optical constants of evaporated SubPc **3a** thin film and coated SubPc **3b** thin film in the visible region. The curves of extinction coefficient k are structurally similar to their absorption spectra. The strongest peaks of refractive index n are located at 630 and 595 nm, respectively, which are near the optical recording wavelength of DVD-R. The extinction coefficients in the wavelength range of 630–650 nm are very small (<0.05). These properties are advantageous for the applications in DVD-R because a higher n and a lower k are necessary to obtain high initial reflectivity and required modulation [17].

2.12.3. Static short-wavelength optical recording properties of SubPc thin films

For the evaporated SubPc **3a** thin film, its reflectivity is very much lower at the wavelength

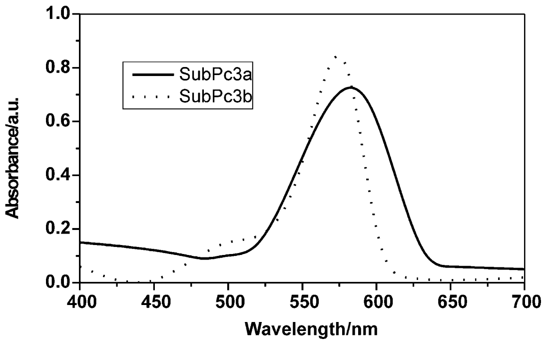

Fig. 3. Absorption spectra of SubPc evaporated films.

(632.8 nm) of the He–Ne laser used in static optical recording test. It can be higher and appreciable after sublimation of Al onto the film, and so is Ag on SubPc **3b** film.

The results of static optical recording test of the evaporated SubPc **3a** thin film on a K9 glass substrate are shown in Fig. 6. It shows the reflectivity contrast of the film as a function of laser pulse width at different laser powers. For a laser power of 10 mW, the reflectivity contrast increases with increasing writing pulse width in the beginning, and then reaches a maximum value of 63% when the writing pulse width is about 600 ns, shown in Fig. 7. Maximum values of 63 and 51% are also observed for laser powers of 9 and 8 mW at a writing pulse width of about 700 and 900 ns, respectively.

As to the evaporated SubPc **3a** film, Fig. 6 gives optical writing characteristics of it. For laser

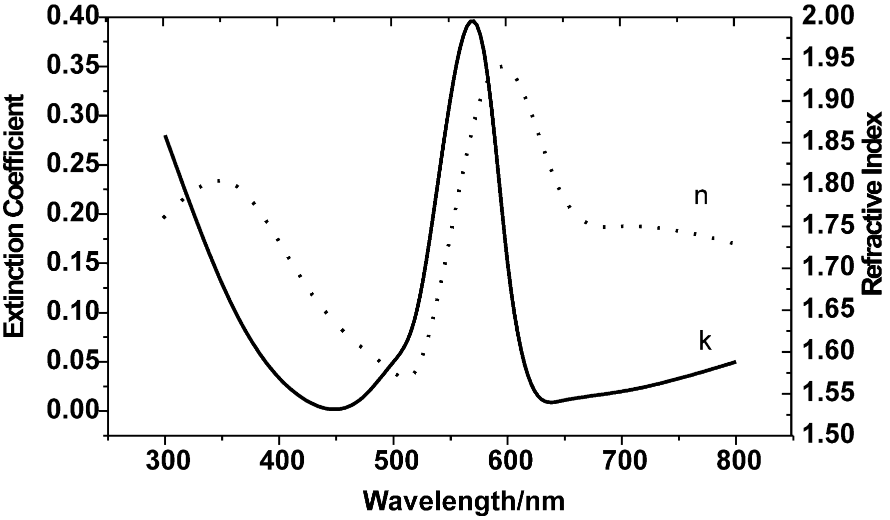

Fig. 4. Refractive index of the evaporated SubPc **3a** film.

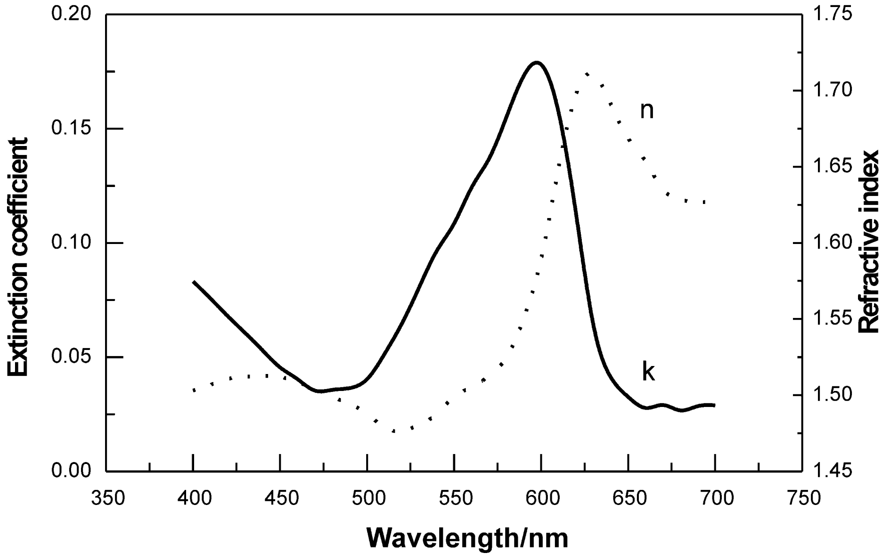

Fig. 5. Refractive index of the coated SubPc **3b** film.

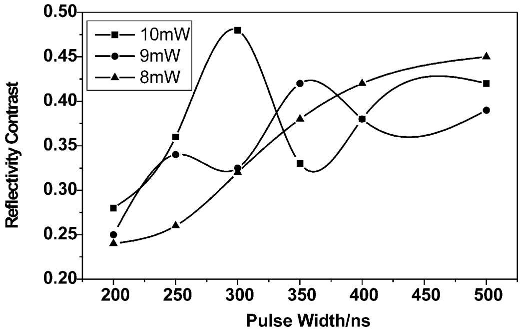

Fig. 6. Static optical recording property of evaporated SubPc **3a** film.

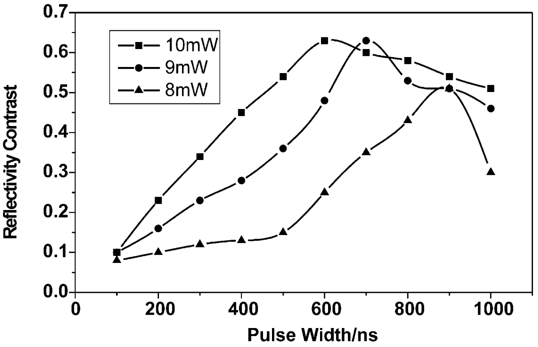

Fig. 7. Static optical recording property of coated SubPc **3b** film.

Table 1
Static optical recording properties of the compound films (632.8 nm, 300 ns)

Compounds	SubPc **3a**	SubPc **3b**	CuPc [18]
Power (mW)	10	10	10
Reflectivity contrast	34%	48%	<10%

powers of 10, 9 and 8 mW, maximum values of the reflectivity contrast are accordingly 48, 39 and 45%. From Table 1, the static optical recording property of SubPcs is better than that of phthalocyanine.

3. Conclusions

Five SubPcs are synthesized and the structures are determined. The spectral properties of these compounds and their evaporated and coated films show that they have strong and broad absorption and acceptable reflection in the wavelength range of 500–650 nm. The appropriate optical constants near 630 nm and high reflectivity contrast ($\lambda = 632.8$ nm) of the evaporated/coated film indicate the great potential of SubPc as a practical recording material for DVD-R. The dynamic optical recording test will be expected.

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