

## Discotic liquid crystals of transition metal complexes 48<sup>†</sup>: Synthesis of novel phthalocyanine-fullerene dyads and effect of a methoxy group on their clearing points

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**ABSTRACT:** In our previous work, we could successfully synthesize the 1:1 phthalocyanine-fullerene (Pc-C<sub>60</sub>) dyads, (OFbaC<sub>60</sub>)PcCu(OCH<sub>3</sub>) **2**, in very high yields (81 ~ 96%) by using Prato reaction. In this study, we have prepared novel Pc-C<sub>60</sub> dyads, (OFbaC<sub>60</sub>)PcM (M = Co (**a**), Ni (**b**), Cu (**c**), metal free (**d**)) **3a–3d** without the methoxy group. The target Pc-C<sub>60</sub> dyads **3a–3d** could be successfully synthesized in good yields also by Prato reaction. It is surprising for us that removal of a very small methoxy group from the big (OFbaC<sub>60</sub>)PcCu(OCH<sub>3</sub>) molecule (**2**) significantly lowers the cp of (OFbaC<sub>60</sub>)PcCu (**3c**) by about 70 °C in comparison with that of **2** having the methoxy group. Very interestingly, each of the novel dyads **3a–3d** synthesized here shows perfect homeotropic alignment in the tetragonal columnar phase (Col<sub>tet</sub>). Moreover, it is noteworthy that **3c** and **3d** show only one Col<sub>teto</sub> mesophase having ordered stacking distance with perfect homeotropic alignment. Such simple phase transition can contribute to maintain stable performance in wide temperature range, when they will be applied to organic thin film solar cells.

**KEYWORDS:** discotic liquid crystal, phthalocyanine, fullerene, phthalocyanine-fullerene dyad, homeotropic alignment, organic thin film solar cell.

## **INTRODUCTION**

Liquid crystalline donor–acceptor (D–A) complexes may display superb performance in organic thin film solar cells [1–25]. They can greatly reduce their costs to manufacture the solar cells. Liquid crystalline D–A systems are broadly classified into three groups: smectic liquid crystals [1–4], liquid crystalline copolymers [5–12] and discotic columnar liquid crystals [13–25]. In 2004, Kim *et al.* reported that an organic photovoltaic cell was fabricated by using liquid crystalline N,N'-diheptyl-3,4,9,10-perylenetetracarboxylicdiimide (PTCDI-C7) as the electron acceptor and zinc phthalocyanine (ZnPc) as the electron donor [1]. The two long chain-substituted PTCDI-C7 shows, however, a liquid crystalline phase at very high temperature range (214-403 °C). In 2007, Hashimoto et al. reported that they synthesized a novel liquid crystalline oligothiophene(D)-fullerene(A) dyad to investigate the photovoltaic properties [2]. Moreover, they revealed that the dyad shows a smectic A phase. Liquid crystalline donor-acceptor block copolymers have been also used for photovoltaic applications [5–12]. Morphologies of the vertically oriented mesophase of D-A separated block copolymers are very favorable for organic photovoltaics. Furthermore, the covalent

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bond between the donor and acceptor blocks is not only desired to improve morphology control, but also to enhance long term stability of the device [8]. However, it seems that the mesophase structure difference between smectic liquid crystals and discotic columnar liquid crystals has been not so much concerned in this field. In comparison with smectic mesophases, discotic columnar mesophases are much easier to realize one-dimensional columnar structure perpendicular to both two electrodes (= homeotropic alignment) [14, 23, 25]. Columnar mesophases in homeotropic alignment are so favorable to obtain higher photoelectric conversion efficiency which can be attributable to larger  $\pi$ - $\pi$  stacking of the  $\pi$ -conjugated macrocycles [19].

Discotic liquid crystals are well known to spontaneously form one-dimensional columnar structure in their columnar mesophases. Generally, a discotic columnar liquid crystal is composed of a plane and hard central core and several flexible peripheral chains [26]. Especially, triphenylene [27], phthalocyanine (Pc) [28], and porphyrin [28] are often utilized as a central core part. One-dimensional columns can be formed by piling up such disk-like molecules. The column can be a charge carrier path. In order to achieve efficient charge transfer, it is favorable to form perfect homeotropic alignment [14, 19, 23, 25, 29]. On the contrary, it is unfavorable to form both defects and polydomains in the homeotropic alignment [29]. Up to date, there have been some donor-acceptor dyads showing columnar liquid crystalline mesophases [13-25]. For example, Bushby et al. reported in 2005 that a triphenylene derivative connected with fullerene showed columnar mesomorphism columnar liquid crystalline [13]. This triphenylene-fullerene dyad partially showed homeotropic alignment, but it has many defective parts. Recently, columnar liquid crystalline phthalocyanine-fullerene dyads [14, 18, 20, 23–25] have been also synthesized.

In 2001, we succeeded in synthesis of phthalocyanine derivatives showing perfect homeotropic alignment in large area at high

temperatures [29]. Furthermore, in 2007 we reported the first liquid crystalline phthalocyanine-fullerene dyad, (OMalC<sub>60</sub>)PcCu (**1** in Fig. 1), exhibiting perfect homeotropic alignment in the hexagonal columnar phase (Col<sub>h</sub>) at high temperatures [14]. For the synthesis of this phthalocyanine-fullerene dyad **1**, Bingel reaction [30] was adopted to connect phthalocyanine and fullerene. However, it gave polyads connected with two or three phthalocyanines per one fullerene, as the by-products at



Fig. 1. Molecular formulae of the previous  $Pc-C_{60}$  dyads (1, 2) and the present  $Pc-C_{60}$  dyad (3)

the same time. Accordingly, the yield of the target 1:1 phthalocyanine-fullerene dyad **1** was very low (20%). Therefore, we changed the synthetic method from Bingel reaction to Prato reaction [31]. By using Prato reaction illustrated in Scheme 1, the 1:1 phthalocyanine-fullerene dyads, (OFbaC<sub>60</sub>)PcM(OCH<sub>3</sub>) (**2** in Fig. 1 and Scheme 1), could be synthesized in very high yields (81~96%) with negligible amount of undesirable 2:1 phthalocyanine-fullerene by-product [25]. Thus, Prato reaction was more



**Scheme 1.** Synthetic route for the previous  $Pc-C_{60}$  dyad, (OFba $C_{60}$ )PcCu(OCH<sub>3</sub>): **2**, by using Prato reaction. (i)  $Br_2/(C_2H_5)_2O \cdot BF_3$ , CHCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>; (ii) CuCN, DMF; (iii) BrC<sub>12</sub>H<sub>24</sub>OH, K<sub>2</sub>CO<sub>3</sub>/DMF; (iv) DBU/CuCl<sub>2</sub>, *n*-hexanol; (v) *p*-formylbenzoic acid, DMAP/DCC, CH<sub>2</sub>Cl<sub>2</sub>; (vi) *N*-methylglycine,  $C_{60}$ /toluene. DMAP = 4-dimethylaminopridine. DCC = *N*,*N*-dicyclohexylcarbodiimide

favorable to obtain phthalocyanine-fullerene dyads than Bingel reaction. The Prato 1:1 phthalocyanine-fullerene dyads **2** also showed perfect homeotropic alignment in the tetragonal columnar phase (Col<sub>tet</sub>) at high temperatures [25].

In this work, we have synthesized novel phthalocyanine-fullerene dyads, (OFbaC<sub>60</sub>)PcCu (**3** in Fig. 1), by a synthetic route using Prato reaction and another commercially available starting material, as illustrated in Scheme 2. Very interestingly, each of the novel dyads **3** shows perfect homeotropic alignment in the tetragonal columnar phase (Col<sub>tet</sub>). Moreover, it is surprising for us that removal of a very small methoxy group from the big (OFbaC<sub>60</sub>)PcM(OCH<sub>3</sub>) molecule (**2** in Fig. 1) significantly lowers the cp of (OFbaC<sub>60</sub>)PcCu (**3c** in Fig. 1) by about 70 °C in comparison with that of **2** having the methoxy group. We wish to report here the synthesis and very interesting mesomorphic properties and effect of methoxy group on the clearing points of the dyads **3**.

### **EXPERIMENTAL**

#### Synthesis

The synthetic route is shown in Scheme 2. The phthalonitrile derivative, 4,5-bis(3,4-didodecyloxyphenoxy)-1,2-dicyanobenzene (7) was prepared by our

previously reported method [29]. The phthalocyanine precursors, (OH)PcM (11) (a: Co, b: Ni, c: Cu, d: metal free), were synthesized from two different phthalonitriles 7 and 10 in a molecular ratio of 3:1. The terminal OH group in 11 was esterified with *p*-formyl benzoic acid by Steglich reaction [32] to afford (OFba) PcM (12). Finally, (OFbaC<sub>60</sub>)PcM (3) was synthesized from 12 with *N*-methylglycine and fullerene by Prato reaction [31]. These procedures are described below in detail.

4-(12-hydroxydodecyloxy)phthalonitrile (10).A mixture of 4-hydroxyphthalonitrile (0.250 g, 1.73 mmol), 12-bromododecanol (0.600 g, 2.25 mmol), K<sub>2</sub>CO<sub>3</sub> (0.500 g, 3.62 mmol), and dry DMF (12 mL) was stirred at 160 °C under N<sub>2</sub> for 1 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over  $Na_2SO_4$ and evaporated in vacuo. The residue was purified by column chromatography (silica gel, chloroform:ethyl acetate = 4:1,  $R_f = 0.85$ ). After removal of solvent, 0.479 g of white solid was obtained. Yield 84.4%, mp 69.7 °C. IR (KBr): v, cm<sup>-1</sup> 3536 (-OH), 2918, 2852 (-CH<sub>2</sub>-), 2234 (-CN), 1598 (Ar). <sup>1</sup>H NMR (4:00 MHz;  $CDCl_3$ ; TMS):  $\delta_H$ , ppm 7.66 (d, 1H, Ar-H), 7.24 (d, 1H, Ar-H), 7.15 (d, 1H, Ar-H), 4:01 (t, 2H, -OCH<sub>2</sub>), 3.62 (t, 2H, -OCH<sub>2</sub>), 2.15 (s, 2H, -CH<sub>2</sub>-), 1.53 (s, 16H, -CH<sub>2</sub>-), 1.48 (s, 2H, -CH<sub>2</sub>-).



**Scheme 2.** Synthetic route for novel Pc-C<sub>60</sub> dyads, (OFbaC<sub>60</sub>)PcM: **3a–3d**, by using Prato reaction. (i)  $BrC_{12}H_{24}OH$ ,  $K_2CO_3/DMF$ ; (ii)  $MCl_2$  DBU, *n*-hexanol; (iii) *p*-formylbenzoic acid, DMAP/DCC,  $CH_2Cl_2$ ; (iv) *N*-methylglycine,  $C_{60}$ /toluene. DMF = *N*.*N*'-dimethylformamide, DBU = 1,8-diazabicyclo[5,4,0]-7-undecene, DMAA = *N*,*N*-dimethylacetamide, DCC = *N*,*N*'-dicyclohexyl-carbodiimide, and DMAP = *N*,*N*-dimethyl-4-aminopyridine

2-(12-hydroxydodecyloxy)-9,10,16,17,23,24-hexakis(3,4-didodecyloxy)phthalocyaninato cobalt(II) ((OH)PcCo: 11a). A mixture of 4-(12-hydroxydodecyloxy) phthalonitrile (10) (70.0 mg, 0.213 mmol), 4,5-bis(3,4didodecyloxyphenoxy)-1,2-dicyanobenzene (7) (0.600 g, 0.572 mmol), CoCl<sub>2</sub> (33.0 mg, 0.256 mmol), 1-hexanol (11 mL), and DBU (7 drops) was stirred at 150–160 °C under N<sub>2</sub> for 24 h. Ethanol was poured into the reaction mixture to precipitate the target compound. The ethanolic layer was removed by filtration. The residue was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, chloroform,  $R_f = 0.63$ ) and then recrystallized from ethyl acetate to give 0.155 g of green solid. Yield 20.5%. MS (MALDI-TOF): *m/z* 3538.11 (calcd. 3536.23).

2-(12-hydroxydodecyloxy)-9,10,16,17,23,24-hexakis(3,4-didodecyloxy)phthalocyaninato nickel(II) ((OH)PcNi: 11b). A mixture of 4-(12-hydroxydodecyloxy)phthalonitrile (10) (70.0 mg, 0.213 mmol), 4,5bis(3,4-didodecyloxyphenoxy)-1,2-dicyanobenzene (7) (0.600 g, 0.572 mmol), NiCl<sub>2</sub> (36.0 g, 0.278 mmol), 1-hexanol (11 mL), DBU (7 drops) was stirred at 150– 160 °C under N<sub>2</sub> for 17 h. Ethanol was poured into the reaction mixture to precipitate the target compound. The ethanolic layer was removed by filtration. The residue was extracted with chloroform and washed with water. The organic layer was dried over  $Na_2SO_4$  and evaporated *in vacuo*. The rude product was purified by column chromatography (silica gel, chloroform,  $R_f = 0.63$ ) and then recrystallized from ethyl acetate to give 0.162 g of green solid. Yield 23.7%. MS (MALDI-TOF): *m/z* 3537.22 (calcd. 3536.23).

2-(12-hydroxydodecyloxy)-9,10,16,17,23,24-hexakis(3,4-didodecyloxy)phthalocyaninato copper(II) ((OH)PcCu: 11c). A mixture of 4-(12-hydroxydodecyloxy)phthalonitrile (10) (72.0 mg, 0.219 mmol), 4,5bis(3,4-didodecyloxyphenoxy)-1,2-dicyanobenzene (7) (0.621 g, 0.591 mmol), CuCl<sub>2</sub> (38.3 mg, 0.285 mmol), 1-hexanol (12 mL), and DBU (7 drops) was stirred at 150–160 °C under N<sub>2</sub> for 24 h. Ethanol was poured into the reaction mixture to precipitate the target compound. The ethanolic layer was removed by filtration. The residue was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, chloroform, R<sub>f</sub> = 0.55) and then recrystallized from ethyl acetate to give 0.229 g of green solid. Yield 29.5%. MS (MALDI-TOF): *m/z* 354:0.54 (calcd. 354:0.85).

2-(12-hvdroxydodecyloxy)-9,10,16,17,23,24-hexakis(3,4-didodecyloxy)phthalocyanine ((OH)PcH<sub>2</sub>: mixture of 4-(12-hydroxydodecyloxy) 11d). А phthalonitrile (10) (70.0 mg, 0.213 mmol), 4,5-bis(3,4didodecyloxyphenoxy)-1,2-dicyanobenzene (7) (0.600 g, 0.572 mmol), 1-hexanol (11 mL), DBU (7 drops) was stirred at 150-160 °C under N<sub>2</sub> for 24 h. Ethanol was poured into the reaction mixture to precipitate the target compound. The ethanolic layer was removed by filtration. The residue was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, chloroform:nhexane = 3:1,  $R_f = 0.50$ ) and then recrystallized from ethyl acetate to give 0.188 g of green solid. Yield 27.9%. MS (MALDI-TOF): m/z 3482.63 (calcd. 3479.32).

**Cobalt benzoic derivative ((OFba)PcCo: 12a).** A mixture of (OH)PcCo (**11a**) (0.120 g, 0.0339 mmol), *p*-formyl benzoic acid (11.5 mg, 0.0763 mmol), *N*,*N*<sup>-</sup>dicyclohexylcarbodiimide (70.0 mg, 0.339 mmol), *N*,*N*-dimethyl-4-aminopyridine (12.4 mg, 0.102 mmol), and dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred at rt under N<sub>2</sub> for 30 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, chloroform, R<sub>f</sub> = 0.90) and then recrystallized from ethyl acetate to give 0.108 g of green solid. Yield 87.3%. MS (MALDI-TOF): *m/z* 3671.58 (calcd. 3667.34).

Nickel benzoic derivative ((OFba)PcNi: 12b). A mixture of (OH)PcNi (11b) (0.120 g, 0.0339 mmol), *p*-formyl benzoic acid (11.2 mg, 0.0747 mmol), *N*,*N*<sup>-</sup>dicyclohexylcarbodiimide (70.0 mg, 0.339 mmol), *N*,*N*-dimethyl-4-aminopyridine (12.4 mg, 0.102 mmol), and dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred at rt under N<sub>2</sub> for 24 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, chloroform, R<sub>f</sub> = 0.89) and then recrystallized from ethyl acetate to give 0.122 g of green solid. Yield 98.7%. MS (MALDI-TOF): *m/z* 3670.47 (calcd. 3667.34).

**Copper benzoic derivative ((OFba)PcCu: 12c).** A mixture of (OH)PcCu (**11c**) (0.150 g, 0.0424 mmol), *p*-formyl benzoic acid (9.53 mg, 0.0635 mmol), *N*,*N*-dicyclohexylcarbodiimide (13.1 mg, 0.0635 mmol), *N*,*N*-dimethyl-4-aminopyridine (31.0 mg, 0.254 mmol), and dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was stirred at rt under N<sub>2</sub> for 24 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, chloroform, R<sub>f</sub> = 0.90) and then recrystallized from ethyl acetate to 0.102 g of give green solid. Yield 65.0%. MS (MALDI-TOF): *m/z* 3676.71 (calcd. 3671.96).

Metal free benzoic derivative ((OFba)PcH<sub>2</sub>: 12d). A mixture of (OH)PcH<sub>2</sub> (11d) (0.120 g, 0.0349 mmol), *p*-formyl benzoic acid (7.76 mg, 0.0517 mmol), *N*,*N*'dicyclohexylcarbodiimide (10.7 mg, 0.0517 mmol), *N*,*N*-dimethyl-4-aminopyridine (25.3 mg, 0.207 mmol), and dry CH<sub>2</sub>Cl<sub>2</sub> (11 mL) was stirred at rt under N<sub>2</sub> for 24 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, chloroform::nhexane = 10:1, R<sub>f</sub> = 0.93) and then recrystallized from ethyl acetate to give 0.0844 g of green solid.. Yield 66.5%. MS (MALDI-TOF): *m/z* 3614.27 (calcd. 3610.43).

**Cobalt fullerene derivative** ((**OFbaC**<sub>60</sub>)**PcCo: 3a**). A mixture of (OFba)PcCo (**12a**) (50.0 mg, 0.0136 mmol),  $C_{60}$  fullerene (19.6 mg, 0.0272 mmol), *N*-methylglycine (2.91 mg 0.0326 mmol), and dry toluene (80 mL) was stirred at 120 °C under N<sub>2</sub> for 24 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. Unreacted fullerene was removed by chromatography (silica gel, toluene,  $R_f = 1.0$ ), and the residue in silica gel was flushed out with THF. The crude product was recrystallized from ethyl acetate at rt and THF at -20 °C, respectively. After removal of solvent, 47.9 mg of green solid was obtained. Yield 79.8%. MS (MALDI-TOF): *m/z* 4416.57 (calcd. 4415.07).

Nickel fullerene derivative ((OFbaC<sub>60</sub>)PcNi: 3b). A mixture of (OFba)PcNi (12b) (60.0 mg, 0.0164 mmol), C<sub>60</sub> fullerene (23.6 mg, 0.0327 mmol), *N*-methylglycine (2.92 mg 0.0328 mmol), and dry toluene (90 mL) was stirred at 120 °C under N<sub>2</sub> for 14 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. Unreacted fullerene was removed by chromatography (silica gel, toluene,  $R_f = 1.0$ ), and the residue in silica gel was flushed out with THF. The crude product was recrystallized from ethyl acetate at rt and THF at -20 °C, respectively. After removal of solvent, 70.1 mg of green solid was obtained. Yield 96.8%. MS (MALDI-TOF): *m/z* 4424.4 (calcd. 4415.07).

**Copper fullerene derivative** ((**OFbaC**<sub>60</sub>)**PcCu: 3c**). A mixture of (OFba)PcCu (**12c**) (60.0 mg, 0.0163 mmol), C<sub>60</sub> fullerene (23.4 mg, 0.0325 mmol), *N*-methylglycine (3.47 mg 0.0389 mmol), and dry toluene (60 mL) was stirred at 120 °C under N<sub>2</sub> for 14 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. Unreacted fullerene was removed by chromatography (silica gel, toluene,  $R_f = 1.0$ ), and the residue in silica gel was flushed out with THF. The crude product was recrystallized from ethyl acetate at rt and THF at -20 °C, respectively. After removal of solvent, 61.3 mg of green solid was obtained. Yield 85.1%. MS (MALDI-TOF): *m/z* 4424.18 (calcd. 4419.69).

Metal free fullerene derivative (( $OFbaC_{60}$ )PcH<sub>2</sub>: 3d). A mixture of (OFba)PcH<sub>2</sub> (12d) (47.0 mg, 0.0130 mmol),  $C_{60}$  fullerene (18.7 mg, 0.0259 mmol), *N*-methylglycine (2.77 mg 0.0311 mmol), and dry toluene (65 mL) was stirred at 120 °C under N<sub>2</sub> for 14 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. Unreacted fullerene was removed by chromatography (silica gel, toluene, R<sub>f</sub> = 1.0), and the residue in silica gel was flushed out with THF. The crude product was recrystallized from ethyl acetate at rt and THF at -20 °C, respectively. After removal of solvent, 43.0 mg of green solid was obtained. Yield 75.8%. MS (MALDI-TOF): *m/z* 4366.84 (calcd. 4358.16).

#### Measurements

The <sup>1</sup>H NMR measurements were carried out by using <sup>1</sup>H NMR (BRUKER Ultrashield 400 MHz). The elemental analyses were performed by using a Yanaco CHN CORDER MT-3. The MALDI-TOF mass spectral measurements were carried out by using a PerSeptive Biosystems Voyager DE-Pro spectrometer (matrix: dithranol). Infrared absorption spectra were recorded by using a Nicolet NEXUS670 FT-IR. Electronic absorption (UV-vis) spectra were recorded by using a HITACHI U-4100 spectrophotometer. Phase transition behavior of the present compounds was observed with polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage and a Mettler FP-90 Central Processor, and differential scanning calorimeter (Perkin-Elmer Diamond DSC.) The mesophases were identified by using a wide angle X-ray diffractometer (Rigaku Rad) equipped with Cu-K $\alpha$ radiation and a handmade hot stage equipped with a temperature controller [33].

### **RESULTS AND DISCUSSION**

# Synthesis of the novel Pc compounds: 11a–11d, 12a–12d, and 3a–3d

Table 1 summarizes MALDI-TOF mass spectra data, elemental analysis results, and yields of **11a-11d**, **12a-12d**, and **3a–3d**. The 3:1 precursors, (OH)PcM (**11**), could be prepared in 20–30% of yields. These low yields resulted from the inevitable by-product of the 4:0 phthalocyanine composed of only 4,5-bis(3,4-didodecyloxyphenoxy)-1,2-dicyanobenzene units. On the other hand, the precursors, (OFba)PcM (**12**), could be prepared in good yields by Steglich esterification [32]. The

Table 1. MALDI-TOF mass spectral data and elemental analysis data of (OH)PcM: 11a–11d, (OFba)PcM: 12a–12d, and (OFba $C_{60}$ ) PcM: 3a–3d.

Compound	ompound Mol. formula Mass observed Elemental analysis: Found(Calco			Calcd.)(%)	) Yield	
			Ν	С	Н	(70)
11a: (OH)PcCo	C <sub>224</sub> H <sub>352</sub> N <sub>8</sub> O <sub>20</sub> Co (3536.23)	3538.11	3.10 (3.17)	76.4 (76.08)	10.26 (10.03)	20.5
11b: (OH)PcNi	C <sub>224</sub> H <sub>352</sub> N <sub>8</sub> O <sub>20</sub> Ni (3535.99)	3537.22	3.17 (3.17)	75.94 (76.09)	10.15 (10.03)	23.7
11c: (OH)PcCu	$\begin{array}{c} C_{224}H_{352}N_8O_{20}Cu\\ (3540.85)\end{array}$	3540.54	3.20 (3.16)	76.14 (75.98)	10.21 (10.02)	29.5
<b>11d:</b> (OH)PcH <sub>2</sub>	$\begin{array}{c} C_{224}H_{354}N_8O_{20}\\ (3479.32) \end{array}$	3482.63	3.13 (3.22)	76.96 (77.33)	10.61 (10.26)	27.9
12a: (OFba)PcCo	$\begin{array}{c} C_{232}H_{355}N_8O_{22}Co\\ (3667.34) \end{array}$	3671.58	2.96 (3.06)	76.15 (75.98)	10.11 (9.76)	87.3
12b: (OFba)PcNi	C <sub>232</sub> H <sub>355</sub> N <sub>8</sub> O <sub>22</sub> Ni (3667.10)	3670.47	3.09 (3.06)	75.72 (75.99)	10.09 (9.76)	98.7
12c: (OFba)PcCu	C <sub>232</sub> H <sub>355</sub> N <sub>8</sub> O <sub>22</sub> Cu (3671.96)	3676.71	3.01 (3.05)	76.24 (75.89)	10.14 (9.74)	65.0
<b>12d:</b> (OFba)PcH <sub>2</sub>	$\begin{array}{c} C_{232}H_{357}N_8O_{22}\\ (3610.43)\end{array}$	3614.27	3.09 (3.10)	77.23 (77.18)	10.31 (9.97)	66.5
<b>3a:</b> (OFbaC <sub>60</sub> )PcCo	C <sub>294</sub> H <sub>360</sub> N <sub>9</sub> O <sub>21</sub> Co (4415.07)	4416.57, 3695.94	—	—	_	79.8
<b>3b:</b> (OFbaC <sub>60</sub> )PcNi	C <sub>294</sub> H <sub>360</sub> N <sub>9</sub> O <sub>21</sub> Ni (4414.83)	4424.47, 3700.34		_	—	96.8
<b>3c:</b> (OFbaC <sub>60</sub> )PcCu	$\begin{array}{c} C_{294}H_{360}N_9O_{21}Cu\\ (4419.69)\end{array}$	4424.18, 3705.23				85.1
<b>3d:</b> (OFbaC <sub>60</sub> )PcH <sub>2</sub>	$\begin{array}{c} C_{294}H_{362}N_9O_{21}\\ (4358.16)\end{array}$	4366.84, 3643.64	_		_	75.8

corresponding dyads, (OFbaC<sub>60</sub>)PcM (3), were synthesized by Prato reaction [31]. All the products gave satisfactory molecular weights by MALDI-TOF mass spectra. The elemental analysis data of the precursors 11 and 12 are in agreement with the theoretical values. However, the dyads **3a–3d** did not completely burn out at the measurement temperature (850 °C). Therefore, these elemental analysis data are not listed up in Table 1. Electronic absorption (UV-vis) spectra were recorded in order to confirm the existence of the phthalocyanine and fullerene parts. In Table 2 are listed electronic spectral data of all the compounds, 11, 12 and 3. The UV-vis spectra are illustrated in Fig. 2. As can be seen from these table and figure, each of the compounds 11, 12 and 3, shows Q-band (600-700 nm) and Soret band (300-400 nm) characteristic to the phthalocyanine macrocycle. As can be seen from Fig. 2d, each of the Pc compounds 3d, 11d and 12d gave split O-band characteristic to a metal free phthalocyanine. Each of the dyads 3a-3d gave an additional absorption peak at ca. 250 nm attributed to fullerene moiety, whereas the other phthalocyanine precursors, 11a-11d and 12a-12d, did not give this peak. This fact clearly supports that fullerene is connected with phthalocyanine in the dyads 3a-3d. Thus, we confirmed that all the target Pc-fullerene dyads 3 could be successfully synthesized.

Although we tried to measure <sup>1</sup>H NMR spectra of the diamagnetic Pc derivatives, **11b**, **11d**; **12b**, **12d** and **3b**, **3d**, all our attempts were in vain. As is well-known,

phthalocyanine discotic liquid crystals tend to aggregate even in a very dilute chloroform solution like as 10<sup>-6</sup> M. We could not measure <sup>1</sup>H NMR spectra for such a dilute solution. So, we need to increase the concentration to ca. 10<sup>-3</sup> M for the NMR measurements. However, very strong aggregation took place in such a concentrated solution, and it always gave the very broad meaningless NMR spectra. Accordingly, we used the other solvents, DMSO-d<sub>6</sub> and/or THF-d<sub>8</sub>, for the Pc-C<sub>60</sub> dyads, **3b**, **3d**, but the dyads were totally insoluble in DMSO and less soluble in THF than chloroform. Even for the saturated solution in hot THFd<sub>8</sub>, it gave a very broad meaningless <sup>1</sup>H NMR spectrum due to the strong aggregation. Thus, all our trials were in vain for the NMR measurements. However, as mentioned above we confirmed from MALDI-TOF mass spectra and the UV-vis spectra that all the target Pc-fullerene dyads 3 could be successfully synthesized.

#### Unusual phase transition behavior of 11 and 12

The phase transition behavior of the PcM precursors (**11** and **12**) and the PcM-C<sub>60</sub> dyads (**3**) is summarized in Table 3. Their X-ray data of **11**, **12** and **3** are listed in Table 4. The phase transition behavior was revealed by polarization microscopy (POM), differential scanning calorimetry (DSC), temperature-dependent X-ray diffraction measurements and temperature-dependent electronic spectrometry.

Table 2. Electronic spectral data of (OH)PcM: 11 ( $\mathbf{a} = Co$ ,  $\mathbf{b} = Ni$ ,  $\mathbf{c} = Cu$ , and  $\mathbf{d} = H_2$ ), (OFba)PcM: 12 ( $\mathbf{a} = Co$ ,  $\mathbf{b} = Ni$ ,  $\mathbf{c} = Cu$ , and  $\mathbf{d} = H_2$ ), and (OFbaC<sub>60</sub>)PcM: 3 ( $\mathbf{a} = Co$ ,  $\mathbf{b} = Ni$ ,  $\mathbf{c} = Cu$ , and  $\mathbf{d} = H_2$ ).

Compound	Concentration <sup>a</sup>	$\lambda max (nm) (log \epsilon)$						
	(X10 <sup>-3</sup> mol/l)	C <sub>60</sub> peak	S	Soret-bar	nd		Q-band	
(OH)PcCo: 11a	1.2				327.7 (4.9)	608.8 (4.6)	643.4 (sh)	677.1 (5.2)
(OH)PcNi: 11b	1.0		289.4 (5.0)	306.6 (5.0)	330.3 (sh)	628.4 (4.6)	646.2 (sh)	675.6 (5.3)
(OH)PcCu: 11c	1.8		290.8 (4.9)		340.2 (5.0)	615.4 (4.7)	651.8 (4.6)	686.7 (5.3)
(OH)PcH <sub>2</sub> : <b>11d</b>	0.98		291.1 (4.8)		342.9 (4.9)	608.3 (4.4)	644.8 669.8 (4.6) (5.1)	704.3 (5.1)
(OFba)PcCo: 12a	1.0				327.1 (5.3)	608.6 (4.6)	642.7 (sh)	675.9 (5.2)
(OFba)PcNi: 12b	1.0		288.6 (5.0)	305.3 (5.0)	330.2 (sh)	608.6 (4.6)	647.6 (sh)	675.9 (5.3)
(OFba)PcCu: 12c	1.6		291.3 (4.9)		341.3 (4.9)	615.0 (4.6)	652.5 (sh)	685.0 (5.3)
(OFba)PcH <sub>2</sub> : <b>12d</b>	1.2		291.5 (4.8)		345.3 (4.9)	607.4 (4.9)	643.9 670.0 (0.51) (5.1)	702.8 (5.1)
(OFbaC <sub>60</sub> )PcCo: <b>3a</b>	0.63	245.0 (5.2)	292.8 (5.1)			609.2 (4.5)	642.9 (sh)	677.2 (5.2)
(OFbaC <sub>60</sub> )PcNi: <b>3b</b>	0.54	248.0 (5.1)	283.3 (5.0)	309.2 (5.0)	328.2 (sh)	610.9 (4.5)	647.8 (sh)	676.1 (5.1)
(OFbaC <sub>60</sub> )PcCu: <b>3c</b>	0.52	255.6 (5.2)	292.7 (sh)		340.3 (5.0)	618.1 (4.7)	652.2 (sh)	684.9 (5.2)
(OFbaC <sub>60</sub> )PcH <sub>2</sub> : <b>3d</b>	0.53	254.5 (5.1)	288.6 (5.0)		338.8 (4.9)	610.9 (4.5)	641.4 669.7 (4.6) (5.0)	704.3 (5.1)

<sup>a</sup>: in chloroform.

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**Fig. 2.** UV-vis spectra in CH<sub>3</sub>Cl at room temperature: (a) PcCo (**11a**, **12a**, and **3a**), (b) PcNi (**11b**, **12b**, and **3b**), (c) PcCu (**11c**, **12c**, and **3c**), and (d) PcH<sub>2</sub> (**11d**, **12d**, and **3d**)

As can be seen from Table 3, each of the (OH)PcM derivatives (11a-11d) shows very interesting phase transition sequence, e.g.  $K(R) \rightarrow Col_{tet}(R) \rightarrow Col_{h}(F) \rightarrow$  $Col_{tet}(F) \rightarrow I.L.$  for (OH)PcNi (11b) on heating stage. (R) and (F) mean roof-top-shaped dimer stacking and face-to-face stacking, respectively. On cooling from I.L., it gave Cub(Pn3m). On further cooling the Cub phase relaxed into  $\text{Col}_{tet}(F)$  and then it transformed into  $\text{Col}_{h}(F)$ . The  $Col_h(F)$  mesophase was supercooled till rt. Thus, the (OH)PcNi (11b) derivative gave a very peculiar phase transition like as  $\operatorname{Col}_{tet}(R) \rightarrow \operatorname{Col}_{h}(F) \rightarrow \operatorname{Col}_{tet}(F)$ . As can be seen from Table 3, the (OFba)PcNi (12b) derivative also showed unusual phase transitions like as  $K(R) \rightarrow$  $\operatorname{Col}_{tet}(R) \rightarrow \operatorname{Col}_{tet}(F) \rightarrow I.L.$  on heating stage, and I.L.  $\rightarrow$  $\operatorname{Cub}(\operatorname{Pn3m}) \rightarrow \operatorname{M}_{x} \rightarrow \operatorname{Col}_{h}(R) \rightarrow \operatorname{Col}_{tet}(R) \rightarrow \operatorname{K}(R)$  on cooling stage. These unusual phase transition sequences of 11 and 12 are resulted from formation, deformation, and reformation of roof-top-shaped dimers.

#### Formation, deformation and reformation of the rooftop-shaped dimers of 11 and 12

UV-vis spectra of the thin film certified the roof-topshaped dimer formation, which is based on Kasha's rule [34] for the excited energy levels as illustrated in Fig. 3. As can be seen from Fig. 3d, when roof-top-shaped dimers are formed, the excited energy level is split into two levels. Hence, the Q-band of phthalocyanine should be split into two peaks only in the roof-top-shaped dimer. Representative UV-vis spectra of the thin films of 11b, 12b, and 3b are shown in Fig. 4. The Col<sub>tet</sub>(R) mesophase of 11b at 80 °C gave a shoulder at ca. 750 nm. The peak at ca. 680 nm and the shoulder at ca. 750 nm correspond to two split Q-bands. However, the shoulder at ca. 750 nm disappeared with heating and did not appear again on cooling. On the other hand, the  $Col_{tet}(R)$  mesophase of **12b** at 80 °C gave a much clearer shoulder at *ca*. 750 nm. Although the shoulder at ca. 750 nm disappeared on further heating, it appeared again for the  $Col_{h}(R)$ mesophase on cooling stage.

These spectral changes agree with the stacking distances in the XRD data listed in Table 4. As can be seen from this table, the  $Col_{tet}(R)$  mesophase of **11b** at 80 °C, for example, gave a sharp peak at 4.87 Å (h<sub>1</sub>) and a broad peak at *ca*. 9.4 Å (h<sub>2</sub>: approximately two times of 4.87 Å). Taking into account these two stacking distances at 4.87 Å and two times of the stacking distance at *ca*. 9.2 Å, it is consistent with formation



Table 3. Phase transition temperatures and enthalpy changes of all compounds

(a) Phase nomenclature: K = crystal,  $Col_h = hexagonal columnar mesophase$ ,  $Col_{tet,0} = tetragonal ordered columnar mesophase$ ,  $Col_{tet,0} = tetragonal disordered columnar mesophase$ , I.L. = isotropic liquid, (R) = roof-top-shaped dimer stacking and (F) = face-to-face stacking. \* = the DSC peak was too small to estimate the enthalpy change, + = gradual decomposition after clearing, # = two peaks were too close to determine the enthalpy changes,  $\Box$  = mesophase shawing homeotropic alignment, and ¶ = This mesophase gave only one XRD peak in the low angle region. Although the mesophase was impossible to be established from the one peak, it was tentatively identified as a  $Col_{tet}$  mesophase.

of the roof-top-shaped dimers in the columns. When it was further heated up into the  $\text{Col}_h(F)$  mesophase at 105 °C, the peak at 4.87 Å disappeared and a broad peak appeared at *ca.* 3.5 Å instead, as listed in this table. Stacking distance of *ca.* 3.5 Å is a typical stacking distance of phthalocyanine disks stacked faceto-face. Therefore, the roof-top-shaped dimers in the  $\text{Col}_{tet}(R)$  mesophase changed into face-to-face stacking in the  $\text{Col}_h(F)$  mesophase at the phase transition from  $\text{Col}_{tet}(R)$  to  $\text{Col}_h(F)$  at 92.0 °C. As can be seen from Table 3, the  $\text{Col}_h(F)$  mesophase changed into another tetragonal mesophase,  $\text{Col}_{tet}(F)$ , at 110.3 °C, which cleared into isotropic liquid (I.L.) at 172.3 °C. It is very interesting that a Cub mesophase, Cub(Pn3m),

Compound	<b>Tt</b>	Spacing/A		Miller indices
	Lattice constants/A	Observed	Calculated	(hkl)
(OH)PcCo:11a	Col <sub>tet</sub> (R) at 85°C	33.2	33.2	(1 0 0)
		23.0	23.5	(1 1 0)
	a = 33.2	14.6	14.8	(2 1 0)
	$h_2 = ca. 9.3$	ca. 9.3		h <sub>2</sub>
	$h_1 = 4.89$	4.89		$h_1$
	$Z = 0.92$ for $\rho = 1.0$	ca. 4.5		#
	Col <sub>h</sub> (F) at 115°C	33.7	33.7	(1 0 0)
	a = 38.9	19.9	19.5	(1 1 0)
		13.1	12.7	(2 1 0)
		ca. 4.6	_	#
	Col <sub>tot</sub> (F) at 160°C	30.2	30.5	(1 0 0)
	a = 30.5	21.5	21.5	(1 1 0)
		ca. 4.6	_	#
	Cub(Pn3m) at 163°C on cooling	39.4	39.4	(3 2 1)
	a = 147	35.0	35.0	(3 3 0)
		33.4	33.4	(3 3 1)
		30.2	30.2	(4 2 2)
		20.5	20.5	(6 4 0)
		ca. 13.2	_	#
		ca. 9.4	_	#
		ca. 4.7		#
		<i>ca</i> . 3.6		h
(OH)PcNi: 11b	Col <sub>tet</sub> (R) at 80°C	33.7	33.7	(1 0 0)
	a = 33.7	23.0	23.8	(1 1 0)
	$h_2 = ca. 9.4$	ca. 9.4	—	$h_2$
	$h_1 = 4.87$	4.87	—	$\mathbf{h}_1$
	$Z = 1$ for $\rho = 1.2$	ca. 4.4	—	#
	Col <sub>h</sub> (F) at 105°C	34.0	34.0	(1 0 0)
		20.3	19.6	(1 1 0)
	a = 39.3	13.3	12.9	(2 1 0)
	h = ca. 3.5	ca. 9.0		#
	$Z = 1$ for $\rho = 1.2$	ca. 4.5		#
		ca. 3.5		h
	Col <sub>tet</sub> (F) at 130°C	31.5	31.2	(1 0 0)
	a = 31.2	22.1 ca. 4.6	22.1	(1 1 0) #

Table 4 X-ray data of (OH)PcM (11a–11d), (OFba)PcM (12a–12d) and (OFbaC<sub>60</sub>)PcM (3a–3d).

# = Halo of the molten alkoxy chains.  $h_1$  = stacking distance between the monomers.  $h_2$  = stacking distance between the dimers.  $\P$  = This mesophase gave only one XRD peak in the low angle region. Although the mesophase was impossible to be established from the one peak, it was tentatively identified as a Coltet mesophase.

(Continued)

Table 4. (Continued).						
	Cub(Pn3m) at 160°C on cooling	34.5	34.5	(3 2 1)		
	a = 129	30.7	30.7	(3 3 0)		
		29.6	29.6	(3 3 1)		
		21.9	21.9	(5 3 1)		
		ca. 8.9	_	#		
		ca. 4.6	_	#		
		ca. 3.4	_	h		
(OH)PcCu: 11c	Col <sub>h</sub> (F) at 120°C	34.5	34.5	(1 0 0)		
	a = 40.7	20.3	19.9	(1 1 0)		
		17.3	17.2	(2 0 0)		
		13.1	13.0	(2 1 0)		
		11.6	11.5	(3 0 0)		
		ca. 4.4	_	#		
	Col <sub>tet</sub> (F) at160°C	30.7	30.9	(1 0 0)		
	a = 30.9	21.9	21.9	(1 1 0)		
		ca. 9.6	_	#		
		ca. 4.7	_	#		
	Cub(Pn3m) at 154°C on cooling	38.4	38.4	(3 2 1)		
	a = 144	34.0	34.0	(3 3 0)		
		33.2	33.2	(3 3 1)		
		32.0	32.0	(4 2 0)		
		30.9	30.9	(3 3 2)		
		22.6	22.7	(6 2 1)		
		ca. 8.6	_	#		
		ca. 4.6	_	#		
		ca. 3.5		h		
(OH)PcH <sub>2</sub> : <b>11d</b>	M <sub>x</sub> (R) at 70°C	35.9	_	_		
	If this mesophase is $Col_{tet}(R)$ , a = 35.9.	22.4	—	—		
		ca. 9.5		$h_2$		
		4.81		$\mathbf{h}_1$		
		ca. 4.5		#		
	Col <sub>tet</sub> (F) at 110°C	34.5	34.5	(1 0 0)		
	a = 34.5	24.4	24.4	(1 1 0)		
		ca. 4.5		#		
	Cub(Pn3m) at 130°C on cooling	38.7	39.0	(3 1 1)		
	a = 129	37.1	37.3	(2 2 2)		

Table 1 (Continued)

(Continued)

		,		
		32.5	32.3	(4 0 0)
		23.7	23.6	(5 2 1)
		ca. 4.5		#
(OFba)PcCo: 12a	Col <sub>tet</sub> (R) <sub>1</sub> at 85°C	33.2	32.5	(1 0 0)
	a = 32.5	23.0	23.0	(1 1 0)
	$h_2 = ca. 9.5$	14.6	14.5	(2 1 0)
	$h_1 = 4.89$	ca. 9.5	_	$h_2$
	$z = 0.88$ for $\rho = 1.0$	4.89	_	$\mathbf{h}_1$
		ca.4.5	—	#
	M <sub>x</sub> at 118°C	32.2	_	_
	If this mesophase is	21.2	_	_
	$Col_{tet}(R)_2, a = 32.2$	13.3	_	_
		ca. 9.5	_	$h_2$
		4.89	—	$h_1$
		ca. 4.5	—	#
	Col <sub>tet</sub> (F) at 160°C	30.2	30.6	(1 0 0)
	a = 30.6	21.6	21.6	(1 1 0)
		11.0	10.8	(2 2 0)
		<i>ca</i> . 4.6	_	#
	Cub(Pn3m) at 155°C on cooling	37.4	37.4	(3 2 1)
	a = 140	32.9	32.9	(3 3 0)
		32.0	32.0	(3 3 1)
		29.8	29.8	(3 3 2)
		22.2	22.2	(6 2 0)
		ca. 9.9	_	#
		ca. 4.7	—	#
		ca. 3.4	—	h
(OFba)PcNi: 12b	$\text{Col}_{\text{tet}}(R)$ at 90°C	32.2 21.7	32.2 22.8	$(1 \ 0 \ 0)$ $(1 \ 1 \ 0)$
	a = 33.2	13.5	14.4	(2 1 0)
	$h_2 = ca. 9.3$	11.0	10.7	(3 0 0)
	$h_1 = 4.85$	ca. 9.3		$h_2$
	$Z=0.83 \ for \ \rho=1.0$	4.85	_	$h_1$
		ca. 4.5	—	#
	Col <sub>tet</sub> (F) at 160°C	30.0	30.5	(1 0 0)
	a = 30.5	21.5	21.5	(1 1 0)
		ca. 9.0	_	#
		ca. 4.7	—	#
		ca. 3.5	—	h
	Cub(Pn3m) at 155°C on cooling	39.1	39.0	(3 1 0)
	a = 124	37.7	37.7	(3 1 1)

 Table 4. (Continued).

(Continued)

Table 4. (Continued). 35.6 35.6  $(2\ 2\ 2)$ 32.7 32.7  $(3\ 2\ 1)$ 29.6 29.6 (330)21.9 21.8  $(4\ 4\ 0)$ ca. 9.2 # # ca. 4.6 ca. 3.5 h \_\_\_\_  $Col_h(R)$  at 90°C on cooling  $(1\ 0\ 0)$ 35.0 35.0 20.6 20.6  $(1\ 1\ 0)$ a = 41.3 17.9 17.9  $(2\ 0\ 0)$  $h_2 = ca. 95$ 13.7 13.5  $(2\ 1\ 0)$  $h_1 = 4.85$ ca. 9.5 \_\_\_\_\_  $h_2$ Z = 1.2 for  $\rho = 1.0$ 4.85 h<sub>1</sub> \_\_\_\_ ca. 4.4 # \_\_\_\_ (OFba)PcCu: 12c Col<sub>tet</sub> (R)<sub>1</sub> at 80°C 32.7 32.3  $(1\ 0\ 0)$ a = 32.3 22.9 22.9  $(1\ 1\ 0)$ h = 4.85 ca. 12 (2 2 0)+(3 0 0) \_\_\_\_ 4.85 h # ca. 4.3 \_\_\_\_ Col<sub>tet</sub>(R)<sub>2</sub> at 107°C 35.0 35.0  $(1\ 0\ 0)$ a = 35.0 23.2 24.8  $(1\ 1\ 0)$ 17.7 17.5  $(2\ 0\ 0)$  $(2\ 2\ 0)+(3\ 0\ 0)$ ca. 12 ca. 12 8.73 8.76  $(4\ 0\ 0)$ # ca. 4.4 \_\_\_\_ Col<sub>tet</sub>(F) at 145°C 31.1 31.1  $(1\ 0\ 0)$ a = 31.1 22.5 22.0  $(1\ 1\ 0)$  $(2\ 2\ 0)+(3\ 0\ 0)$ ca. 12 \_\_\_\_ # ca. 4.3 \_\_\_\_ Cub(Pn3m) at 155°C 38.7 (3 1 1)38.7 a = 128 37.1 37.0  $(2\ 2\ 2)$ 34.0 33.9 (3 2 1) 30.7 30.6 (330)ca. 12.2 # ca.4.4 # \_\_\_\_ (OFba)PcH<sub>2</sub>: 12d Col<sub>tet</sub>(R) at 80°C 33.4 33.4  $(1\ 0\ 0)$ 23.5 23.5  $(1\ 1\ 0)$ a = 33.4 14.4 15.0  $(2\ 1\ 0)$ h = 4.84 $(3\ 0\ 0)$ 11.1 11.1 4.84 \_ h ca. 4.4 # \_\_\_\_ Col<sub>tet</sub>(F) at 110°C 32.0  $(1\ 0\ 0)$ 32.0 22.9 a = 32.0 22.6  $(1\ 1\ 0)$ 

(110)

(Continued)

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	Table 4. (Co	ommuea).		
		14.0	14.3	(2 1 0)
		ca. 4.4	_	#
	Cub(Pn3m) at 125°C	39.4	39.3	(2 2 2)
	a = 138	34.8	34.7	(4 0 0)
		31.5	31.5	(3 3 1)
		30.7	30.6	(4 2 0)
		21.9	21.8	(6 2 0)
		ca. 12.8	—	#
		ca. 4.4	_	#
(OFbaC <sub>60</sub> )PcCo: <b>3a</b>	Col <sub>tet.1</sub> ¶ at 65°C	33.2	33.2	(1 0 0)
	a = 33.2	ca. 9.8	_	#
		ca. 4.5	_	#
	Col <sub>tet.2</sub> ¶ at 90°C	33.7	33.7	(1 0 0)
	a = 33.7	ca. 9.5	_	#
		<i>ca</i> . 4.7	—	#
(OFbaC <sub>60</sub> )PcNi: <b>3b</b>	Col <sub>tet.o</sub> at 70°C	33.4	33.4	(1 0 0)
	a = 33.4	14.2	15.0	(2 1 0)
	h = 4.84	ca. 9.3	_	#
		4.84	—	h
		<i>ca</i> . 4.4	—	#
	Col <sub>tet.d</sub> at 90°C	33.2	33.2	(1 0 0)
		23.6	23.5	(1 1 0)
	a = 33.2	ca. 9.2	—	#
		ca. 4.5	—	#
(OFbaC <sub>60</sub> )PcCu: 3c	Col <sub>tet.o</sub> at 90°C	33.2	33.2	(1 0 0)
	a = 33.2	23.4	23.5	(1 1 0)
	h = 4.85	ca.11.5	_	#
		4.85	_	h
		ca. 4.5	_	#
(OFbaC <sub>60</sub> )PcH <sub>2</sub> : <b>3d</b>	Col <sub>tet.o</sub> at 75°C	34.0	34.0	(1 0 0)
		23.9	24.0	(1 1 0)
	a = 34.0	ca. 9.1		#
	h = 4.81	4.81		h
		ca. 4.5	—	#

Table 4. (Continued)

appeared only on cooling from I.L. and it also gave a short stacking distance at *ca.* 3.5 Å (h). On further cooling below 110.3, the  $Col_h(F)$  mesophase appeared again *via*  $Col_{tet}(F)$ . The  $Col_h(F)$  mesophase gave again the broad peak at *ca.* 3.5 Å in the X-ray diffraction pattern. On further cooling, the  $Col_h(F)$  mesophase was suppercooled until room temperature and the stacking distance at *ca.* 3.5 Å was maintained.

For another example, the  $Col_{tet}(R)$  mesophase of **12b** at 90 °C also gave two stacking distances at 4.85 Å (h<sub>1</sub>)

and *ca.* 9.3 Å (h<sub>2</sub>: approximately two times of 4.85 Å), whereas the higher temperature mesophase  $\text{Col}_{\text{tet}}(F)$  at 160 °C gave a short stacking distance at *ca.* 3.5 Å (h), as can be seen from Table 4. Very interestingly, the Cub(Pn3m) mesophase of **12b** also appeared only on cooling from I.L. and it gave a short tacking distance at *ca.* 3.5 Å (h). On further cooling,  $\text{Col}_h(R)$  mesophase appeared and gave two stacking distances at 4.85 Å (h<sub>1</sub>) and *ca.* 9.5 Å (h<sub>2</sub>). These formation, deformation and reformation of the roof-top-shaped dimer are compatible



Oblique (herringbone) transition dipoles: band-splitting case (d)



Fig. 3. Kasha's rules: exciton energy diagrams for various dimers

with the UV-vis spectral changes of the thin film of 12b mentioned above.

These unique phase structural changes of the representative (OFba)PcNi (12b) derivative are illustrated in Fig. 5, together with the phase transition sequence.

#### Phase transition behavior of 3

As can be seen from Table 3, each of the  $Pc-C_{60}$ dyads, (OFbaC<sub>60</sub>)PcM (**3a–3d**), shows only tetragonal columnar (Col<sub>tet</sub>) mesophase(s). As can be seen from Table 4, the Col<sub>tet o</sub> mesophases of **3b–3d** gave a longer stacking distance at ca. 4.85 Å, which was observed

as a roof-top-shaped dimer stacking distance for the Pc precursors, 11a-11d and 12a-12d. However, as can be seen from Fig. 4, the representative  $Pc-C_{60}$ dyad 3b did not show split O-bands, and the UV-vis spectra did not change at all for the heating and cooling cycle. Therefore, it can be concluded that **3b** does not form the roof-top-shaped dimers, and that the faceto-face stacking shape maintains at all temperatures.

This phenomenon may be attributed to the size of substituent group. The precursors 11 and 12 having a relatively small terminal substituent group of hydroxyl or *p*-formyl benzoate hardly move in more frozen alkyl chains at lower temperatures. Accordingly, the phthalocyanine core parts having the relatively small terminal substituent groups may tend to form roof-topshaped dimers in the lower temperature mesophases of  $\operatorname{Col}_{tet}(R)$  and  $\operatorname{Col}_{h}(R)$ . On the other hand, these relatively small terminal substituent group can easily move in more melted alkyl chains in Col<sub>tet</sub>(F) mesophase at higher temperatures. As a result, phthalocyanine core parts easily stack face-to-face in the higher temperature mesophases of Col<sub>tet</sub>(F) and Cub(Pn3m). Therefore, two longer stacking distances of 4.85 Å and ca. 9.5 Å appear at lower temperature mesophases, whereas a short stacking distance at ca. 3.5 Å appears at higher temperature mesophases. The Pc disks of Pc-C<sub>60</sub> dyad **3b** having very bulky terminal substituent group of fullerene may not tilt to form roof-top-shaped dimer due to the bulkiness of fullerene at all the temperatures. Therefore, the dyad **3b** may keep their stacking shape faceto-face at 4.85 Å.

Compared with the clearing points (cps) in Table 3 for all the present derivatives **11a–11d**, **12a–** 12d, and 3a–3d having a different terminal group, the cps of 12a–12d having benzoic acid group are lower by about 6 °C on the average than those of 11a-11d having OH group. The cps of **3a–3d** having fullerene group is lower by about 67 °C on the average than those of 12a-12d having benzoic acid group. Therefore, the bulkier the terminal substituted group becomes in an order of OH < benzoic acid < fullerene, the more Col<sub>tet</sub> mesophase only tends to appear.

Additionally, the dyads **3a–3d** only showed gradual decomposition over their cps. It may be resulted from charge transfer from Pc moiety to fullerene. Further studies are needed to clarify the origin of this decomposition.



**Fig. 4.** UV-vis spectra of the thin films of (OH)PcNi: **11b**, (OFba)PcNi: **12b**, and (OFbaC<sub>60</sub>)PcNi: **3b**. Q = Q-band; SptQ = split Q-band; A = aggregated band

## Effect of an additional methoxy group directly substituted to Pc core on clearing points

In our previous work [25], we successfully synthesized PcCu derivatives, (OH)PcCu(OCH<sub>3</sub>) (8), (OFba) PcCu(OCH<sub>3</sub>) (9) and (OFbaC<sub>60</sub>)PcCu(OCH<sub>3</sub>) (2), which have an additional methoxy group directly substituted to Pc core, as shown in Scheme 1. In contrast to these previous derivatives, the present PcCu derivatives, (OH)PcM (11c), (OFba)PcM (12c) and (OFbaC<sub>60</sub>) PcM (3c), have no additional methoxy group, as can be seen from Scheme 2. Therefore, it is very interesting for us to investigate the effect of an additional methoxy group on their phase transition behavior. Table 5 lists the phase transition behavior of the representative derivatives in both series for comparison.

Comparing these clearing points, the present PcCu compounds (11c, 12c and **3c**) give lower clearing points than the previous methoxy-group-substituted PcCu derivatives (8, 9 and 2): the cp of 11c is lower about 15 °C than that of 8; the cp of **12c** is about 10 °C than that of 9; and the cp of 3c is about 70 °C than that of **2**. It is surprising for us that removal of such a small methoxy group from the big  $(OFbaC_{60})PcM(OCH_3)$  (2) molecule significantly lowers the cp of  $(OFbaC_{60})PcCu$  (**3c**) by about 70 °C in comparison with that of 2 having the methoxy group. Although the reason of the cp lowering is not clear at the present stage, we tentatively speculate it as follows. The present PcCu compounds (11c, 12c and 3c) have larger open space around Pc macrocycle than the methoxy-group-substituted previous PcCu derivatives (8, 9 and 2). Therefore, the bulky terminal fullerene group of the neighboring molecule may reach more closely to the Pc macrocycle and perturb the stacking of Pc disks to destroy the columnar structure effectively at much lower temperatures; it may cause the cp lowering the present PcCu compounds (11c, 12c and 3c).

As can be seen from Table 5, each of the PcCu derivatives in both series shows homeotropic alignment in the highest temperature Col<sub>tet</sub> mesophase.

#### Homeotropic alignment

As can be seen from Table 3, each of the present novel Pc compounds, **11** and **12**, shows homeotropic alignment in the highest temperature  $\text{Col}_{\text{tet}}$  mesophase. On the other hand, each of the Pc-C<sub>60</sub> dyads **3** shows homeotropic alignment in all the  $\text{Col}_{\text{tet}}$  mesophases. When perfect homeotropic alignment can be achieved, it will give complete darkness between cross polarizers. As can be seen from the photomicrographs in Fig. 6, the (OFbaC<sub>60</sub>)



Fig. 5. The mechanism of phase transition for (OFba)PcNi (12b)

Table 5. Phase transition temperatures and enthalpy changes of the previous  $PuCu(OCH_3)$  compounds (8, 9 and 2) and the present Cu compounds (11c, 12c and 3c).



(a) Phase nomenclature: K = crystal,  $Col_h = hexagonal columnar mesophase$ ,  $Col_{tet.o} = tetragonal ordered columnar mesophase$ ,  $Col_{tet.d} = tetragonal disordered columnar mesophase$ ,  $M_x = unidentified mesophase$ , Cub = cubic mesophase, I.L. = isotropic liquid, + = gradual decomposition over *ca*. 120 °C, and  $\Box$  = mesophase shawing homeotropic alignment.



**Fig. 6.** Photomicrographs of the (OFbaC<sub>60</sub>)PcM: (a) (OFbaC<sub>60</sub>)PcCo: **3a** at 90.0 °C on the first heating, (b) (OFbaC<sub>60</sub>)PcNi: **3b** at 85.0 °C on the first heating, (c) (OFbaC<sub>60</sub>)PcCu: **3c** at 87.0 °C on the first heating, and (d) (OFbaC<sub>60</sub>)PcH<sub>2</sub>: **3d** at 87.0 °C on the first heating (all the photos were taken under crossed polarizers)

PcM (M = Co, Ni, Cu, H<sub>2</sub>) dyads, **3a–3d**, in the Col<sub>tet</sub> mesophases exhibited complete darkness characteristic to perfect homeotropic alignment. It is noteworthy that **3c** and **3d** show only one Col<sub>tet.o</sub> mesophase having ordered stacking distance with perfect homeotropic alignment. Such simple phase transition can contribute to maintain stable performance in wide temperature range, when they will be applied to organic thin film solar cells.

#### **CONCLUSION**

In this study, we have successfully prepared novel PcM compounds, **11a–11d** and **12a–12d**, and Pc-C<sub>60</sub> dyads **3a–3d** (M = Co (a), Ni (b), Cu (c), metal free (d)). The Pc-C<sub>60</sub> dyads **3a–3d** could be obtained in good yields by Prato reaction. We established their unique mesomorphism using temperature-dependent X-ray diffraction measurements and temperature-dependent electronic spectroscopy. It is surprising that a small methoxy group largely affects the cps of these big molecules, especially cps of Pc-C<sub>60</sub> dyads. The cp of **3c** having no methoxy group is lower about 70 °C than that of **2** having the methoxy group. Each of the present novel Pc compounds, **11** and **12**, shows homeotropic alignment in the highest temperature Col<sub>tet</sub> mesophase. On the other

hand, each of the  $Pc-C_{60}$  dyads **3** shows homeotropic alignment in all the  $Col_{tet}$  mesophases. Very interestingly, the  $Pc-C_{60}$  dyads **3c** and **3d** showed simple phase transition with perfect homeotropic alignment in  $Col_{tet,o}$  mesophase having ordered stacking distance. These properties are very suitable for organic solar cell fabrication.

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#### REFERENCES

- Kim JY and Bard AJ. Chem. Phys. Lett. 2004; 383: 11–15.
- Nishizawa T, Tajima K and Hashimoto K. J. Mater. Chem. 2007; 17: 2440–2445.
- Roland T, Ramirez GH, Léonard J, Méry S and Haacke S. J. Phys.: Conference Series 2011; 276: 012006(1–6).
- Lincker F, Heinrich B, Bettignies R, Rannou P, Pecaut J, Grevin B, Pron A, Donnio B and Demadrille R. *J. Mater. Chem.* 2011; 21: 5238–5247.

- Barrau S, Heiser T, Richard F, Brochon C, Ngov C, van de Wetering K, Hadziioannou G, Anokhin DV and Ivanov DA. *Macromolecules*. 2008; 41: 2701–2710.
- 6. Kim DH, Lee BL, Moon H, Kang HM, Jeong EJ, Park JI, Han KM, Lee S, Yoo BW, Koo BW, Kim JY, Lee YH, Cho K, Becerril HA and Bao Z. *J. Am. Chem. Soc.* 2009; **131**: 6124–6132.
- Liang TC, Chiang IH, Yang PJ, Kekuda D, Chu CW and Lin HC. *J. Poly. Sci.: Part A Poly. Chem.* 2009; 47: 5998–6013.
- 8. Sommer M, Huettner S and Thelakkat M. *J. Mater. Chem.* 2010; **20**: 10788–10797.
- Yao K, Chen Y, Chen L, Li F, Li X, Ren X, Wang H and Liu T. *Macromolecules*. 2011; 44: 2698–2706.
- Yasuda T, Yonezawa K, Ito M, Kamioka H, Han L and Moritomo Y. J. Photopolym. Sci. Technol. 2012; 25: 271–276.
- 11. Han Y, Chen L and Chen Y. J. Poly. Sci. Poly. Chem. 2012; published online: DOI: 10.1002/pola.26394.
- Li F, Chen W and Chen Y. J. Mater. Chem. 2012; 22: 6259–6266.
- 13. Bushby JR, Hamley IW, Liu Q, Lozman OR and Lydon EJ. *J Mater Chem.* 2005; **15**: 4429–4434.
- Uchida S, Kude Y, Nishikitani Y and Ota (= Ohta) K. Jpn. Kokai Tokkyo Koho. JP 2008214227(A)-2008-09-18 (Priority number: JP2007060604; Submission Date: 2007-03-09)
- Zhou X, Kang SW, Kumar S, Kulkarni RR, Cheng SZD and Li Q. *Chem. Mater.* 2011; **20**: 3551–3553.
- 16. de la Escosura A, Martinez-Diaz MV, Barbera J and Torres T. J. Org. Chem. 2008; **73**: 1475–1480.
- Tashiro K and Aida T. J. Amer. Chem. Soc. 2008; 130: 13812–13813.
- Geerts YH, Debever O, Amato C and Sergeyev S. Beilstein J. Org. Chem., Beilstein J. Org. Chem. 2009; 5: 1–9.
- 19. Thiebaut O, Bock H and Grelet E. J. Am. Chem. Soc. 2010; **132**: 6886–6887.

- Hayashi H, Nihashi W, Umeyama T, Matano Y, Seki S, Shimizu Y and Imahori H. J. Am. Chem. Soc. 2011; 133: 10736–10739.
- Bagui M, Dutta T, Chakraborty S, Melinger JS, Zhong H, Keightley A and Peng Z. J. Phys. Chem. A 2011; 115: 1579–1592.
- Haverkate LA, Zbiri M, Johnson MR, Deme B, de Groot HJM, Lefeber F, Kotlewski A, Picken SJ, Mulder FM and Kearley GJ. *J. Phys. Chem. B* 2012; 116: 13098–13105.
- 23. Ota (= Ohta) K. *Jpn. Kokai Tokkyo Koho*, JP2011132180(A)-2011–07–07 (Priority number: JP20090293501; Submission Date: 2009-12-24).
- 24. Ince M, Martinez-Diaz MV, Barbera J and Torres T. *J. Mater. Chem.* 2011; **21**: 1531–1536.
- 25. Kamei T, Kato T, Itoh E and Ohta K. J. Porphyrins Phthalocyanines 2012; 16: 1261–1275
- Demus D, Goodby J, Gray GW, Spiess HW and Vill V. *Handbook of Liquid Crystals*, Vol. 2B, Wiley-VCH: New York, 1998; pp 693–798.
- 27. Kumar S. Chemistry of Discotic Liquid Crystals: From Monomers to Polymers, CRC Press: 2010.
- Ohta K, Nguyen-Tran H.-D, Tauchi L, Kanai Y, Megumi T and Takagi Y. In *The Handbook of Porphyrin Science*, Vol. 12, Kadish KM, Smith KM and Guilard R. (Eds.) World Scientific Publishing: Singapore, 2011; pp 1–120.
- Hatsusaka K, Ohta K, Yamamoto I and Shirai H. J. Mater. Chem. 2001; 11: 423–433.
- 30. Bingel C. Chem. Ber. 1993; 126: 1957-1959.
- Maggini M, Scorrano G and Prato M. J. Am. Chem. Soc. 1993; 115: 9798–9799.
- 32. Neises B and Steglish W. Angew. Chem. Int. Ed. 1978; 17: 522–524.
- Hasebe H. Master Thesis, Sinshu University (1991); Ema H. Master Thesis, Sinshu University (1988).
- Kasha M, Rawls HR and El-Bayoumi MA. Pure. Appl. Chem. 1965; 11: 371.