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An Application of the Stille Coupling for the Preparation of Arylated Phthalonitriles and Phthalocyanines

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Dedicated to Professor Göran Bergson on the occasion of his 65th birthday

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The substituted phthalonitriles 4-phenylphthalonitrile (**2a**), 4-(2,5-dimethoxyphenyl)phthalonitrile (**2b**) and 2-(3,4-dicyanophenyl)-4-methylpyridine (**2c**) have been prepared in good yields from 4-iodophthalonitrile **3**, the synthesis of which is also discussed, using the Stille coupling method. Such phthalonitriles are precursors for phthalocyanines with the possibility of biphenyl-like orientation of a peripheral substituent with respect to the macrocycle ring plane. As an example, **2b** was used in the preparation of tetra(dimethoxyphenyl)phthalocyanine **1a**. Both **1a** and the corresponding zinc(II) complex show good solubility in non-polar solvents such as dichloromethane.

Phthalocyanines (Fig. 1) constitute a group of macrocyclic compounds with applications in fields as diverse as materials for optical data storage, phototherapy for cancer, and redox catalysis.[1–3] Furthermore, the iron complex of the parent macrocycle can be used as an ink color base in ballpoint pens,[4] and various substituted copper phthalocyanines are employed in color photography.[5]

One reason for their usefulness is that phthalocyanines strongly absorb visible light in the far-red/near-IR region. This, in combination with the stability of the macrocycle, also make them potentially attractive for use in solar energy conversion.[1,6] A problem is their often poor solubility in many solvents. However, by proper choice of substituents on the periphery of the macrocycle or use of ligands occupying the axial positions in octahedral or square pyramidal metal phthalocyanine complexes, the problem can be diminished or even eliminated.[1] Phthalocyanines soluble in aqueous media have been prepared and studied,[7] as well as phthalocyanines which form Langmuir–Blodgett films or discotic mesophases.[3,8] The introduction of substituents can also affect the electronic absorption properties, resulting in shifts of the Q-band absorption wavelength.[1,9,10]

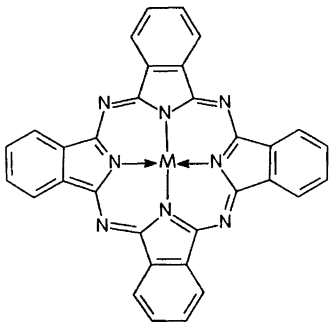

Fig. 1. Metallophthalocyanine.

Perhaps the most important requirement for applications of phthalocyanines in dye-sensitized nanocrystalline TiO_2-based photoelectrochemistry[6,11] is that they have to be soluble in solvents which are compatible with the semiconductor and which favor the adsorption of a non-aggregated monolayer of the macrocycle on the surface of the nanoparticles. If this requirement is fulfilled, questions of HOMO and LUMO energy levels, absorption maxima and photostability can be adressed – the answers of which will probably lead to further modifications of the substitution of the macrocycle.

A general objective of the current project has been to find a convenient general strategy (retrosynthetically outlined in Scheme 1) for the synthesis of peripherally substituted phthalocyanines (**1**). An important step is the formation of a bond between the substituent-to-be and the macrocycle. For practical reasons, the substitu-

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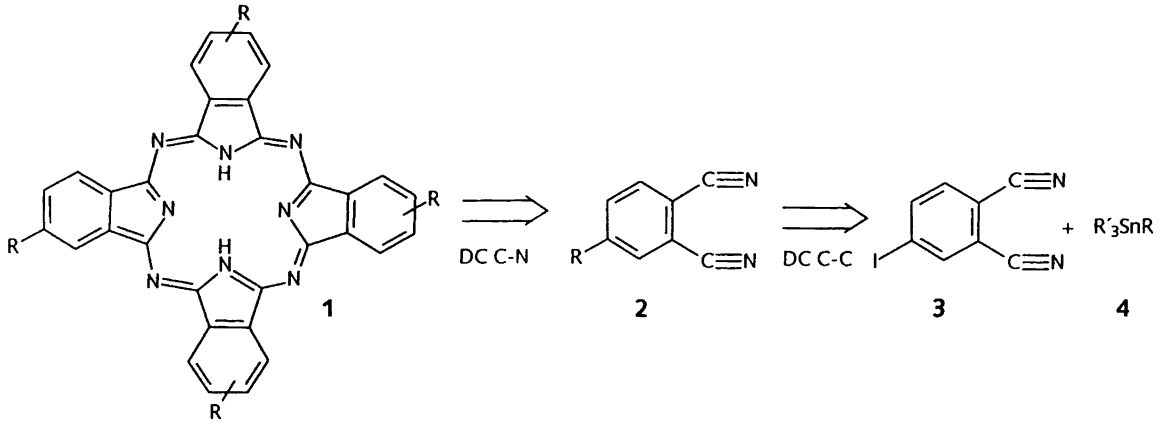


Scheme 1. Retrosynthetic scheme for the preparation of peripherally substituted phthalocynanines.

ents should be attached prior to phthalocyanine formation, i.e. the substituent should be on the phthalocyanine precursor, phthalonitrile (**2**). For stability reasons, carbon–carbon bonds are preferred over heteroatom linkages. This means that a key step in the synthetic process will be the formation of a carbon–carbon bond between a reagent containing the phthalonitrile unit (**3**) and a reagent containing the substituent group (**4**).

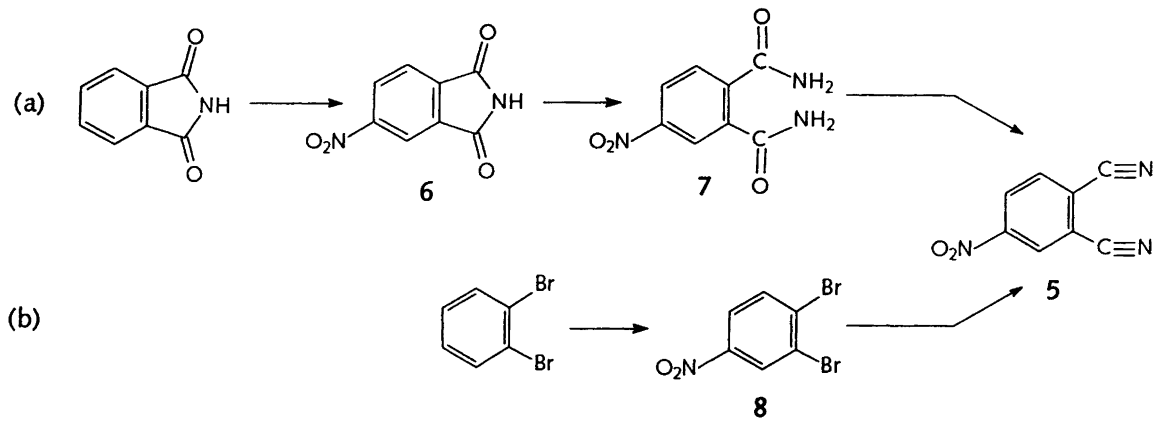
Here we present the use of the Stille coupling reaction for the preparation of precursors for arylated phthalocyanines with possibility of biphenyl-like orientation of substituent with reference to the macrocycle ring plane. Further, the use of one arylated phthalonitrile in phthalocyanine synthesis is discussed.

1. Arylated phthalonitriles by Stille coupling. Among the methods for transition-metal-catalyzed formation of carbon–carbon bonds between aromatic carbon atoms, the Stille coupling is among the most versatile. In this reaction [eqn. (1)], an organic electrophile is reacted with an organotin reagent in the presence of a palladium(0) catalyst.[12,13]

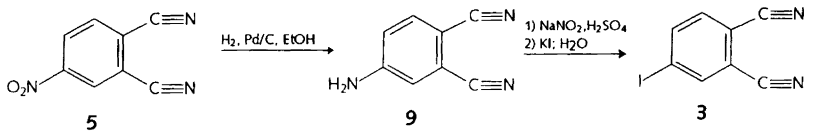
$$\text{Ar–LG} + \text{R–SnR}'_3 \xrightarrow{\text{cat. Pd(0)}} \text{Ar–R} \qquad (1)$$

Because of the electronic properties of the nitrile groups, the phthalonitrile should be the electrophile in the Stille coupling, and 4-iodophthalonitrile **3** was considered a good candidate. The substituent-to-be should thus be a tin derivative containing the desired substituent as the most easily transferred group.

In Schemes 2 and 3, the synthesis of 4-iodophthalonitrile (**3**) is outlined. An important intermediate is 4-nitrophthalonitrile (**5**), which, by the traditional pathway,[14] can be obtained in three steps from phthalimide (Scheme 2, route a). Quite unexpectedly, the dehydration of the intermediate 4-nitrophthalamide (**7**) turned out to be problematic. For some reason, the most commonly employed procedures (based on Ac_2O) yielded only small amounts of the desired product. A more powerful method, trifluoroacetic anhydride in dry pyridine–dioxane, however gave a good yield of **5**.[15] Since route (a) also, in the first step, involved a troublesome and poor-yielding recrystallisation of **6**, we decided to investigate an alternative two-step route to **5** (Scheme 2, route b). Nitration of 1,2-dibromobenzene proceeded in good yield, whereas the cyanation of 1,2-dibomo-4-nitrobenzene **8** was more difficult. Although this kind of reaction is described in the literature,[16,17] a substantial number of products was formed, non-colored as well as colored. The ideal reaction conditions and work-up



Scheme 2. Two routes to 4-nitrophthalonitrile.



Scheme 3. Preparation of 4-iodophthalonitrile.

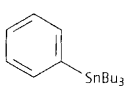
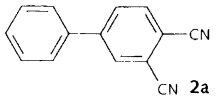
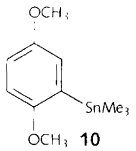
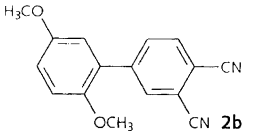
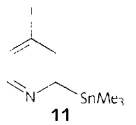
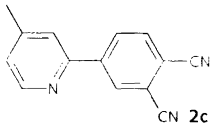
procedure for the transformation of **8** into **5** have not yet been found.

Reduction of the nitro group of **5**, directly followed by substitution of the amino group of **9** by iodide via the diazonium salt gave **3** in a reasonable yield (Scheme 3).[18]

A wide range of tetraorganotin reagents are available from the reaction of triorganotin halides with various organic anions.[12] Most reagents can be isolated, purified and stored. A disadvantage is that, although the toxicity of this group of compounds is not fully investigated, all organotin compounds should be considered toxic and handled with care. In spite of this, we considered that the advantages of the method outweighed the disadvantages, especially considering the small quantities of reagents to be handled. In Scheme 4, the straightforward preparation of two of the reagents (**10** and **11**) used in the present study is outlined.

The efficiency of the Stille coupling reaction varies for different substrates. Also the choice of the the palladium catalyst is of importance. Perhaps the most common source of Pd(0) is $Pd(PAr_3)_4$, either added as such or formed *in situ* from a Pd(0) precursor and the desired phosphine ligand. For our combinations of reagents, $Pd(PPh_3)_4$ was not the ideal catalyst. Although it promoted the coupling between iodobenzene and **3**, no coupling product was obtained between **3** and **10**. Instead, the air-stable dibenzylideneacetone complex $Pd_2dba_3 \times CHCl_3$ in DMF without added phosphine ligands, was found give good to satisfactory results, summarised in Table 1.

Table 1. Stille coupling of organostannanes with 4-iodophthalonitrile **3**.[a]

Organostannate	Coupling product	Yield[b]
		72%
		75%
		66%

[a]The reactions were carried out in DMF on a 0.1–0.5 mmol scale using 4–5 mol% of $Pd_2dba_3 \times CHCl_3$. For further details see Experimental section. [b]Isolated yield after column chromatography.

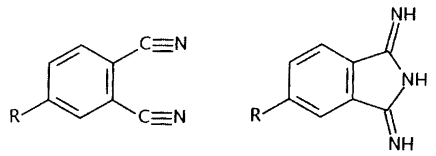
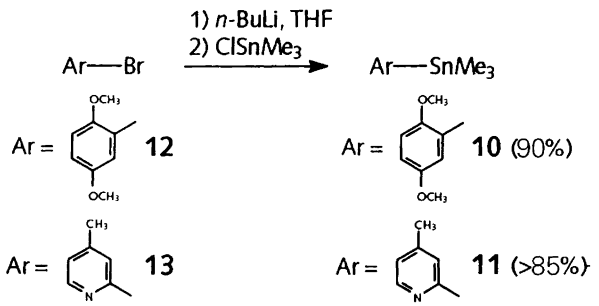


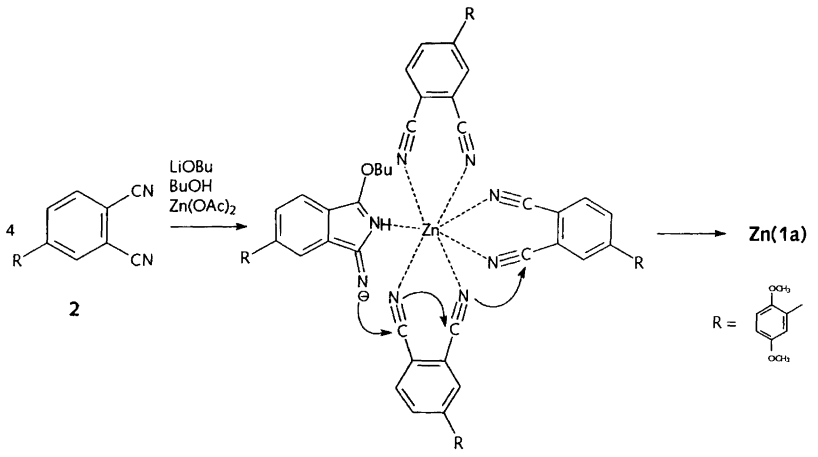
Fig. 2. Two phthalocyanine precursors, phthalonitrile and diiminoisoindole.

2. Phthalocyanine formation. The construction of the phthalocyanine macrocycle can be accomplished in various ways.[1,19,20] In the current work, pthhtalocyanine formation was accomplished using phthalonitrile **2b** as a precursor, rather than from the corresponding diiminoisoindole (Fig. 2). The formation of a phthalocyanine from four phthalonitriles involves the formation of eight new C–N bonds. Even if each of these steps proceeds in high yield, the isolated yield of phthalocyanine is usually poor to moderate, partly because of losses of material during the purification of the product mixtures.



Scheme 4. Preparation of organotin reagents **10** and **11**.

Acceptable amounts of **1a** (R = 2,5-dimethoxyphenyl) with the the green color typical of phthalocyanines was obtained following a standard procedure.[19] A problem encountered was the removal of by-products such as dimers and polymers of the phthalonitrile. During the design of the target phthalocyanine, solubility was an important issue, and **1a** is actually unusually soluble in non-polar solvents such as dichloromethane, a property which greatly simplified the purification procedure. In addition to precipitations, column chromatography on silica could also be employed with good results. Analyses (MS, UV–VIS, elemental) all gave the results expected for a phthalocyanine product. The appearance of the absorption bands in the visible region indicated that the



Scheme 5. Zn(III) as a template ion in the synthesis of a zinc phthalocyanine.

phthalocyanine is monomeric in dilute solution, whereas the broad overlapping signals in the aromatic region of the ^{1}H NMR spectrum indicated aggregation and/or that it exists as a mixture of isomers. When the reaction was carried out in the presence of a template ion (Scheme 5),[1,21] zinc(II), Zn(**1a**) was obtained. The presence of the metal was verified by the characteristic change of the absorption in the visible region compared with what was observed for **1a**.

Concluding remarks and outlook. The Stille coupling method has been shown to be applicable to the synthesis of substituted phthalonitriles. The synthesis of an aryl-substituted phthalocyanine with good solubility in non-polar solvents such as dichloromethane has been accomplished. Investigations[22] of the properties of a range of metallophthalocyanine–nanocrystalline TiO_2 systems by UV-VIS emission and fluorescence spectroscopy and by femtosecond laser spectroscopy indicate that this class of compounds might be useful for photoelectrochemical applications, provided that the right conditions for the adsorption of the right compound to the semiconductor are found. There will certainly be a demand for new phthalocyanines!

Experimental

All reagents were from commercial sources and were used without further purification. Solvents were HPLC grade and were used without further purification, except THF, which was distilled from sodium–benzophenone ketyl and diisopropyl amine (DIPA) which was distilled from CaH_2. Butyllithium (BuLi) was stored in a desiccator under argon, and used as fresh (no precipitate) 1.6 M solutions in hexane. Column chromatography was performed on Merck silica gel (230–400). Thin-layer chromatography (TLC) was carried out on Merck pre-coated silica gel 60-F_{254} plates.

NMR spectroscopy. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Unity 400 spectrometer for samples in $CDCl_3$. The chloroform signal at 7.26 ppm (for ^{1}H) or 77.0 ppm (for ^{13}C) was used as indirect reference to TMS.

UV–VIS spectroscopy. Absorption spectra of the phthalocyanines were recorded on a Cary 2000 spectrophotometer (2.5×10^{-5} M in CH_2Cl_2 solution).

Mass spectrometry. GC–mass spectra were recorded with Finnigan gas chromatography mass spectrometry (GC–MS) equipment using Et_2O solutions. Electrospray mass spectra were recorded by pneumatically assisted electrospray mass spectrometry (ES–MS) on a Micromass Vg platform apparatus using a direct inlet of a solution in CH_2Cl_2.

4-Nitrophthalimide (**6**) was prepared according to a slightly modified literature procedure.[15] To a mixture of conc. H_2SO_4 and conc. HNO_3 (4:1, 125 ml) at 15 °C were added 20 g of phthalimide in portions. The temperature was the raised slowly to 35 °C and the reaction was stirred for 45 min. The reaction mixture was then cooled to 0 °C and poured onto ice (700 g). The product was collected by vacuum filtration and washed with cold water. The wet crude product was recrystallised from EtOH. After filtration of the hot solution and slow cooling, the desired product (10.7 g, 55.78 mmol, 41%) was collected and dried. Physical and spectroscopic data were in agreement with the literature.

4-Nitrophthalamide (**7**). 10.7 g (55.7 mmol) of **7** in 105 ml of concentrated aq. NH_4OH were stirred at ambient temperature for 24 h. The product was collected by filtration, washed with cold water and dried to give 8.7 g (41.53 mmol, 76%) of **7** as a colorless powder. Physical and spectroscopic data were in agreement with the literature.[15]

4-Nitrophthalonitrile (**5**) was prepared according to a modified literature procedure.[20a] Under an argon atmosphere, 4-nitrophthalamide (**7**) (12.27 g, 58.71 mmol)

was suspended in 125 ml of a 4:1 dioxane–pyridine mixture. The suspension was cooled with an ice-bath and 20.6 ml of trifluoroacetic anhydride were added dropwise. When the addition was complete, the ice-bath was removed and the reaction mixture was diluted to 2.5 times its volume with water. The product was then extracted with EtOAc (4 × 75 ml). The combined organic phases were washed with water, 20% HCl, water and sat. NaCl. After drying over $MgSO_4$ and evaporation of the solvent, 9.26 g (53.33 mmol, 91%) of **5** was obtained as a creamy white solid. ^{1}H NMR ($CDCl_3$): δ 8.67 (d, J = 2 Hz, 1 H, ArH), 8.59 (dd, J = 2 Hz, J = 8.6 Hz, 1 H, ArH), 8.08 (d, J = 8.6 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 135.1, 128.4, 127.8, 121.2, 117.8, 113.7, 113.5, 108.9.

4-Aminophthalonitrile (**9**) was prepared according to a modified literature procedure.[15] A suspension of **5** (5.19 g, 30 mmol) and 0.6 g of 10% palladium on charcoal in 150 ml of 95% EtOH was placed in a 500 ml jar in a Parr hydrogenation apparatus and hydrogenated at 3.80 bar for 48 h. The palladium catalyst was removed by filtration and the solvent was evaporated off. Subsequent recrystallisation from MeOH yielded 3.78 g, (26.43 mmol, 88%) of **9**. Physical and spectroscopic data were in agreement with the literature.

4-Iodophthalonitrile (**3**) was prepared according to a modified literature procedure.[15] A suspension of **9** (3.7 g, 25.87 mmol) in 51 ml of 25% aq. H_2SO_4 was cooled to −5 °C. Keeping the temperature constant, a solution of 2.07 g of $NaNO_2$ in 6 ml of water was added dropwise with stirring. After 30 min, KI in water (4.66 g in 30 ml) was added and the resulting black mixture was allowed to warm to ambient temperature (1.5 h) before the product was extracted with EtOAc. The combined EtOAc phases were washed consecutively with cold water, $NaHCO_3$, cold water, saturated $Na_2S_2O_3$ and cold water, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by chromatography (*n*-pentane–EtOAc, 9:1) to yield 3.29 g (12.94 mmol, 50%) of **3**. Physical and spectroscopic data were in agreement with the literature.

1,2-Dibromo-4-nitrobenzene (**8**). 1.50 ml of a mixture of conc. H_2SO_4 and conc. HNO_3 (4:1, v/v) was cooled to 15 °C. Dibromobenzene (0.300 g, 1.18 mmol) was added in small portions over 5 min. The temperature was then slowly raised to 50 °C and the mixture was stirred for 1 h at this temperature. The reaction mixture was slowly neutralised with sat. $NaHCO_3$ and extracted with EtOAc (2 × 50 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated off to give 0.380 g of a 9:1 (by ^{1}H NMR) mixture of **8** and 1,2-dibromo-3-nitrobenzene. ^{1}H NMR (**8**, $CDCl_3$): δ 8.46 (d, J = 2.4 Hz, ArH, 1 H), 8.02 (dd, J = 2.4 Hz, J = 8.8 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 136.4, 134.2, 132.7, 128.5, 125.7, 123.4, 123.0.

1,4-Dimethoxy-2-trimethylstannylbenzene (**10**) was prepared from dimethoxybenzene via 2-bromo-1,4-dimethoxybenzene (**12**).

(A) Dimethoxybenzene (10 g, 72.4 mmol) was dissolved in 100 ml of acetic acid. A solution of Br_2 in acetic acid (4.00 ml in 50 ml) was then added dropwise over 1 h. The reaction was stirred for 1 h. Water was then added and the product was extracted with diethyl ether (2 × 50 ml). The organic layer was washed (1 × H_2O, 1 × NaOH), dried (Na_2SO_4) and evaporated off to give 14.15 g (65.21 mmol, 90%) of **12** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.13 (dd, 1 H, ArH), 6.83 (d, 1 H, ArH), 6.82 (d, 1 H, ArH), 3.85 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3).

(B) Under an argon atmosphere, 2-bromo-1,4-dimethoxybenzene (**12**) (4.0 g, 18.5 mmol) in 160 ml of THF was cooled to −78 °C with stirring. BuLi (17 ml) was then added dropwise, and the temperature was slowly raised to −10 °C. The reaction was cooled to −40 °C after which $ClSnMe_3$ (4.463 g, 22.4 mmol) in THF (24 ml) was slowly added to the reaction flask. The temperature was slowly (overnight) allowed to reach ambient temperature. The reaction mixture was then washed with 50 ml of 25% aq. NH_4OH and extracted with 50 ml of diethyl ether. The organic phase was washed with 50 ml of aq. sat. NaCl and dried over $MgSO_4$. Evaporation of the solvents followed by chromatography of the residue (*n*-pentane–ether, 10:1) gave 4.9 g (16.5 mmol, 90%) of **10** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.13 (m, 2 H, ArH), 6.82 (m, 1 H, ArH), 3.84 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 0.3 [s, 9 H, $Sn(CH_3)_3$].

4-Methyl-2-trimethylstannylpyridine (**11**) was prepared from 2-amino-4-methyl pyridine via 2-bromo-4-methylpyridine (**13**).[23]

(A) 2-Amino-4-methylpyridine (5.0 g, 46 mmol) was dissolved in hydrobromic acid (20.35 ml of an 48% aq. solution) and cooled to −10 °C. Then, keeping the temperature below 0 °C, Br_2 (6.15 ml, 125 mmol) and subsequently, a solution of sodium nitrite (7.05 g, 100 mmol in 10 ml H_2O) were added over 15–20 min. After a further 30 min of stirring, aq. NaOH (15.45 g in 15.45 g of H_2O) was added dropwise. Solid NaOH (5.15 g) was then added to make the solution strongly alkaline. After extraction with diethyl ether (250 ml), drying of the organic phase over $MgSO_4$ and evaporation of the solvent, 6.32 g (39.9 mmol, 85%) of **13** were obtained. The NMR spectrum showed a pure product. ^{1}H NMR ($CDCl_3$): δ 8.20 (d, 1 H, ArH), 7.30 (d, 1 H, ArH), 7.05 (dd, 1 H, ArH), 2.32 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 150.2, 149.6, 142.23, 128.6, 123.8, 20.6. GC–MS: m/z (%) 171 (M^+), 92, 65.

(B) Under an argon atmosphere, 2-bromo-4-methylpyridine (**13**) (0.500 g, 2.92 mmol) in 10 ml of THF was cooled to −78 °C with stirring. BuLi (2.07 ml, 3.21 mmol) was then added dropwise, and the mixture was stirred at this temperature for 30 min. $ClSnMe_3$

(0.639 g, 3.21 mmol) in THF (5 ml) was then slowly added to the reaction flask. The mixture was stirred for 4 h while the temperature was allowed to rise to room temperature. The reaction mixture was then treated with 50 ml of 25% aq. NH_4OH and the product was extracted with diethyl ether (2 × 50 ml). The organic phases were washed with aq. sat. NaCl (50 ml) and dried over $MgSO_4$. The solvents were evaporated off to yield **11** (0.689 g, ≈2.6 mmol, >85%), which was used without further purification in the cross-coupling. ^1H NMR ($CDCl_3$): δ 8.58 (d, 1 H, J=5 Hz, aromatic), 7.27 (s, 1 H, ArH), 6.97 (d, 1 H, J=5 Hz, ArH), 2.30 (s, 3 H, CH_3), 0.33 [s, 9 H, $Sn(CH_3)_3$]. ^{13}C NMR ($CDCl_3$): δ 172.6, 150.2, 144.3, 132.7, 123.3, 20.9, −9.5. GC–MS: m/z (%) 256 (M^+), 242, 224, 212, 135.

4-Phenylphthalonitrile (**2a**). Under an argon atmosphere, **3** (0.082 g, 0.33 mmol) in DMF (1 ml) was added to $Pd_2(dba)_3$ (0.012 g, 0,013 mmol) in 1 ml of DMF and the mixture was stirred for 5 min. Tributylstannylbenzene (0.100 g, 0.27 mmol) in DMF (1 ml) was then added, and the mixture was stirred for 5 min before the temperature was raised to 80–85 °C. The reaction was stirred at this temperature overnight and was then poured into 15 ml of 10% aq. KF. The product was extracted with EtOAc (2 × 50 ml). The combined organic phases were washed with water (2 × 100 ml) and dried over $MgSO_4$. After concentration, the crude product was chromatographed (n-pentane–Et_2O, 4:1) to give 0.040 g (0.20 mmol, 72%) of **2a** as a colorless solid. Elemental analysis: found C 78.28, H 4.06, N 13.67 ($C_{14}H_8N_2 \times 1/2$ H_2O, $C_{14}H_8N_2$ requires C 82.34, H 3.95, N 13.72). ^1H NMR ($CDCl_3$): δ 8.010 (d, J=1.6 Hz, 1 H, ArH), 7.93 (dd, J=1.6 Hz, J=8.4 Hz, 1 H, ArH), 7.87 (d, J=8.4 Hz, 1 H, ArH), 7.60–7.49 (m, 5 H, ArH). ^{13}C NMR ($CDCl_3$): δ 146.4, 136.8, 133.9, 131.4, 129.7, 129.4, 127.1, 116.4, 115.44, 115.38, 113.9. GC–MS: m/z (%) 204 (M^+), 177, 165, 151.

4-(2,5-Dimethoxyphenyl)phthalonitrile (**2b**). Under an argon atmosphere, **3** (0.101 g, 0.4 mmol) in DMF (1 ml) was added to $Pd_2(dba)_3$ (0.023 g, 0,025 mmol) in 1 ml of DMF and the mixture was stirred for 5 min. Compound **10** (127 g, 0.42 mmol) in DMF (1 ml) was then added and the mixture was stirred for another 5 min. The reaction temperature was raised to 45–50 °C and stirred at this temperature overnight. The reaction was diluted with water, and extracted with CH_2Cl_2 (2 × 5 ml). The combined organic phases were washed with water (2 × 100 ml) and dried over $MgSO_4$. After concentration, the crude product was chromatographed (n-pentane–ether, 9:1) to give 78 mg (0.3 mmol, 75%) of **2b** as a colorless solid. Elemental analysis: found C 70.80, H 4.49, N 10.32 ($C_{16}H_{12}N_2O_2 \times 1/3$ $CH_3COOC_2H_5$. $C_{16}H_{12}N_2O_2$ requires C 72.72, H 4.58, N 10.60). ^1H NMR ($CDCl_3$): δ 8.01 (d, J=1.6 Hz, 1 H, ArH), 7.87 (dd, J=1.6 Hz, J=8 Hz, 1 H, ArH), 7.81 (d, J=8 Hz, 1 H, ArH), 6.96 (m, 2 H, ArH), 6.85 (m, 1 H, ArH), 3.81 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 154.0, 150.4, 144.0, 134.6, 133.9, 133.6, 133.2, 133.1, 126.9, 116.2, 115.6, 115.5, 113.5, 112.7, 56.1, 55.9. GC–MS: m/z (%) 264 (M^+), 249, 234, 221, 206.

2-(3,4-Dicyanophenyl)-4-methylpyridine (**2c**). **2c** was prepared from **3** (0.164 g, 0.65 mmol in 1 ml DMF), **11** (0.182 g, 0.71 mmol in 1 ml DMF) and $Pd_2(dba)_3$ (0.029 g, 0,03 mmol in 1 ml DMF), following the same procedure as described for **2a**. After concentration, the crude product was chromatographed (n-pentane–Et_2O, 4:1) to give 0.103 g (0.41 mmol, 66%) of **2c** as a colorless solid. Elemental analysis: found: C 74.78, H 3.88, N 19.38 ($C_{14}H_9N_3 \times 1/3$ H_2O. $C_{14}H_9N_3$ requires C 76.70, H 4.14, N 19.17). ^1H NMR ($CDCl_3$): δ 8.61 (d, J=4.8 Hz, 1 H, ArH), 8.51 (d, J=1.6 Hz, 1 H, ArH), 8.37 (dd, J=1.6 Hz, J=8 Hz, 1 H, ArH), 7.90 (d, 1 H, J=8 Hz, ArH), 7.64 (d, J=0.4 Hz, 1 H, ArH), 7.23 (dd, J=0.4 Hz, J=4.8 Hz, 1 H, ArH), 2.49 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 149.9, 148.7, 144.2, 133.7, 133.4, 133.1, 131.7, 130.8, 125.2, 121.9, 116.2, 115.4, 115.3, 21.1. GC–MS: m/z (%) 219 (M^+), 204, 192, 177, 165.

Tetra(2,5-dimethoxyphenyl)phthalocyanine (**1a**). This is an adaptation of a litterature procedure.[19] Under an argon atmosphere, 4-(2,5-dimethoxyphenyl)phthalonitrile (**2b**) (1.006 g, 3.79 mmol) was refluxed in n-butanol (4 ml) for 1 h. Li (0.281 g, 40.5 mmol) was added in small pieces, and the mixture was refluxed for another hour. The deep green solution was allowed to cool to room temperature, then 6 ml of AcOH were added and stirring was continued for another hour. The solvent was removed using a rotary evaporator and the residue was dissolved in CH_2Cl_2 (25 ml), washed with dil. aq. HCl (2:3 conc. HCl–H_2O, 100 ml) and water (4 × 100 ml), and dried over $MgSO_4$. The organic phase was concentrated and after repeated chromatography on silica with EtOAc–CH_2Cl_2 (1:1 and then 1:9) as the eluent, 0.27 g (0.27 mmol, 27%) of **1a** was obtained. Elemental analysis: found C 71.07, H 4.50, N 10.52. $C_{64}H_{50}N_8O_8$ requires C 72.58, H 4.76, N 10.58. UV–VIS: 705, 671, 645, 611, 343. ES–MS: m/z: 1058 (M^+).

[Tetra(2,5-dimethoxyphenyl)]phthalocyaninatozinc[Zn-(**1a**)]. Under an argon atmosphere, 4-(2,5-dimethyoxyphenyl) phthalonitrile (**2b**) (0.206 g, 0.8 mmol) and dry $Zn(OAc)_2$ (0.073 g, 0.4 mmol) was refluxed in n-butanol (6.5 ml) for 1 h. Li (0.060 g, 8.7 mmol) was added in small pieces, and the mixture was refluxed for 2.5 h. The deep green solution was allowed to cool to room temperature, then 12 ml of AcOH were added and stirring was continued for another hour. The solvent was removed using a rotary evaporator and the residue was dissolved in CH_2Cl_2 (25 ml), washed with dil. HCl (1:4, conc. HCl–H_2O, 100 ml) and water (4 × 100 ml), and dried over $MgSO_4$. The organic phase was concentrated and chromatographed on silica using EtOAc–CH_2Cl_2 (1:1 and then 1:9) as the eluent to yield 0.018 g (0.016 mmol,

8%) of Zn(**1a**). Elemental analysis, found: C 67.65, H 4.79, N 9.07. $C_{64}H_{48}N_8O_8Zn$ requires C 68.48, H 4.31, N 9.98. UV-VIS 683, 618, 349.

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