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Synthesis and Characterization of Monoisomeric 1,8,15,22-Substituted (A_3B and A_2B_2) Phthalocyanines and Phthalocyanine−Fullerene Dyads

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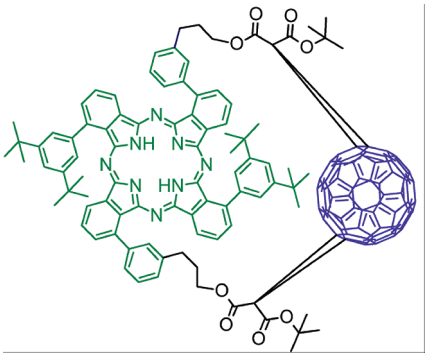

Synthesis and characterization of three phthalocyanine−fullerene (*Pc*-C_{60}) dyads, corresponding monoisomeric phthalocyanines (*Pc*), and building blocks, phthalonitriles, are described. Six novel bisaryl phthalonitriles were prepared by the Suzuki−Miyaura coupling reaction from trifluoromethanesulfonic acid 2,3-dicyanophenyl ester and various oxaborolanes. Two phthalonitriles were selected for the synthesis of A_3B- and A_2B_2-type phthalocyanines. Phthalonitrile **4** has a bulky 3,5-di-*tert*-butylphenyl substituent at the α-phthalo position, which forces only one regioisomer to form and greatly increases the solubility of phthalocyanine. Phthalonitrile **8** has a 3-phenylpropanol side chain at the α-position making further modifications of the side group possible. Synthesized monoisomeric A_3B- and A_2B_2-type phthalocyanines are modified by attachment of malonic residues. Finally, fullerene is covalently linked to phthalocyanine with one or two malonic bridges to produce *Pc*-C_{60} dyads. Due to the monoisomeric structure and increased solubility of phthalocyanines, the quality of NMR spectra of the compounds is enhanced significantly, making detailed NMR analysis of the structures possible. The synthesized dyads have different orientations of phthalocyanine and fullerene, which strongly influence the electron transfer (ET) from phthalocyanine to fullerene moiety. Fluorescence quenchings of the dyads were measured in both polar and nonpolar solvents, and in all cases, the quenching was more efficient in the polar environment. As expected, most efficient fluorescence quenching was observed for dyad **20b**, with two linkers and phthalocyanine and fullerene in face-to-face orientation.

Introduction

Phthalocyanines (*Pc*'s), structural analogues of porphyrins, are planar 18 π-electron aromatic macrocycles perfectly suited for their integration in light energy conversion systems. Compared to porphyrins, phthalocyanines have an advantage of a higher absorption around 700 nm where the maximum of the solar photon flux occurs. During the past decade several systems bearing *Pc* as electron donor and C_{60} as electron acceptor have been synthesized and studied by many research groups.[1−15]

The structural characterization and photochemical studies of phthalocyanines have always been a challenge for researchers due to the poor solubility and the number of

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regioisomers formed during the reaction. Cyclotetramerization of monosubstituted phthalonitriles usually results in the formation of four regioisomers. These four isomers possess C_{4h}, C_s, C_{2v}, and D_{2h} molecular symmetry and, assuming a statistical distribution, are prepared in a relative yield of 1:4:2:1, respectively.[16] In some cases these isomers can be separated from each other by HPLC methods.[17,18] The presence of isomers has few important consequences. Apart from differences in absorption spectra[18] and redox potentials, different isomers offer different positions for further substitution. The latter means that covalent bonding of phthalocyanine with another chromophore (e.g., fullerene) produces a mixture of regioisomerical dyads, which differ not only by phthalocyanine substituents positions, but as well by location of interchromophore bridges. To overcome this problem, few approaches are usually employed. One is to use a chelated atom in the phthalocyanine's central cavity as a binding site for the second component of the dyad.[19] Another option is to link the dyad components only by one bridge at the α- or β-phthalo position of *Pc*. Finally, two bridges can be located at the same phthalo ring, which makes the geometry of the dyad more predictable.[20] Complementary to such arrangements of functional bridge, the use of α,α or β,β bis-substituted phthalonitriles in phthalocyanine synthesis allows the isomer formation to be completely avoided. However, these methods are not suitable for the synthesis of 1,8,15,22-substituted phthalocyanines with two linkers or functional substituents.

The need for selective synthetic approaches in *Pc* synthesis was discussed long ago.[21] While so-called A_3B-type phthalocyanines are relatively easy to prepare by expanding subphthalocyanines, and the *adjacently* substituted AABB macrocycles by the templated approach, the *oppositely* substituted ABAB structures can be synthesized chiefly by statistical condensation. This means that the yield of ABAB *Pc* will not exceed 12.5%, which could be acceptable if the whole product would be a single regioisomer. Indeed, from the viewpoint of analysis and characterization the isomer with C_{4h} symmetry is preferred. Numerous attempts to prepare such molecules demonstrated that the C_{4h} isomer formation is favored by low reaction temperature (usually 80 °C), use of specific alkoxide (mostly lithium octoxide), and bulky substituents at position 3 of phthalonitriles. Impressive results in the synthesis of monoisomeric α-substituted phthalocyanines were achived,[16,22−25] but to our knowledge these phthalocyanines were not used as components in dyads.

Here we propose the approach to functionalized monoisomeric phthalocyanines using sterically restricting substituents in α-phthalo positions of the macrocycle. As we have found, the proper substituent at the 3-position of phthalonitrile plays the major role in controlling the isomers formation regardless the reaction temperature and alkoxide employed. We have designed and synthesized 3-(di(*tert*-butyl)phenyl)-phthalonitrile, which produced corresponding C_{4h} phthalocyanine with high yield and selectivity. The structure of the product was evident from ^{1}H NMR and was additionally supported by COSY and gHSQC measurements. We have found that combining 3-(di(*tert*-butyl)phenyl)phthalonitrile with other 3-arylphthalonitriles in mixed synthesis yielded the same "cartwheel" isomers of A_3B, AABB, and ABAB phthalocyanines.

Following this approach, we have synthesized a set of *Pc*-C_{60} dyads, where fullerene is covalently linked to monoisomeric phthalocyanine. Phthalocyanines and the dyads are well soluble in variety of solvents, which improves the quality of the NMR analysis and simplifies further photochemical studies and applications.

The mutual orientation and distance between donor and acceptor have been recognized as important factors in dyad design.[14,26−29] We have designed our dyads so that the bridge between fullerene and phthalocyanine is similar in length to that of previously synthesized porphyrin−fullerene dyads.[28] We prepared a set of molecules in which dyad **20a** has one linker whereas dyads **20b** and **20c** have two linkers in

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1,15- and 1,8-positions, respectively. In the case of dyad **20b** the phthalocyanine and fullerene moieties are oriented face-to-face while in dyad **20c** they are oriented face-to-edge. As expected, in dyad **20b** with face-to-face orientation the electron transfer from phthalocyanine to fullerene is the most efficient, as evidenced by steady-state fluorescence measurements.

Results and Discussion

The design of phthalocyanines is with no doubt a question of phthalonitrile chemistry. Unlike benzaldehydes in porphyrin synthesis, the choice of commercially available phthalonitriles is rather limited both in number and variety of the substituents. This especially concerns 3-substituted phthalonitriles, from which no compounds with bulky groups are commercially available. Our previous efforts in making 3-substituted phthalonitriles[14] and their corresponding phthalocyanines and dyads have demonstrated that 3-aryloxyphthalonitriles are not sterically restricting enough to produce a "cartwheel" C_{4h} isomer with good selectivity. Even at lower temperatures (< 90 °C) the yield of this isomer did not exceed 50%, and the separation of monoisomeric product was not possible. Neither did the choice of alkoxide help in solving the problem; albeit the "cartwheel" formation was evidently more efficient when the *Pc* synthesis was done with litium octoxide, but further purification of the reaction products from octanol solution was always problematic, if possible at all. A possible explanation is that the aryloxy (or alkoxy) group does not protrude in plane with the *Pc* macrocycle due to sp^3-hybridization of the oxygen atom, which allows the substituents to lift off the plane and form a "card pile" thus not restricting the formation of 4,5-substituted phthalocyanines. Compared to aryloxy group, the aryl group at the α-phthalo position is more "straight" and rigid, and therefore is suitable for direct synthesis of 1,8,15,22-substituted Pcs.[31,32] It should be noted that octakis[α-aryl]phthalocyanines are also known,[33,34] but the presence of the aryl group at position 3 of the phthalonitrile does not guarantee the C_{4h} isomer formation. On the other hand, octaarylphthalocyanines are sufficiently nonplanar macrocycles, which are prepared at high temperatures with moderate yields, thus the sterical hindrance of the α-aryl substituent should be combined with mild conditions of macrocyclization if a "cartwheel" phthalocyanine needs to be synthesized.

We have designed the phthalonitriles so that one phthalonitrile has solubility-improving substituents and another one bears a functional substituent. As a solubility-improving and sterically restricting group we decided to use the di(*tert*-butyl)phenyl fragment. Similar phthalonitrile was prepared with low yield by Brewis et al.[16] by reaction of 3-nitrophthalonitrile with the corresponding phenol. Synthesis of 3-arylphthalonitriles with functional groups (hydroxy, carboxy, amino) by Suzuki coupling is not yet described. We decided to prepare bulky phthalonitrile **4**, as well as hydroxyl-functionalized phthalonitriles **8** (Scheme 1) and **12**−**14** (Scheme 2), by Suzuki−Miyaura coupling using trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** as the key intermediate[31] bearing the phthalonitrile fragment, and the corresponding oxaborolanes **1**, **7**, **9**−**11** as arylboronic components.

Synthesis of Trifluoromethanesulfonic Acid 2,3-Dicyanophenyl Ester 3. 3-Hydroxyphthalonitrile **2** was prepared according to literature procedure.[30] The product **2** was treated with trifluoromethanesulfonyl chloride and triethylamine in dichloromethane at 0 °C followed by warming to ambient temperature. The reaction mixture was then stirred overnight to give trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** in 89% yield.

Borylation Reaction. The synthesis of the dioxaborolane **1a** was optimized by using 1-bromo-3,5-di-*tert*-butylbenzene as starting material. Different borylation reagents (4,4,5,5-tetramethyl-1,3,2-dioxaborolane and bis(pinacolato)diboron), bases (KOAc and Et_3N), solvents (THF, DMSO, and dioxane), and catatalysts ($PdCl_2(dppf)\cdot CH_2Cl_2$, $Pd(OAc)_2$, and $Pd(PPh_3)_4$) were used to maximize the yield. Reaction time was varied from 12 h to 4 days, and temperatures were varied from room temperature to 100 °C. When 4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used as borylation reagent and Et_3N as base with different catalysts, no product formation was observed. Bis(pinacolato)diboron as borylation reagent, KOAc as base, $PdCl_2(dppf)\cdot CH_2Cl_2$ as catalyst, and DMSO or dioxane as solvent gave better results. When the reaction mixture was stirred at 80 °C for 4 days in DMSO, the dimer **1b** was formed. We suggested that by reducing the reaction time or temperature it should be possible to suppress the formation of compound **1b** and increase the yield of target product **1a**. In further experiments at the room temperature, even after 3 days of stirring neither the product **1a** nor the dimer **1b** was observed. However, when the temperature was set to 80 °C and reaction time to 12−24 h the target product **1a** was formed in 75−94% yields. The best yield (94%) was obtained with bis(pinacolato)diboron as borylation agent, KOAc as base, DMSO as solvent, and $PdCl_2(dppf)\cdot CH_2Cl_2$ as catalyst when the reaction mixture was heated at 80 °C for 24 h. Optimization conditions are shown in Table 1.

Synthesis of the dioxaborolane **7a** was more complex. At first, 3-(3-bromophenyl)propionic acid was reduced to 3-(3-bromophenyl)propan-1-ol **5** with $BH_3\cdot THF$. The hydroxy group was then protected to give acetic acid 3-(3-bromophenyl)propyl ester **6**, which was necessary for further Suzuki coupling, since the unprotected hydroxyl derivative did not produce the target phthalonitrile at all. Borylation of compound **6** was optimized by using KOAc/DMSO/$PdCl_2$-$(dppf)\cdot CH_2Cl_2$ as base/solvent/catalyst combination. The reaction time was varied from 6 to 21 h, while the temperature was set to 80 °C. Yields of 85% and 51% were obtained for the product **7a** in 6 and 21 h, respectively, and the dimer **7b** was isolated in trace amounts. The optimization conditions are shown in Table 2.

Synthesis of Phthalonitriles by the Suzuki−Miyaura Coupling Reaction. The phthalonitriles **4** and **8a** were synthesized from trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** and the corresponding dioxaborolane **1a** or **7a** by the Suzuki−Miyaura coupling reaction. The reaction conditions for synthesis of di(*tert*-butyl)phenylphthalonitrile **4** were optimized by using different bases (KOAc and K_3PO_4)

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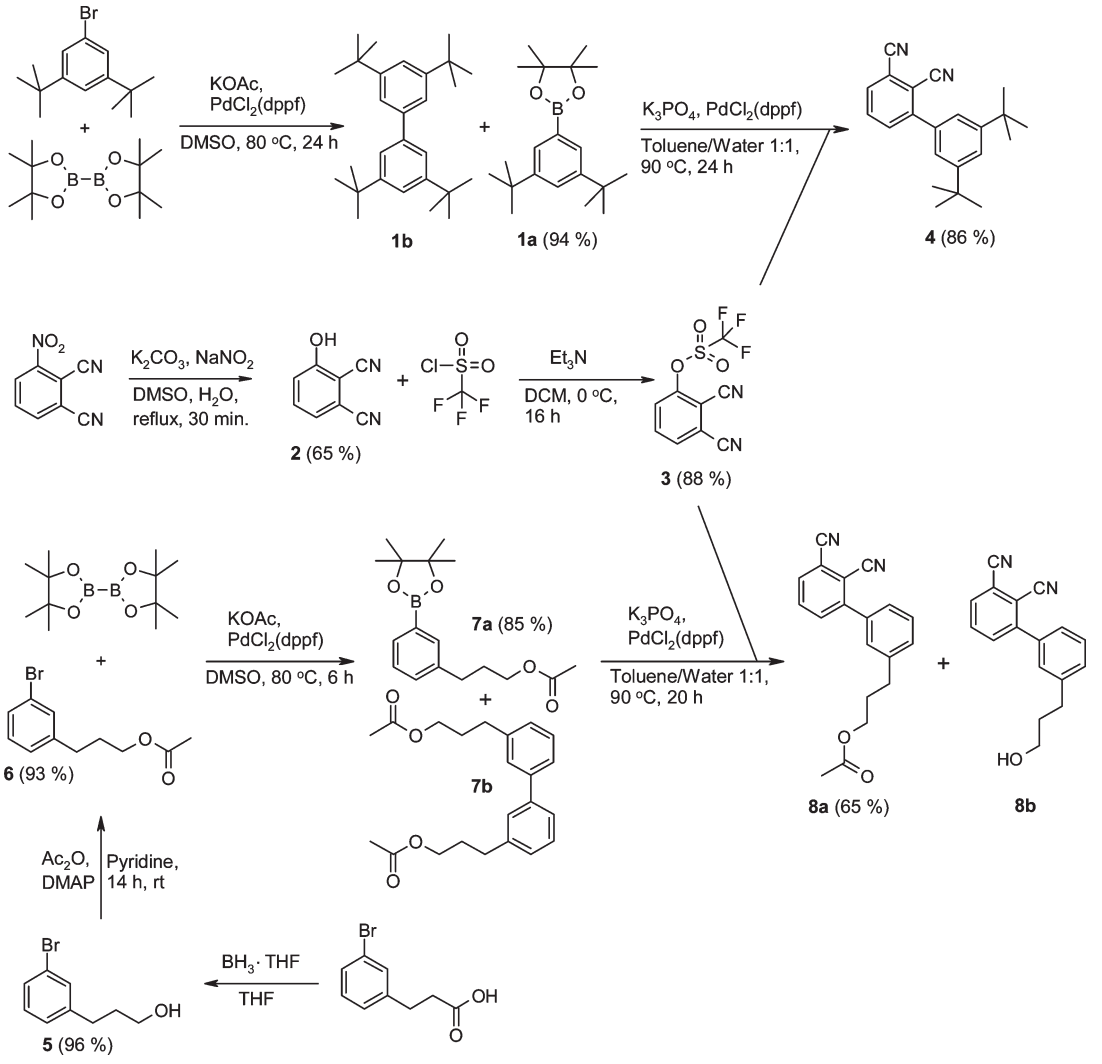
SCHEME 1. Synthesis of Phthalonitriles 4 and 8



and solvents (dioxane, DMSO, and toluene/water 1:1). $PdCl_2(dppf)\cdot CH_2Cl_2$ was used as catalyst in all experiments, the reaction time was set to 22−24 h, and the temperature was varied from 80 to 90 °C. When KOAc was used as base, no product formation was observed. However, the combination of K_3PO_4 as base and toluene/water 1:1 mixture as solvent gave the yield of target compound **4** as high as 86% in 24 h at 90 °C. Reaction conditions are shown in Table 3.

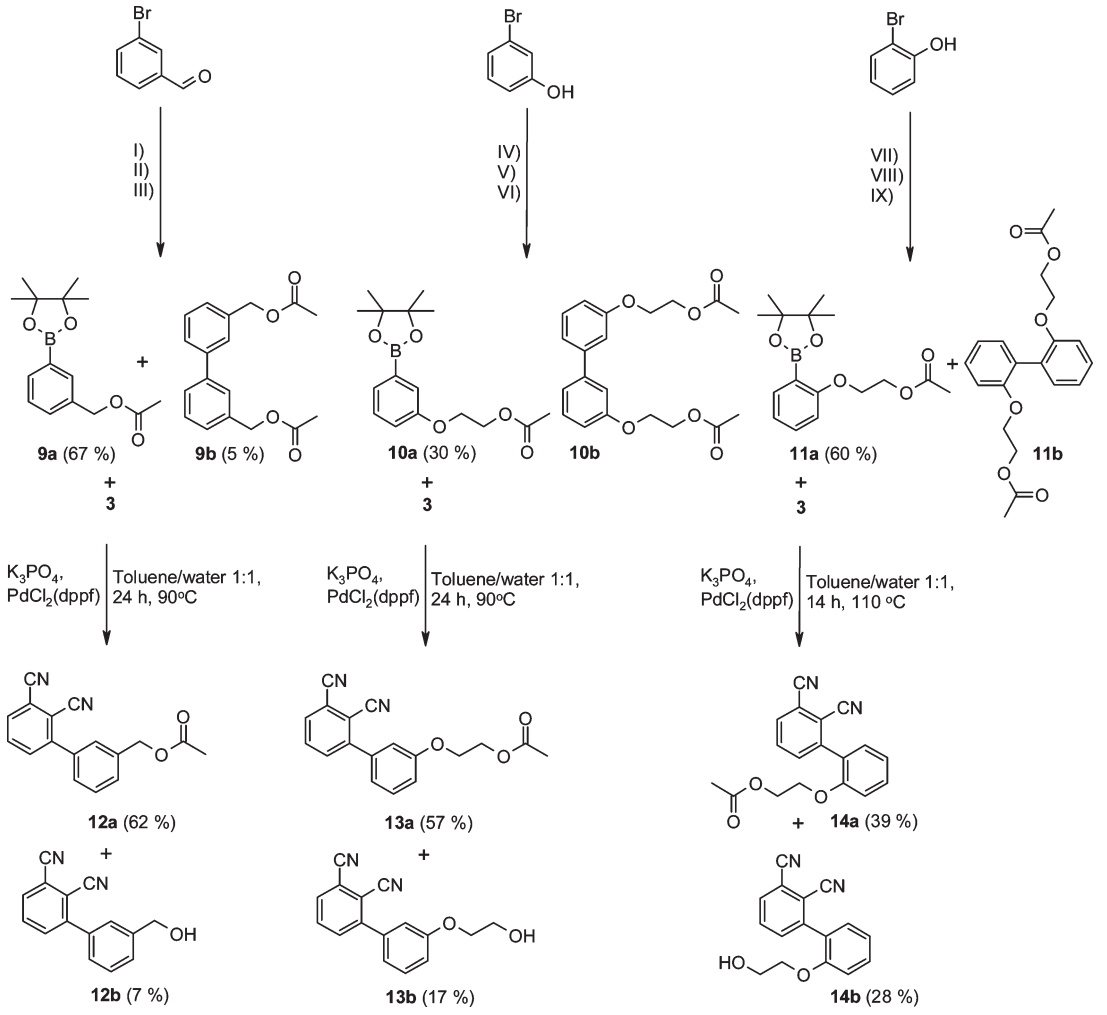
The synthesis of phthalonitrile **8a** was carried out in the presence of K_3PO_4 and $PdCl_2(dppf)\cdot CH_2Cl_2$ with toluene/water 1:1 mixture as solvent at 90 °C. Yields of 50% and 68% were obtained in 5 and 20 h, respectively. In addition to the protected product **8a**, also a small amount of the deprotected compound **8b** was observed (Table 4).

We have also prepared a few other dioxaborolanes **9a**−**11a** and phthalonitriles **12a**−**14a** (Scheme 2). Compounds **12**−**14** differ by the position and length of the hydroxyl-terminated bridge, which can be used for further functionalization. However, the yields of dioxaborolanes **10a** and **11a** were lower and the purification procedure was difficult due to a significant amount of dimer formed in the reaction. The mobility of the dimers was very close to that of dioxaborolanes, which required repetitive and time-consuming chromatographic purification. It is interesting to note that deprotection of acetoxy groups during Suzuki coupling occurred to a much higher degree for hydroxyethoxyphthalonitriles **13** and **14**, while deprotected phthalonitriles **8b** and **12b** were isolated only in minor amounts.

Synthesis of A_4-Type Phthalocyanines 15−17. The synthesis of phthalocyanines **15**−**17** is presented in Scheme 3. The aim was to find phthalonitriles, which produce phthalocyanines with a reduced number of regioisomers, and to determine the yields of A_4-type *Pc*'s. The product **15** with *tert*-butyl groups was evidently a good candidate, but the main challenge was to select the hydroxyl-containing phthalonitrile for further reactions, as it was not evident which of the phthalonitriles **8**, **12**−**14** was the best suitable for efficient phthalocyanine synthesis and further *Pc*-fullerene dyad preparation.

Phthalocyanine **15** with di-*tert*-butylphenyl substituents was synthesized first to ensure that only one regioisomer forms in the reaction. The syntheses were carried out in two different solvents (butanol, pentanol), and with different lithium alkoxide concentrations. Reaction time was varied

SCHEME 2. Synthesis of Compounds 9−14a,b[a]



[a]Reaction conditions: (I) $NaBH_4$, EtOH, 0 °C, 1 h; (II) acetic anhydride, DMAP, pyridine, rt, 3 d; (III) bis(pinacolato)diboron, KOAc, $PdCl_2(dppf)\cdot CH_2Cl_2$, 80 °C, 4 h, DMSO; (IV) 2-chloroethanol, K_2CO_3, acetone, 60 °C, 7 d; (V) acetic anhydride, DMAP, pyridine, 58 °C, 16 h; (VI) bis(pinacolato)diboron, KOAc, $PdCl_2(dppf)\cdot CH_2Cl_2$, 80 °C, 22 h, DMSO; (VII) 2-chloroethanol, K_2CO_3, acetone, 54 °C, 4d; (VIII) acetic anhydride, DMAP, pyridine, rt, 17 h; (IX) bis(pinacolato)diboron, KOAc, $PdCl_2(dppf)\cdot CH_2Cl_2$, 80 °C, 17.5 h, DMSO.

TABLE 1. Optimization Conditions of the Synthesis of Compound 1a

borylation agent	base	catalyst	solvent	temp/°C	time/h	product (yield/%)
4,4,5,5-tetramethyl-1,3,2-dioxaborolane	Et_3N	$PdCl_2(dppf)\cdot CH_2Cl_2$	THF	80	48	
	Et_3N	$Pd(OAc)_2$	THF	80	24	
	Et_3N	$Pd(PPh_3)_4$	THF	80	48	
	Et_3N	$PdCl_2(dppf)\cdot CH_2Cl_2$	THF	80	24	
	Et_3N	$PdCl_2(dppf)\cdot CH_2Cl_2$	THF	100	72	
bis(pinacolato) diboron	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	80	96	**1b**
	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	rt	72	
	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	80	12	**1a** (83)
	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	dioxane	80	12	**1a** (75)
	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	80	24	**1a** (94)

TABLE 2. Optimization Conditions of the Synthesis of Compound 7a

borylation agent	base	catalyst	solvent	temp/°C	time/h	yield/%
bis(pinacolato)diboron	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	80	21	51
	KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	80	6	85

from 5 to 22 h. The best yield was achieved when compound **4** was refluxed in lithium pentoxide/pentanol for 5 h (Table 5). After purification the monoisomeric phthalocyanine **15** was obtained in 23% yield, which is much higher than the results published[16] for similar tetrakis[3,5-di(*tert*-butyl)-4-hydroxyphenyl]phthalocyanine. The NMR data and isomer analysis will be discussed in the next section, but it should be noticed that only the C_{4h} isomer formed efficiently at high

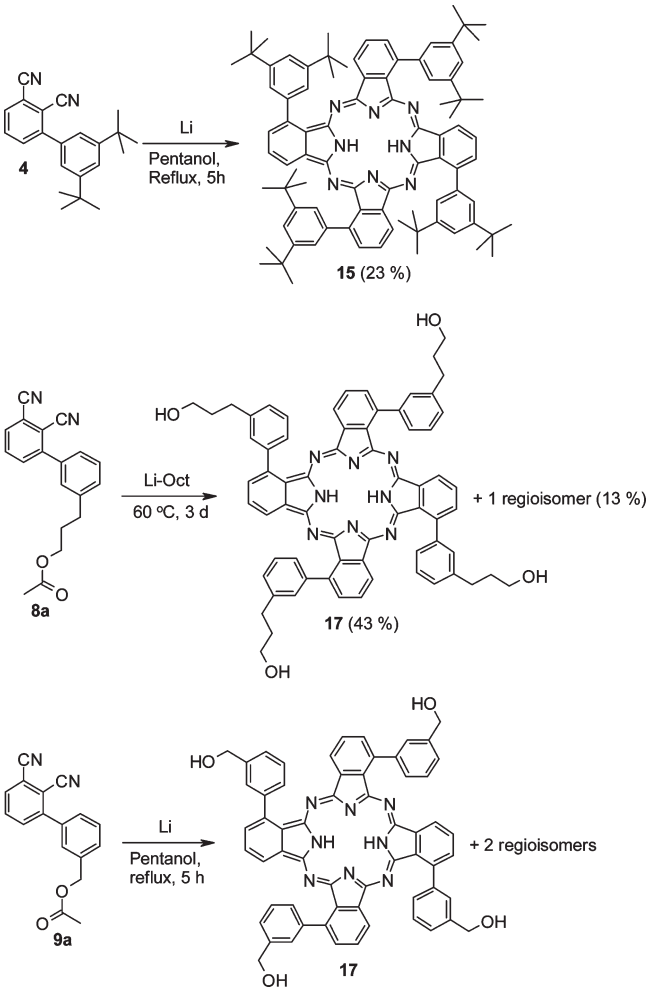
TABLE 3. Optimization Conditions of the Synthesis of Compound 4

base	catalyst	solvent	temp/°C	time/h	yield/%
KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	dioxane	80	22	
KOAc	$PdCl_2(dppf)\cdot CH_2Cl_2$	DMSO	80	22	
K_3PO_4	$PdCl_2(dppf)\cdot CH_2Cl_2$	toluene/water 1:1	90	24	86

TABLE 4. Optimization Conditions of the Synthesis of Compound 8a

base	catalyst	solvent	temp/°C	time/h	yield/%
K_3PO_4	$PdCl_2(dppf)\cdot CH_2Cl_2$	toluene/water 1:1	90	5	50
K_3PO_4	$PdCl_2(dppf)\cdot CH_2Cl_2$	toluene/water 1:1	90	20	68

SCHEME 3. Synthesis of Phthalocyanines 15−17



temperature in pentanol, which greatly simplified further purification of the product.

Phthalocyanine **16** was synthesized from phthalonitrile **8a** in lithium octoxide/octanol solution. The reaction mixture was stirred under argon atmosphere at 60 °C for 3 days. The protective acetyl groups cleaved during the reaction, and tetrahydroxyphthalocyanine was precipitated out by hexane addition. After purification, C_{4h} phthalocyanine **16** was obtained as the main product in 43% yield. Another regioisomer formed in the reaction as the minor product (13%). Separation of the two regioisomers was achieved easily by column chromatography on silica eluting with $CHCl_3$/EtOH 10:1.

TABLE 5. Optimization Conditions of Phthalocyanine 15

compd **4** (mg)	solvent (mL)	lithium/mg	time/h	yield/%
100	pentanol (5)	4.4	22	7.5
50	butanol (5)	2.2	22	1.2
50	pentanol (5)	5.0	5	11
50	pentanol (5)	21.2	5	23

Phthalocyanine **17** was also synthesized, but the yield was low, and the purification was difficult due to poor solubility of the compound. In addition, three different regioisomers were formed in the reaction, and the ^{1}H NMR spectrum was complex due to aggregation of phthalocyanines.

Phthalonitriles **13**−**14** were not suitable for efficient phthalocyanine synthesis. Few attempts to prepare corresponding phthalocyanines in lithium pentoxide/pentanol at the boiling point and in lithium octoxide/octanol at 95 °C were done, but in all cases the hydroxyethoxy side chains exchanged partly to alkoxide groups from solvent, thus forming a complex mixture of products with low yield of the target *Pc*. Taking into account the troublesome preparation of phthalonitriles **13**−**14**, we decided to choose phthalonitriles **4** and **8a**, which produced one and two *Pc* regioisomers, respectively, for further reactions. We expected that two or three di-*tert*-butylphenyl substituents in the phthalocyanine core are enough to ensure the formation of monoisomeric phthalocyanines **18a**−**c**.

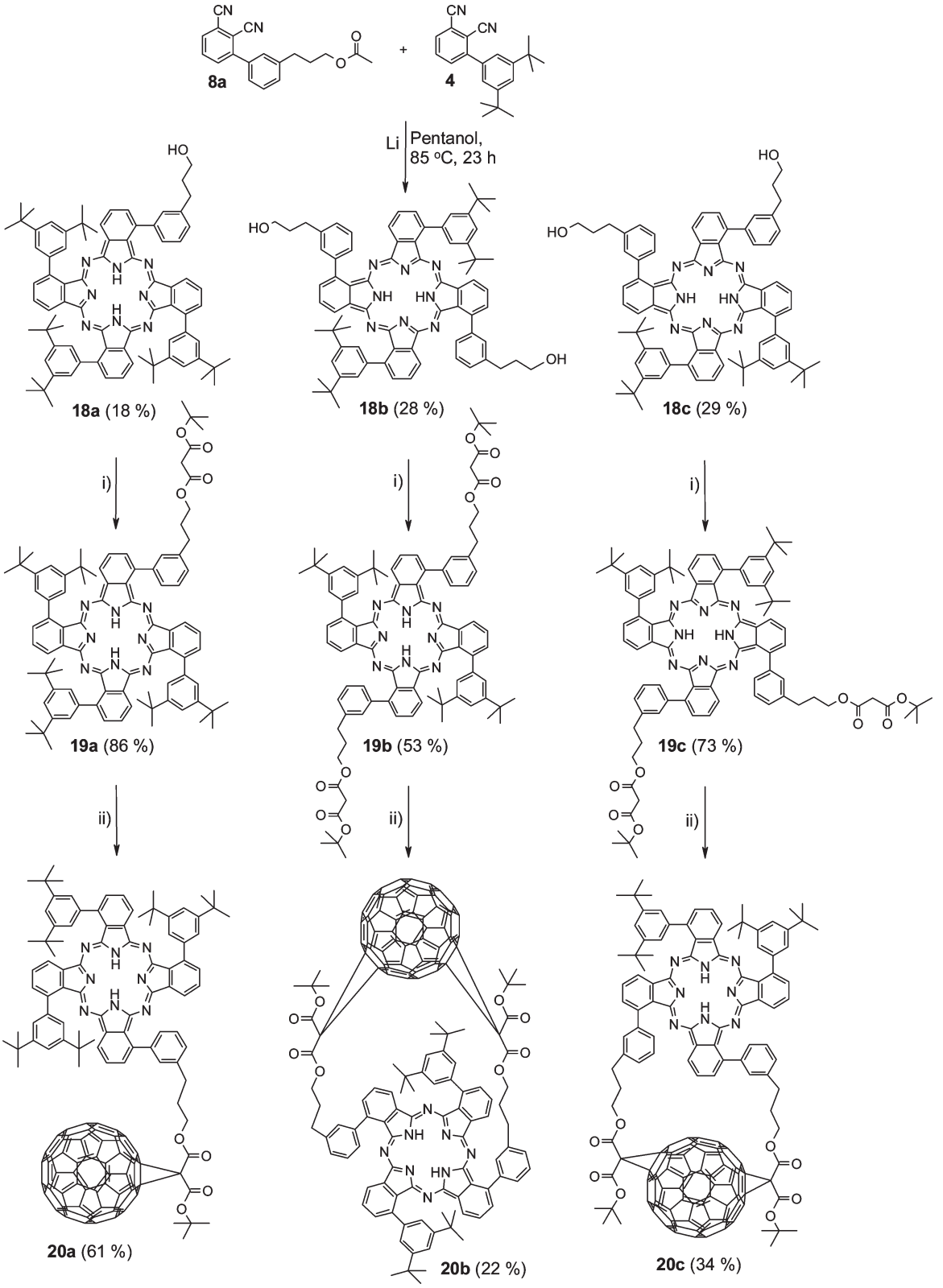
Synthesis of Phthalocyanines 18−**19a**−**c and Dyads 20a**−**c.** The syntheses of phthalocyanines **18**−**19a**−**c** and the dyads **20a**−**c** are presented in Scheme 4. Phthalocyanines **18a**−**c** were prepared by heating the mixture of phthalonitriles **4** and **8a** (molar ratio 7:5) in lithium pentoxide/pentanol at 85 °C for 23 h. During the reaction, the protective acetyl groups were cleaved by lithium pentoxide. Altogether seven different phthalocyanines formed in the reaction from which phthalocyanines **18a**−**c** were separated and purified for further reactions.

In the next reaction, *tert*-butyl esters of malonic acid were attached to the hydroxyl groups of phthalocyanines **18a**−**c** to yield phthalocyanines **19a**−**c**. Synthesis was done in dichloromethane with a 2-fold excess of *tert*-butylmalonate and 2-chloro-1-methylpyridium iodide, and a 4-fold excess of triethylamine per hydroxy group. Reaction mixtures were stirred overnight at room temperature, and the yields of the products **19a**−**c** after purification were 86%, 56%, and 76%, respectively.

In the synthesis of the dyads **20a**−**c**, C_{60}-fullerene (1.1 equiv/malonate group) was dissolved in toluene, iodine (1 equiv/malonate group) and phthalocyanine **19a**−**c** were then added, and the reaction mixture was stirred for 15 min under argon atmosphere. A 3-fold excess of DBU per malonate group was added and the reaction mixture was stirred 2 h at room temperature under argon atmosphere. The first purification of the dyads was done by column chromatography immediately after the completion of the reaction to avoid decomposition of the target compound by residual iodine. Further purification of the dyads **20b**,**c** was carried out on HPTLC glass plates (Silica gel 60 F_{254}, Merck).

NMR Analysis. The structural characterization of phthalocyanines has always been difficult since *Pc*'s usually have poor solubility and form a number of regioisomers. We designed phthalocyanines to have only one regioisomer

SCHEME 4. Synthesis of Phthalocyanines 18a−c and 19a−c and Dyads 20a−c[a]



[a]Reagents and conditions: (i) *tert*-butyl malonate, 2-chloro-1-methylpyridinium iodide, triethylamine, DCM, 1day, rt; (ii) I_2, DBU, C_{60}, 2 h, rt.

and good solubility in different solvents. These factors improve the quality and applicability of the NMR analysis significantly.

In the ^{1}H NMR spectrum of phthalocyanine **15** (Figure 1), the peaks are well resolved and sharp. Similar to the data reported by Bian[23] and Görlach,[18] the signal of α-phthalo

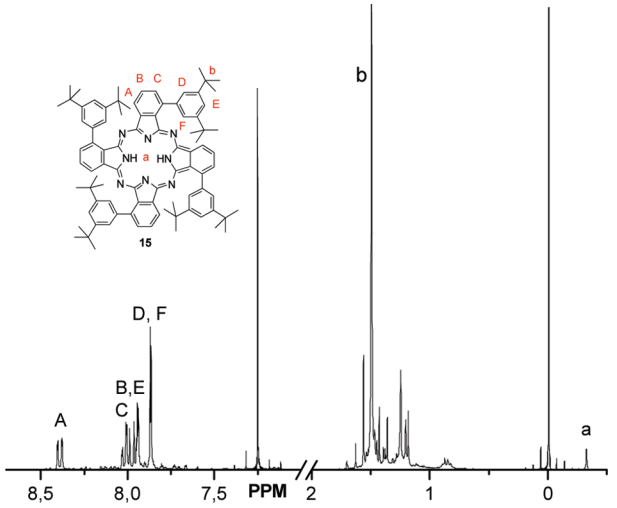


FIGURE 1. The structure and ^{1}H NMR spectrum of compound **15** in $CDCl_3$.

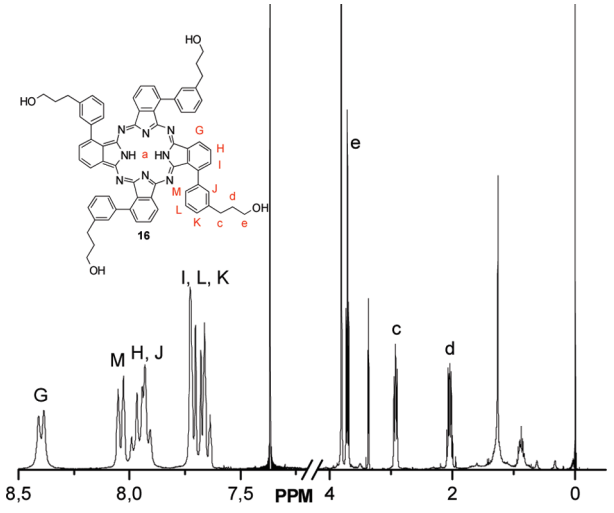


FIGURE 2. The structure and ^{1}H NMR spectrum of compound **16** in $CDCl_3$/MeOD.

protons (A) is well distinguishable and can be found as a doublet of doublets at 8.4 ppm. The protons of the di(*tert*-butyl)phenyl ring give rise to two singnals: a triplet of one proton (E) at 7.95 ppm, and a doublet of two protons (D and F) at 7.87 ppm. Two other phthalo-protons (B and C) produce a multiplet consisting of overlapping doublet and doublet of doublets between 7.98 and 8.02 ppm. Signals for *tert*-butyl protons (b) are observed at 1.5 ppm as a singlet and NH-protons (a) are found at −0.3 ppm as a sharp singlet. The H, H-COSY spectrum (see the Supporting Information) shows clearly the coupling between signals at 8.4 and 8.02−7.98 ppm, and at 7.95 and 7.87 ppm, thus demonstrating the conjugation within separated aromatic rings. The C,H-gHSQC (see the Supporting Information) spectrum shows each proton signal correlating to only one respective carbon, namely 8.4−123, 8.02−132, 7.98−129, 7.95−122, and 7.87−124 ppm. The only explanation for such a clear spectrum is that only one highly symmetrical regioisomer is present in the sample, otherwise the signals (especially those of phthalo-protons) would have much higher multiplicity, and many C,H-correlations would be observed in gHSQC. Indeed, this highly symmetrical compound could be either C_{4h} or D_2 type, but from the sterical point of view the C_{4h} *Pc* is much more favorable. Considering the facts mentioned above and previous literature examples,[18,23] we assign the structure of compound **15** as 1,8,15,22-tetrakis[(3,5-di-*tert*-butyl)phenyl]phthalocyanine.

In the ^{1}H NMR spectrum of the main isomer of phthalocyanine **16** (Figure 2) the peaks are well distinguishable as well, though broadened due to aggregation of the macrocycles. In fact, whereas compound **15** was well soluble in neat $CDCl_3$, the product **16**, which had four hydroxyl groups, was soluble only upon addition of MeOD, which affected the chemical shifts. Thus, α-phthalo protons (G) show a doublet with no fine structure at 8.4 ppm. Another doublet at 8.04 ppm originates from the proton M of the 3-(3-hydroxypropyl)phenyl group. Two other phthalo-protons (H and I) and proton of the aryl ring (J) form a multiplet at 8.00−7.88 ppm, and the rest of the aryl protons (K and L) produce a multiplet at 7.7.3−7.60 ppm. The signals of the alkyl chain protons appear as a sharp triplet, triplet, and quintet at 3.71 (e), 2.93 (c), and 2.05 ppm (d), respectively. According to our previous experience,[14] the signals of side substituents split into a few multiplets if more than one isomer is present in the sample, the same way as α-phthalo protons do. For compound **16**, however, the simplicity of NMR signals is evidence for a highly symmetrical monoisomeric structure, which is 1,8,15,22-tetrakis[3-(3-hydroxypropyl)phenyl]phthalocyanine.

The ^{1}H NMR spectra of the monofunctionalized compounds **18**−**20a** in $CDCl_3$ are presented in Figure 3. Signal assignments are based on COSY and gHSQC data (see the Supporting Information). In the aromatic region of the spectrum of **18a** signals of the α-phthalo protons G and A are found at 8.70−8.64 and 8.45−8.38 ppm, respectively. The signal of proton G is a doublet of doublets, which indicates that only one isomer is present in the sample. Three protons A are nonequivalent and produce a narrow multiplet around 8 ppm, which correspond well to the spectrum of **15**. As revealed by H,H-COSY, a doublet around 8.12 ppm with additional fine structure originates from the proton at position M. The doublet is coupled with the signals of protons at positions L and K, which in turn appear as a triplet at 7.79 ppm and as a doublet at 7.70 ppm, respectively. The multiplet at 8.09−8.06 ppm is due to the protons at positions H and J. Overlapped signals of protons at positions B and C appear as a multiplet at 8.06−7.98 ppm. The proton at position E gives a singlet at 7.96 ppm, which is overlapped with the multiplet of the proton at position I. The multiplet at 7.91−7.87 ppm corresponds to the six protons at positions D and F. In the aliphatic region of the spectrum of compound **18a** three signals for $-CH_2-$ protons are visible: a quartet at 3.77 ppm, a triplet at 3.04 ppm, and a multiplet at 2.16−2.05 ppm corresponding to the protons at positions e, c, and d, respectively. Signals for *tert*-butyl protons (b) are observed at 1.51 ppm and −NH protons (a) are found at −0.29 ppm as a singlet.

The aromatic region of the spectrum of **19a** is almost identical with that of **18a**. The signal of the proton at position M is shifted to higher frequency (8.14 ppm), and the signal of the proton at position K is shifted to lower frequency (7.68 ppm). In the aliphatic region of the spectrum of **19a** four signals for methylene groups are observed instead of three: a quartet at 4.27 ppm, a singlet at 3.27 ppm, a triplet at 3.04

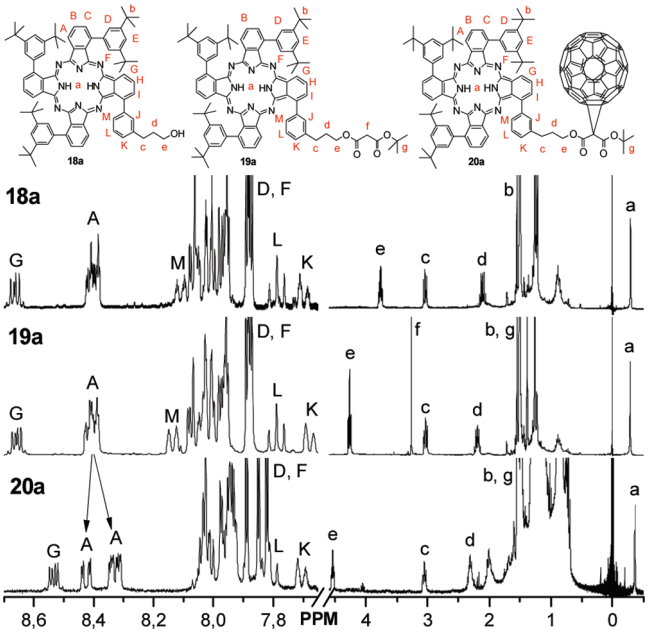


FIGURE 3. Structures of compounds **18**−**20a** (above) and ^{1}H NMR spectra of compounds **18**−**20a** (below) in $CDCl_3$.

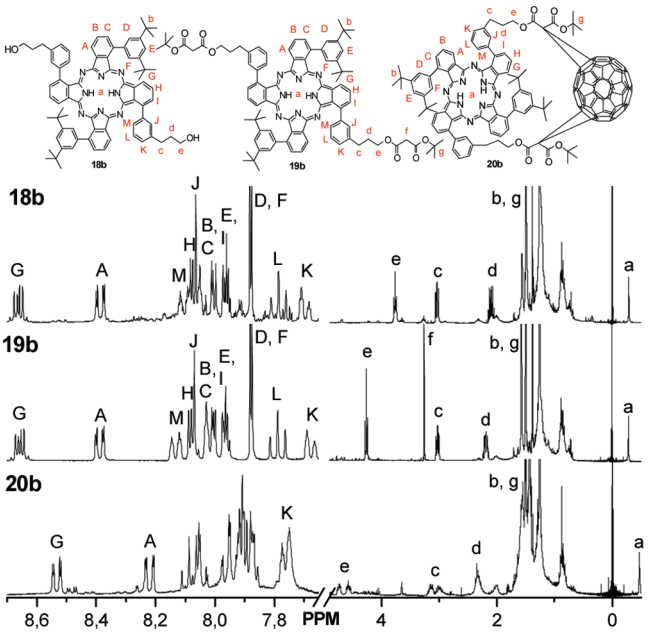


FIGURE 4. Structures of compounds **18**−**20b** (above) and ^{1}H NMR spectra of compounds **18**−**20b** (below) in $CDCl_3$.

ppm, and a multiplet at 2.26−2.12 ppm corresponding to the protons at positions e, f, c, and d, respectively. The signals for protons at positions e and d are shifted to higher frequency, and one additional singlet appears at 3.27 ppm corresponding to the $-CH_2-$ protons of the malonic linker. Signals for *tert*-butyl protons at position b (1.51 ppm) and −NH protons at position a (−0.29 ppm) are identical with those of **18a**. *tert*-Butyl ester protons of the malonic linker group (g) are observed at 1.39 ppm.

The spectrum of the dyad **20a** differs significantly from the spectra of **18a** and **19a**. In the aromatic region of the spectrum, the signal of the α-phthalo proton at position G is shifted to lower frequency (8.56 − 8.52 ppm) and the signal of the α-phthalo protons at position A is split into two: a doublet of doublets at 8.43 ppm corresponding to one proton and a multiplet at 8.36−8.30 ppm corresponding to two protons. The difference can be explained by the shielding effect of fullerene, which apparently forms a stable conformer with phthalocyanine, even though the two chromophores are linked by one flexible bridge only. The signals of protons at positions H−J, M, B−C, and E appear as two multiplets at 8.07−7.99 and 7.99−7.91 ppm. In the dyad, the six protons at positions D and F give three doublets at 7.89, 7.85, and 7.82 ppm. The doublets are partly overlapped with the triplet at 7.81 ppm, which is the signal of the proton at position L. A doublet is observed at 7.71 ppm, which corresponds to the proton at position K. In the aliphatic region the signals of $-CH_2-$ protons at positions e, c, and d appear as a triplet at 4.54 ppm, another triplet at 3.06 ppm, and a multiplet at 2.37−2.25 ppm, respectively. The singlet that is visible at 3.27 ppm in the spectrum of compound **19a** disappears due to the attachment of fullerene. *tert*-Butyl ester protons of the malonic linker (g) appear as a singlet at 1.55 ppm and the *tert*-butyl protons of phthalocyanine (b) are observed as a singlet at 1.54 ppm and as two overlapping singlets at 1.48 ppm. NH protons (a) are visible as a singlet at −0.36 ppm.

^{1}H NMR spectra of ABAB-type compounds **18**−**20b** are presented in Figure 4. Two doublets of doublets are visible at 8.7 and 8.4 ppm, corresponding to two pairs of α-phthalo protons (G and A) of symmetrical isomer. Unlike in A_3B *Pc*'s **18a**−**19a**, the protons D−E of two di(*tert*-butyl)phenyl groups of **18b**−**19b** are magnetically equivalent and produce a sharp triplet and doublet at 7.95 and 7.88 ppm.

In the spectrum of dyad **20b** α-phthalo protons at positions G and A are observed as a doublet of doublets at 8.54 and 8.22 ppm, respectively. The signals from other aromatic protons appear as a set of multiplets in the region 8.12−7.72 ppm, which can be explained by the close proximity of the fullerene sphere. In the aliphatic region, the signals for $-CH_2-$ protons are visible as multiplets at 4.79−4.52, 3.22−2.93, and 2.43−2.25 ppm. The signal of the dyad oxymethylene protons e around 4.6 ppm is split into two due to asymmetry introduced by fullerene addition. Eighteen *tert*-butyl protons at position g are observed as a singlet at 1.51 ppm and the 36 *tert*-butyl protons at position b are found as a singlet at 1.44 ppm. NH protons (a) of the dyad are visible as a singlet at −0.47 ppm.

Mass Spectrometry. The identification of the chromatographically pure compounds was proved by mass spectrometry. A high-resolution ESI-TOF instrument was used in measurements. To obtain an accurate mass value, the solution of reference compound (leucine enkephaline) was infused simultaneously with analyte, and the experimental spectra were processed according to the routine of accurate mass measurements (peak centering and lock-mass TOF correction).

The mass spectra of compounds **19**−**20a** are shown in Figure 5. In the spectrum of phthalocyanine **19a**, the $[M]^+$ peak was observed at *m*/*z* 1354.7708. For the "single handed" dyad **20a** the $[M]^+$ peak was found at *m*/*z* 2072.7576.

The mass spectra of compounds **19**−**20b** are shown in Figure 6. For phthalocyanine **19b** the $[M + Na]^+$ peak was observed at *m*/*z* 1465.7451. Molecular ion peak $[M + H]^+$ appeared at *m*/*z* 2159.7175 for the dyad **20b**.

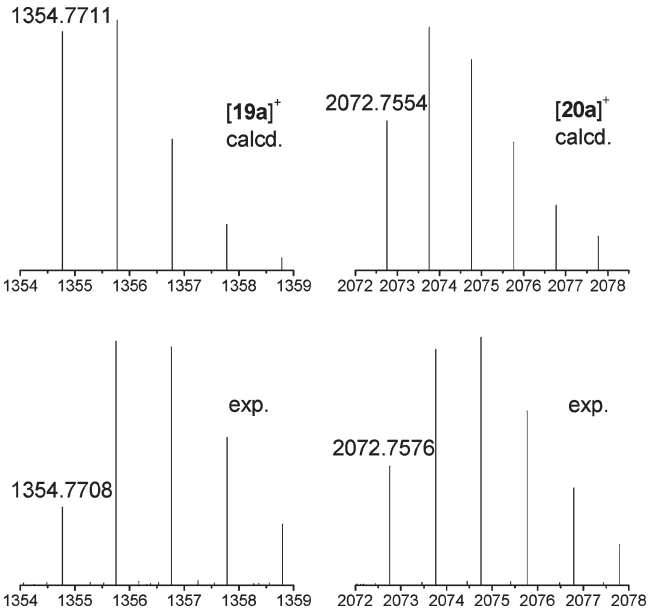


FIGURE 5. Mass spectra of compounds **19**−**20a**. **19a**: $[M]^+$ (left); and **20a**: $[M]^+$ (right).

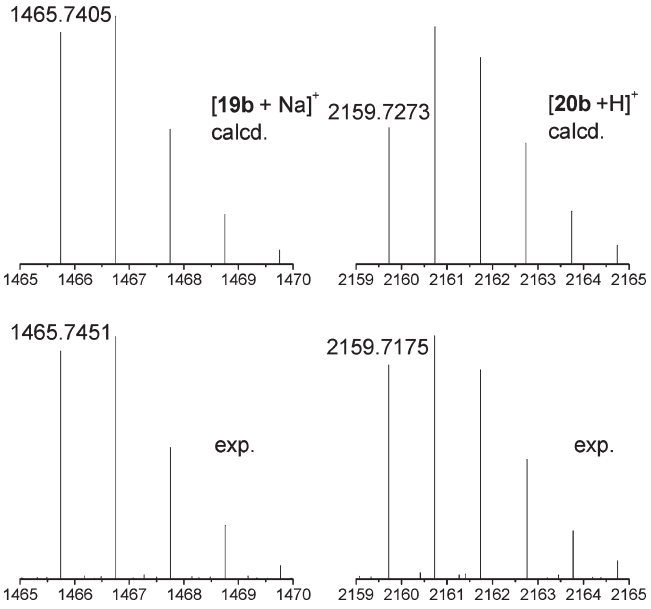


FIGURE 6. Mass spectra of compounds **19**−**20b**. **19b**: $[M + Na]^+$ (left); and **20b**: $[M + H]^+$ (right).

The mass spectra of compounds **19**−**20c** are shown in Figure 7. For phthalocyanine **19c**, the $[M]^+$ peak appeared at m/z 1442.7501. In the spectrum of the dyad **20c** the $[M - H]^-$ peak was found at m/z 2157.7124.

Steady-State Absorption. Steady-state absorption spectra were measured in toluene. Figures 8−10 show the absorption spectra of compounds **19**−**20a**−**c**. For the reference compounds **19a**−**c** the Q bands around 700 nm were split into two having absorption maxima at 675 and 709 nm. The Q bands of the dyads **20a**−**c** were similar in shape, but red-shifted by 2 nm for the dyad **20a** and by 6 nm for the dyads **20b** and **20c** compared to the spectra of the reference compounds. In addition, the spectra of the dyads were broadened

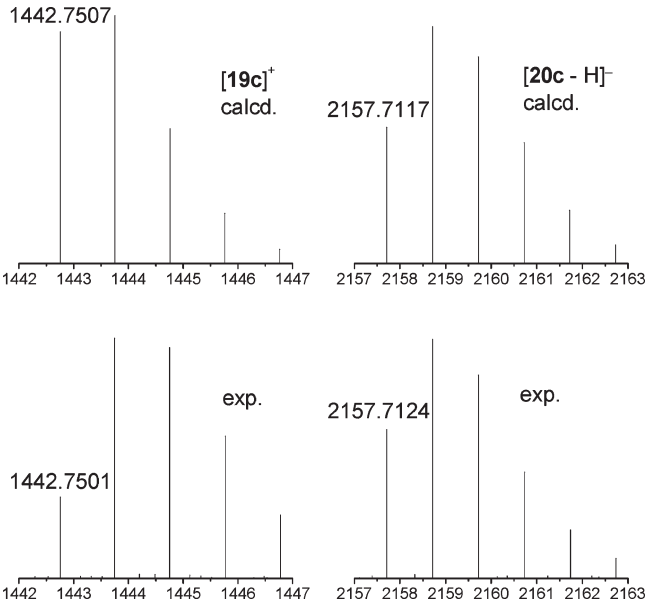


FIGURE 7. Mass spectra of compounds **19**−**20c**. **19c**: $[M]^+$ (left); and **20c**: $[M - H]^-$ (right).

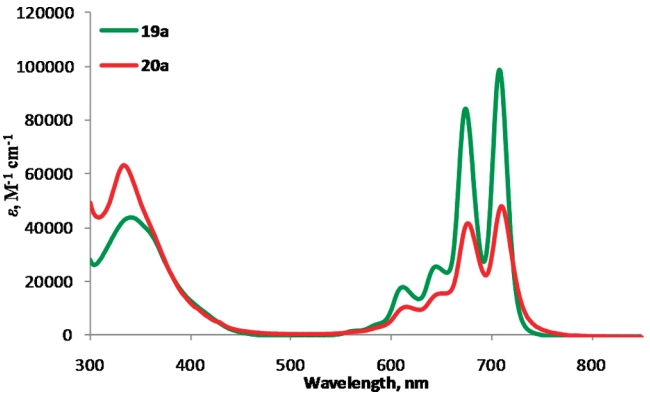


FIGURE 8. Absorption spectra of **19a** and **20a** in toluene.

indicating interaction between the chromophores in the dyads.[14]

Steady-State Fluorescence. Steady-state emissions were measured in polar (benzonitrile) and nonpolar (toluene) solvents. Emission spectra of the dyad **20a** and the corresponding reference **19a** in benzonitrile are given in Figure 11. The spectrum of the dyad (red line) has been multiplied by 18 (dotted line) for comparison. Similarly, the emissions of the dyads **20b** and **20c** in benzonitrile are 395 and 194 times weaker, respectively, compared to those of **19b** and **19c** (Figures 12 and 13), indicating that electron transfer (ET) from phthalocyanine to fullerene may be the cause of the quenching.[14] In addition, the emission spectra of the dyads **20b** and **20c** are red-shifted by 9 and 5 nm, respectively, compared to the spectra of compounds **19b** and **19c**.

In toluene, the emissions of compounds **20a**−**c** are quenched 13.5, 12.9, and 6.3 times, respectively. The emission spectrum of compound **20b** is red-shifted by 10 nm compared to compound **19b**, and the spectrum of compound **20c** is red-shifted by 6 nm compared to compound **19c**. Results from the steady-state fluorescence measurements are collected to Table 6.

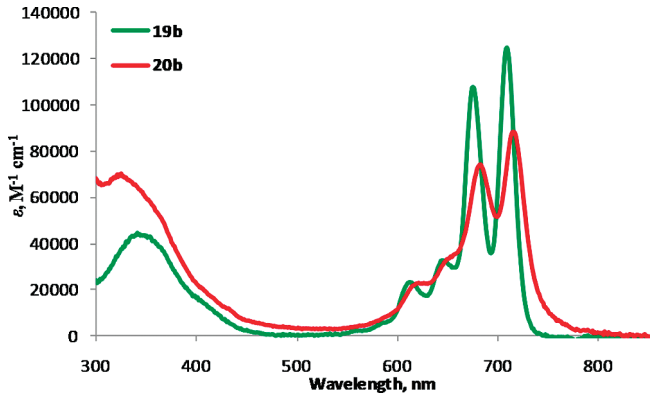


FIGURE 9. Absorption spectra of **19b** and **20b** in toluene.

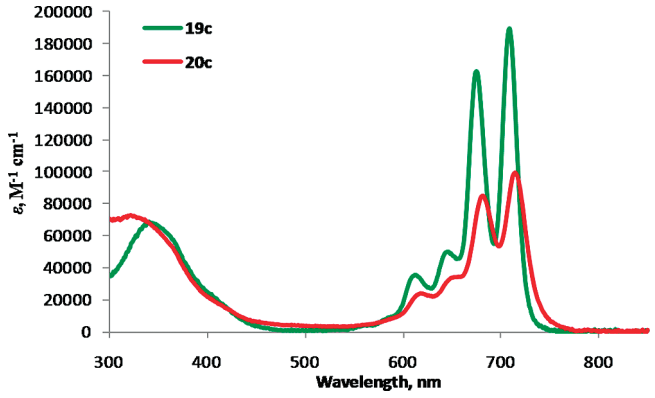


FIGURE 10. Absorption spectra of **19c** and **20c** in toluene.

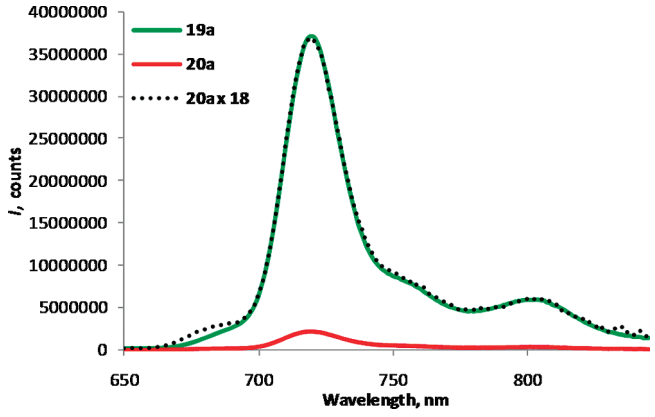


FIGURE 11. Fluorescence spectra of **19a** and **20a** in benzonitrile excited at 606 nm. The spectrum of dyad **20a** has been multiplied by 18 for comparison as indicated in the figure.

Porphyrin−fullerene dyads show distinct exciplex emission in the region 700−950 nm, but for *Pc*-C_{60} dyads the emission of exciplex is not so clearly visible.[14] The dyads **20b** and **20c** (Figures 12 and 13) show stronger emission around 775−825 nm compared to the reference compounds **19b** and **19c**. That feature will be studied more carefully by time-resolved spectroscopy methods in our research.[35]

(35) Lemmetyinen, H.; Kumpulainen, T.; Niemi, M.; Efimov, A.; Ranta, J.; Stranius, K.; Tkachenko N. V., *Photochem. Photobiol. Sci.* Submitted for publication.

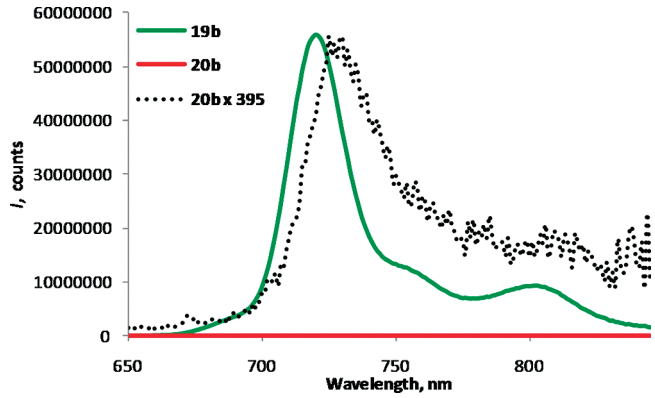


FIGURE 12. Fluorescence spectra of **19b** and **20b** in benzonitrile excited at 606 nm. The spectrum of dyad **20b** has been multiplied by 395 for comparison as indicated in the figure.

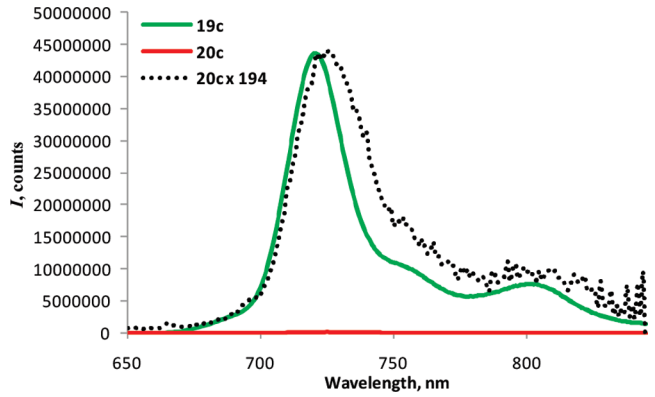


FIGURE 13. Fluorescence spectra of **19c** and **20c** in benzonitrile excited at 601 nm. The spectrum of dyad **20c** has been multiplied by 194 for comparison as indicated in the figure.

Conclusions

We have designed and prepared six novel bisaryl phthalonitriles by Suzuki−Miyaura coupling from trifluoromethanesulfonic acid 2,3-dicyanophenyl ester and a set of oxaborolanes. Phthalonitriles **4** and **8** (with two *tert*-butyl or one hydroxypropyl substituents, correspondingly) produced phthalocyanines with C_{4h} symmetry with high selectivity and good yields. A_3B- and A_2B_2-type phthalocyanines substituted at 1,8,15,22-positions were synthesized by mixed phthalonitrile condensation and were successfully isolated. Phthalocyanines were further modified by a covalent fullerene moiety attachment to yield a set of *Pc*-C_{60} dyads. Dyad **20a** has one linker whereas dyads **20b** and **20c** have two linkers. In dyad **20b**, phthalocyanine and fullerene are in a face-to-face orientation, but in dyad **20c** they are in a face-to-edge orientation. The orientation affects strongly the electron transfer from phthalocyanine to fullerene moiety.[35] Fluorescence quenchings of all the dyads were measured in toluene and benzonitrile. In all cases, fluorescence quenching was strongest in benzonitrile, and, as expected, for dyad **20b**, with the face-to-face orientation.

The products were characterized by ^{1}H NMR and mass spectrometry. The analysis of NMR spectra clearly indicates that synthesized phthalocyanines possess a 1,8,15,22-substitution pattern. Thus, we propose a way to selectively prepare monoisomeric phthalocyanines with high yields.

TABLE 6. Quenching of Compounds 20a−c in Benzonitrile and Toluene at Different Excitation Wavelengths

compd	solvent	λ_{exc} (nm)	$\lambda_{max.}$ (nm)	quenching (times)	quenching (%)
20a	benzonitrile	606	719	18.1	94.5
		618	719	17.4	94.2
		645	719	17.2	94.2
	toluene	599	713	13.5	92.6
		619	714	13.3	92.5
		656	714	13.4	92.5
20b	benzonitrile	606	727	395	99.8
		624	729	326	99.7
		642	729	409	99.8
		651	729	337	99.7
		667	729	419	99.8
	toluene	598	726	12.4	92.0
		619	726	10.3	90.3
		635	725	12.9	92.3
		652	726	11.6	91.4
		661	726	14.1	92.9
20c	benzonitrile	601	725	194	99.5
		626	726	177	99.4
		636	726	193	99.5
		657	725	183	99.5
		662	725	192	99.5
	toluene	602	720	6.3	84.2
		611	720	5.7	82.5
		640	720	6.2	83.9
		663	720	7.0	85.7

The structures we have discovered have enhanced symmetry and bear functional groups, and can be used to construct high-ordered supramolecular assemblies.

Experimental Section

Synthesis of 2-(3,5-Di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1a). 1-Bromo-3,5-di-*tert*-butylbenzene (600 mg, 2.2 mmol), bis(pinacolato)diboron (622 mg, 2.45 mmol), potassium acetate (657 mg, 6.7 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (90 mg, 0.11 mmol) were loaded into a 40 mL vial. The vial was flushed with argon for 5 min. Dry DMSO (20 mL) was added and the reaction mixture was stirred at 80 °C for 20 h, and then cooled to room temperature. The dark brown solution was diluted with toluene, then the organic layer was washed with water (3×50 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 100 eluting with hexane/ethyl acetate 15:1. The product **1a** (663 mg, 94%) was obtained as a white solid. **1a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 2.0 Hz, 2H, arom H), 7.54 (t, J = 2.0 Hz, 1H, arom H), 1.34 (s, 18 H, *tert*-butyl H), 1.34 (s, 12 H, methyl H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.1, 150.1, 129.0, 125.8, 83.8, 35.0, 31.7, 25.1; MS (ESI-TOF, positive mode, acetone/acetonitrile) m/z 317.1258 $[M + H]^+$ (calcd 317.2656 $[C_{20}H_{33}BO_2 + H]^+$). The dimer **1b** was not observed in this reaction, but it was formed when the reaction mixture was stirred at 80 °C for 4 days. **1b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, J = 1.87 Hz, 2H, arom H), 7.37 (d, J = 1.87 Hz, 4H, arom H), 1.38 (s, 36H, *tert*-butyl H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 142.5, 122.4, 121.2, 35.2, 31.8.

Synthesis of 3-Hydroxyphthalonitrile (2)[30]. 3-Nitrophthalonitrile (2.0 g, 11.6 mmol) was dissolved in DMSO (30 mL) and K_2CO_3 (1.8 g, 12.7 mmol) and $NaNO_2$ (0.8 g, 11.6 mmol) were added. The reaction mixture was refluxed for 30 min under argon atmosphere and then cooled to room temperature. The reaction mixture was diluted with water (45 mL) and the mixture was acidified to pH 3 with 2 M HCl and centrifuged. The pellets were collected, resuspended in water, and centrifuged again. The supernatant liquid was discarded and the residue was washed with methanol. The crude product was dissolved in acetone and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica 100 eluting with acetone. Recrystallization from glacial acetic acid gave the product **2** (702 mg, 65%) as a yellow solid. ^{1}H NMR (300 MHz, DMSO) δ 12.04 (s, 1H, arom OH), 7.69 (t, J = 8.03 Hz, 1H, arom H), 7.52 (dd, J_1 = 7.7 Hz, J_2 = 0.9 Hz, 1H, arom H), 7.36 (dd, J_1 = 8.6 Hz, J_2 = 0.9 Hz, 1H, arom H); ^{13}C NMR (75 MHz, DMSO) δ 161.3, 135.4, 124.7,121.7,116.1, 114.9, 114.2, 100.8; MS (ESI-TOF, negative mode, acetonitrile) m/z 143.0256 $[M - H]^-$ (calcd 143.0245 $[C_8H_4N_2O - H]^-$).

Synthesis of Trifluoromethanesulfonic Acid 2,3-Dicyanophenyl Ester (3). 3-Hydroxyphthalonitrile **2** (50 mg, 0.35 mmol) was dissolved in DCM (5 mL). Et_3N (50 μL, 0.35 mmol) was added and the reaction mixture was stirred at room temperature for 30 min under argon atmosphere. The reaction mixture was cooled to 0 °C on an ice bath and trifluoromethanesulfonyl chloride (40 μL, 0.35 mmol) was slowly added. The resulting mixture was stirred at 0 °C for 30 min, followed by stirring for 16 h at room temperature. Diethyl ether (10 mL) was added and the mixture was filtered, washed with brine (10 mL), dried over $MgSO_4$, and evaporated. The triflate **3** was purified by column chromatography on silica 100 eluting with $CHCl_3$. The product **3** (86 mg, 89%) was obtained as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 2H, arom H), 7.77 (dd, J_1 = 6.8 Hz, J_2 = 2.8 Hz 1H, arom H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 135.4, 133.1, 127.2, 120.9, 118.6, 116.6, 114.1, 110.6; ^{19}F NMR (282 MHz, $CDCl_3$) −72.58; MS (ESI-TOF, negative mode, acetone) m/z 274.9731 $[M - H]^-$ (calcd 274.9738 $[C_9H_3F_3N_2O_3S - H]^-$).

Synthesis of 3′,5′-Di-*tert*-butylbiphenyl-2,3-dicarbonitrile (4). 2-(3,5-Di-*tert*-butylphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane **1** (300 mg, 0.95 mmol), trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** (262 mg, 0.95 mmol), K_3PO_4 (604.9 mg, 2.85 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (38.8 mg, 0.048 mmol) were stirred in a mixture of toluene (10 mL) and water (10 mL) at 90 °C for 24 h. The reaction mixture was cooled to room temperature and diluted with water and toluene. The organic layer was separated, washed with water (2 × 30 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$. The product **4** (257 mg, 85%) was obtained as a light brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.74 (m, 3H, arom H), 7.56 (t, J = 1.8 Hz, 1H, arom H), 7.38 (d, J = 1.8 Hz, 2H, arom H), 1.38 (s, 18H, *tert*-butyl H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 148.7, 135.8, 134.4, 132.9, 131.9, 123.8, 123.3, 117.5, 116.0, 115.7, 114.7, 35.3, 31.5; MS (ESI-TOF, positive mode, $CHCl_3$/EtOH) m/z 317.2018 $[M + H]^+$ (calcd 317.2020 $[C_{22}H_{24}N_2 + H]^+$).

Synthesis of 3-(3-Bromophenyl)propan-1-ol (5). 3-(3-Bromophenyl)propionic acid (1.008 g, 4.36 mmol) was dissolved in THF (20 mL), then the mixture was cooled on an ice bath under argon atmosphere for 40 min. $BH_3\cdot THF$ (7 mL, 7 mmol) was added dropwise to the solution. The reaction mixture was stirred on an ice bath for 1 h, and then refluxed under argon atmosphere for 1 h. The reaction was quenched with water (4 mL). The solvents were evaporated, and the residue was extracted with $CHCl_3$ (40 mL). The organic layer was washed with H_2O/$NaHCO_3$ (2 × 80 mL), and then with water (80 mL). The solvent was evaporated under reduced pressure. The product **5** (900 mg, 96%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−7.25 (m, 1H, arom H), 7.25−7.20 (m, 1H, arom H), 7.08−6.99 (m, 2H, arom H), 3.55 (t, J = 6.3 Hz, 2H, $-CH_2-$), 2.58 (t, J = 7.5 Hz, 2H, $-CH_2-$), 2.01 (s, 1H, −OH), 1.82 (m, 2H, $-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 131.8, 130.2, 129.5, 127.5, 122.7, 62.2, 34.1, 32.0.

Synthesis of Acetic Acid 3-(3-Bromophenyl)propyl Ester (6). 3-(3-Bromophenyl)propan-1-ol **5** (900 mg, 4.1 mmol) was dissolved in pyridine (30 mL). Acetic anhydride (0.765 mL,

8 mmol) and DMAP (36 mg, 0.3 mmol) were added. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure. The oily residue was dissolved in $CHCl_3$ (40 mL) and washed first with diluted HCl (pH 3, 80 mL) and then with water (3 × 80 mL). The solvent was evaporated under reduced pressure to yield the product **6** (950 mg, 93%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.21 (m, 2H, arom H), 7.10−6.98 (m, 2H, arom H), 3.98 (t, J = 6.5 Hz, 2H, $-CH_2-$), 2.57 (t, J = 7.5 Hz, 2H, $-CH_2-$), 1.96 (s, 3H, $-CH_3$), 1.91−1.78 (m, 2H, $-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 143.8, 131.7, 130.3, 129.5, 127.4, 122.8, 63.9, 32.1, 30.2, 21.3.

Synthesis of Acetic Acid 3-[3-(4,4,5,5-Tetramethyl[1,3,2]-dioxaborolan-2-yl)phenyl]propyl Ester (7a). Acetic acid 3-(3-bromophenyl)propyl ester **6** (272.7 mg, 1.06 mmol), bis(pinacolato)diboron (334.4 mg, 1.32 mmol), potassium acetate (323.9 mg, 3.3 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (44.9 mg, 0.055 mmol) were suspended in DMSO (10 mL). The vial was flushed with argon for 10 min and sealed. The reaction mixture was stirred at 80 °C for 6 h and then cooled to room temperature. The dark brown solution was diluted with toluene and the organic layer was washed with water (3 × 50 mL). The solvent was evaporated under reduced pressure. The crude product was purified on Combiflash Companion, using hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane 100% (2 min), hexane 100% to hexane/ethyl acetate 70:30 (8 min), hexane/ethyl acetate 70:30 (5 min), hexane 100% (1 min)). The product **7a** (275 mg, 85%) was obtained as a colorless oil from the second fraction (t_R = 6 min). **7a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.61 (m, 2H, arom H), 7.31−7.27 (m, 2H, arom H), 4.08 (t, J = 6.6 Hz, 2H, $-CH_2-$), 2.69 (t, J = 7.6 Hz, 2H, $-CH_2-$), 2.06 (s, 3H, $-CH_3$), 2.02−1.90 (m, 2H, $-CH_2-$), 1.35 (s, 12H, methyl H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 140.7, 135.0, 132.8, 131.8, 128.3, 84.0, 83.7, 64.2, 32.4, 30.5, 25.2, 25.0, 21.5; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 327.1707 $[M + Na]^+$ (calcd 327.1747 $[C_{17}H_{25}BO_4 + Na]^+$). The dimer **7b** was observed only in trace amount in the third fraction (t_R = 8 min). **7b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.32 (m, 6H, arom H), 7.19−7.15 (m, 2H, arom H), 4.12 (t, J = 6.64 Hz, 4H, $-CH_2-$), 2.76 (t, J = 7.55 Hz, 4H, $-CH_2-$), 2.06 (s, 6H, $-CH_3$), 2.02−1.93 (m, 4H, $-CH_2-$).

Synthesis of Acetic Acid 3-(2′,3′-Dicyanobiphenyl-3-yl)propyl Ester (8a). Acetic acid 3-[3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)phenyl]propyl ester **7** (200 mg, 0.66 mmol), trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** (181.6 mg, 0.66 mmol), K_3PO_4 (420.2 mg, 1.98 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (27 mg, 0.033 mmol) were stirred in a mixture of toluene (5 mL) and water (5 mL) at 90 °C for 20 h. The reaction mixture was cooled to room temperature and diluted with toluene and water. The organic layer was washed with water (3 × 30 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane/ethyl acetate 9:1 (1 min), hexane/ethyl acetate 9:1 to hexane/ethyl acetate 1:3 (8 min), hexane/ethyl acetate 1:3 (3 min), hexane 100% (1 min)). The product **8a** (130 mg, 65%) was obtained as a greenish oil from the second fraction (t_R = 6 min). **8a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.75 (m, 3H, arom H), 7.49−7.42 (m, 1H, arom H), 7.40−7.31 (m, 3H, arom H), 4.12 (t, J = 6.5 Hz, 2H, $-CH_2-$), 2.79 (t, J = 7.5 Hz, 2H, $-CH_2-$), 2.06 (s, 3H, $-CH_3$), 2.05−1.96 (m, 2H, $-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 147.6, 142.4, 136.7, 134.4, 133.1, 132.2, 129.9, 129.4, 128.9, 126.6, 117.6, 115.9, 115.5, 114.6, 63.7, 32.3, 30.2, 21.1; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 305.1313 $[M + H]^+$ (calcd 305.1290 $[C_{19}H_{16}N_2O_2 + H]^+$). Side product **8b** was obtained from the third fraction (t_R = 10 min). **8b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.74 (m, 3H, arom H), 7.49−7.32 (m, 4H, arom H), 3.69 (t, J = 6.45 Hz, 2H, $-CH_2-$), 2.82 (t, J = 7.78 Hz, 2H, $-CH_2-$), 2.00−1.89 (m, 2H, $-CH_2-$), 1.42 (s, br, 1H, −OH).

Synthesis of Acetic Acid 3-(4,4,5,5-Tetramethyl[1,3,2]dioxaborolan-2-yl)benzyl Ester (9a). (3-Bromophenyl)methanol: $NaBH_4$ (228 mg, 6 mmol) was added to a mixture of ethanol (4.4 mL) and *m*-bromobezaldehyde (1.28 mL, 11 mmol) on an ice bath. The reaction mixture was stirred on an ice bath for 1 h. The solvent was evaporated under reduced pressure. The white solid was dissolved in water. The water layer was washed with ether (3 × 30 mL). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The product (1.95 g, 95%) was obtained as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, br, 1H, arom H), 7.44−7.39 (m, 1H, arom H), 7.31−7.26 (m, 1H, arom H), 7.24 (t, J = 7.5 Hz, 1H, arom H), 4.67 (d, J = 5.6 Hz, 2H, $-CH_2-$), 1.78 (br, 1H, −OH). **Acetic acid 3-bromobenzyl ester:** (3-Bromophenyl)methanol (880.4 mg, 4.71 mmol) was dissolved in pyridine (20 mL), then DMAP (57.5 mg, 0.47 mmol) and acetic anhydride (0.89 mL, 9.4 mmol) were added, and the reaction mixture was stirred over the weekend at room temperature. The solvent was evaporated under reduced pressure. The reaction mixture was diluted with $CHCl_3$ and washed with water (3 × 20 mL). The solvent was evaporated under reduced pressure. The crude product was purified on silica 100 eluting with $CHCl_3$. The product (1.06 g, 98%) was obtained from the first fraction as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 1H, arom H), 7.47−7.42 (m, 1H, arom H), 7.30−7.25 (m, 1H, arom H), 7.22 (t, J = 7.5 Hz, 1H, arom H), 5.06 (s, 2H, $-CH_2-$), 2.11 (s, 3H, $-CH_3$). **Acetic acid 3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)benzyl ester (9a):** Acetic acid 3-bromobenzyl ester (180.8 mg, 0.8 mmol)·CH_2Cl_2, bis(pinacolato)diboron (220.5 mg, 0.87 mmol), potassium acetate (232.6 mg, 2.37 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (32.3 mg, 0.04 mmol) were loaded into a 40 mL vial. The vial was flushed with argon for 5 min. Dry DMSO (10 mL) was added and the reaction mixture was stirred at 80 °C for 4 h, and then cooled to room temperature. The dark brown solution was diluted with toluene, then the organic layer was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane/ethyl acetate 9:1 (1 min), hexane/ethyl acetate 9:1 to hexane/ethyl acetate 1:1 in 5 min, hexane/ethyl acetate 1:1 (4 min), hexane/ethyl acetate 3:7 (2 min)). The product **9a** (145.3 mg, 67%) was obtained as a colorless oil from the second fraction (t_R = 2 min). The dimer **9b** (10.9 mg, 5%) was obtained from the third fraction as side product (t_R = 3 min). **9a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−7.74 (m, 2H, arom H), 7.48−7.42 (m, 1H, arom H), 7.41−7.32 (m, 1H, arom H), 5.10 (s, 2H, $-CH_2-$), 2.09 (s, 3H, $-CH_3$), 1.34 (s, 12H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 135.3, 134.84, 134.79, 131.4, 128.3, 84.1, 66.6, 25.0, 21.3; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 299.1421 $[M + Na]^+$ (calcd 299.1433 $[C_{15}H_{21}B_2O_4 + Na]^+$). **9b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.52 (m, 4H, arom H), 7.44 (t, J = 7.47 Hz, 2H, arom H), 7.38−7.32 (m, 2H, arom H), 5.17 (s, 4H, $-CH_2-$), 2.12 (s, 6H, $-CH_3$); MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 299.1314 $[M + H]^+$ (calcd 299.1283 $[C_{18}H_{18}O_4 + H]^+$).

Synthesis of Acetic Acid 2-[3-(4,4,5,5-Tetramethyl[1,3,2]dioxaborolan-2-yl)phenoxy]ethyl Ester (10a). 2-(3-Bromophenoxy)-ethanol: 3-Bromophenol (0.5 g, 2.89 mmol), acetone (20 mL), and K_2CO_3 (3.2 g. 23.1 mmol) were mixed in a 40 mL vial. 2-Chloroethanol (0.39 mL, 5.78 mmol) was added and the solution was stirred at 60 °C for 7 days. The reaction mixture was cooled and filtered. The filtration residue was washed with acetone (60 mL). Organic solutions were combined and water (3 mL) was added. The solvents were distilled off at atmospheric pressure. The oily residue was dissolved in $CHCl_3$ then washed with water (4 × 100 mL), and the solvent was evaporated under reduced

pressure. The oily residue of 2-(3-bromophenoxy)ethanol was used in the next step without further purification. **Acetic acid 2-(3-bromophenoxy)ethyl ester:** 2-(3-Bromophenoxy)ethanol (627 mg, 2.89 mmol) was dissolved in pyridine (15 mL). Acetic anhydride (0.57 mL, 5.78 mmol) and DMAP (36 mg, 0.29 mmol) were added and the reaction mixture was stirred at 58 °C overnight. The yellow solution was evaporated. The oily residue was dissolved in $CHCl_3$ (30 mL) and washed with water (5 × 100 mL), and then the solvent was evaporated under reduced pressure. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.05 (m, 3H, arom H), 6.89−6.81 (m, 1H, arom H), 4.41 (t, J = 4.99, 2H, $-CH_2-$), 4.14 (t, J = 5.22, 2H, $-CH_2-$), 2.10 (s, 3H, $-CH_3$); MS (ESI-TOF, positive mode, methanol) m/z 260.9955 $[M + H]^+$ (calcd 260.9950 $[C_{10}H_{11}BrO_3 + H]^+$). **Acetic acid 2-[3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)phenoxy]ethyl ester 10a:** Acetic acid 2-(3-bromophenoxy)ethyl ester (284.2 mg, 1.1 mmol), bis-(pinacolato)diboron (334.4 mg, 1.32 mmol), potassium acetate (323.9 mg, 3.3 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (44.9 mg, 0.055 mmol) were loaded into a 40 mL vial. The vial was flushed with argon for 5 min. Dry DMSO (10 mL) was added and the reaction mixture was stirred at 80 °C for 22 h, and then cooled to room temperature. The dark brown solution was diluted with toluene, then the organic layer was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane 100% (1 min), hexane 100% to hexane/ethyl acetate 7:3 in 8 min, hexane/ethyl acetate 7:3 (5 min), hexane 100% (1 min)). The product **10a** (100 mg, 30%) was obtained as a colorless oil from the third fraction (t_R = 6 min). Side product **10b** was not collected. **10a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.40 (d, J = 6.94 Hz, 1H, arom H), 7.36−7.27 (m, 3H, arom H), 4.42 (t, J = 4.96 Hz, 2H, $-CH_2-$), 4.21 (t, J = 4.96 Hz, 2H, $-CH_2-$), 2.10 (s, 3H, $-CH_3$), 1.34 (s, 12H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 158.1, 129.2, 127.8, 119.6, 118.7, 84.0, 66.0, 63.1, 25.0, 21.0; MS (ESI-TOF, positive mode, methanol) m/z 329.1549 $[M + Na]^+$ (calcd 329.1539 $[C_{16}H_{23}BO_5 + Na]^+$).

Synthesis of Acetic Acid 2-[2-(4,4,5,5-Tetramethyl[1,3,2]dioxaborolan-2-yl)phenoxy]ethyl Ester (11a). 2-(2-Bromophenoxy)-ethanol: 2-Bromophenol (0.5 g, 2.89 mmol), acetone (15 mL), and K_2CO_3 (3.2 g, 23.1 mmol) were mixed in a 40 mL vial. 2-Chloroethanol (0.39 mL, 5.78 mmol) was added and the solution was stirred at 54 °C for 4 days. The reaction mixture was cooled and filtered. The filtration residue was washed with acetone (60 mL). Organic solutions were combined and water (3 mL) was added. The solvents were distilled off at atmospheric pressure. The oily residue was dissolved in $CHCl_3$ then washed with water (3 × 100 mL), and the solvent was evaporated under reduced pressure. The oily residue of 2-(2-bromophenoxy)-ethanol was used in the next step without further purification. MS (ESI-TOF, positive mode, MeOH) m/z 238.9685 $[M + Na]^+$ (calc. 238.9684 $[C_8H_9BrO_2 + Na]^+$). **Acetic acid 2-(2-bromophenoxy)ethyl ester:** 2-(2-Bromophenoxy)ethanol (1.07 g, 4.9 mmol) was dissolved in pyridine (20 mL). Acetic anhydride (0.94 mL, 9.8 mmol) and DMAP (60 mg, 0.49 mmol) were added and the reaction mixture was stirred at room temperature overnight. The solvent was evaporated, and the oily residue was dissolved in $CHCl_3$ (30 mL) and washed with water (5 × 100 mL). The solvent was evaporated under reduced pressure. The residual yellow oil was dissolved in $CHCl_3$ (20 mL). The organic layer was washed with HCl (pH 3, 80 mL) and then with water (4 × 80 mL). The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with $CHCl_3$ (flow rate: 30 mL/min). The product (1.15 g, 91%) was obtained from the first fraction. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, J_1 = 7.52 Hz, J_2 = 1.96 Hz, 1H, arom H), 7.42−7.33 (m, 1H, arom H), 6.97 (t, J = 7.20 Hz, 1H, arom H), 6.84 (d, J = 8.34 Hz, 1H, arom H), 4.43 (t, J = 5.23 Hz, 2H, $-CH_2-$), 4.17 (t, J = 4.74 Hz, 2H, $-CH_2-$), 2.07 (s, 3H, $-CH_3$), 1.34 (s, 12H, $-CH_3$); MS (ESI-TOF, positive mode, MeOH) m/z 260.9965 $[M + H]^+$ (calcd 260.9950 $[C_{10}H_{11}BrO_3 + H]^+$). **Acetic acid 2-[2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenoxy]ethyl Ester 11a:** Acetic acid 2-(2-bromophenoxy)ethyl ester (300 mg, 1.16 mmol), bis(pinacolato)diboron (326 mg, 1.28 mmol), potassium acetate (343 mg, 3.5 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (47 mg, 0.058 mmol) were loaded into a 40 mL vial. The vial was flushed with argon for 5 min. Dry DMSO (10 mL) was added and the reaction mixture was stirred at 80 °C for 17.5 h, and then cooled to room temperature. The dark brown solution was diluted with toluene, then the organic layer was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane 100% (2 min), hexane 100% to hexane/ethyl acetate 7:3 in 7 min, hexane/ethyl acetate 7:3 (5 min), hexane 100% (1 min)). The product **11a** (143 mg, 60%) was obtained as a colorless oil from the second fraction (t_R = 7 min). The dimer **11b** was obtained from the third fraction as side product (t_R = 10 min). **11a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, J_1 = 7.23 Hz, J_2 = 1.85 Hz, 1H, arom H), 7.42−7.32 (m, 1H, arom H), 6.97 (t, J = 7.40 Hz, 1H, arom H), 6.84 (d, J = 8.41 Hz, 1H, arom H), 4.43 (t, J = 5.21 Hz, 2H, $-CH_2-$), 4.17 (t, J = 5.04 Hz, 2H, $-CH_2-$), 2.07 (s, 3H, $-CH_3$), 1.34 (s, 12 H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 163.4, 136.4, 132.5, 121.2, 112.7, 83.7, 67.0, 63.3, 25.0, 21.1; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 307.1731 $[M + H]^+$ (calcd 307.1720 $[C_{16}H_{23}BO_5 + H]^+$). **11b:** MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 381.1352 $[M + Na]^+$ (calcd 381.1314 $[C_{20}H_{22}O_6 + Na]^+$).

Synthesis of Acetic Acid 2′,3′-Dicyanobiphenyl-3-ylmethyl Ester (12a). Acetic acid 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)benzyl ester **9a** (100 mg, 0.36 mmol), trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** (100 mg, 0.36 mmol), K_3PO_4 (229.2 mg, 1.08 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (14.7 mg, 0.018 mmol) were stirred in a mixture of toluene (5 mL) and water (5 mL) at 90 °C for 24 h. The reaction mixture was cooled to room temperature, then diluted with water and toluene. The organic layer was separated, washed with water (2 × 30 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 100 eluting with $CHCl_3$/EtOH 18:1. The protected product **12a** (61.2 mg, 62%) was obtained from the second fraction (t_R = 6 min) as a light brown solid. The deprotected compound **12b** (19.2 mg, 7%) was obtained from the third fraction as side product (t_R = 10 min). **12a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.76 (m, 3H, arom H), 7.56−7.50 (m, 4H, arom H), 5.19 (s, 2H, $-CH_2-$), 2.13 (s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 147.2, 137.4, 137.0, 134.4, 133.3, 132.4, 129.6, 129.5, 128.7, 128.6, 117.6, 115.8, 115.3, 114.8, 65.8, 21.1; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 299.0782 $[M + Na]^+$ (calcd. 299.0797 $[C_{17}H_{12}N_2O_2 + Na]^+$). **12b:** ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (dd, J_1 = 6.48 Hz, J_2 = 2.50 Hz, 1H, arom H), 7.96 (d, J = 4.42 Hz, 1H, arom H), 7.95 (s, 1H, arom H), 7.54 (m, 4H, arom H), 5.32 (t, J = 5.74 Hz, 1H, −OH), 4.58 (d, J = 5.74 Hz, 2H, $-CH_2-$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.3, 143.5, 136.3, 134.7, 134.1, 132.9, 128.7, 127.5, 127.2, 126.7, 116.3, 116.0, 115.8, 113.3, 62.5; MS (ESI-TOF, positive mode, MeOH) m/z 257.0686 $[M + Na]^+$ (calcd 257.0691 $[C_{15}H_{10}N_2O + Na]^+$).

Synthesis of Acetic Acid 2-(2′,3′-Dicyanobiphenyl-3-yloxy)-ethyl Ester (13a). Acetic acid 2-[3-(4,4,5,5-tetramethyl[1,3,2]-dioxaborolan-2-yl)phenoxy]ethyl ester **10a** (50 mg, 0.16 mmol), trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** (44.2 mg, 0.16 mmol), K_3PO_4 (104 mg, 0.49 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (6.5 mg, 0.008 mmol) were stirred in a mixture of toluene (3 mL) and water (3 mL) at 90 °C for 24 h. The reaction mixture was cooled to room temperature, then diluted with

water and toluene. The organic layer was separated, washed with water (2 × 30 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane/ethyl acetate 9:1 (1 min), hexane/ethyl acetate 9:1 to hexane/ethyl acetate 1:1 in 7 min, hexane/ethyl acetate 1:1 (7 min)). The protected product **13a** (28.1 mg, 57%) was obtained as a white solid from the second fraction (t_R = 6.5 min). The deprotected compound **13b** (7.3 mg, 17%) was obtained from the third fraction (t_R = 12 min) as side product. **13a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86−7.74 (m, 3H, arom H), 7.44 (t, J = 8.06 Hz, 1H, arom H), 7.14 (d, J = 7.54, 1H, arom H), 7.10−7.02 (m, 2H, arom H), 4.45 (t, J = 5.28 Hz, 2H, $-CH_2-$), 4.24 (t, J = 4.53 Hz, 2H, $-CH_2-$), 2.11 (s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3. 158.9, 147.2, 138.0, 134.3, 133.1, 132.4, 130.6, 121.7, 117.5, 116.1, 115.8, 115.3, 115.2, 114.7, 66.4, 62.8, 21.2; MS (ESI-TOF, positive mode, MeOH) m/z 329.0916 $[M + Na]^+$ (calcd. 329.0902 $[C_{18}H_{14}N_2O_3 + Na]^+$). **13b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.74 (m, 3H, arom H), 7.45 (t, J = 7.92 Hz, 1H, arom H), 7.16−7.04 (m, 3H, arom H), 4.16 (t, J = 4.19 Hz, 2H, $-CH_2-$), 4.04 − 3.96 (br, 2H, $-CH_2-$), 1.25 (s, 1H, −OH); ^{13}C NMR (75 MHz, DMSO) δ 158.8, 146.0, 137.8, 134.8, 134.0, 132.9, 130.1, 121.0, 116.3, 116.0, 115.86, 115.83, 114.8, 113.5, 69.8, 59.6; MS (ESI-TOF, positive mode, MeOH/DMSO) m/z 387.0789 $[M + Na]^+$ (calcd 287.0797 $[C_{16}H_{12}N_2O_2 + Na]^+$).

Synthesis of Acetic Acid 2-(2′,3′-Dicyanobiphenyl-2-yloxy)-ethyl Ester (14a). Acetic acid 2-[2-(4,4,5,5-tetramethyl[1,3,2]-dioxaborolan-2-yl)phenoxy]ethyl ester **11a** (96 mg, 0.31 mmol), trifluoromethanesulfonic acid 2,3-dicyanophenyl ester **3** (85 mg, 0.31 mmol), K_3PO_4 (197 mg, 0.93 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (12.7 mg, 0.0155 mmol) were stirred in a mixture of toluene (4 mL) and water (4 mL) at 110 °C for 14 h. The reaction mixture was cooled to room temperature and diluted with water and toluene. The organic layer was separated, washed with water (4 × 100 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by Combiflash chromatography eluting with hexane/ethyl acetate gradient (flow rate: 30 mL/min, hexane/ethyl acetate 9:1 (1 min), hexane/ethyl acetate 9:1 to hexane/ethyl acetate 1:1 in 4 min, hexane/ethyl acetate 1:1 (9 min), hexane 100% (1 min)). The protected product **14a** (34 mg, 39%) was obtained from the second fraction (t_R = 6 min). The deprotected compound **14b** (21 mg, 28%) was obtained from the third fraction as side product (t_R = 12 min). **14a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.66 (m, 3H, arom H), 7.45 (t, J = 7.98 Hz, 1H, arom H), 7.25 (dd, J_1 = 6.81 Hz, J_2 = 1.74 Hz, 1H, arom H), 7.10 (t, J = 7.39 Hz, 1H, arom H), 7.02 (d, J = 8.25 Hz, 1H, arom H), 4.37−4.28 (m, 2H, $-CH_2-$), 4.27−4.19 (m, 2H, $-CH_2-$), 2.09 (s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 155.4, 144.5, 135.2, 132.8, 132.0, 131.6, 131.0, 126.1, 121.8, 117.1, 116.6, 116.1, 115.5, 112.3, 66.5, 62.4, 21.2; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 329.0902 $[M + Na]^+$ (calcd 329.0902 $[C_{18}H_{14}N_2O_3 + Na]^+$). **14b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.67 (m, 3H, arom H), 7.46 (t, J = 7.95 Hz, 1H, arom H), 7.25 (dd, J_1 = 7.65 Hz, J_2 = 1.84 Hz, 1H, arom H), 7.14−7.02 (m, 2H, arom H), 4.19 (t, J = 4.90 Hz, 2H, $-CH_2-$), 3.91 (q, br, 2H, $-CH_2-$), 2.00 (t, br, J = 6.27 Hz, 1H, −OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 144.8, 135.6, 133.1, 132.2, 131.8, 131.3, 125.9, 121.7, 116.8, 116.6, 116.0, 112.7, 105.0, 70.0, 61.5; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 287.0807 $[M + Na]^+$ (calcd 287.0797 $[C_{16}H_{12}N_2O_2 + Na]^+$).

Synthesis of 1,8,15,22-Tetrakis[(3,5-di-*tert*-butyl)phenyl]phthalocyanine (15). Lithium shots (21.2 mg, 3.05 mmol) were dissolved in pentanol (5 mL) at heating under argon atmosphere. 3′,5′-Di-*tert*-butylbiphenyl-2,3-dicarbonitrile **4** (50 mg, 0.16 mmol) was added, and the reaction mixture was flushed with argon and refluxed for 5 h. The dark green solution was cooled to room temperature and diluted with $CHCl_3$, then the organic layer was washed with water (3 × 50 mL). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 100 eluting with $CHCl_3$. The product **15** (11.6 mg, 23%) was obtained from the first fraction as a dark green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (dd, J_1 = 7.32 Hz, J_2 = 1.27 Hz, 4H, arom H), 8.02 (dd, J_1 = 7.46 Hz, J_2 = 1.41 Hz, 4H, arom H), 8.00−7.94 (m, 8H, arom H), 7.87 (d, J = 1.74 Hz, 8H, arom H), 1.50 (s, 72 H, $-CH_3$), −0.32 (s, br, 2H, −NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 141.4, 140.3, 132.1, 129.1, 124.4, 122.9, 122.1, 35.5, 32.1, 29.9; MS (ESI-TOF, negative mode, $CHCl_3$/EtOH) m/z 1266.7869 $[M - H]^-$ (calcd 1266.7853 $[C_{88}H_{98}N_8 - H]^-$).

Synthesis of 3,3′,3″,3‴-(29*H*,31*H*-Phthalocyanine-1,8,15,22-tetrayltetra-3,1-phenylene)tetrapropan-1-ol (16). Lithium shots (400 mg, 57.6 mmol) and octanol (40 mL) were refluxed under argon atmosphere for 1 h. Acetic acid 3-(2′,3′-dicyanobiphenyl-3-yl)propyl ester **8a** (20 mg, 0.066 mmol) was added to warm lithium octoxide solution (5 mL) under argon atmosphere. The reaction mixture was stirred at 60 °C over the weekend. The dark green solution was cooled to room temperature, and diluted with H_2O/MeOH 1:1 solution. The organic layer was washed with water (2 × 30 mL), then water and methanol were evaporated under reduced pressure. Hexane (60 mL) was added to the residual octanol/phthalocyanine mixture, which was then left to crystallize overnight. The precipitate was filtered, washed with hexane and ether, and then dissolved in $CHCl_3$/EtOH mixture. The solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica 100 eluting with $CHCl_3$/EtOH 10:1. Two fractions were observed. The product **16** (7.4 mg, 43%) was obtained from the second fraction as a blue solid. Another regioisomer (2.2 mg, 13%) was obtained from the first fraction. **16:** ^{1}H NMR (300 MHz, $CDCl_3$ + MeOD) δ 8.40 (d, J = 6.92 Hz, 4H, arom H), 8.04 (d, J = 7.16 Hz, 4H, arom H), 8.01−7.88 (m, 8H, arom H), 7.75−7.62 (m, 12 H, arom H), 3.71 (t, J = 6.45 Hz, 8H, $-CH_2-$), 2.93 (t, J = 8.12 Hz, 8H, $-CH_2-$), 2.11−1.98 (m, 8H, $-CH_2-$); MS (ESI-TOF, negative mode, MeOH) m/z 1049.4500 $[M - H]^-$ (calcd 1049.4503 $[C_{68}H_{58}N_8O_4 - H]^-$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.1, 139.83, 139.82, 131.0, 129.4, 128.3, 128.0, 61.0, 35.0, 32.6.

Synthesis of 1,8,15,22-Tetrakis[3-(hydroxymethyl)phenyl]phthalocyanine (17). Lithium shots (3.5 mg, 0.51 mmol) were dissolved in pentanol (5 mL) at heating under argon atmosphere. Acetic acid 3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)benzyl ester **9a** (70 mg, 0.25 mmol) was added, and the reaction mixture was flushed with argon and refluxed for 5 h. The dark green solution was cooled to room temperature and diluted with $CHCl_3$, then the organic layer was washed with water (3 × 40 mL). The solvent was evaporated under reduced pressure. In TLC three different green fractions were visible. The crude product was purified by column chromatography on silica 100 eluting with $CHCl_3$/EtOH 10:1. Purification of the products is very difficult due to insolubility of phthalocyanines. ^{1}H NMR spectra of the fractions were complex due to aggregation of phthalocyanines. MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 939.3442 $[M + H]^+$ (calcd 939.3407 $[C_{60}H_{42}N_8O_4 + H]^+$).

Synthesis of Phthalocyanines (18a−c): 3-{3-[8,15,22-Tris(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanin-1-yl]phenyl}propan-1-ol (18a), 3,3′-{[8,22-Bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,15-diyl]di-3,1-phenylene}dipropan-1-ol (18b), 3,3′-{[8,15-Bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,22-diyl]di-3,1-phenylene}dipropan-1-ol (18c). Lithium shots (100 mg, 14.4 mmol) were dissolved in pentanol (10 mL) at heating under argon atmosphere. 3′,5′-Di-*tert*-butylbiphenyl-2,3-dicarbonitrile **4** (70 mg, 0.22 mmol) and acetic acid 3-(2′,3′-dicyanobiphenyl-3-yl)propyl ester **8a** (50 mg, 0.16 mmol) were added. The reaction mixture was flushed with argon and stirred at 80 °C for 23 h. The dark green solution was

cooled to room temperature and diluted with $CHCl_3$. The organic layer was washed with water (3 × 30 mL) and the solvents were evaporated under reduced pressure. Altogether seven different phthalocyanines were formed in the reaction from which phthalocyanines **18a**−**c** were separated and purified for further reactions. The reaction products **18a**−**c** were separated by column chromatography on silica 60 eluting at first with $CHCl_3$ and then with $CHCl_3$/ethanol 10:1. Compound **18a** was obtained from the second green fraction, and **18b** and **18c** were obtained from the third and fourth fractions, respectively. Compound **18a** was further purified by column chromatography on silica 60 eluting with $CHCl_3$. The product **18a** (8.8 mg, 18%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70−8.64 (m, 1H, arom H), 8.43−8.38 (m, 3H, arom H), 8.14−8.10 (m, 1H, arom H), 8.09 (d, J = 1.80 Hz, 1H, arom H), 8.08−8.05 (m, 3H, arom H), 8.05−8.00 (m, 4H, arom H), 7.99 (s, 1H, arom H), 7.98−7.95 (m, 3H, arom H), 7.91−7.87 (m, 6H, arom H), 7.79 (t, J = 7.56 Hz, 1H, arom H), 7.70 (d, J = 7.92 Hz, 1H, arom H), 3.77 (t, J = 6.44 Hz, 2H, $-CH_2-$), 3.05 (t, J = 7.93 Hz, 2H, $-CH_2-$), 2.16−2.05 (m, 2H, $-CH_2-$), 1.51 (d, J= 0.75 Hz, 36H, *tert*-butyl H), 1.50 (s, 18H, methyl H), −0.29 (s, 2H, −NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.69, 150.68, 150.66, 141.62, 141.57, 141.4, 140.6, 140.21, 140.19, 140.1, 132.4, 132.24, 132.17, 131.0, 129.4, 129.17, 129.12, 128.4, 128.3, 128.2, 124.3, 123.2, 123.0, 122.3, 122.12, 122.07, 62.6, 35.4, 34.5, 32.5, 32.0; MS (ESI-TOF, negative mode, $CHCl_3$/MeOH) m/z 1211.7081 $[M - H]^-$ (calcd 1211.7003 $[C_{83}H_{88}N_8O - H]^-$). Phthalocyanines **18b** and **18c** were separated by column chromatography on silica 60 eluting with $CHCl_3$. **18b** was purified by column chromatography on silica 60 eluting with $CHCl_3$/ethanol 10:1. The product **18b** (13.1 mg, 28%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (m, 2H, arom H), 8.39 (dd, J_1 = 7.20 Hz, J_2 = 1.50 Hz, 2H, arom H), 7.86−8.04 (m, 8H, arom H), 8.01 (m, 3H, arom H), 7.98−7.94 (m, 3H, arom H), 7.88 (d, J = 1.90 Hz, 4H, arom H), 7.79 (t, J = 7.50 Hz, 2H, arom H), 7.70 (d, J = 7.70 Hz, 2H, arom H), 3.76 (t, J = 6.30 Hz, 4H, $-CH_2-$), 3.04 (t, J = 7.90 Hz, 4H, $-CH_2-$), 2.15−2.04 (m, 4H, $-CH_2-$), 1.50 (s, 36H, *tert*-butyl H), −0.28 (s, 2H, −NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 141.65, 141.57, 140.5, 140.2, 140.1, 132.4, 132.2, 131.0, 129.4, 129.2, 128.4, 128.3, 128.2, 124.2, 123.2, 122.4, 122.1, 62.6, 35.4, 34.5, 32.5, 32.0, 31.7; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 1159.6279 $[M]^+$ (calcd 1159.6261 $[C_{78}H_{78}N_8O_2]^+$). **18c** was purified by column chromatography on silica 60 eluting with $CHCl_3$/ethanol 10:1. The product **18c** (13.8 mg, 29%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.61 (m, 2H, arom H), 8.40 (dd, J_1 = 7.15 Hz, J_2 = 1.40 Hz, 2H, arom H), 8.14−7.94 (m, 14H, arom H), 7.88 (dd, J_1 = 4.36 Hz, J_2 = 1.92 Hz, 4H, arom H), 7.79 (t, J = 7.41 Hz, 2H, arom H), 7.69 (d, J = 7.61 Hz, 2H, arom H), 3.77 (m, 4H, $-CH_2-$), 3.04 (t, J = 7.40 Hz, 4H, $-CH_2-$), 2.16−2.04 (m, 4H, $-CH_2-$), 1.50 (d, J = 2.32 Hz, 36H, *tert*-butyl H), −0.30 (s, 2H, −NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 161.1, 152.0, 150.48, 150.47, 141.42, 141.41, 141.40, 141.3, 140.5, 140.33, 140.29, 140.1, 140.0, 139.94, 139.92, 137.8, 135.8, 135.2, 132.7, 132.1, 130.7, 128.9, 128.1, 125.2, 124.05, 124.03, 122.85, 122.76, 122.2, 76.5, 62.32, 62.30, 53.4, 35.2, 35.1, 34.3, 31.7, 31.4, 21.4; MS (ESI-TOF, negative mode, $CHCl_3$/MeOH/acetonitrile) m/z 1157.6212 $[M - H]^-$ (calcd 1157.6169 $[C_{78}H_{78}N_8O_2 - H]^-$).

Synthesis of *tert*-Butyl 3-{3-[8,15,22-Tris(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanin-1-yl]phenyl}propyl Malonate (19a). 3-{3-[8,15,22-Tris(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanin-1-yl]phenyl}propan-1-ol **18a** (12 mg, 0.01 mmol), *tert*-butyl malonate (3.2 mg, 0.02 mmol), 2-chloro-1-methylpyridinium iodide (5.1 mg, 0.02 mmol), and Et_3N (5.6 μL, 0.04 mmol) were stirred in DCM (5 mL) at room temperature for 1 day. The reaction mixture was diluted with $CHCl_3$ and the organic layer was washed with water (3 × 30 mL). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$. The product **19a** (13.6 mg, 86%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.63 (m, 1H, arom H), 8.44−8.37 (m, 3H, arom H), 8.14 (d, J = 7.46 Hz, 1H, arom H), 8.10−7.94 (m, 12H, arom H), 7.79 (t, J = 7.46 Hz, 1H, arom H), 7.68 (d, J = 7.64 Hz, 1H, arom H), 4.27 (t, J = 6.55 Hz, 2H, $-CH_2-$), 3.27 (s, 2H, $-CO-CH_2-CO-$), 3.04 (t, J = 7.82 Hz, 2H, $-CH_2-$), 2.25−2.14 (m, 2H, $-CH_2-$), 1.51 (d, J = 1.68 Hz, 54H, *tert*-butyl H), 1.39 (s, 9H, *tert*-butyl H), −0.29 (s, 2H, −NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 165.9, 150.69, 105.68, 150.66, 141.6, 141.4, 140.9, 140.6, 140.21, 140.20, 140.19, 140.0, 132.4, 132.23, 132.17, 130.9, 129.4, 129.2, 129.1, 128.7, 128.3, 128.1, 124.3, 123.2, 123.0, 122.3, 122.11, 122.10, 122.07, 82.1, 77.4, 64.9, 43.1, 35.4, 32.5, 32.0, 30.4, 28.0; UV/vis (toluene) λ_{max}, nm (ε, M^{-1} cm^{-1}) 340 (43728), 612 (17900), 645 (25504), 674 (84039), 708 (98490); MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 1354.7711 $[M]^+$ (calcd 1354.7708 $[C_{90}H_{98}N_8O_4]^+$).

Synthesis of 2,2′-[[8,22-Bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,15-diyl]bis(3,1-phenylenepropane-3,1-diyl)] 3,3′-Di-*tert*-butyl Dimalonate (19b). 3,3′-{[8,22-Bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,15-diyl]di-3,1-phenylene}dipropan-1-ol **18b** (6.3 mg, 5 μmol), *tert*-butyl malonate (3.2 mg, 20 μmol), 2-chloro-1-methylpyridinium iodide (5.1 mg, 20 μmol) and Et_3N (5.6 μL, 40 μmol) were stirred in DCM (5 mL) at room temperature for 1 day. The reaction mixture was diluted with $CHCl_3$ and the organic layer was washed with water (3 × 30 mL). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$. The product **19b** (7.2 mg, 53%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70−8.62 (m, 2H, arom H), 8.39 (dd, J_1 = 6.95 Hz, J_2 = 1.59 Hz, 2H, arom H), 8.14 (d, J = 7.80 Hz, 2H, arom H), 8.09 (d, J = 2.81 Hz, 2H, arom H), 8.07 (s, 2H, arom H), 8.05−7.99 (m, 5H, arom H), 7.98−7.95 (m, 3H, arom H), 7.88 (d, J = 1.83 Hz, 4H, arom H), 7.79 (t, J = 7.56 Hz, 2H, arom H), 7.68 (d, J = 7.68 Hz, 2H, arom H), 4.26 (t, J = 6.46 Hz, 4H, $-CH_2-$), 3.26 (s, 4H, $-CO-CH_2-CO-$), 3.03 (t, J = 8.17 Hz, 4H, $-CH_2-$), 2.25−2.12 (m, 4H, $-CH_2-$), 1.50 (s, 36H, *tert*-butyl H), 1.38 (s, 18H, *tert*-butyl H), −0.29 (s, 2H, −NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 166.3, 165.9, 150.7, 141.7, 140.9, 140.6, 140.2, 140.0, 132.5, 130.9, 129.5, 129.5, 129.3, 128.7, 128.36, 128.34, 128.2, 124.2, 123.2, 122.3, 122.1, 82.1, 81.8, 64.9, 44.5, 43.1, 35.4, 32.5, 32.0, 30.4, 28.1, 28.0; UV/vis (toluene) λ_{max}, nm (ε, M^{-1} cm^{-1}) 341 (38519), 612 (12725), 645 (18171), 675 (61809), 709 (71615); MS (ESI-TOF, positive mode, $CHCl_3$/MeOH 1:1) m/z 1466.7505 $[M + Na]^+$ (calcd 1466.7438 $[C_{92}H_{98}N_8O_8 + Na]^+$).

Synthesis of 2,2′-[[8,15-Bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,22-diyl]bis(3,1-phenylenepropane-3,1-diyl)] 3,3′-Di-*tert*-butyl Dimalonate (19c). 3,3′-{[8,15-Bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,22-diyl]di-3,1-phenylene}dipropan-1-ol **18c** (5.0 mg, 4 μmol), *tert*-butyl malonate (2.6 mg, 16 μmol), 2-chloro-1-methylpyridinium iodide (4.1 mg, 16 μmol), and Et_3N (4.5 μL, 32 μmol) were stirred in DCM (5 mL) at room temperature for 1 day. The reaction mixture was diluted with $CHCl_3$ and the organic layer was washed with water (3 × 30 mL). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$. The product **19c** (5.8 mg, 73%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68−8.61 (m, 2H, arom H), 8.40 (d, J = 7.02 Hz, 2H, arom H), 8.13 (d, J = 7.39 Hz, 2H, arom H), 8.09−8.04 (m, 4H, arom H), 8.04−7.99 (m, 5H, arom H),7.99−7.93 (m, 3H, arom H), 7.87 (dd, J_1 = 4.60 Hz, J_2 = 1.84 Hz, 4H, arom H), 7.79 (t, J = 7.70 Hz, 2H, arom H), 7.71−7.65 (m, 2H, arom H), 4.26 (m, 4H, $-CH_2-$), 3.26 (d, J = 2.43 Hz, 4H, $-CO-CH_2-CO-$), 3.03 (t, J = 7.56 Hz, 4H, $-CH_2-$), 2.25−2.12 (m, 4H, $-CH_2-$), 1.50 (d, J = 2.50 Hz, 36H, *tert*-butyl H), 1.39 (d, J = 1.97 Hz, 18H, *tert*-butyl H), −0.29 (s, 2H, −NH); UV/vis (toluene) λ_{max}, nm (ε, M^{-1} cm^{-1}) 341 (51583), 612 (19697), 645 (28047), 675 (92713), 709 (107582); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.21, 167.20, 165.9, 150.70, 150.69, 141.7,

141.5, 140.94, 140.91, 140.6, 140.23, 140.17, 140.15, 140.0, 132.5, 132.4, 132.3, 132.2, 130.8, 129.54, 129.49, 129.24, 129.18, 128.7, 128.4, 128.3, 128.2, 128.1, 124.16, 124.24, 123.2, 123.0, 122.5, 122.3, 122.13, 122.12, 122.09, 82.1, 65.0, 64.9, 43.1, 35.4, 32.50, 32.47, 32.0, 30.43, 30.41, 28.02, 28.01; MS (ESI-TOF, positive mode, $CHCl_3$/MeOH) m/z 1442.7507 $[M]^+$ (calcd 1422.7501 $[C_{92}H_{98}N_8O_8]^+$).

Synthesis of Dyad 20a. C_{60} (9.4 mg, 13.1 μmol) was dissolved in toluene (100 mL) on ultrasonic bath for 15 min. I_2 (3.0 mg, 11.9 μmol) and *tert*-butyl 3-{3-[8,15,22-tris(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanin-1-yl]phenyl}propyl malonate **19a** (16.1 mg, 11.9 μmol) were added and the reaction flask was flushed with argon for 15 min. DBU (5.3 μL, 35.7 μmol) was added and the reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Water (1 mL) was added and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$. The product **20a** (15.0 mg, 61%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (dd, J_1 = 5.9 Hz, J_2 = 2.9, 1H, arom H), 8.43 (dd, J_1 = 7.0 Hz, J_2 = 1.7 Hz, 1H, arom H), 8.36−8.30 (m, 2H, arom H), 8.06 − 8.00 (m, 5H, arom H), 8.00−7.91 (m, 8H, arom H), 7.89 (d, J = 1.8 Hz, 2H, arom H), 7.85 (d, J = 1.8 Hz, 2H, arom H), 7.82 (d, J = 1.8 Hz, 2H, arom H), 7.81 (t, J = 7.6 Hz, 1H, arom H), 7.71 (d, J = 7.6 Hz, 1H, arom H), 4.54 (t, J = 5.6 Hz, 2H, $-CH_2-$), 3.06 (t, J = 7.5 Hz, 2H, $-CH_2-$), 2.16 − 2.25 (m, 2H, $-CH_2-$), 1.55 (s, 9H, *tert*-butyl H), 1.54 (s, 18H, *tert*-butyl H), 1.48 (d, J = 1.29 Hz, 36H, *tert*-butyl H), −0.36 (s, 2H, −NH); UV/vis (toluene) λ_{max} (ε, M^{-1} cm^{-1}) 333 (63056), 616 (10625), 651 (15595), 677 (41516), 710 (47868) nm; MS (ESI-TOF, positive, $CHCl_3$/MeOH) m/z 2073.7573 $[M]^+$ (calcd 2073.7588 $[C_{150}H_{96}N_8O_4]^+$).

Synthesis of Dyad 20b. C_{60} (4.5 mg, 6.3 μmol) was dissolved in toluene (80 mL) on ultrasonic bath for 15 min. I_2 (2.9 mg, 11.4 μmol) and 2,2′-[[8,22-bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,15-diyl]bis(3,1-phenylenepropane-3,1-diyl)] 3,3′-di-*tert*-butyl dimalonate **19b** (8.2 mg, 5.7 μmol) were added and the reaction mixture was flushed with argon for 15 min. DBU (5.1 μL, 34.2 μmol) was added and the reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Water (1 mL) was added and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$ and then on HPTLC glass plates (Silica gel 60 F_{254}, Merck) eluting with toluene. The product **20b** (2.7 mg, 22%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (dd, J_1 = 7.1 Hz, J_2 = 1.4 Hz, 2H, arom H), 8.22 (dd, J_1 = 7.4 Hz, J_2 = 1.0 Hz, 2H, arom H), 8.12−8.02 (m, 4H, arom H), 8.00−7.94 (m, 3H, arom H), 7.94−7.85 (m, 9H, aromH), 7.81−7.72 (m, 6H, arom H), 4.79−4.51 (m, 4H, $-CH_2-$), 3.21−2.86 (m, 4H, $-CH_2-$), 2.41−2.20 (m, 4H, $-CH_2-$), 1.51 (s, 18H, *tert*-butyl H), 1.44 (s, 36H, *tert*-butyl H), −0.47 (s, 2H, −NH); UV/vis (toluene) λ_{max}, nm (ε, M^{-1} cm^{-1}) 325 (43140), 621 (8762), 682 (30087), 715 (36320); MS (ESI-TOF, positive mode, $CHCl_3$/EtOH) m/z 2160.7285 $[M + H]^+$ (calcd 2160.7305 $[C_{152}H_{94}N_8O_8 + H]^+$).

Synthesis of Dyad 20c. C_{60} (10.8 mg, 15.0 μmol) was dissolved in toluene (80 mL) on ultrasonic bath for 15 min. I_2 (6.9 mg, 27.2 μmol) and 2,2′-[[8,15-bis(3,5-di-*tert*-butylphenyl)-29*H*,31*H*-phthalocyanine-1,22-diyl]bis(3,1-phenylenepropane-3,1-diyl)] 3,3′-di-*tert*-butyl dimalonate **19c** (19.6 mg, 13.6 μmol) were added and the reaction mixture was flushed with argon for 15 min. DBU (12.2 μL, 81 μmol) was added and the reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Water (1 mL) was added and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica 60 eluting with $CHCl_3$ and then on HPTLC glass plates (Silica gel 60 F_{254}, Merck) eluting with toluene. The product **20c** (10.1 mg, 34%) was obtained as a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47−8.20 (m, 4H, arom H), 8.15−7.59 (m, 22H, arom H), 4.86 (m, 4H, $-CH_2-$), 3.33−2.63 (m, 4H, $-CH_2-$), 2.47−1.97 (m, 4H, $-CH_2-$), 1.61−1.44 (m, 54H, *tert*-butyl H), −0.46 to −0.71 (m, 2H, −NH); UV/vis (toluene) λ_{max}, nm (ε, M^{-1} cm^{-1}) 324 (88204), 619 (27832), 681 (100044), 715 (117381); MS (ESI-TOF, negative mode, $CHCl_3$/MeOH) m/z 2158.7148 $[M - H]^-$ (calcd 2158.7139 $[C_{152}H_{94}N_8O_8 - H]^-$).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.