Novel Synthesis of 1,4-Dialkoxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes through Electron Transfer from Mg Metal and Efficient Development of New Naphthalocyanines

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Abstract: Novel methods for efficient synthesis of 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes were successfully developed, starting from easily available 2,3-dicyanohydroquinone as a common single compound through only three steps, the first dibromination of 2,3-dicyanohydroquinone, the second Mitsunobu dialkylation of 2,3-dicyano-5,6-diboromo-1,4-hydroquinone, and the last Diels–Alder-type of cycloaddition between 1,4-alkoxy-2,3-dicyano-5,6-diboromobenzenes and multisubstituted furans, followed by reductive deoxygenation with Mg turning. The obtained 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes were easily transformed into the corresponding naphthalocyanines in 20–45% yields which showed their λ_{max} at 867–892 nm.

Key words: multisubstituted-2,3-dicyanonaphthalenes, Mg metal naphthalocyanines, benzyne, ν_{max} at 867–892 nm

Although phthalocyanines have been so far well-known as useful color and dye stuffs[1a–d] and employed for many actual purposes because of high stability for sunlight, heat, chemicals, water, and so on, naphthalocyanines have been recently expected as much better functional materials for optical memory, semiconductivity, and electrochromic display.[2a–c]

Approximately two important properties have been required for those remarkable optically highly functional materials. The first one is high solubility to usual organic solvents and for this purpose, introduction of substituents with long alkyl chains to the naphthalocyanine molecular is needed (Figure 1). As the second necessary property, λ_{max} of the absorption band of those color materials should be present between 800 and 900 nm. Since introduction of conjugate systems such as aryl or vinyl groups to a naphthalocyanine skeleton is expected to show λ_{max} of the absorption band at longer than 800 nm, the naphthalocyanines having those conjugated systems could be required.

On the other hand, since direct regioselective introduction of those organic conjugate substituents into a naphthalocyanine skeletone should be very difficult, it is probably much more reasonable and realistic to introduce many kinds of organic conjugate substituents in the course of synthesis of 2,3-dicyanonaphthalenes in the regioselective manner. However, the hitherto known methods[3a–c,4,5] of 2,3-dicyanonaphthalene derivatives through bromination of the benzylic positions of xylene derivatives by *N*-bromosuccimide may possess many of unfavorite demerits such as multistep synthesis, low overall yields, much limitation for introduction of substituents into 2,3-dicyanonaphthalene molecules, especially much difficulty in the case of alkyl and aryl groups as those introduced substituents.

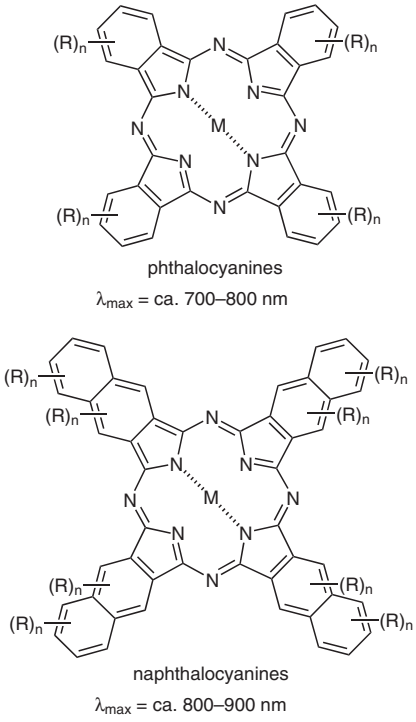

Figure 1

Therefore, facile and general novel synthesis of 2,3-dicyanonaphthalenes should be quite important and strongly required for development of new naphthalocyanines which are easily soluble to usual organic solvents and also have their λ_{max} absorption at the area of 800–900 nm at the same time.

In this study, we would like to present the successful development of an efficient, facile, general, and novel synthesis of 1,4-dialkoxy-2,3-dicyano-5,6,7,8-multisubstituted naphthalenes and the successful development of the corresponding new naphthalocyanines, which are not

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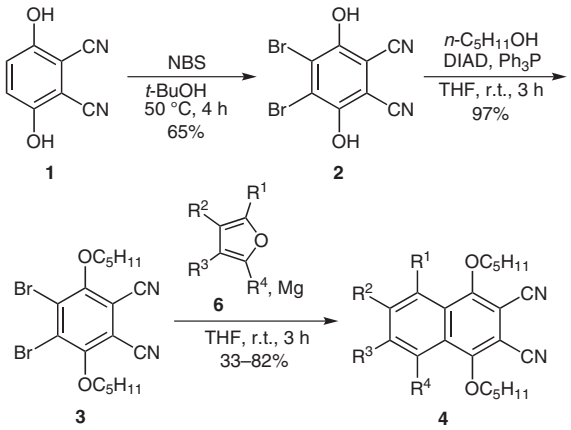
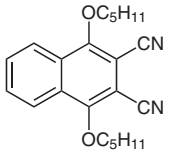
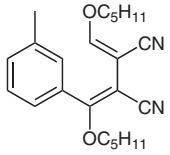
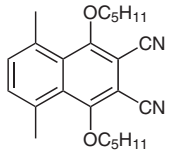
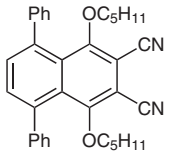
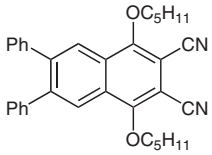
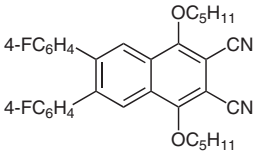
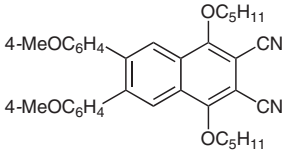
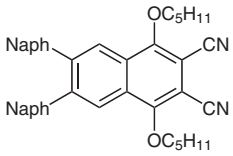
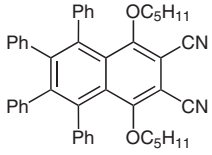
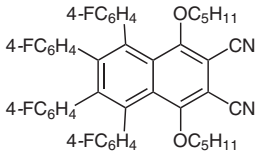
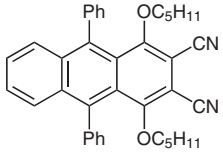
only easily soluble to usual organic solvents, but also show their absorption of λ_{max} at 800–900 nm.

According to the reaction scheme developed by this study, dibromonation of 2,3-dicyanohydroquinone (**1**) by NBS followed by Mitsunobu reaction[6a–c] of the resulting 5,6-dibromo-1,4-dicyanohydroquinone (**2**)[7] using *n*-pentanol, diisopropyl azodicarboxylate, and triphenylphosphine in tetrahydrofuran (THF) brought about effective formation of 1,4-diamyloxy-2,3-dibromo-5,6-dicyanobenzene (**3**) in a 63% overall yield. The subsequent treatment of **3** with Mg turnings used for Grignard reaction in the presence of a variety of substituted furans **6a–k**[8] in THF at room temperature for 3 hours resulted in an efficient formation of the desired corresponding 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes **4a–k** in 82–33% yields, as shown in Scheme 1.



Scheme 1 Novel synthesis of 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyano-naphthalenes **4a–k**

Table 1 Isolated Yields of **4a–k** Starting from the Reaction of **3** with Various Furans **5a–k**

Entry	Product	Yield (%)
1	 **4a**	82
2	 **4b**	61
3	 **4c**	75
4	 **4d**	37
5	 **4e**	68
6	 **4f**	52
7	 **4g**	37
8	 **4h**	36
9	 **4i**	36
10	 **4j**	37
11	 **4k**	33

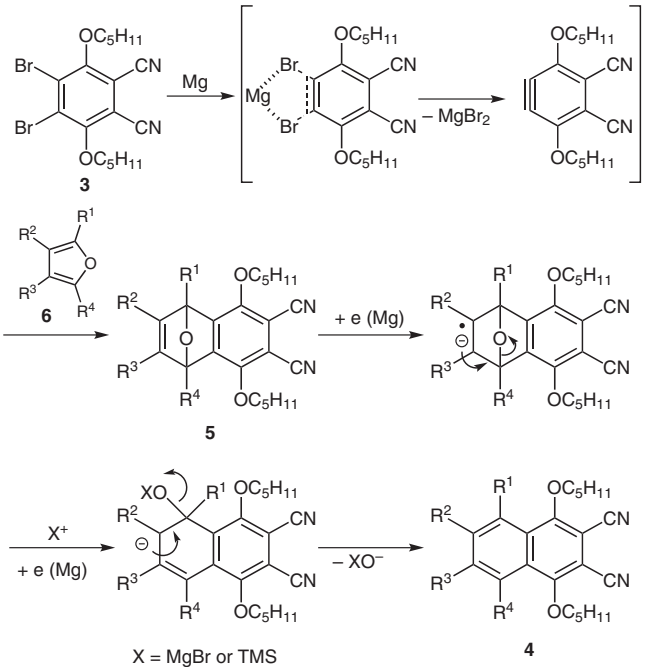
This three-step reaction scheme may be highly successful from the viewpoint of safety and easy availability of reagents, good total yields, and easy availability of substituted furans. Isolated yields for each of 1,4-diamyloxy-

5,6,7,8-multisubstututed-2,3-dicyanonaphthalenes **4a–k** are summarized in Table 1.

Interestingly, shortening of reaction time from 4 hours to 1 hour in the reactions of **3** with some of multisubstituted furans (**6a**,**e–g**) resulted in formation of the mixtures (ca. 1:1) of the corresponding 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes **4a**,**e–g** and the corresponding epoxy adducts **5a**,**e–g**, as shown in Table 2. This experimental fact clearly indicates that those substituted 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes **4** are formed through Diels–Alder-type of [4+2] cycloaddition between various substituted furans with the corresponding benzyne intermediate,[9] generated from the reaction of Mg metal with 1,4-diamyloxy-2,3-dibromo-5,6-dicyanobenzene (**3**), to give the corresponding epoxy adducts **5**. Furthermore, cationic participation[10] of the generated $MgBr_2$ to the epoxy adduct **5** was excluded because of no reaction on treatment of **5** with an equivalent molecular amount of $MgBr_2$.

On the other hand, treatment of the epoxy adduct **5** with Mg turnings for Grignard reaction and $MgBr_2$ (or TMSCl), indicating subsequent electron transfer from Mg metal[11] may produce the corresponding anion radicals, which gave the corresponding ring-opened products. And finally, the desired 1,4-di(amyloxy)-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes **4** were obtained smoothly, as shown in Scheme 2.

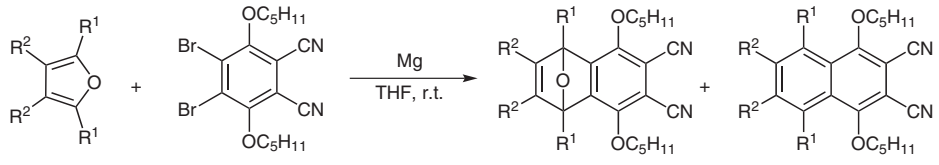
From these obtained 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes **4a**,**e–g**, the corresponding naphthalocyanines **7a**,**e–g** were easily synthesized using Li metal in *n*-pentanol in 20–45% yields according to the usual procedure,[12] which showed their λ_{max} at 867–892 nm ($\varepsilon = 2.51–3.31 \cdot 10^5\ M^{-1}cm^{-1}$). Furthermore, these new organic color stuffs were found to be easily soluble to organic solvents such as chloroform, toluene, ethanol, etc., indicating that they can have much potentiality for semiconductors, electrochromic display, optical and electronic materials, and absorption materials of infrared light.



Scheme 2 Proposed reaction scheme for the conversion of 1,4-diamyloxy-2,3-dibromo-6,7-dicyanobenzene (**3**) to 1,4-diamyloxy-substituted-2,3-dicyanonaphthalenes **4** through the epoxy adducts **5**

As a conclusion, in this study we have successfully developed a new efficient synthetic method of 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyano-naphthalenes **4**, and some of their derived new naphthalocyanines **7** (Table 3), which are not only easily soluble to many of organic solvents but also show their absorption of λ_{max} at 800–900 nm. Those new organic functional materials are expected to show much potentiality and possibility as new promising functional materials for optical memory, semiconductivity, electrochromic display, and infrared light absorption.

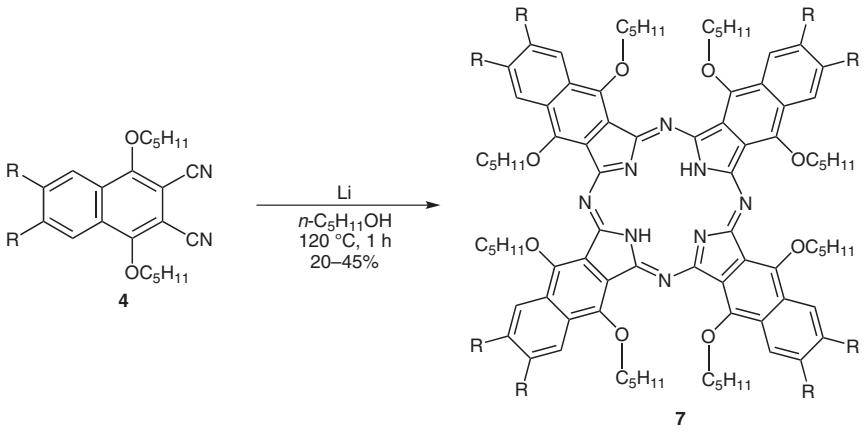
Table 2 Trapping of the Epoxides **5a**,**e–g** as Intermediates of the Cycloaddition of **3** with Furans **6a**,**e–g**[a]



R^1	R^2	Furan	Yield of **5a**,**e–g** (%)[b]	Yield of **4a**,**e–g** (%)[b]
H	H	**6a**	**5a** 36	**4a** 20
H	Ph	**6e**	**5e** 35	**4e** 26
H	4-FC_6H_4	**6f**	**5f** 42	**4f** 33
H	4-$MeOC_6H_4$	**6g**	**5g** 35	**4g** 24

[a] 3,6-Dialkoxy-4,5-dibromophthalonitrile (2.0 mol equiv), Mg (4.0 mol equiv), THF (4 mL), r.t., under N_2 atmosphere, 1 h (after starting material was consumed).
[b] Isolated yield.

Table 3 Synthesis of New Naphthalocyanines Soluble in Organic Solvents



R	Yield (%)	λ_{max} ($CHCl_3$)	ε ($M^{-1}cm^{-1}$)
4a H	**7a** 34	867 nm	$2.51 \cdot 10^5$
4e Ph	**7e** 30	888 nm	$2.95 \cdot 10^5$
4f 4-F(C_6H_4)	**7f** 45	886 nm	$3.31 \cdot 10^5$
4g 4-MeO(C_6H_4)	**7g** 20	892 nm	$3.24 \cdot 10^5$

Preparation of 3,6-Dihydroxy-4,5-dibromophthalonitrile (2)
Into the solution of 2,3-dicyanohydroquinone (**1**, 30.0 g, 187 mmol) in *t*-BuOH (200 mL), NBS (135.2 g, 720 mmol) were carefully added in a small portion for 15 min at 45 °C, then the reaction mixture was continued to stir for another 2 h. After the reaction, the reaction mixture was poured into an aq $NaHSO_3$ solution with vigorous stirring. The resulting precipitate was filtered under reduced pressure to wash adequately with H_2O, and then was dried further under vacuum. The product was identified by comparison with its authentic sample (65% yield).

Preparation of 3,6-Diamyloxy-4,5-dibromophthalonitrile (3)
Into the solution of *n*-amyl alcohol (12.5 g, 142 mmol), 4,5-dibromo-3,6-dihydroxyphthalonitrile (**2**, 18.0 g, 56.6 mmol), Ph_3P (35.9 g, 136 mmol) in anhyd THF (80 mL), a solution of diisopropyl azodicarboxylate (28.8 g, 142 mmol) dissolved in THF (120 mL) was added dropwise at 0 °C during 45 min, and then the mixture was continued to be stirred for 5 h. After the reaction, evaporation of the reaction solvent followed by addition of Et_2O gave Ph_3P, which was removed by filtration and then washed with the solvent. Evaporation of Et_2O from the filtrate under reduced pressure gave the desired product, which was purified by column chromatography and recrystallization, and was characterized by spectroscopic methods and elemental analysis.

3,6-Diamyloxy-4,5-dibromophthalonitrile (3)
Mp 68.8–69.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (t, 4 H, *J* = 6.4 Hz), 1.94–1.87 (m, 4 H), 1.56–1.36 (m, 8 H), 0.95 (t, 6 H, *J* = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.38, 129.62, 112.36, 109.21, 76.69, 29.63, 27.73, 22.34, 13.93 ppm. IR (KBr): 2959, 2858, 2234, 1548, 1466, 1423, 1361, 1231, 1072, 1044, 1006, 936, 889, 835, 729, 536, 499 cm^{-1}. MS (APCI): *m/z* = 459 $[M + H]^+$. Anal. Calcd for $C_{18}H_{22}Br_2N_2O_2$: C, 47.18; H, 4.84; N, 6.11. Found: C, 47.29; H, 4.80; N, 6.06.

General Method for the Synthesis of 1,4-Diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonaphthalenes 4a–k and 1,4-Diamyloxy-5,8-epoxy-5,8-dihydro-2,3-dicyanonaphthalene 5a,e–g
Into anhyd THF (40 mL) of Mg turning for Gnignard reaction (1.0 g, 41 mmol) was introduced, and the solution was stirred at r.t. under N_2 atmosphere. Then 4,5-dibromo-3,6-di(amyloxy)-4,5-dibromophthalonitrile (**3**, 9.01 g, 20 mmol) and one of multisubstituted furans **6a–k** (10 mmol) was added to the solution with stirring, and the resulting solution was continuously stirred at r.t. until all the starting furans consumed.

After the reaction of 4 h, the product mixture was poured into aq NH_4Cl solution, and was extracted with three portions of CH_2Cl_2 (3 × 50 mL). The combined CH_2Cl_2 solution was washed with H_2O, and then dried over anhyd $MgSO_4$. After evaporation of the solvent, the organic layer was subjected to column chromatograph (elution: CH_2Cl_2–hexane = 1:2) to give the desired product, each of 1,4-diamyloxy-5,6,7,8-multisubstituted-2,3-dicyanonapthalenes **4a–k**.

Shortening the reaction time from 4 h to 1 h for the reaction of the starting multisubstituted furans **6a,e–g** with **3** brought about formation of almost the same ratio (1:1) of two products **4a**,**e–g** and **5a**,**e–g**, which were found by isolation, chromatographic and spectroscopic analyses.

1,4-Diamyloxy-2,3-dicyanonaphthalene (4a)
Mp 52.6–53.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, 2 H, *J* = 3.0, 6.2 Hz), 7.79 (dd, 2 H, *J* = 3.0, 6.2 Hz), 4.42 (t, 4 H, *J* = 6.8 Hz), 1.97 (quint, 4 H, *J* = 6.8 Hz), 1.60–1.40 (m, 8 H), 0.97 (t, 6 H, *J* = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.23, 130.45, 130.15, 123.53, 114.41, 98.7 ppm. MS (APCI): *m/z* = 351 $[M + H]^+$. Anal. Calcd for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.69; H, 7.60; N, 7.90.

1,4-Diamyloxy-2,3-dicyano-5-methylnaphthalene (4b)
Mp 62.0–63.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (1 H, d, *J* = 7.2 Hz), 7.62 (t, 1 H, *J* = 7.2 Hz), 7.53 (d, 1 H, *J* = 7.2 Hz), 4.35 (t, 2 H, *J* = 6.9 Hz), 4.22 (t, 2 H, *J* = 6.9 Hz), 2.88 (s, 3 H), 2.02–1.92 (m, 4 H), 1.59–1.40 (m, 8 H), 0.97 (t, 6 H, *J* = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.35, 157.42, 136.30, 133.94, 131.68, 129.75, 121.69, 114.44, 114.07, 101.29, 98.92, 77.00, 29.68, 27.72, 23.46, 22.28, 13.78 ppm. IR (KBr): 2939, 2872, 2228, 1571, 1496, 1459, 1409, 1350, 1330, 1208, 1044, 1021, 972, 888, 810, 782 cm^{-1}. MS (APCI): *m/z* = 365 $[M + H]^+$. Anal. Calcd for $C_{23}H_{28}N_2O_2$: C, 75.79; H, 7.74; N, 7.69. Found: C, 76.00; H, 7.70; N, 7.63.

1,4-Diamyloxy-2,3-dicyano-5,8-dimethylnaphthalene (4c)
Mp 95.0–95.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (s, 2 H), 4.14 (t, 4 H, *J* = 6.8 Hz), 2.83 (s, 6 H), 1.97 (quint, 4 H, *J* = 6.8 Hz), 1.56–1.38 (m, 8 H), 0.96 (t, 6 H, *J* = 7.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.70, 134.12, 133.71, 131.39, 114.22, 101.66, 77.64, 29.37, 27.68, 23.80, 22.33, 13.76 ppm. IR (KBr): 2938, 2872, 2226, 1459, 1338, 1214, 1042, 1015, 962, 850, 729, 566 cm^{-1}. MS (APCI): *m/z* = 379 $[M + H]^+$. Anal. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.45; H, 7.88; N, 7.19

1,4-Diamyloxy-2,3-dicyano-5,8-diphenylnaphthalene (4d)
Mp 192.5–194.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 2 H), 7.44–7.35 (m, 10 H), 3.61 (t, 4 H, *J* = 6.8 Hz), 1.16 (quint, 4 H, *J* = 6.8 Hz), 1.06 (quint, 4 H, *J* = 6.8 Hz), 0.93 (quint, 4 H, *J* = 6.8 Hz), 0.82 (t, 6 H, *J* = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.80, 141.99, 139.74, 133.64, 129.50, 128.84, 127.38, 127.13, 113.92, 102.95, 77.05, 28.21, 27.28, 22.18, 13.75 ppm. IR (KBr): 3057, 2956, 2870, 2230, 1599, 1573, 1489, 1411, 1353, 1280, 1233, 1074, 1027, 960, 855, 758, 699 cm^{-1}. MS (APCI): *m/z* = 503 $[M + H]^+$. Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.42; H, 6.83; N, 5.30.

1,4-Diamyloxy-2,3-dicyano-6,7-diphenylnaphthalene (4e)
Mp 119.5–121.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 2 H), 7.18–7.09 (m, 10 H), 4.33 (t, 4 H, *J* = 6.6 Hz), 1.83 (quint, 4 H, *J* = 6.6 Hz), 1.47–1.25 (m, 8 H), 0.82 (t, 6 H, *J* = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.08, 143.66, 139.75, 129.64, 129.22, 128.10, 127.48, 125.12, 114.44, 98.78, 76.31, 29.73, 27.87, 22.27, 13.86 ppm. IR (KBr): 3061, 2956, 2870, 2223, 1565, 1495, 1340, 1041, 1025, 965, 908, 781, 768, 702, 565, 532 cm^{-1}. MS (APCI): *m/z* = 503 $[M + H]^+$. Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.44; H, 6.85; N, 5.38.

1,4-Diamyloxy-2,3-dicyano-6,7-bis(4′-fluorophenyl)naphthalene (4f)
Mp 228.5–230.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 2 H), 7.17–7.13 (m, 4 H), 7.01 (t, 4 H, *J* = 8.7 Hz), 4.47 (t, 4 H, *J* = 7.0 Hz), 1.95 (quint, 4 H, *J* = 7.0 Hz), 1.54 (quint, 4 H, *J* = 7.0 Hz), 1.41 (sext, 4 H, *J* = 7.0 Hz), 0.93 (t, 6 H, *J* = 7.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.40 (d, $^1J_{CF}$ = 247.7 Hz), 157.14, 142.58, 135.71 (d, $^4J_{CF}$ = 4.0 Hz), 131.36 (d, $^3J_{CF}$ = 8.0 Hz), 129.47, 125.25, 115.36 (d, $^2J_{CF}$ = 20.0 Hz), 114.51, 99.12, 76.45, 29.83, 27.98, 22.36, 13.95 ppm. IR (KBr): 3070, 2960, 2874, 2226, 1905, 1603, 1509, 1339, 1220, 1161, 1015, 966, 842, 817, 546 cm^{-1}. MS (APCI): *m/z* = 538 $[M]^+$. Anal. Calcd for $C_{34}H_{32}F_2N_2O_2$: C, 75.82; H, 5.99; N, 5.20. Found: C, 75.74; H, 6.07; N, 5.16.

1,4-Diamyloxy-2,3-dicyano-6,7-bis(4′-methoxyphenyl)naphthalene (4g)
Mp 128.0–130.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 2 H), 7.13 (d, 4 H, *J* = 8.6 Hz), 6.84 (d, 4 H, *J* = 8.6 Hz), 4.45 (t, 4 H, *J* = 7.2 Hz), 3.82 (s, 6 H), 1.95 (quint, 4 H, *J* = 7.2 Hz), 1.54 (quint, 4 H, *J* = 7.2 Hz), 1.42 (sext, 4 H, *J* = 7.2 Hz), 0.94 (t, 6 H, *J* = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.15, 157.30, 143.43, 132.36, 130.87, 129.28, 124.95, 114.66, 113.75, 98.80, 76.43, 55.23, 29.85, 27.98, 22.38, 13.96 ppm. IR (KBr): 3070, 2956, 2871, 2224, 1608, 1515, 1338, 1295, 1251, 1179, 1029, 835, 560 cm^{-1}. MS (APCI): *m/z* = 562 $[M]^+$. Anal. Calcd for $C_{36}H_{38}N_2O_4$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.99; H, 6.83; N, 4.79.

1,4-Diamyloxy-2,3-dicyano-6,7-bis(1′-naphthyl)naphthalene (4h)
Mp 142.1–142.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 8.44 (s, 1 H), 7.80 (dd, 1 H, *J* = 2.0, 7.6 Hz), 7.71 (dd, 1 H, *J* = 1.6, 7.3 Hz), 7.67–7.61 (m, 4 H), 7.49–7.42 (m, 2 H), 7.29–7.24 (m, 3 H), 7.09 (t, 1 H, *J* = 7.9 Hz), 7.04 (t, 1 H, *J* = 7.9 Hz), 6.95 (dd, 1 H, *J* = 1.2, 7.1 Hz), 4.54–4.44 (m, 4 H), 1.88 (sext, 4 H, *J* = 6.6 Hz), 1.49–1.26 (m, 8 H), 0.83 (t, 3 H, *J* = 7.4 Hz), 0.80 (t, 3 H, *J* = 7.3 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.41, 143.79, 143.60, 137.15, 137.13, 133.31, 133.20, 132.00, 131.18, 129.38, 129.24, 128.38, 128.33, 128.12, 128.07, 127.99, 127.05, 126.58, 126.52, 126.27, 125.78, 125.62, 125.59, 125.41, 124.66, 124.46, 114.65, 99.11, 99.05, 76.63, 76.61, 29.78, 29.75, 27.84, 27.80, 22.30, 22.27, 13.85, 13.82 ppm. IR (KBr): 3047, 2955, 2871, 2224, 1592, 1560, 1509, 1426, 1340, 1177, 1011, 802, 775 cm^{-1}. MS (APCI): *m/z* = 603 $[M]^+$. Anal. Calcd for $C_{42}H_{38}N_2O_2$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.70; H, 6.55; N, 4.45.

1,4-Diamyloxy-2,3-dicyano-5,6,7,8-tetraphenylnaphthalene (4i)
Mp 201.4–203.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.02 (m, 10 H), 6.82–6.77 (m, 6 H), 6.61–6.58 (m, 4 H), 3.66 (t, 4 H, *J* = 6.9 Hz), 1.15 (sext, 4 H, *J* = 6.9 Hz), 1.05 (quint, 4 H, *J* = 6.9 Hz), 0.95 (quint, 4 H, *J* = 6.9 Hz), 0.79 (t, 6 H, *J* = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.03, 145.52, 140.49, 138.88, 137.86, 130.60, 129.90, 129.88, 126.70, 126.47, 126.11, 125.60, 114.19, 103.41, 76.68, 28.37, 27.28, 22.27, 13.81 ppm. IR (KBr): 3056, 3025, 2957, 2228, 1601, 1567, 1542, 1493, 1442, 1358, 1279, 1027, 963, 759, 697 cm^{-1}. MS (APCI): *m/z* = 673 $[M + H_2O]^+$. Anal. Calcd for $C_{46}H_{42}N_2O_2$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.22; H, 6.64; N, 4.13.

1,4-Diamyloxy-2,3-dicyano-5,6,7,8-tetrakis(4′-fluorophenyl)-naphthalene (4j)
Mp 199.8–201.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (dd, 4 H, *J* = 5.3, 8.6 Hz), 6.84 (t, 4 H, *J* = 8.6 Hz), 6.60–6.51 (m, 8 H), 3.67 (t, 4 H, *J* = 6.9 Hz), 1.21–1.03 (m, 12 H), 0.82 (t, 6 H, *J* = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.50 (d, $^1J_{CF}$ = 246.6 Hz), 160.65 (d, $^1J_{CF}$ = 246.6 Hz), 158.78, 144.75, 137.36, 136.23 (d, $^4J_{CF}$ = 3.6 Hz), 134.53 (d, $^4J_{CF}$ = 3.6 Hz), 132.01 (d, $^3J_{CF}$ = 8.1 Hz), 131.26 (d, $^3J_{CF}$ = 8.1 Hz), 130.03, 114.13 (d, $^2J_{CF}$ = 20.7 Hz), 114.04 (d, $^2J_{CF}$ = 21.6 Hz), 113.96, 103.95, 77.26, 28.60, 27.34, 22.29, 13.76 ppm. IR (KBr): 3052, 1900, 1599, 1514, 1498, 1238, 1160, 840, 818, 647, 622, 511 cm^{-1}. MS (APCI): *m/z* = 727 $[M]^+$. Anal. Calcd for $C_{46}H_{38}F_4N_2O_2$: C, 76.02; H, 5.27; N, 3.85. Found: C, 76.27; H, 5.26; N, 3.62.

1,4-Diamyloxy-2,3-dicyano-5,10-diphenylanthracene (4k)
Mp 213.6–214.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.35 (m, 14 H), 3.75 (t, 4 H, *J* = 7.4 Hz), 1.22 (quint, 4 H, *J* = 7.4 Hz), 1.15 (m, 8 H), 0.85 (t, 6 H, *J* = 7.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.37, 140.55, 138.48, 133.60, 129.57, 127.71, 127.63, 127.54, 127.19, 125.70, 114.59, 99.78, 76.86, 28.52, 27.37, 22.36, 13.89 ppm. IR (KBr): 3056, 2954, 2925, 2869, 2227, 1575, 1471, 1401, 1380, 1335, 1274, 1033, 956, 948, 771, 759, 701, 517 cm^{-1}. MS (APCI): *m/z* = 571 $[M + H_2O]^+$. Anal. Calcd for $C_{38}H_{36}N_2O_2$: C, 82.58; H, 6.57, N, 5.07. Found: C, 82.85; H, 6.65; N, 4.77.

2,3-Dicyano-5,8-epoxy-5,8-dihydro-1,4-diamyloxynaphthalene (5a)
Mp 77.6–78.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (s, 2 H), 6.02 (s, 2 H), 4.21 (dt, 2 H, *J* = 9.2, 6.0 Hz), 4.06 (dt, 2 H, *J* = 9.2, 6.0 Hz), 1.82 (quint, 4 H, *J* = 6.0 Hz), 1.52–1.35 (m, 8 H), 0.95 (t, 6 H, *J* = 6.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.81, 145.79, 142.48, 113.24, 108.47, 81.06, 74.94, 29.44, 27.80, 22.30, 13.91 ppm. IR (KBr): 2955, 2871, 2231, 1578, 1447, 1376, 1288, 1062, 1034, 983, 892, 862, 710, 520 cm^{-1}. MS (APCI): *m/z* = 385 $[M + H_2O]^+$. Anal. Calcd for $C_{22}H_{26}N_2O_3$: C, 72.11; H, 7.15; N, 7.64. Found: C, 71.81; H, 7.20; N, 7.62.

2,3-Dicyano-5,8-epoxy-5,8-dihydro-1,4-diamyloxy-6,7-diphenylnaphthalene (5e)
Mp 101.2–101.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 10 H), 6.23 (s, 2 H), 4.10 (dt, 2 H, *J* = 8.8, 6.6 Hz), 3.94 (dt, 2

H, *J* = 8.8, 6.6 Hz), 1.77–1.68 (m, 4 H), 1.38–1.25 (m, 8 H), 0.90 (t, 6 H, *J* = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.95, 146.53, 146.22, 132.23, 128.89, 128.81, 126.92, 113.36, 108.84, 85.79, 75.35, 29.35, 27.62, 22.17, 13.87 ppm. IR (KBr): 3081, 3056, 3022, 2931, 2870, 2233, 1597, 1574, 1498, 1442, 1377, 1340, 1279, 984, 920, 863, 761, 695 cm^{-1}. MS (APCI): *m/z* = 536 [M + H_2O]$^+$, Anal. Calcd for $C_{34}H_{34}N_2O_3$: C, 78.74; H, 6.61; N, 5.40. Found: C, 78.59; H, 6.83; N, 5.43.

2,3-Dicyano-5,8-epoxy-5,8-dihydro-6,7-bis(4′-fluorophenyl)-1,4-diaoxynamyloxyphthalene (5f)

Mp 160.5–161.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.23 (m, 4 H), 7.02 (t, 4 H, *J* = 8.4 Hz), 6.17 (s, 2 H), 4.13 (dt, 2 H, *J* = 8.9, 6.6 Hz), 3.95 (dt, 2 H, *J* = 8.9, 6.6 Hz), 1.83–1.68 (m, 4 H), 1.40–1.27 (m, 8 H), 0.91 (t, 6 H, *J* = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.82 (d, $^1J_{CF}$ = 250.4 Hz), 149.98, 145.98, 145.63, 128.85 (d, $^3J_{CF}$ = 8.1 Hz), 128.18 (d, $^4J_{CF}$ = 3.6 Hz), 116.26 (d, $^2J_{CF}$ = 21.6 Hz), 113.29, 109.11, 85.74, 75.45, 29.42, 27.70, 22.20, 13.90 ppm. IR (KBr): 3072, 2932, 2873, 2228, 1599, 1513, 1503, 1443, 1377, 1338, 1280, 1221, 1162, 983, 920, 865, 839, 685, 567, 538 cm^{-1}. MS (APCI): *m/z* = 572 [M + H_2O]$^+$.

2,3-Dicyano-5,8-epoxy-5,8-dihydro-6,7-bis(4′-methoxyphenyl)-1,4-dipentyloxynaphthalene (5g)

Mp 105.8–106.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, 4 H, *J* = 8.6 Hz), 6.84 (d, 4 H, *J* = 8.6 Hz), 6.16 (s, 2 H), 4.10 (dt, 2 H, *J* = 8.9, 6.6 Hz), 3.95 (dt, 2 H, *J* = 8.9, 6.6 Hz), 3.81 (s, 6 H), 1.79–1.71 (m, 4 H), 1.39–1.29 (m, 8 H), 0.91 (t, 6 H, *J* = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.86, 149.91, 146.56, 144.31, 128.33, 124.86, 114.34, 113.45, 108.79, 85.76, 75.41, 55.26, 29.44, 27.71, 22.24, 13.93 ppm. IR (KBr): 2977, 2934, 2871, 2229, 1604, 1573, 1517, 1505, 1439, 1376, 1341, 1292, 1248, 1179, 982, 924, 863, 834, 679, 577, 547 cm^{-1}. MS (APCI): *m/z* = 596 [M + H_2O]$^+$.

General Method for the Synthesis of Metal-Free Multisubstituted Naphthalocyanines (7a,e–g)

Into a solution of one of 1,4-diamyloxy-6,7-disubstituted-2,3-dicyanonaphthalenes (**4a**,**e**–**g**, 1.5 mmol) dissolved in 1-pentanol (5.0 mL), was added Li metal (20 mol equiv) in a small portion with stirring, and then the solution was heated at 100–120 °C for 1.0 h. After cooling to r.t., the solution was poured into diluted aq AcOH (100 mL), and then the solution was extracted with CH_2Cl_2 (3 × 50 mL). After the CH_2Cl_2 solution was dried over anhyd $MgSO_4$, the drying agent was filtered, and the filtrate was concentrated under reduced pressure to give a black solid product, which was subjected to column chromatography (silica gel–CH_2Cl_2) to give the corresponding naphthalocyanines (**7a**,**e**–**g**) in 20–45% yield.

1,6,10,15,19,24,28,33-Octaamyloxy-37*H*,39*H*-naphthalocyanine (7a)

Mp 285.0–287.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (dd, 8 H, *J* = 3.2, 6.4 Hz), 7.89 (dd, 8 H, *J* = 3.2, 6.4 Hz), 5.17 (t, 16 H, *J* = 6.8 Hz), 2.48 (s, 2 H), 2.28 (quint, 16 H, *J* = 6.8 Hz), 1.62 (quint, 16 H, *J* = 6.8 Hz), 1.49 (sext, 16 H, *J* = 6.8 Hz), 0.97 (t, 24 H, *J* = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.97, 130.82, 126.99, 124.50, 122.79, 76.96, 30.37, 28.52, 22.78, 14.18 ppm. IR (KBr): 3298, 3069, 2957, 2929, 2859, 1583, 1349, 1249, 1155, 1127, 1095, 1049, 766, 730 cm^{-1}. MS–FAB: *m/z* = 1403 [M]$^+$. UV/vis ($CHCl_3$): 867, 765, 475, 448, 412, 328, 260, 242 nm; λ_{max} (ε) = 2.51·10^5 M^{-1}cm^{-1}. Anal. Calcd for $C_{88}H_{108}N_8O_8$: C, 75.29; H, 7.601; N, 7.98. Found: C, 75.08; H, 7.35; N, 8.15.

1,6,10,15,19,24,28,33-Octaamyloxy-3,4,12,13,21,22,30,31-octaphenyl-37*H*,39*H*-naphthalocyanine (7e)

Mp 266.8–267.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.05 (s, 8 H), 7.50–7.20 (m, 40 H), 5.24 (t, 16 H, *J* = 8.0 Hz), 2.63 (br, 2 H), 2.26 (quint, 16 H, *J* = 8.0 Hz), 1.68 (quint, 16 H, *J* = 8.0 Hz), 1.50 (sext, 16 H, *J* = 8.0 Hz), 0.92 (t, 24 H, *J* = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.11, 141,80, 140.21, 130.25, 130.06, 128.09, 126.83, 126.47, 123.08, 77.05, 30.47, 28.78, 22.86, 14.18 ppm. IR (KBr): 3297, 3059, 2953, 2669, 1599, 1573, 1495, 1427, 1334, 1278, 1203, 1178, 1110, 1075, 982, 903, 768, 700, 588 cm^{-1}. MS–FAB: *m/z* = 2013 [M]$^+$. UV/vis ($CHCl_3$): 888, 781, 491, 342, 277, 244 nm; λ_{max} (ε) = 2.95·10^5 M^{-1}cm^{-1}. Anal. Calcd for $C_{136}H_{138}N_8O_8$: C, 81.16; H, 6.91; N, 5.57. Found: C, 81.46; H, 7.04; N, 5.28.

3,4,12,13,21,22,30,31-Octakis(4′-fluorophenyl)-1,6,10,15,19,24,28,33-octaamyloxy-37*H*,39*H*-naphthalocyanine (7f)

Mp 286.5–287.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (s, 8 H), 7.43–7.40 (m, 16 H), 7.12 (t, 16 H, *J* = 8.0 Hz), 5.22 (t, 16 H, *J* = 8.0 Hz), 2.57 (br, 2 H), 2.23 (quint, 16 H, *J* = 8.0 Hz), 1.66 (quint, 16 H, *J* = 8.0 Hz), 1.44 (sext, 16 H, *J* = 8.0 Hz), 0.91 (t, 24 H, *J* = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.14 (d, $^1J_{CF}$ = 246.7 Hz), 150.01, 139.08, 137.53 (d, $^4J_{CF}$ = 3.0 Hz), 131.68 (d, $^3J_{CF}$ = 8.0 Hz), 130.02, 126.38, 125.75, 123.19, 115.23 (d, $^2J_{CF}$ = 21.0 Hz), 77.05, 30.42, 28.73, 22.80, 14.14 ppm. IR (KBr): 3300, 3069, 2954, 2867, 1604, 1510, 1333, 1226, 1178, 1111, 1039, 836, 583 cm^{-1}. MS–FAB: *m/z* = 2157 [M]$^+$. UV/vis ($CHCl_3$): 886, 780, 491, 344, 278, 242, 217 nm; λ_{max} (ε) = 3.31·10^5 M^{-1}cm^{-1}. Anal. Calcd for $C_{136}H_{130}F_8N_8O_8$: C, 75.74; H, 6.08; N, 5.20. Found: C, 75.57; H, 6.12; N, 5.05.

1,6,10,15,19,24,28,33-Octaamyloxy-3,4,12,13,21,22,30,31-octakis(4′-methoxyphenyl)-37*H*,39*H*-naphthalocyanine (7g)

Mp 289.9–291.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 8 H), 7.40 (d, 16 H, *J* = 8.0 Hz), 6.96 (d, 16 H, *J* = 8.0 Hz), 5.19 (t, 16 H, *J* = 8.0 Hz), 3.91 (s, 24 H), 2.61 (br, 2 H), 2.23 (quint, 16 H, *J* = 8.0 Hz), 1.65 (quint, 16 H, *J* = 8.0 Hz), 1.44 (sext, 16 H, *J* = 8.0 Hz), 0.92 (t, 24 H, *J* = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.63, 149.98, 139.78, 134.36, 131.27, 129.90, 126.10, 122.89, 113.60, 76.91, 55.30, 30.41, 28.74, 22.83, 14.19 ppm. IR (KBr): 3302, 2953, 2869, 2835, 1607, 1573, 1514, 1465, 1333, 1246, 1176, 1108, 1042, 832, 585 cm^{-1}. MS–FAB: *m/z* = 2153 [M]$^+$. UV/vis ($CHCl_3$): 892, 784, 493, 462, 336, 287, 249 nm; λ_{max} (ε) = 3.24·10^5 M^{-1}cm^{-1}. Anal. Calcd for $C_{144}H_{154}N_8O_{16}$: C, 76.77; H, 6.89; N, 4.97. Found: C, 76.86; H, 7.00; N, 4.68.

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