Supporting information

A near-infrared fluorescent phthalocyanine liquid developed through controlling intermolecular interactions

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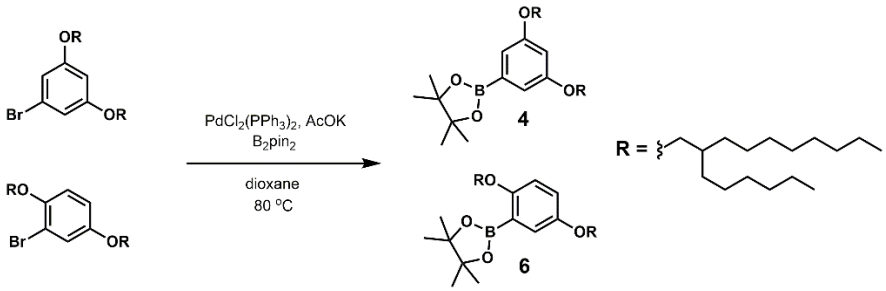
Experimental section

Materials and equipment

All commercial available chemicals were used without further purifications unless otherwise noted. 4A molecular sieves and potassium acetate (AcOK) were dried at 200 °C *in vacuo* in prior to use. 1-Butanol and 1-dodecanol for synthesis of phthalocyanines were dried over 4A molecular sieves in prior to use. 2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (Sphos) and tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$) were purchased from Sigma Aldrich. Palladium acetate ($Pd(OAc)_2$), dichlorobis-(triphenylphosphine)palladium (II) ($PdCl_2(PPh_3)_2$), AcOK, tripotassium phosphate (K_3PO_4), potassium carbonate (K_2CO_3), Li metal, and all solvents were purchased from WAKO pure chemical. Bis(pinacolato)diboron was purchased from Matrix Scientific. 2-Hexyldecylbromide and 2, 5-dimethoxyphenyl boronic acid were purchased from Tokyo Chemical Industry. ^1H and ^{13}C NMR measurements were carried out by using a Bruker BioSpin AVANCE NEO 400 OneBay (400.13 and 100.61 MHz for ^1H and ^{13}C, respectively). Chemical shifts are reported relative to internal tetramethylsillane (TMS). Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, dd = double doublet, t = triplet, quin = quintet, m = multiplet, brs = broad singlet, br = broad. High resolution atmospheric pressure chemical ionization time-of-flight (HR-APCI-TOF)-Mass spectra were recorded with Bruker micrOTOF-II. Fourier transfer infra-red (FT-IR) absorption spectra were recorded on Shimazu IR Prestige-21 with Dura Sample IR II (Kyoto, Japan).UV-visible absorption spectra were recorded with Shimazu UV-2600 for solution state spectra and JASCO V-650 for neat state spectra. Fluorescence spectra were recorded with JASCO spectrofluorometer FP-8600. Excitation wavelength was 625 nm for solution and thin film, respectively. Polarizing optical microscopic observation was carried out with polarizing optical microscope (NIKON ECLIPSE LV100ND) equipped with a hot stage (METTLER TOLEDO FP82HT Hot Stage). Recycling preparative HPLC was carried out with LC-908W (Japan Analytical Industry). Thermogravimetric analyses (TGA) were carried out with Seiko Instruments EXSTAR TG/DTA6200 under nitrogen gas flow at scan rate 10 °C/min. Differential scanning calorimetry (DSC) was carried out with Hitachi High-tech Science DSC7020 with liquid nitrogen cooling under nitrogen gas flow. X-ray diffractogram was recorded with Rigaku X-ray diffractometer RINT-Ultima / S2K (Cu K_α source). Column chromatography was carried out on silica gel (Wako gel C-200). Thin layer chromatography (TLC) was carried out on commercial Merck plates coated with silica gel 60F254. Photostability experiments were conducted with solar simulator (100W m^{-2}, Xe lamp, AM 1.5G, SAN-EI ELECTRIC, XES-151S). Quartz cells were filled with dilute chloroform solution of the samples (c=10^{-5} M). The cells were stored under simulated sunlight over 3 hours. Proceeding of photo-degradation was monitored by absorption and fluorescence spectral change each 30 minutes.

Synthesis



Scheme S1. Sythetic route for di(2-hexyldecyloxy)benzene boronic acid pinacol ester (**4** and **6**).

3, 5- Di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (4 in **Scheme S1)**[S1]

The title compound was prepared by palladium-catalyzed Miyaura-Ishiyama borylation.[S2] A flask containing 3, 5-di(2-hexyldecyloxy)bromobenzene[S1] (612 mg, 0.960 mmol), AcOK (280 mg, 2.85 mmol, 3eq.), bis(pinacolato)diboron (B_2pin_2) (366 mg, 1.43 mmol, 1.5eq.) and $PdCl_2(PPh_3)_2$ (73 mg, 0.095 mmol, 0.1eq.) was filled with Ar. Deoxygenaized dioxane (3.2 mL) was added to the mixture with syringe through septum. The mixture was heated at 80 °C for 72 hs. After cooling to r.t, the reaction mixture was diluted with *n*-hexane. This mixture was filtrated to remove insoluble chemicals. The filtrate was washed with water and brine. The organic layer was dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. The crude product was purified with recycling preparative HPLC ($CHCl_3$) to obtain colorless oil. Yield: 67% ^{1}H NMR (400.13 MHz, $CDCl_3$) δ(ppm): 6.92(d, *J*=2.4Hz, H_a, 2H), 6.56(t, *J*=2.2Hz, H_b, 1H), 3.84(d, *J*=5.6Hz, -OCH_2-(H_c), 4H), 1.74(brs, -OCCH-(H_d), 2H), 1.43-1.27(m, -(CH_2)$_{12}$- and -CH_3 of pinacol unit, 60H), 0.90-0.86(m, -CH_3(H_f), 12H). ^{13}C NMR (100.16MHz, $CDCl_3$) δ(ppm):160.65, 112.63, 105.35, 84.15, 71.07, 38.54, 32.35, 32.32, 32.30, 31.88, 30.47, 30.14, 30.04, 29.77, 27.31, 25.25, 23.11, 14.52. HR-APCI-TOF-Mass (positive) found *m/z*: 683.6046, calcd. for $C_{44}H_{81}O_4B$ *m/z*: 683.6259 $[M]^+$.

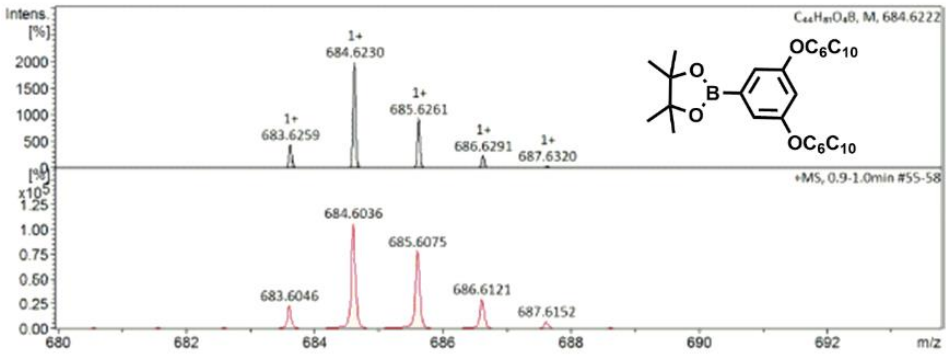


Fig. S1 HR-APCI-TOF-Mass spectrum of 3, 5-di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**4**).

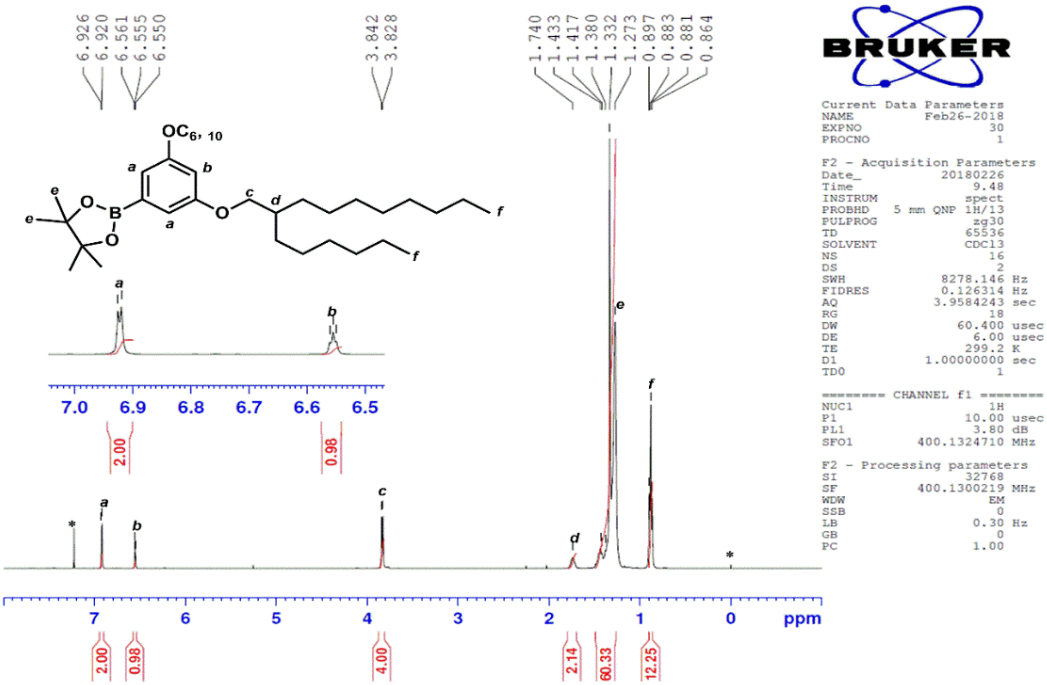


Fig. S2 ^{1}H NMR spectrum of 3, 5-di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**4**) in $CDCl_3$. Peaks marked with asterisk denote residual solvent and internal standard.

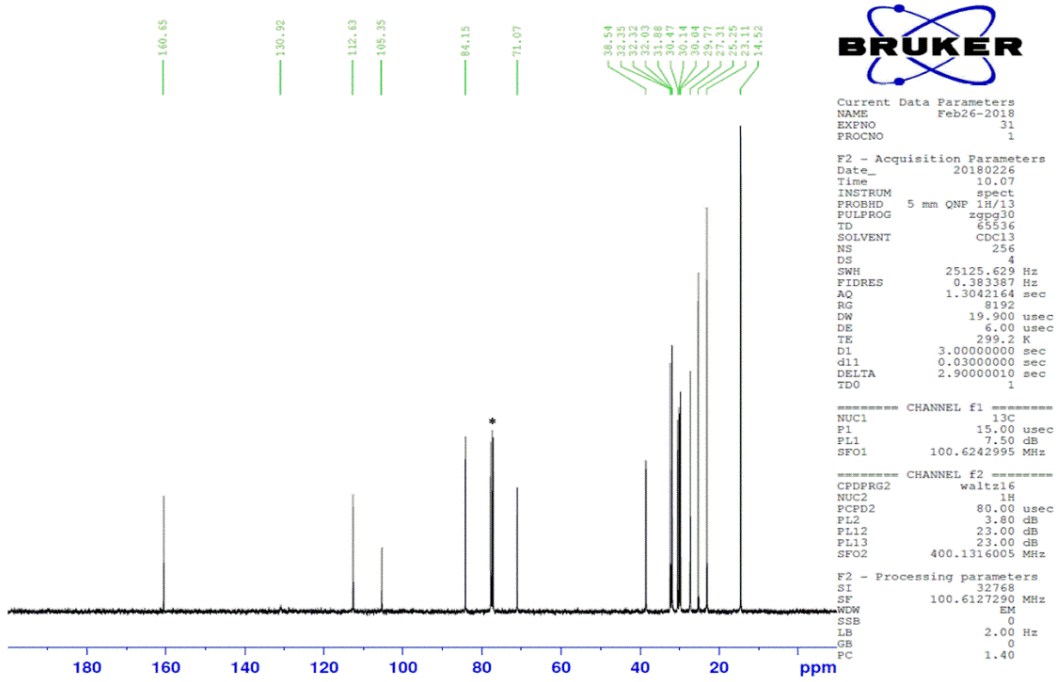


Fig. S3 ^{13}C NMR spectrum of 3, 5-di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**4**) in $CDCl_3$. The peak marked with asterisk denotes residual solvent.

2, 5- Di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (6 in **Scheme S1)**[S1]

The synthetic method was the same for that of **4**. 2, 5-di(2-hexyldecyloxy)bromobenzene [S1] was used as the starting material instead of 3, 5-di(2-hexyldecyloxy)bromobenzene. The target compound was obtained as colorless oil. Yield: 51% ^{1}H NMR (400.13 MHz, $CDCl_3$) δ(ppm): 7.18(d, J=3.2Hz, H_a, 1H), 6.89(dd, J=3.2, 5.6Hz, H_b, 1H), 6.75(d, J=9.2Hz, H_c, 1H), 3.78(d, J=5.2Hz, -OCH_2-(H_d), 4H), 1.78-1.56(m, -OCCH-(H_e), 2H), 1.54-1.32(m, -(CH_2)$_{12}$- and -CH_3 of pinacol unit, 60H), 0.89-0.86(m, -CH_3(H_g), 12H). ^{13}C NMR (100.16MHz, $CDCl_3$) δ(ppm):158.61, 153.34, 122.33, 118.68, 115.78, 113.18, 83.70, 72.18, 71.81, 38.77, 38.60, 32.35, 32.33, 32.30, 31.83, 31.58, 30.59, 30.13, 30.09, 30.02, 29.79, 29.76, 27.36, 27.32, 27.29, 25.31, 23.09, 14.52. HR-APCI-TOF-Mass (positive) found m/z: 683.6341, calcd. for $C_{44}H_{81}O_4B$ m/z: 683.6259 $[M]^+$.

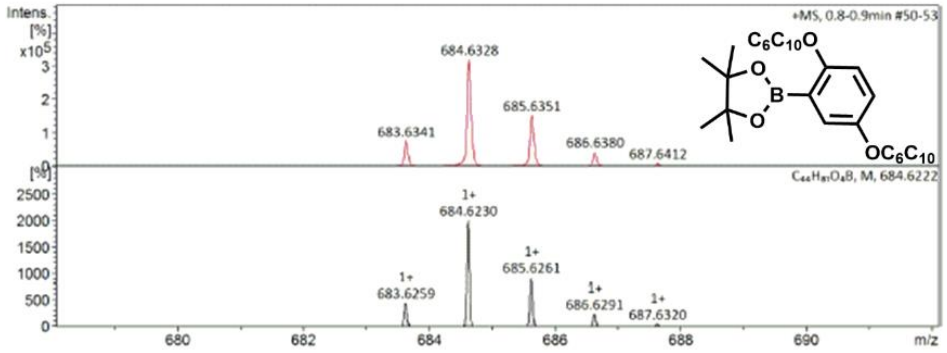


Fig. S4 HR-APCI-TOF-Mass spectrum of 2, 5-di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**6**).

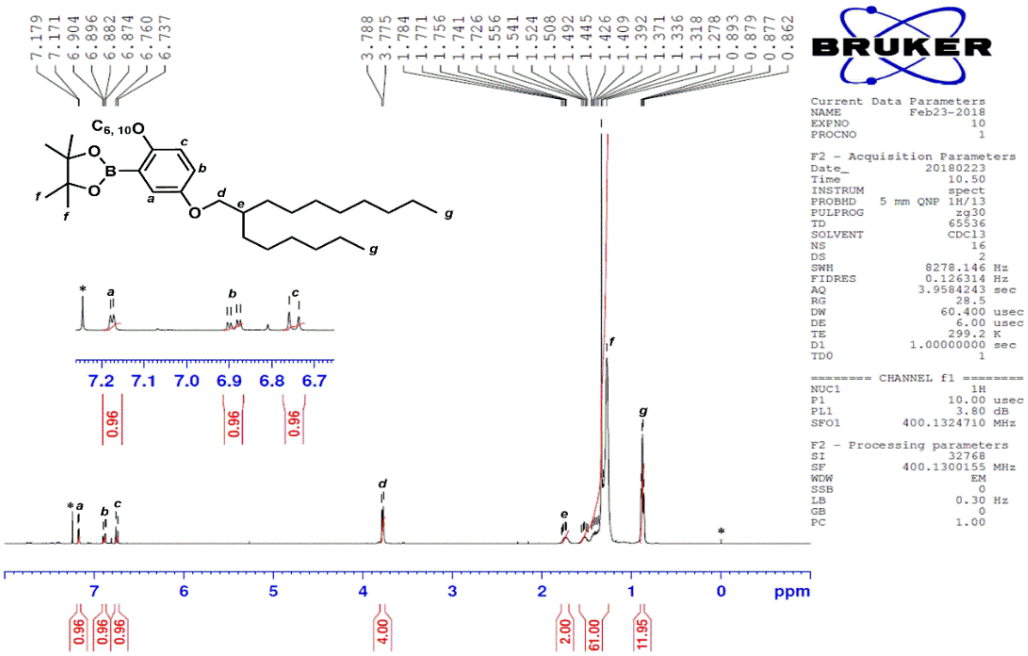


Fig. S5 ^{1}H NMR spectrum of 2, 5-di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**6**) in $CDCl_3$. Peaks marked with asterisk denote residual solvent and internal standard.

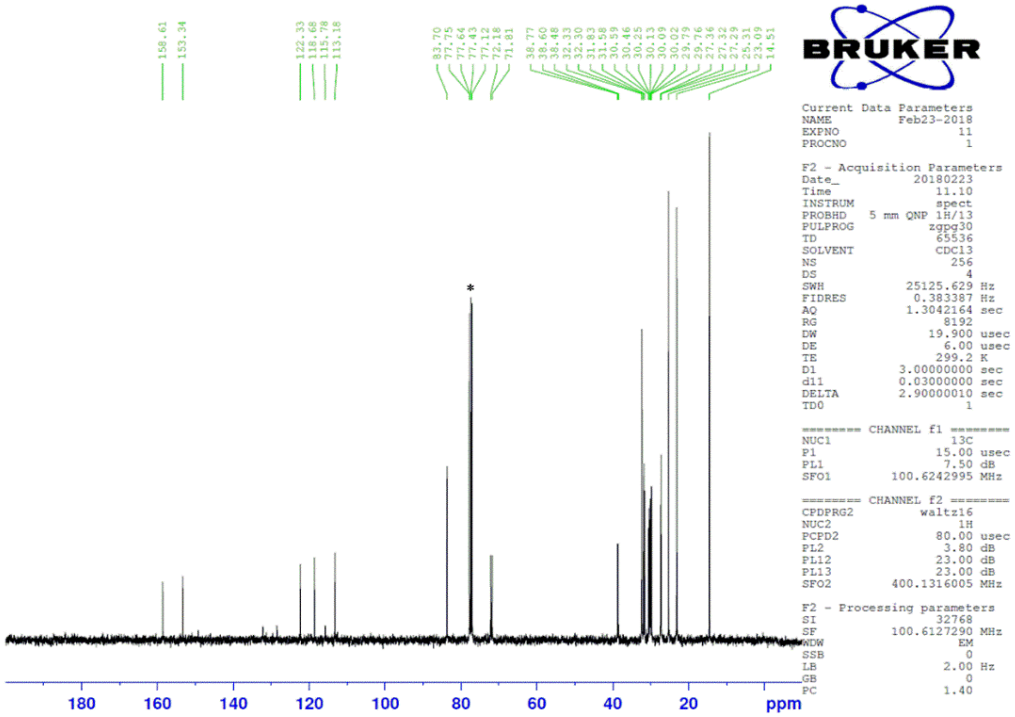
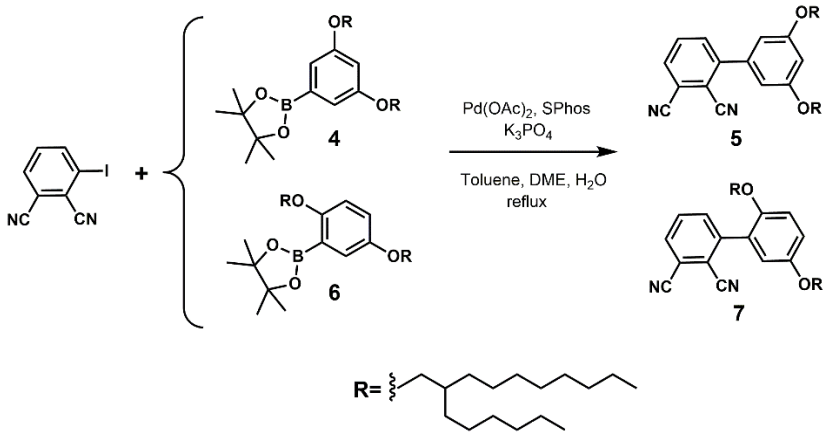


Fig. S6 ^{13}C NMR spectrum of 2, 5-di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**6**) in $CDCl_3$. The peak marked with asterisk denotes residual solvent.



Scheme S2. Synthetic route for 3-di(2-hexyldecyloxyphenyl)phthalonitriles (**5** and **7**).

3-[3′, 5′-Di(2-hexyldecyloxy)phenyl)phthalonitrile (5 in **Scheme S2)**

The title compound was prepared by palladium-catalyzed Suzuki-Miyaura coupling in using SPhos as a ligand.[S3] The reaction condition was followed to previous report.[S4] A flask containing 3-iodophthalonitrile[S5] (118 mg, 0.454 mmol, 1.3eq.), 3, 5- Di(2-hexyldecyloxy)benzeneboronic acid pinacol ester (**4**) (245 mg, 0.358 mmol), K_3PO_4 (310 mg, 1.40 mmol, 4eq.), $Pd(OAc)_2$ (14 mg, 0.035 mmol, 0.1eq.) and SPhos (29mg, 0.070 mmol, 0.2eq.) was filled with Ar. 6.9 mL of deoxygenaized mixed solvent (toluene / 1,2-dimethoxyehane (DME) / H_2O, 1:1:2, v/v/v) was added to the mixture

with syringe through septum. The mixture was refluxed for 72 hs. The reaction mixture was cooled to r.t, and extracted with ethyl acetate. The organic layer was washed with water and brine. The organic layer was dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. The crude product was purified with silica gel column chromatography (R_f = 0.33, AcOEt : *n*-hexane = 1 :15, v/v) and recycling preparative HPLC ($CHCl_3$) to obtain as colorless oil. Yield: 65% ^{1}H NMR (400.13 MHz, $CDCl_3$) δ(ppm): 7.82-7.73(m, H_{abc}, 3H), 6.65-6.59(m, H_{de}, 3H), 3.89(d, J=7.2Hz, -OCH_2-(H_f), 4H), 1.81-1.78(m, -OCCH-(H_f), 2H), 1.49-1.30(m, -(CH_2)$_{12}$-, 48H), 0.92-0.88(m, -CH_3(H_h), 12H). ^{13}C NMR (100.16MHz, $CDCl_3$) δ(ppm):160.86, 147.54, 137.98, 134.04, 132.68, 132.01, 117.27, 115.71, 115.15, 114.50, 107.24, 102.54, 71.23, 37.97, 31.91, 31.86, 31.37, 30.01, 29.68, 29.58, 29.33, 26.85, 26.83, 22.68, 14.11. HR-APCI-TOF-Mass (negative) found *m/z*: 684.5661, calcd. for $C_{46}H_{72}N_2O_2$ *m/z*: 684.5588 $[M]^-$. FT-IR (ATR) ν/ cm^{-1}: 2233.57 (-CN)

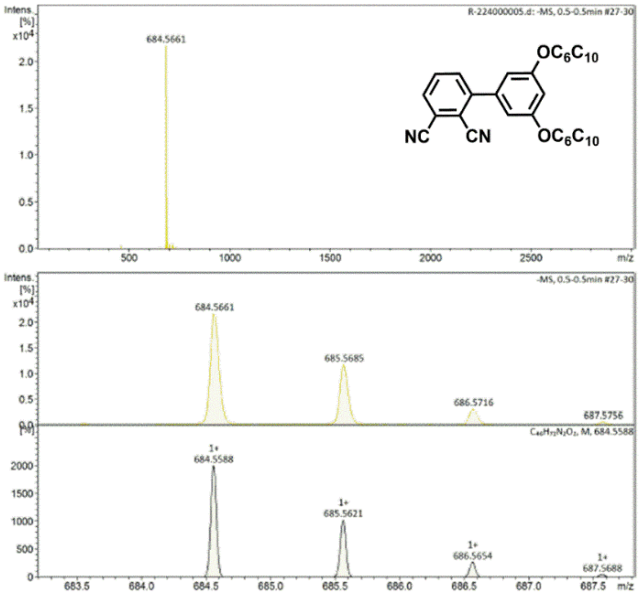


Fig. S7 HR-APCI-TOF-Mass spectrum of 3-[3′, 5′-di(2-hexyldecyloxy)phenyl]phthalonitrile (**5**).

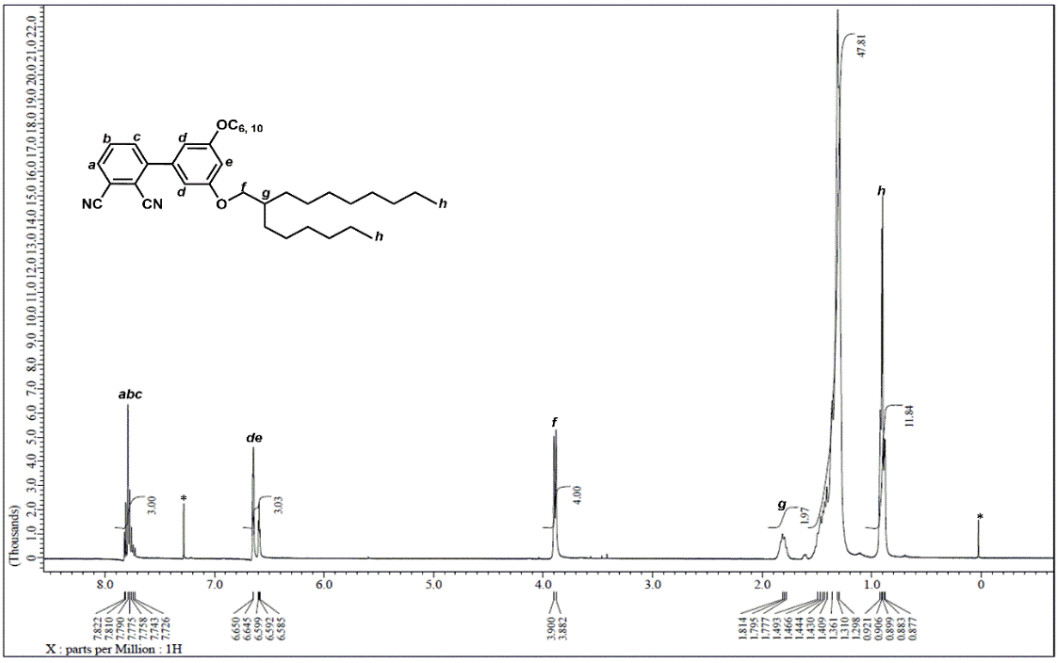


Fig. S8 ^{1}H NMR spectrum of 3-[3′, 5′-di(2-hexyldecyloxy)phenyl]phthalonitrile (**5**) in $CDCl_3$. Peaks marked with asterisk denotes residual solvent and internal standard.

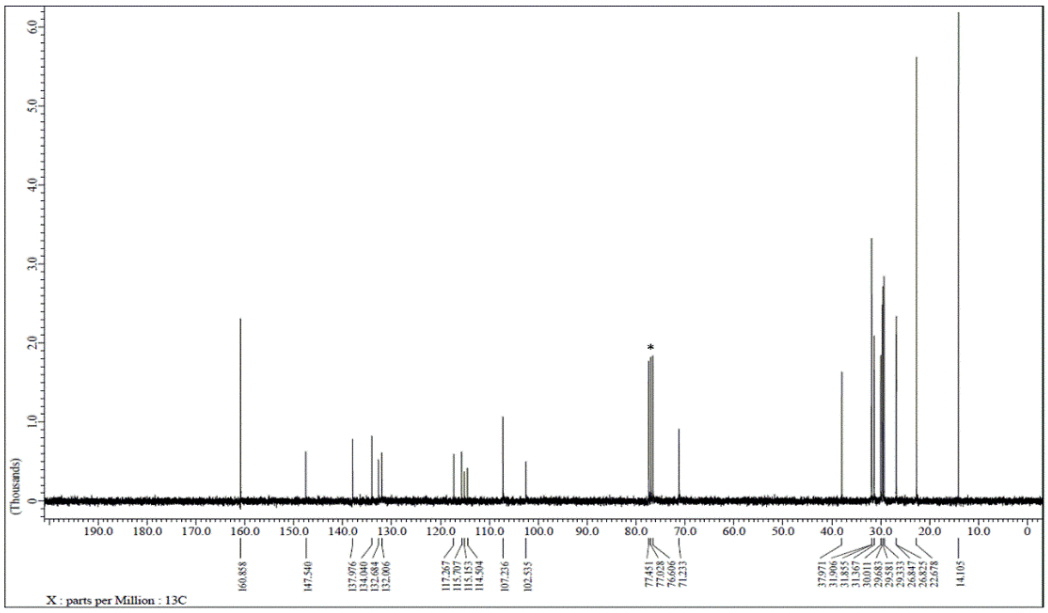


Fig. S9 ^{13}C NMR spectrum of 3-[3′, 5′-di(2-hexyldecyloxy)phenyl]phthalonitrile (**5**) in $CDCl_3$. The peak marked with asterisk denotes residual solvent.

3-[2′, 5′-Di(2-hexyldecyloxy)phenyl]phthalonitrile (7 in **Scheme S2)**

The synthetic method and purifications were the same for that of **5.** 2, 5-Di(2-hexyldecyloxy)benzeneboronic acid pinacol etster (**6**) was used as the starting material instead of 3, 5-di(2′-hexyldecyloxy)benzeneboronic acid pinacol ester. The target compound was obtained as colorless oil. Yield: 45% TLC (silica gel): R_f = 0.55 (AcOEt : *n*-hexane = 1:30, v/v) ^{1}H NMR (400.13 MHz, $CDCl_3$) δ(ppm): 7.76-7.67(m, H_{abc}, 3H), 6.97-6.91(m, Ar*H*, 2H), 6.82(d, *J*=2.8Hz, Ar*H*, 1H), 3.80-3.79(m, -OCH_2-(H_d), 4H), 1.77-1.73(m, -OCC*H*-(H_e), 1H), 1.62(brs, -OCC*H*-(H_f), 1H), 1.46-1.18(m,-(CH_2)$_{12}$-, 48H), 0.90-0.85(m, -CH_3(H_g), 12H). ^{13}C NMR (100.16MHz, $CDCl_3$) δ(ppm):153.67, 150.35, 145.12, 135.62, 132.45, 132.06, 126.64, 117.18, 117.11, 116.70, 116.16, 115.49, 113.86, 72.18, 38.47, 38.32, 32.31, 32.26, 32.21, 31.86, 31.77, 30.43, 30.39, 30.10, 30.04, 29.97, 29.73, 27.23, 27.15, 23.08, 14.51. HR-APCI-TOF-Mass (negative) found *m/z*: 684.5552, calcd. for $C_{46}H_{72}N_2O_2$ *m/z*: 684.5588 $[M]^-$. FT-IR (ATR) ν/ cm^{-1}: 2233.55 (-CN)

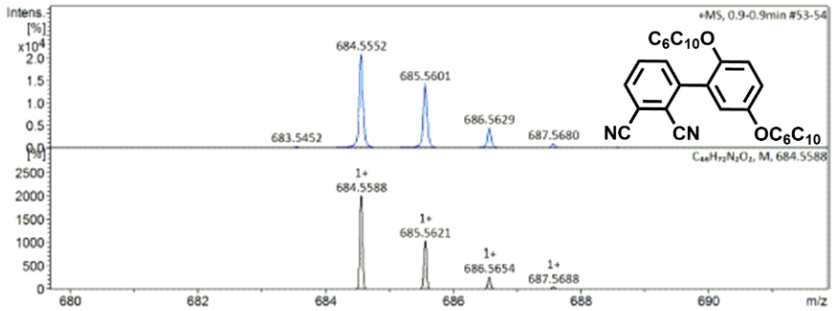


Fig. S10 HR-APCI-TOF-Mass spectrum of 3-[2′, 5′-di(2-hexyldecyloxy) phenyl]phthalonitrile (**7**).

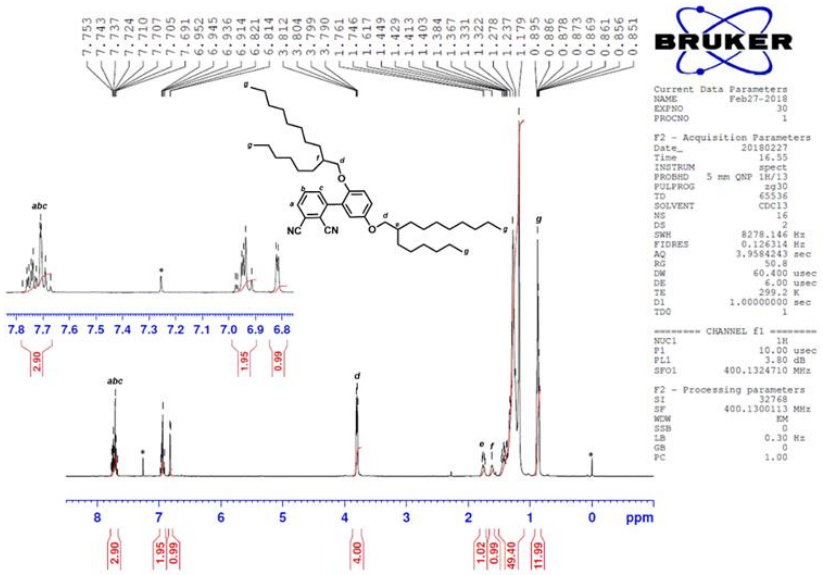


Fig. S11 ^{1}H NMR spectrum of 3-[2′, 5′-di(2-hexyldecyloxy)phenyl]phthalonitrile (**7**) in $CDCl_3$. Peaks marked with asterisk denote residual solvent and internal standard.

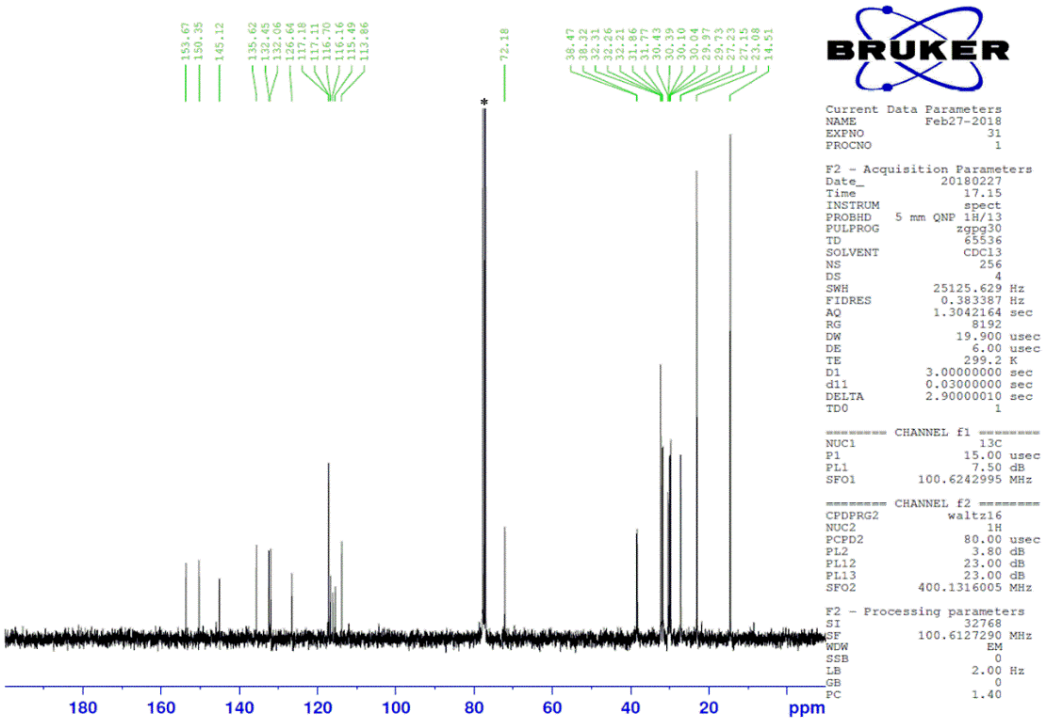
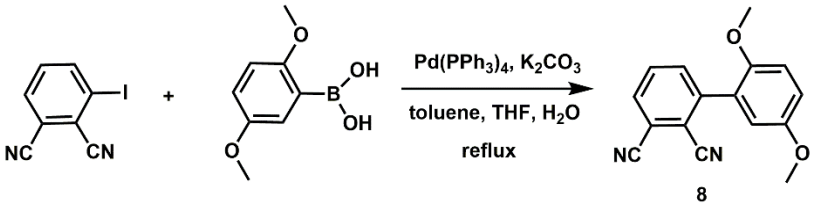


Fig. S12 ^{13}C NMR spectrum of 3-[2′, 5′-di(2-hexyldecyloxy)phenyl]phthalonitrile (**7**) in $CDCl_3$. The peak marked with asterisk denotes residual solvent.



Scheme S3. Synthetic route for 3-(2′, 5′-dimethoxyphenyl)phthalinitrile (**8**).

3-(2′, 5′-Dimethoxyphenyl)phthalonitrile (8 in **Scheme S3)**

A flask containing 3-iodophthalonitrile[S5] (401 mg, 1.58 mmol), 2, 5-dimethoxyphenylboronic acid (373 mg, 2.05 mmol), K_2CO_3 (468 mg, 3.39 mmol) and $Pd(PPh_3)_4$ (181 mg, 0.156 mmol) was filled with Ar. Degassed mixed solvent (5.6 ml, toluene/THF/H_2O (3:1:1.6 v/v/v)) was added to the mixture. The mixture was refluxed for 36 hs under Ar atmosphere. The reaction mixture was cooled to room temperature, and extracted with ethyl acetate. The organic layer was washed with water and brine, and dried over Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. The crude product was purified with column chromatography (SiO_2, eluent: CH_2Cl_2:AcOEt = 20:1) and recycling preparative HPLC ($CHCl_3$) to obtain a white solid (62%). ^{1}H NMR (400.13 MHz, $CDCl_3$); δ (ppm): 7.77-7.69 (m, Ar*H*, 3H), 6.97 (m, Ar*H*, 2H), 6.81-6.80 (m, Ar*H*, 1H), 3.78 (s, -OC*H*$_3$, 3H), 3.77 (s, -OC*H*$_3$, 3H). ^{13}C NMR (100.16MHz, $CDCl_3$); δ (ppm): 154.03, 150.80, 144.58, 135.66, 133.24, 132.34, 126.44, 116.86,

116.83, 116.71, 116.43, 116.39, 115.78, 113.04, 56.35, 56.28. FT-IR (ATR); υ (cm^{-1}): 2233.57 (-CN). HR-APCI-TOF-Mass; found *m/z*: 264.0880, calcd. for $C_{16}H_{12}O_2N_2$ *m/z*: 264.0893 [M].

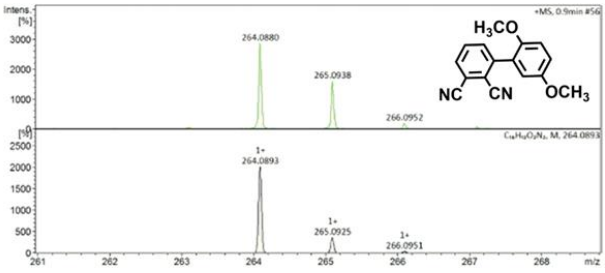


Fig. S13 HR-APCI-Mass spectrum of 3-(2′, 5′-dimethoxy phenyl)phthalonitrile (**8**).

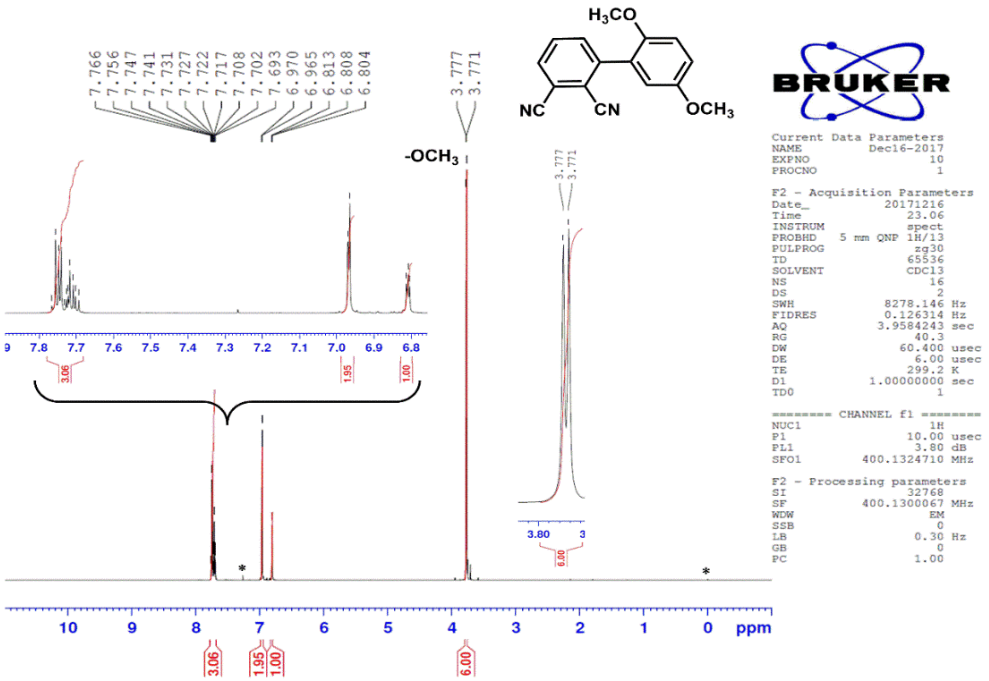


Fig. S14 ^{1}H NMR spectrum of 3-[2′, 5′-di(2-hexyldecyloxy)phenyl]phthalonitrile (**8**) in $CDCl_3$. Peaks marked with asterisk denote residual solvent and internal standard.

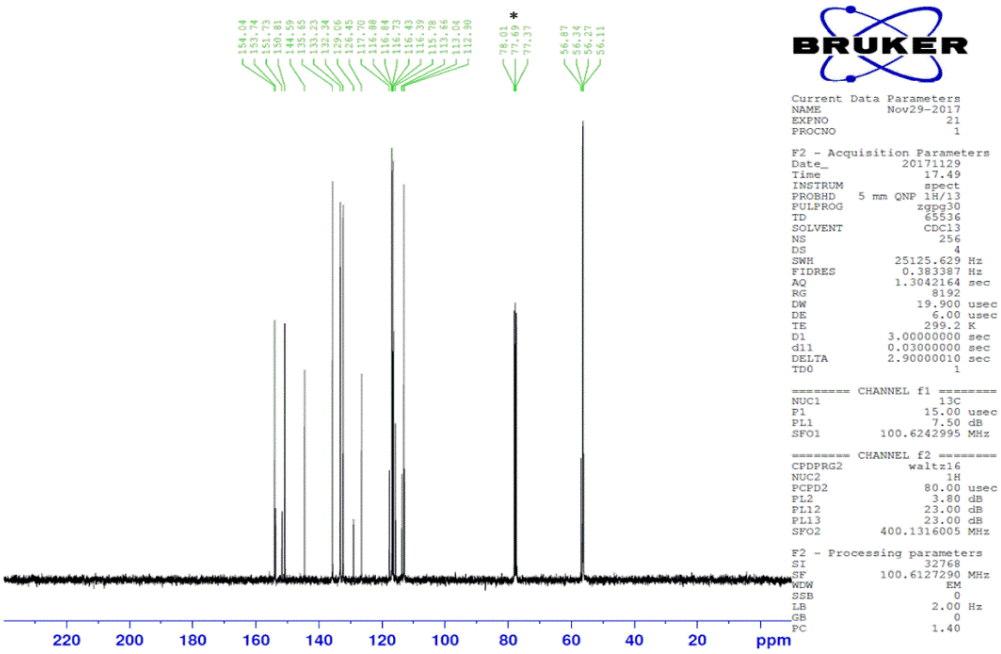
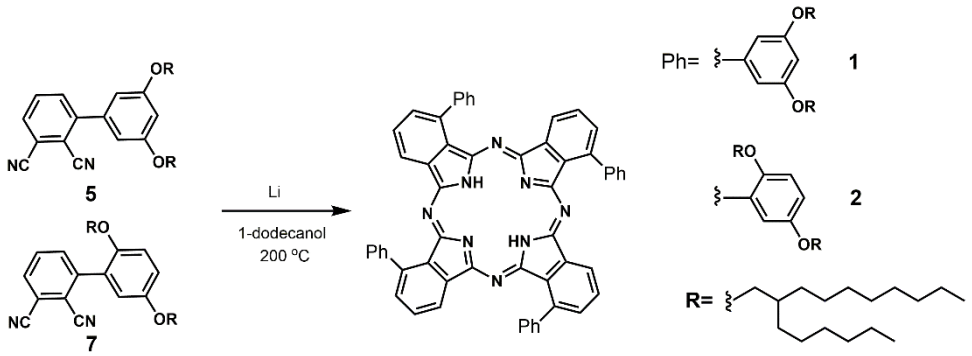


Fig. S15 ^{13}C NMR spectrum of 3-(2′, 5′-dimethoxyphenyl)phthalonitrile (**8**) in $CDCl_3$. The peak marked with asterisk denotes residual solvent.



Scheme S4. Synthetic route for **Pc1** and **Pc2.**

1, 8, 15, 22-Tetra[3′, 5′-di(2-hexyldecyloxyphenyl)]phthalocyanine (1 in **Scheme S4)**

The title compound was prepared by Linstead's method.[S6] Li metal (27 mg, 3.9 mmol) was dissolved in dry 1-dodecanol (3.5 mL) at 100 °C under Ar. After Li was perfectly dissolved, the mixture was cooled to r.t. To this mixture 3-[3′, 5′-di(2-hexyldecyloxyphenyl)]phthalonitrile (**5**) (239mg, 0.349 mmol) was added. The mixture was heated at 200 °C for 10hs under Ar. After cooling to r.t, the reaction mixture was diluted with methanol. The precipitate was collected with filtration and residue was washed with methanol several times. The crude product was purified with column chromatography (Al_2O_3 / CH_2Cl_2, R_f=1.0). Further purification was carried out with recycling preparative HPLC ($CHCl_3$). The title Pc derivative was obtained as dark green viscous oil. Yield: 29% ^{1}H NMR (400.13 MHz, $CDCl_3$) δ(ppm): 8.87 (dd, J=2.0, 3.2Hz, H_a, 4H), 8.10-8.07(m, H_{bc}, 8H), 7.41(d, J=2.0Hz, H_d,

8H), 6.97(t, *J*=2.2Hz, H_e, 4H), 3.99(d, *J*=5.6Hz, -OCH_2-(H_f), 16H), 1.81(quin, *J*=6.0Hz, -OCC*H*-(H_g), 8H), 1.46-0.61(m, aliphatic -CH_2-, 240H), -0.23(s, -N*H*(H_f), 2H). HR-APCI-Mass (negative) found *m/z*: 2740.2675, calcd.for $C_{184}H_{290}N_8O_8$ *m/z*: 2740.2526 $[M]^-$. UV-vis (in $CHCl_3$) : $\lambda_{max}(\log\varepsilon)$ = 715(4.99), 681 (4.96), 653 (4.55), 619(4.38), 341(4.79). Fluorescence (in $CHCl_3$, λ_{ex} = 625 nm): λ_{FL} =718 nm.

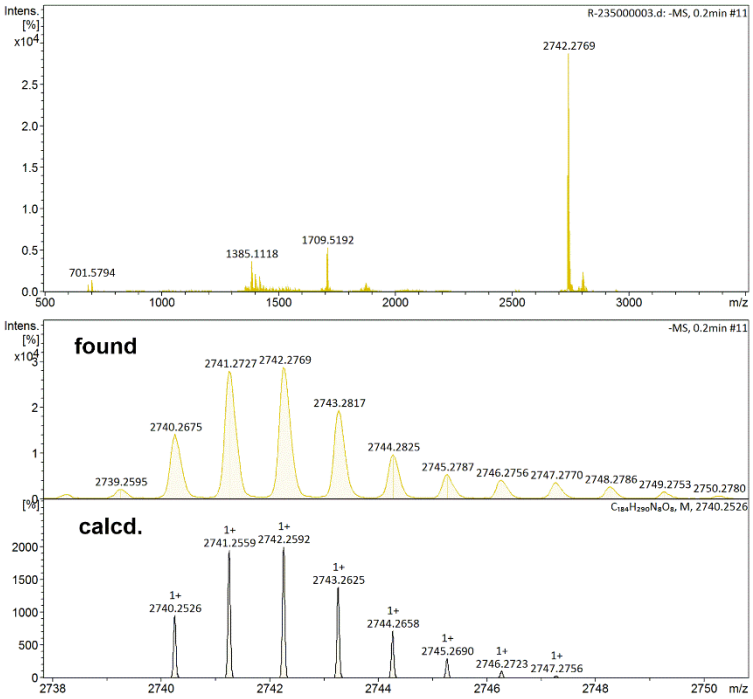


Fig. S16 HR-APCI-TOF-Mass spectrum of **1**.

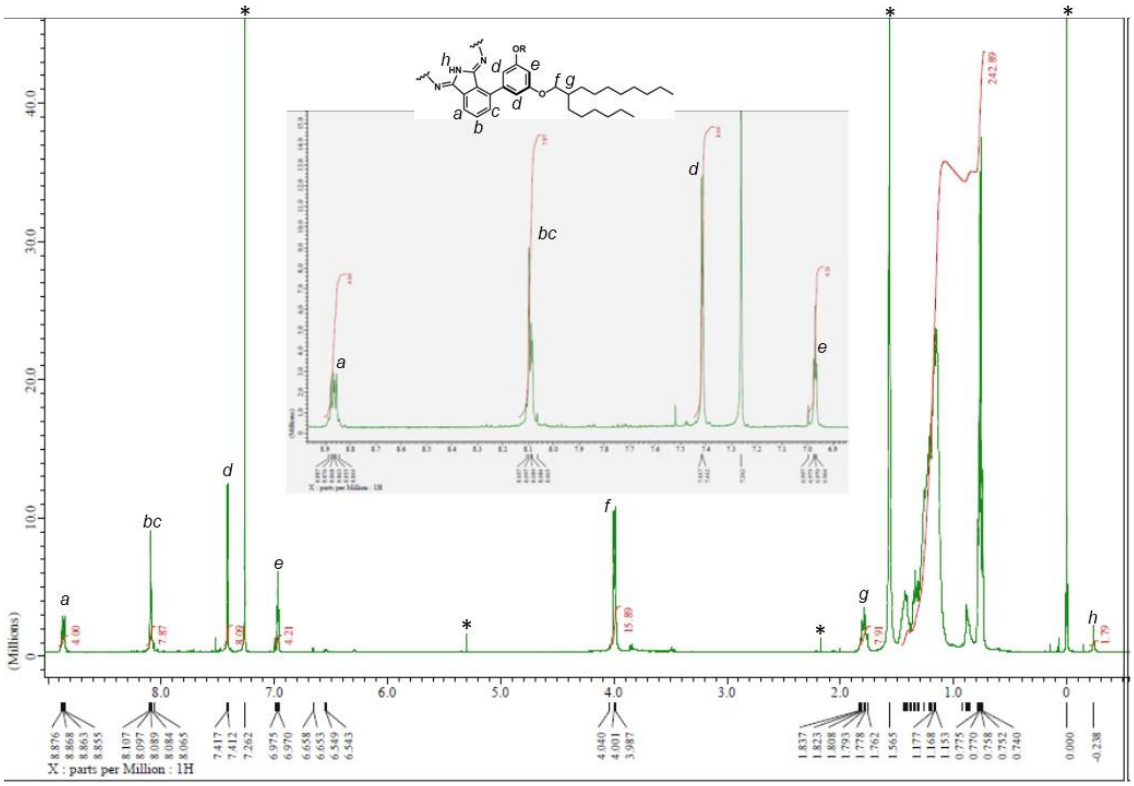


Fig. S17 ^{1}H NMR spectrum of **1** in $CDCl_3$. Peaks marked with asterisk denote residual solvent and internal standard.

1, 8, 15, 22-Tetra[2′, 5′-di(2-hexyldecyloxyphenyl)]phthalocyanine (2 in **Scheme S4)**

The synthetic method and purifications were the same for that of **1**. 3-[2′, 5′-Di(2-hexyldecyloxyphenyl)]phthalonitrile (**7**) was used as the starting material instead of **5.** The title Pc derivative was obtained as dark green oil. Yield: 6% ^{1}H NMR (400.13 MHz, $CDCl_3$) δ(ppm): 8.72(br, H_a, 4H), 8.04(br, H_{bc}, 8H), 7.58-7.29(m, H_{def}, 12H), 3.99-3.59(m, -OCH_2-(H_{hg}), 16H), 1.83(br, *exo*-OCCH-(H_i), 4H), 1.48-0.15(m, aliphatic -CH_2-, 244H), -0.51(s, -NH(H_j), 2H). HR-APCI-Mass (negative) found *m/z*: 2740.2132, calcd.for $C_{184}H_{290}N_8O_8$ *m/z*: 2740.2526 $[M]^-$. UV-vis (in $CHCl_3$) : λ_{max}(logε) = 707(5.05), 673 (5.00), 646(4.54), 611(4.37), 346(4.75). Fluorescence (in $CHCl_3$, λ_{ex} = 625 nm): λ_{FL} =709 nm.

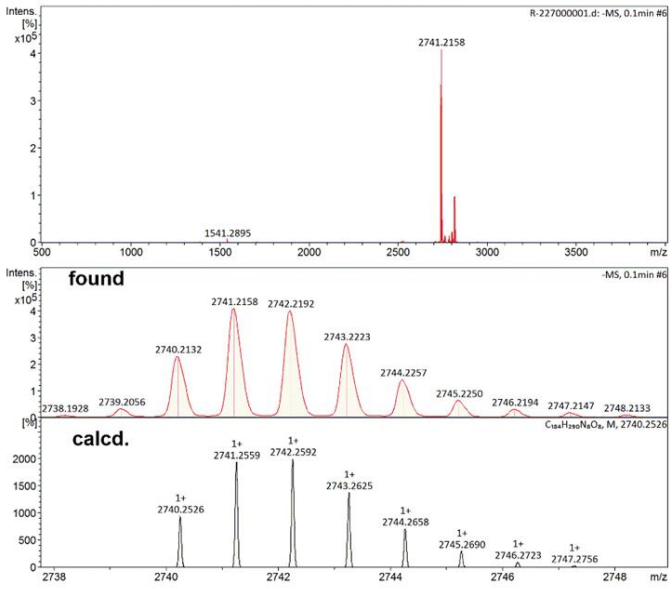


Fig. S18 HR-APCI-TOF-Mass spectrum of **2**.

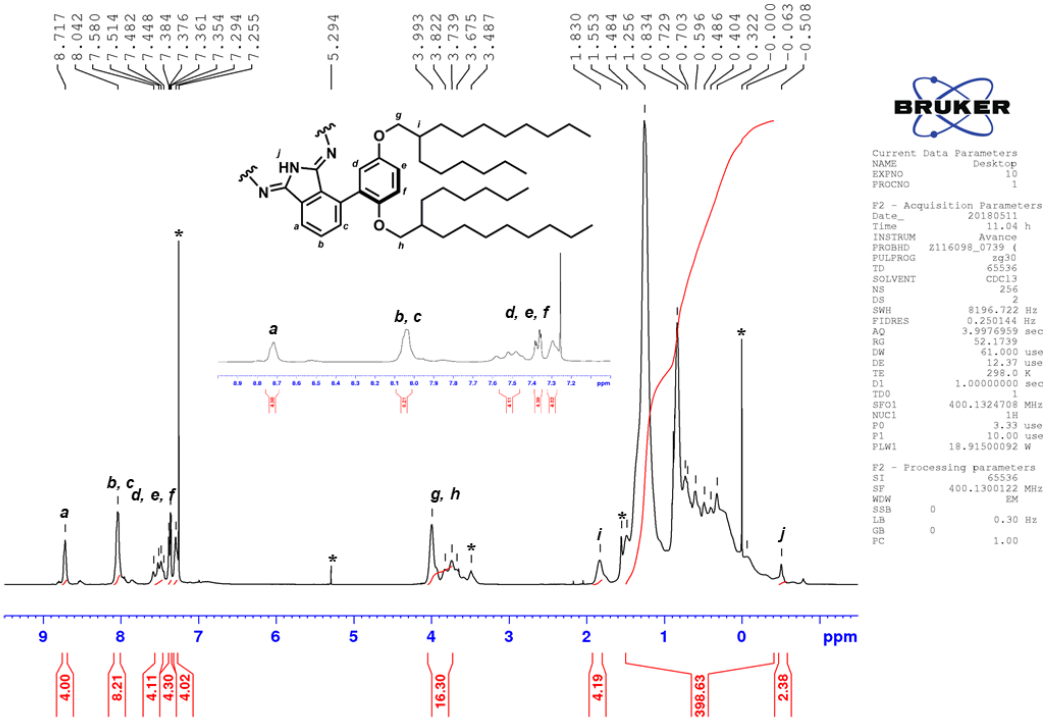
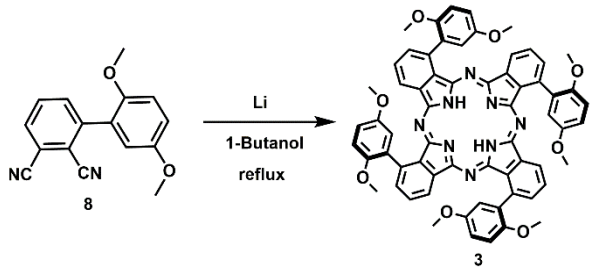


Fig. S19 ^{1}H NMR spectrum of **2** in $CDCl_3$. Peaks marked with asterisk denote residual solvents and internal standard.



Scheme S5. Synthetic route for **Pc3**.

1, 8, 15, 22-Tetra(2′, 5′-dimethoxyphenyl)phthalocyanine (3 in **Scheme S5)**

Li metal (13 mg, 1.9 mmol) was dissolved in dry 1-butanol (3.8 mL) at 70 ºC under Ar. The mixture was cooled to room temperature, and 3-(2′, 5′-dimethoxyphenyl)phthalonitrile (**8)** (100 mg, 0.378 mmol) was added to this mixture. The mixture was refluxed for 4 hs under Ar. After cooling to room temperature, the reaction was quenched with acetic acid and methanol. The precipitate was collected with filtration, and washed with methanol for several times. The crude product was purified with the recrystallization (CH_2Cl_2 / acetone) to isolate *C*$_{4h}$-regioisomer, and the precipitated solid was collected with filtration. Yield:13% ^{1}H NMR (400.13 MHz, $CDCl_3$); δ (ppm): 8.70 (d, *J*=7.2Hz, H_a, 4H), 8.11 (t, *J*=7.4Hz, H_b, 4H), 8.05 (d, *J*=7.2Hz, H_c, 4H), 7.48-7.33 (m, H_{def}, 12H), 3.96 (s, -OCH_3(H_g), 12H), 3.48 (brs, -OCH_3(H_h), 12H), -0.49 (s, -NH(H_i), 2H). ^{13}C NMR (100.16MHz, $CDCl_3$); δ(ppm): 154.32, 153.16, 136.33, 131.26, 129.86, 123.06, 114.39, 56.58, 56.46. HR-APCI-TOF-Mass; found *m/z*: 1058.3760, calcd. for $C_{64}H_{50}N_8O_8$ *m/z*: 1058.3746 [M]. UV-Vis (in $CHCl_3$): λ_{max} (nm) (logε) = 707 (5.09), 672 (5.06), 643 (4.60), 610 (4.44), 346 (4.81). Fluorescence (in $CHCl_3$, λ_{ex} = 625 nm): λ_{FL} =709 nm.

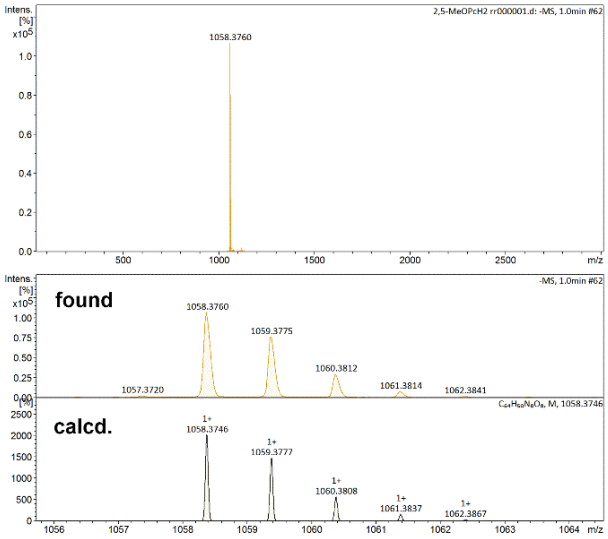


Fig. S20 HR-APCI-TOF Mass spectra for **3**.

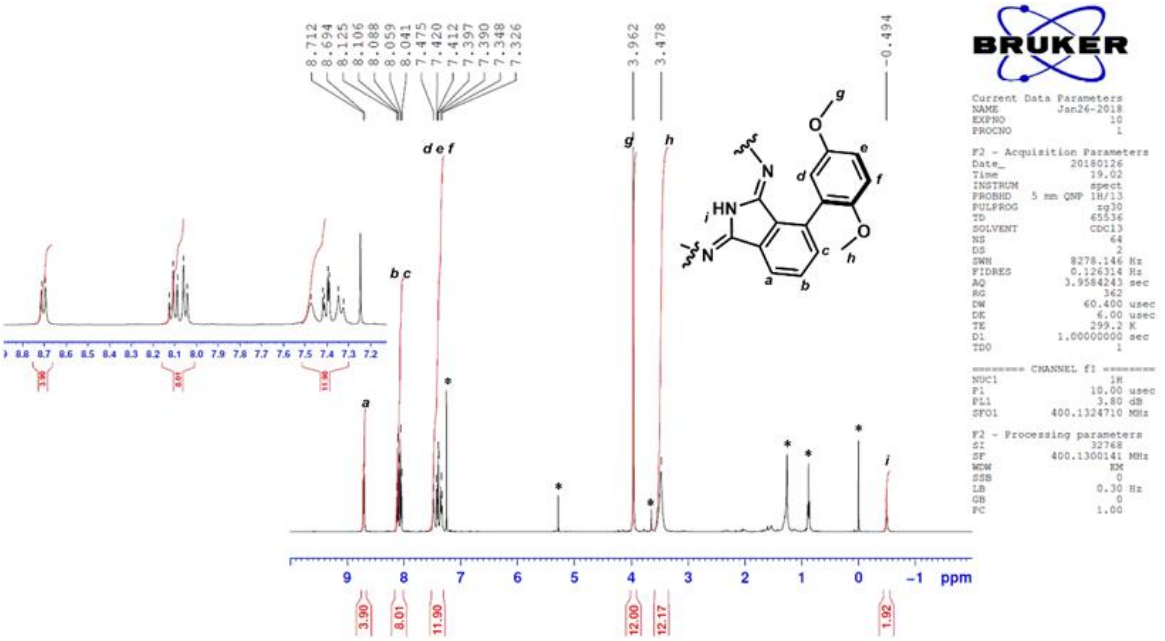


Fig. S21 ^{1}H NMR spectrum for **3** in $CDCl_3$. Peaks marked with asterisk denote residual solvent and internal standard.

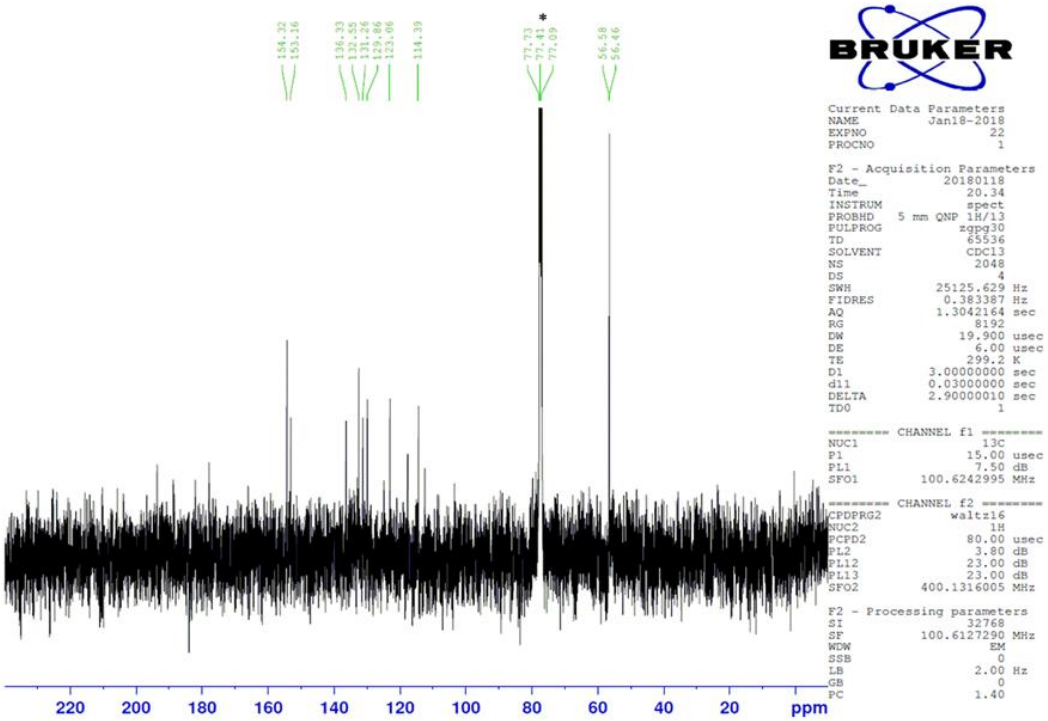


Fig. S22 ^{13}C NMR spectrum for **3** in $CDCl_3$. The peak marked with asterisk denotes residual solvent.

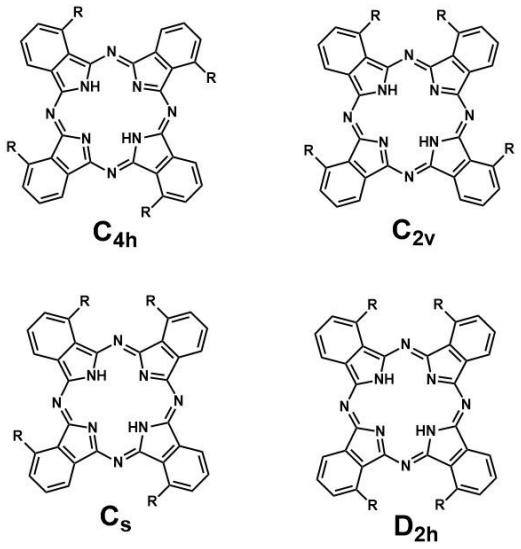


Fig. S23 Possible four regioisomers obtained from cyclotetramerization of 3-substituted phthalonitrile.

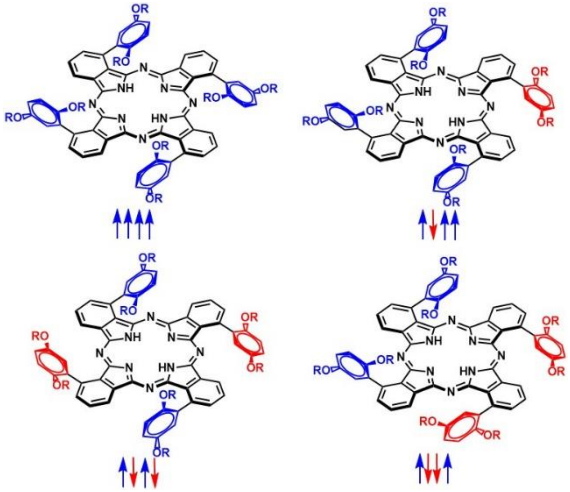


Fig. S24 Possible four conformational isomers of **2** originated from the different orientations of 2-substituted alkoxy chains on the phenyl units. Arrows denote orientations of four alkoxy chains substituted at 2-position on phenyl units relative to phthalocyanine surface (blue: up, red: down). In contrast to the well-resolved and clear ^{1}H NMR spectrum of **1** (Figure S14), **2** with four asymmetric 2, 5-alkoxy chains substituted phenyl units showed broad signals in ^{1}H NMR spectrum (Figure S16, S19), which were probably due to coexistence of several conformational isomers. These isomer mixtures originated from the rotation barrier of single bond between phthalocyanine core and the phenyl unit with steric 2-substitution[S1].

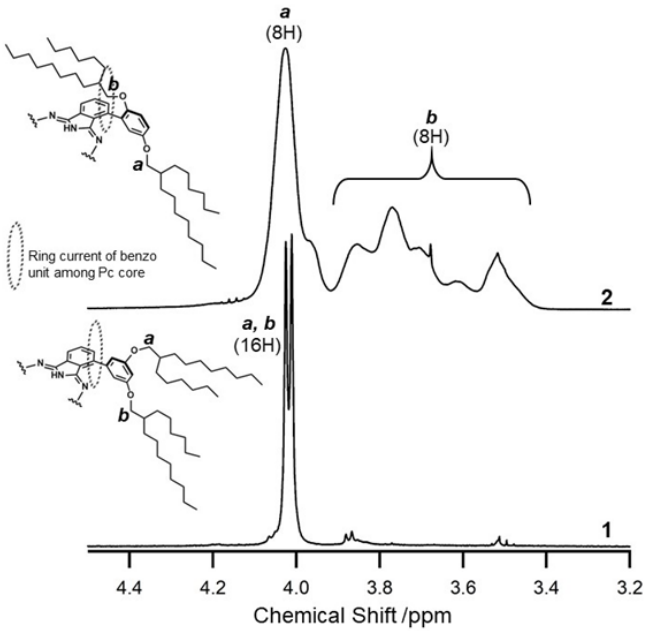


Fig. S25 Selected region of ^{1}H NMR spectra for **1** (lower) and **2** (upper) in $CDCl_3$. Insets mean Side group conformation relative to Pc core.

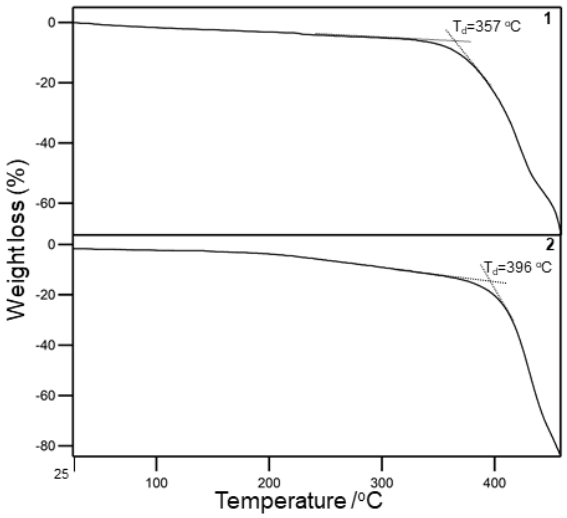


Fig. S26 Thermogravimetric analysis curve for **1** and **2** (under N_2 atmosphere, scan rate 10 °C/ min).

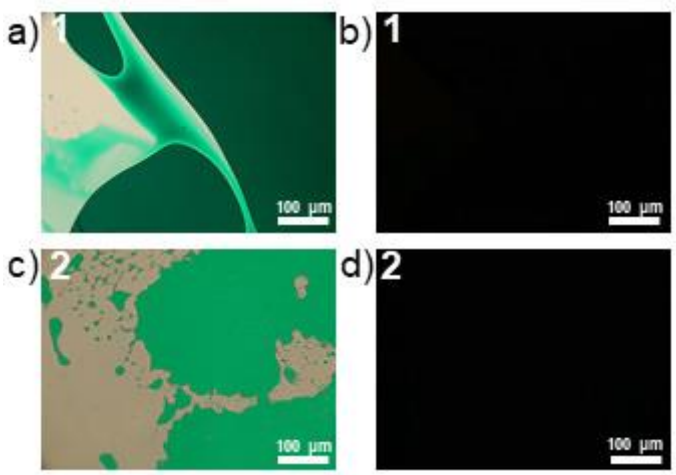


Fig. S27 Polarizing optical microscopic images for **1** and **2** at room temperature. Images a) and c) were taken under open polarizer. Images b) and d) were taken under crossed polarizer.

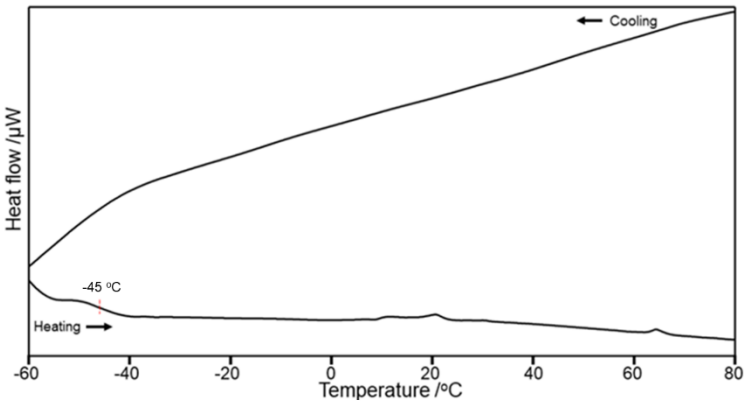


Fig. S28 DSC profiles for **1** at scan rate 10 °C/ min under N_2 flow.

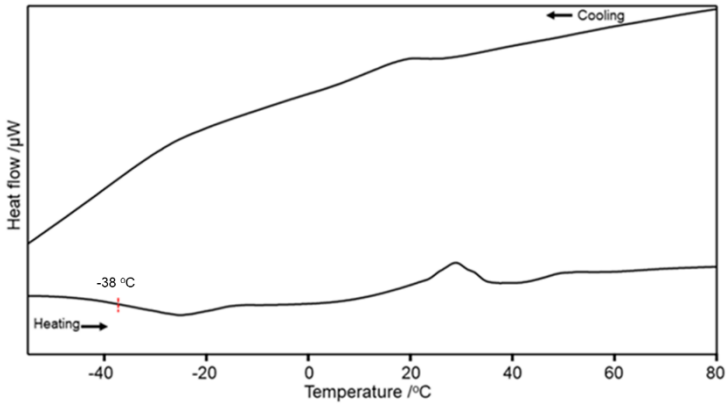


Fig. S29 DSC profiles for **2** at scan rate 10 °C/min under N_2 flow.

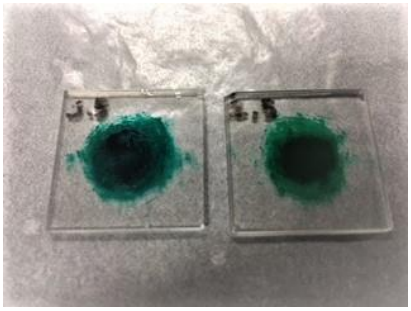


Fig. S30 Liquid thin film sandwiched by two quartz plates for **1** (left) and **2** (right). Small amount of the liquid sample was put on quartz plate by spatula, and then sandwiched by another quartz plate. The sandwiched sample was rubbing with these quartz plates.

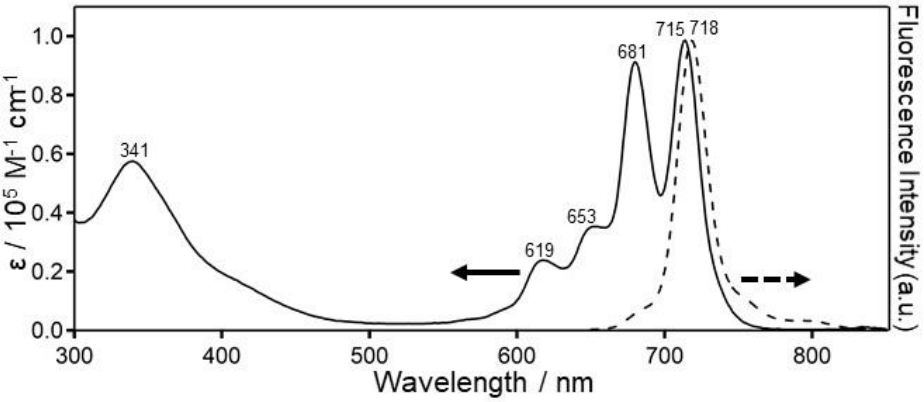


Fig. S31 UV-vis absorption (solid line) and fluorescence (dashed line) spectra for **1** in chloroform solution. ε means molar extinction coefficient. Excitation wavelength for fluorescence spectrum was 625 nm.

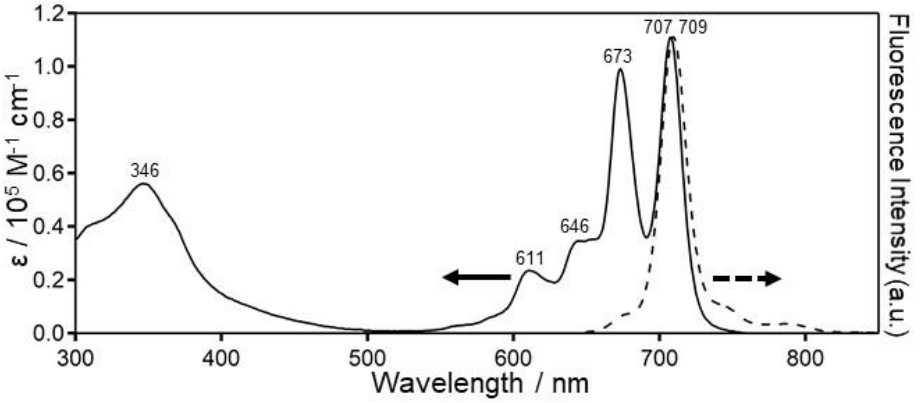


Fig. S32 UV-vis absorption (solid line) and fluorescence (dashed line) spectra for **2** in chloroform solution. ε means molar extinction coefficient. Excitation wavelength for fluorescence spectrum was 625 nm.

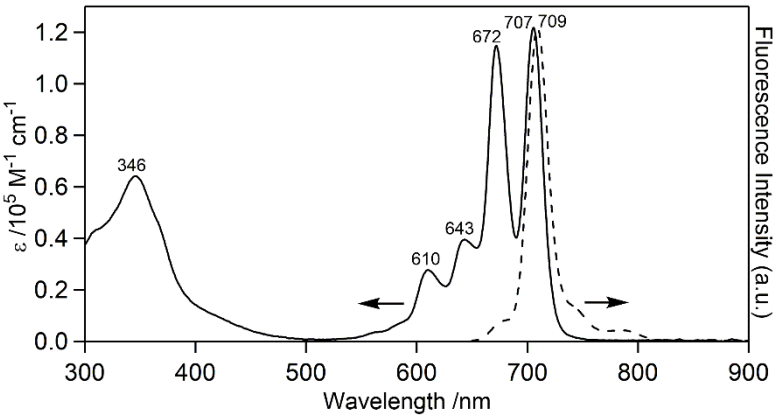


Fig. S33 UV-vis absorption (solid line) and fluorescence (dashed line) spectra for **3** in chloroform solution. $\boldsymbol{\varepsilon}$ means molar extinction coefficient. Excitation wavelength for fluorescence spectrum was 625 nm.

Table S1. Polarity effect of solvents on wavelength of fluorescence.

	λ_{FL} /nm			
Sample	*n*-hexane[a]	toluene[b]	$CHCl_3$[c]	THF[d]
1	714	718	718	717
2	706	709	709	708
3	n.d.[e]	709	709	707

[a] ε=1.90. [b] ε=2.38. [c] ε=4.70. [d] ε=18.5. [e] The datum was not obtained due to the insolubility.

ε means dielectric constant of solvent.

The relative fluorescence quantum yields for **1, 2,** and **3** were obtained from following equation S1. *β*-Tetra-*tert*-butylphthalocyanine was used as a standard sample (Φ_{st}=0.67 in toluene)[S7]. All fluorescence spectra were recorded in toluene. The samples were excited at 625 nm.

$$\Phi = \Phi_{st}\left(\frac{FA}{FA_{st}}\right)\left(\frac{A_{st}}{A}\right) \qquad \text{(Equation S1)}$$

Where Φ and Φ_{st} are fluorescence quantum yield for unknown sample and standard sample (*β*-Tetra-*tert*-butylphthalocyanine), respectively, FA and FA_{st} are integrated area of fluorescence spectra for unknown sample and standard sample, respectively, A and A_{st} are absorbance at excitation wavelength (625 nm) for unknown sample and standard sample, respectively.

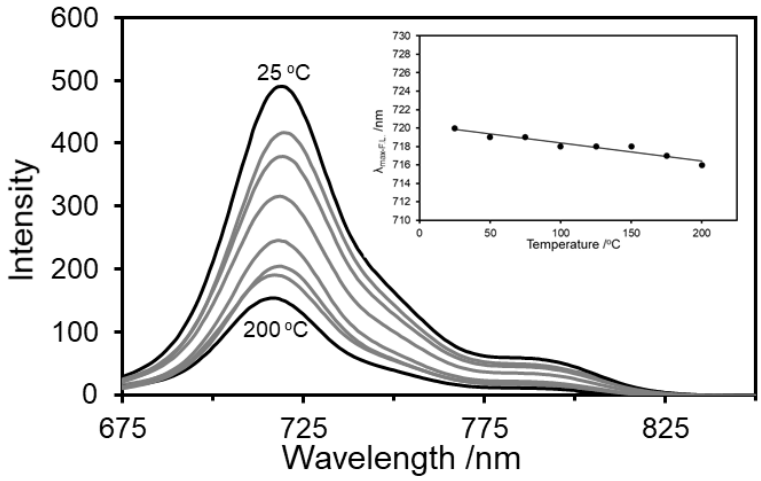


Fig. S34 Fluorescence spectra for heating liquid film of **2**. Liquid film sandwiched by two quartz plates was used for this measurement. The liquid film was heated by hot stage (METTLER TOLEDO FP82HT) for 10 minutes, then the sample was quickly transferred from hot stage to spectrometer and fluorescence of the sample was measured.

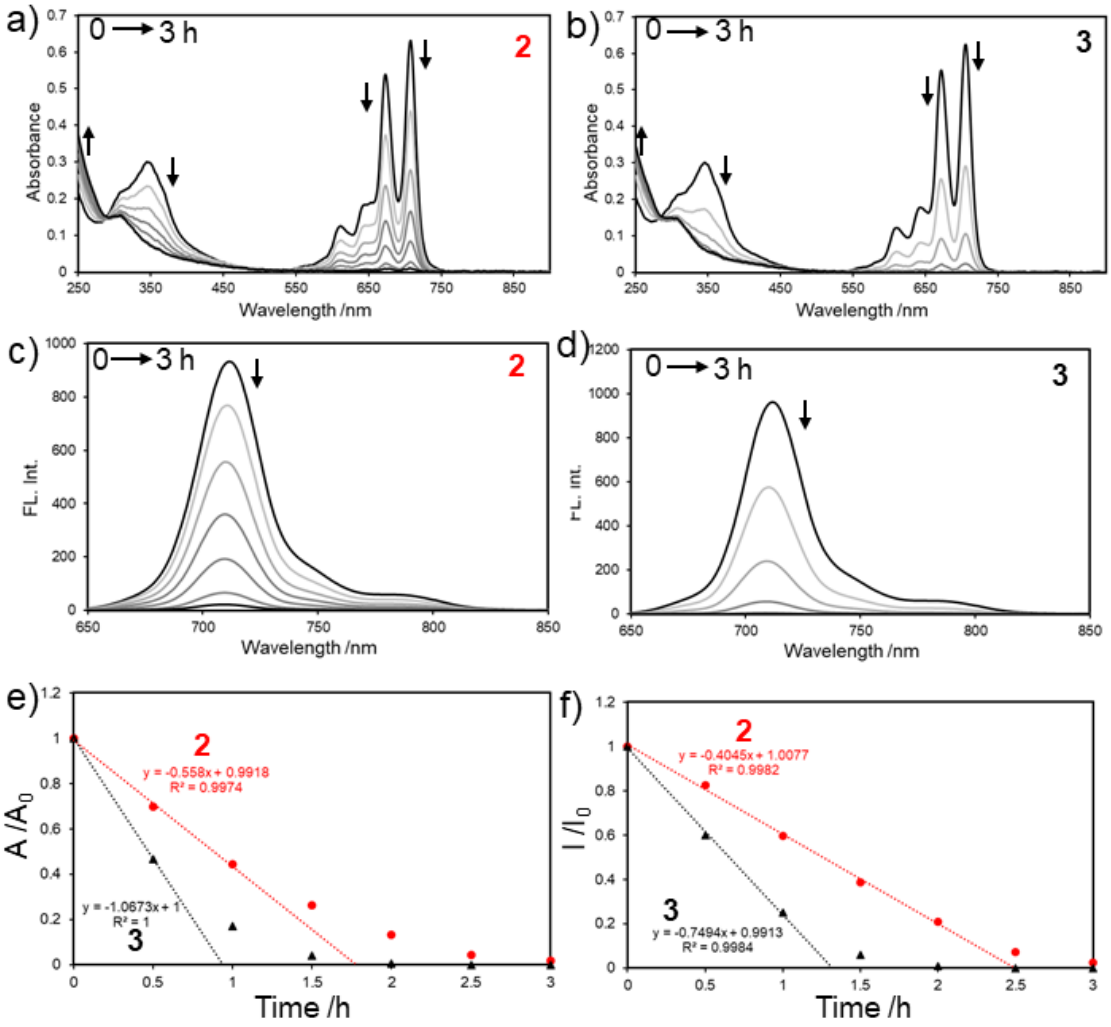


Fig. S35 Comparison of the variation of absorption (a and b) and fluorescence (c and d) spectra for **2** and **3** in chloroform under irradiating by simulated sunlight. Time-dependent change of absorbance (e) or fluorescence intensity (f) ratio at 707 nm. The slopes of least squares line mean photo-degradation rate of the samples.

Supporting references

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