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Iridium-catalysed 3,5-bis-borylation of phthalonitrile enables access to a family of C_{4h} octaarylphthalocyanines†

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Ir-catalysed borylation of phthalonitrile produces both 4-(Bpin) phthalonitrile (1) and 3,5-bis(Bpin)phthalonitrile (2), which are potential divergent intermediates for the synthesis of functionalized phthalocyanines. To exemplify the utility of 2, we have prepared a series of 3,5-bis-arylphthalonitriles that in turn undergo sterically controlled regioselective cyclotetramization to give previously unknown C_{4h} 1,3,8,10,15,17,22,24-octaarylphthalocyanines.

Phthalocyanines (Pcs) have been extensively explored over recent decades for their use in dye-sensitized solar cells,[1–3] single-molecule magnets,[4,5] (photo)catalysis,[6] and various cancer phototherapies,[7–9] making them one of the most important classes of synthetic chromophores.

Pcs are commonly synthesized by the cyclization of four substituted phthalonitrile precursors around a metal-ion template. A recurring issue in Pc chemistry is that the synthesis of substituted phthalonitrile precursors is often lengthy and hindered by the low reactivity of electron-poor phthalonitrile in S_EAr reactions. Here, we report our initial investigation into the use of sterically controlled Ir-catalysed C–H borylation[10–12] to functionalize phthalonitrile that circumvents its unfavourable electronics. This study was further motivated by the ease with which aryl boronic acid pinacol ester (Bpin) groups introduced by this reaction might, in general, be converted to a wide range of other functional groups, including various amines, ethers, thioethers, (hetero)arenes, or to an azide, halide, nitro or alcohol group for further functionalization using known transformations.[13] Such conversions can often be performed using one-pot borylation-functionalization methodologies, such as demonstrated by the cyanation of *in situ* generated arylboronic esters[14] or their conversion to perfluoroalkyl groups,[15] which would make this a versatile route for preparing substituted phthalonitriles.

Based on the steric, rather than electronic selectivity of Ir-catalysed borylation, it was expected that borylation of phthalonitrile using 1.0 eq. B_2pin_2 (pin = pinacolato), 1.5 mol% $[Ir(COD)(OMe)]_2$ and 3.0 mol% dtbpy (dtbpy = 4,4′-bis(^{t}Bu)-2,2′-bipyridyl) in methyl *tert*-butyl ether (MTBE) at room temperature would afford 1,2-dicyano-4-(Bpin)benzene, **1**, selectively (Scheme 1). This reaction did indeed proceed with quantitative consumption of phthalonitrile to give **1** as the major product; however, traces of the bis-borylated 3,5-bis(Bpin)-1,2-dicyanobenzene (**2**) were also observed by ^{1}H NMR spectroscopy. Borylation *ortho* to the relatively low steric-demand cyano group in the absence of more sterically accessible sites, as observed here in the bis-borylation reaction to give unpredicted compound **2**, has been reported for *para*-substituted benzonitriles[16] and was also observed during the borylation of 2-methylbenzonitrile, where 2,4-bis(Bpin)-6-methylbenzonitrile was obtained as a minor by-product.[17] We also note that arylnitrile groups are competent directing groups for a range of metal-catalysed reactions.[18–21]

By increasing the reaction temperature to 55 °C and the amount of B_2pin_2 to 1.1 eq., 70% bis-borylation, 30% mono-borylation and quantitative consumption of phthalonitrile was achieved. Sublimation (150 °C/0.3 mbar) separated **1** from the crude mixture, while recrystallization of the residue from MTBE provided **2**. The structures of **1**·0.25H_2O and **2** were obtained by single-crystal X-ray diffraction (SC-XRD) (Fig. S22, ESI†). Increasing the amount of B_2pin_2 to 1.5 eq. and using a higher reaction concentration (1.3 M *vs.* 1.0 M) increased conversion to **2** (46% isolated yield) and removed the need for the sublimation step.

With the unexpected product **2** in hand, we decided to consider first its potential for the preparation of phthalocyanines for

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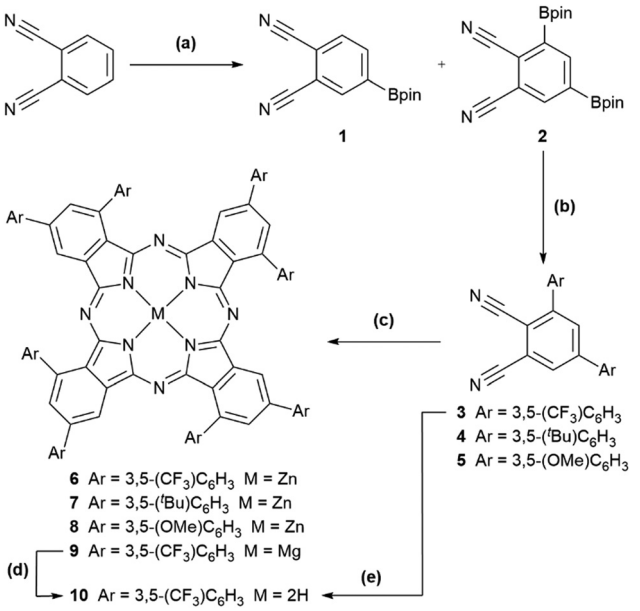
† Electronic supplementary information (ESI) available: Synthetic protocols and other experimental details, copies of NMR spectra, crystallographic data, and absorption and emission spectra. CCDC 1989433–1989438, 1989726 and 1989727. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc03161e



Scheme 1 Synthesis of **6–10** starting from phthalonitrile. (a) Ir-catalysed borylation: 1.0 eq. B_2pin_2, 1.5 mol% $[Ir(COD)(OMe)]_2$, 3.0 mol% dtbpy, MTBE, 1.0 M, r.t., 24 h gave **1** with trace **2**; same conditions except 1.1 eq. B_2pin_2, 55 °C gave 3 : 7 **1** : **2**; same conditions except 1.5 eq. B_2pin_2, 55 °C, 1.3 M gave **2** only [46%]. (b) Suzuki–Miyaura cross-coupling: 2.4 eq. 3,5-bis(R)bromobenzene (R = CF_3, ^{t}Bu, OMe for **3**, **4**, and **5**), 5 mol% $Pd_2(dba)_3$, 20 mol% SPhos, 4.0 eq. CsF, 1,4-dioxane, 65 °C [19% (**3**), 50% (**4**), and 21% (**5**)]. Yield of **3** increased to 68% using 4.0 eq. 3,5-bis(CF_3)iodobenzene, 4.0 eq. Cs_2CO_3. (c) Macrocyclization: 0.2–1.1 eq. $Zn(OAc)_2{\cdot}2H_2O$ (**6–8**) or $Mg(OAc)_2{\cdot}4H_2O$ (**9**), 1-pentanol, 1.0 eq. DBU, 132 °C [39% (**6**), 25% (**7**), 13% (**8**), 5% (**9**)]. (d) Demetallation: acetic acid, 110 °C, 2 h, quantitative by UV-visible absorption spectroscopy. (e) One-pot macrocyclization/demetallation: (i) as (c) with $Mg(OAc)_2{\cdot}4H_2O$; (ii) HCl (1 M, 5 mL), 60 °C, 16 h [5%]. All yields are isolated. See ESI† for further details.

the following reasons. A common problem in the synthesis of functionalized Pcs is that reaction of substituted phthalonitriles lower than C_{2v} symmetry usually produces a 1 : 4 : 2 : 1 statistical, and often inseparable, mixture of C_{4h}, C_s, C_{2v}, and D_{2h} regioisomers.[22] Regardless of which function or application is sought, formation of a single Pc isomer is desirable due to their potentially differing physical, optical and biological properties. In the rare cases where separation of one or more of these four isomers has been possible, it has been necessary to use bespoke HPLC columns[23,24] or repeated column chromatography,[25] limiting the generality of the procedure. Recrystallization has occasionally been successful as part of a multi-step purification of the C_{4h} isomer.[26,27] If, however, bulky substituents, *e.g.* substituted phenyl rings,[28,29] branched alkoxides,[24,26,30] amines,[27,31] or trialkylsilyl groups,[32] are introduced at the 3-position of the phthalonitrile precursor, then exclusive formation of the C_{4h} Pc isomer can sometimes be enforced through steric control or the number of isomers formed in the mixed A/B phthalonitrile synthesis of A_3B-[33,34] and ABAB-type[35,36] Pcs can be reduced. The substituted phthalonitriles used in these previous studies were prepared by cross-coupling of 3-(OTf)phthalonitrile, nucleophilic aromatic substitution of 3-nitrophthalonitrile, or directed *ortho*-lithiation of 4-alkylphthalonitriles, respectively. While successful, these previous reports have been limited in allowing the introduction of further functionalization on to the phthalonitrile, either due to the difficulty of synthesizing the substituted phthalonitriles *via* traditional routes or the incompatibility of desired substituents with organolithium reagents. With this in mind, **2** was seen as a potential precursor to 3,5-bis-substituted phthalonitriles, which could include derivatives having a bulky substituent in the 3-position to direct the regioselective synthesis of C_{4h} phthalocyanines through steric control while also bearing a second substituent in the 5-position.

As a first demonstration of the potential utility of **2** as a divergent intermediate in the synthesis of functionalized regioregular Pcs, a series of 3,5-bis(aryl)phthalonitriles **3–5** with varying steric demand and electronic character was prepared from **2** by Suzuki–Miyaura cross-coupling with 3,5-bis(R)bromobenzenes (R = CF_3, ^{t}Bu, OMe, respectively). 5 mol% $Pd_2(dba)_3$ pre-catalyst, 20 mol% SPhos ligand and 4 eq. CsF base in 1,4-dioxane at 65 °C gave **3–5** in moderate yields (19–50%). Using 3,5-bis(CF_3) iodobenzene and Cs_2CO_3 as the base improved the yield of **3** from 19 to 68%. The SC-XRD structures of **3–5** are shown in Fig. S22 (ESI†). These products were expected to undergo regioselective cyclotetramization to the previously unexplored C_{4h} 1,3,8,10,15,17,22,24-octaarylphthalocyanine family of compounds.

Reaction of **3** with $Zn(OAc)_2{\cdot}2H_2O$ in 1-pentanol in the presence of DBU indeed afforded 1,3,8,10,15,17,22,24-octaarylphthalocyanine **6**. TLC showed only a single dark-green compound, which could be separated by recrystallization in 39% yield, with the mass balance likely being oligomeric by-products. Fig. 1 shows partial ^{1}H and ^{19}F{^{1}H} NMR spectra of **6**, which confirm the high symmetry of the Pc by the single set of sharp resonances for the six aryl proton environments and two inequivalent CF_3 environments, respectively. Only the C_{4h} and D_{2h} isomers would show this equivalence of the rings; these are the least and most sterically encumbered isomers.

Pcs **7** and **8**, starting from precursors **4** and **5**, were synthesized analogously in isolated yields of 25 and 13%, respectively. Sharp, well-defined ^{1}H NMR spectra were obtained for **7** and **8** with six aromatic proton environments clearly observed (Fig. 1).

The SC-XRD structure of **6**, obtained after recrystallization from acetone/pyridine, confirmed the nominal C_{4h} symmetry of **6**, although the Zn atom is additionally ligated by a 3 : 1 mixture

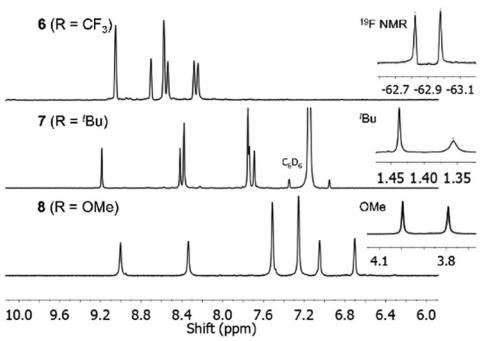


Fig. 1 Partial ^{1}H NMR spectra of **6–8** and ^{19}F{^{1}H} NMR spectrum of **6**. The spectra are consistent with the high symmetry of each Pc.

of pyridine and water (pyridine adduct **6**·NC_5H_5 shown in Fig. 2). Distortion of the Pc ring away from planarity can be seen, with a maximum fold angle of 6.79(9)° for benzo group 1 relative to the *meso*-N_4 plane (N1, N2 and symmetry equivalents). The coordinated Zn atom is 0.49 Å out of the Pc *meso*-N_4 plane and is disordered 50 : 50 either side of the ring. The α-substituents, rings B/D, have mean-plane dihedral angles of 50.49(10)° and 56.30(12)° with respect to adjoining benzo groups 1 and 2, respectively. These large twist angles prevent neighbouring α-substituents from overlapping (unlike when unsubstituted α-phenyl groups are used, which can overlap with distortion of the Pc ring[37]), enforcing the formation of the single C_{4h} isomer. Peripheral β-position rings A/C have dihedral angles of 49.0(1)° and 40.6(1)°.

The SC-XRD structure of **7** was obtained following recrystallization from acetone (Fig. S23, ESI†); however, the quality of this structure is low, due to a large amount of incorporated disordered solvent, the rotational disorder of the ^{t}Bu groups of the two crystallographically independent Pcs **7(A)** and **7(B)**, and the weak diffraction of the crystal. Nonetheless, the Pc rings and the eight aryl substituents of both **7(A)** and **7(B)** were unambiguously refined and the structure conclusively confirms the C_{4h} symmetry of both molecules. Ligation of the Zn atoms can only be defined conclusively for **7(B)** and has been resolved as a water molecule. The large size of the 3,5-bis(^{t}Bu)phenyl groups means that the β-positions are not free to rotate due to close proximity of neighbouring α-substituents, *i.e.* groups A/D and B/C orient concertedly. In comparison, the smaller 3,5-bis(trifluoromethyl)phenyl groups of **6** show less correlation and thus have less restricted rotation.

C_{4h} MgPc **9** was synthesized analogously to **6** in an unoptimized 5% yield by reaction of **3** with $Mg(OAc)_2{\cdot}4H_2O$. The SC-XRD structure of **9** (recrystallized from acetone/hexane, Fig. 2) has disordered solvent in the voids between the cup-like Pcs, but the Pc structure itself is well resolved and the symmetry confirmed. The Mg atom has a ligand that was resolved as water, and sits 0.74 Å out of the Pc plane. The α-substituents have large dihedral angles of 54.8(3)° and 49.0(3)° for B and D respectively. The β-aryl rings A and C are twisted by 36.6(3)° and 51.8(3)°. Similar to **6**, there is no correlation between dihedral angles of close contacting rings: B/C rings twist in the opposite sense, while A/D differ in dihedral angle by about 12° and are therefore assumed to have some rotational freedom.

Successful de-metalation of **9** to free-base Pc **10** by heating in acetic acid was monitored by UV-visible absorption and $^1H/^{19}F$ NMR spectroscopies. Alternatively, **10** can be synthesized in 5% yield with a one-pot procedure using HCl to demetalate the intermediate MgPc. The split Q band in the UV-visible absorption spectrum of **10** confirmed symmetry reduction from C_{4h} to nominal C_{2h} (Fig. S22, ESI†). As free-base Pcs can be metalated with a range of metals other metals could be introduced into these regioregular 1,3,8,10,15,17,22,24-octaarylphthalocyanines.[38]

The presence of eight aryl ring substituents on **6–9** makes them highly soluble in organic solvents of different polarity and coordinating ability, *e.g.* toluene, CH_2Cl_2, $CHCl_3$, THF, acetone, pyridine, and MeCN. The extinction coefficient of **6** at the Q-band maximum (694 nm) is large (3.8×10^5 M^{-1} cm^{-1}, acetone solution). Normalized UV-visible absorption spectra of **6** in acetone solution in the measurable concentration range of 1.7×10^{-7} to 1.7×10^{-4} M were identical within experimental error (Fig. S25, ESI†), indicating that **6** does not aggregate at these concentrations, unlike many common Pc derivatives. The introduction of the eight aryl groups around the Pc core in a regioregular fashion is therefore an effective strategy to inhibit interactions through π-stacking, with the large dihedral angles of the α-substituents being especially beneficial. As aggregation of Pcs often leads to quenching of excited states, and thus lower fluorescence and singlet-oxygen quantum yields, minimizing aggregation is beneficial for most applications.[39]

The Q_{00} bands in the absorption spectra of **6–8** are single peaks (Fig. 3), rather than split into Q_x/Q_y components, consistent with their C_{4h} symmetry and the two-fold degeneracy of the LUMO. Near-infrared emitting **6–9** (λ_{max} = 701–717 nm) have small Stokes shifts (260–280 cm^{-1}) and fluorescence lifetimes of *ca.* 1.9–5.4 ns (Fig. 3, Table 1 and Fig. S24, S26–S31, ESI†). The fluorescence and singlet-oxygen quantum yields of **6** are 0.17 and 0.67, respectively. Thus, encouragingly for potential applications, the eight aryl substituents of **6–9** only lead to a minor increase in non-radiative decay, despite the additional rotational freedom relative to the parent ZnPc, and the triplet state is still sufficiently energetic to sensitize singlet oxygen efficiently. Both the absorption and emission spectra of **7** are significantly broader than **6**, **8** or **9**; the hindered rotation of the aryl groups of **7** observed in its SC-XRD structure may be causing inhomogeneous broadening, *i.e.* there are different solution conformations of **7** that interconvert relatively slowly due to steric crowding. This suggests

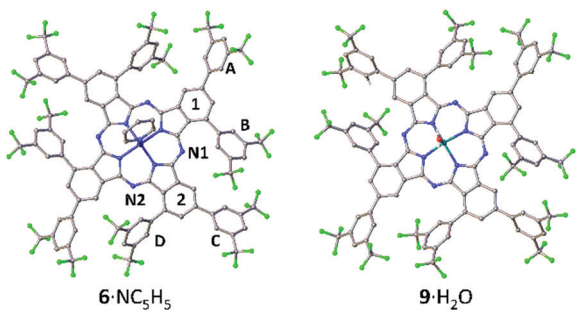


Fig. 2 Structures of **6**·NC_5H_5 and **9**·H_2O from SC-XRD. Disorder and hydrogen atoms are omitted for clarity. Analogous ring labelling to that of **6** is used for all structures.

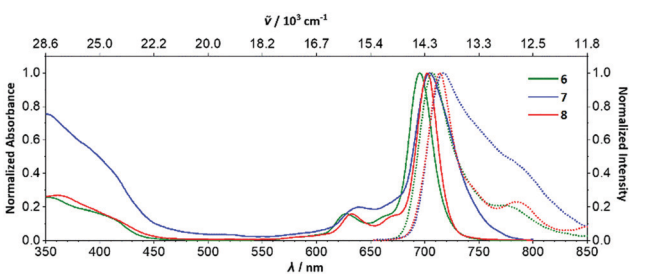


Fig. 3 Normalized absorption (solid lines) and emission (dotted lines) spectra of **6–8** in acetone solution.

Table 1 Room-temperature photophysical properties of **6–9** and unsubstituted ZnPc in acetone solution

	λ_{abs} [nm]	λ_{em} [nm]	τ_f [ns]	Φ_f	k_r [10^7 s^{-1}]	k_{nr} [10^8 s^{-1}]
ZnPc	665	671	4.3[a]	0.17[b]	4.0	1.9
6	694	707	2.72	0.17	6.3	3.1
7	704	717	1.87	0.10	5.4	4.8
8	700	714	2.45	0.20	8.2	3.3
9	695	701	5.39	0.34	6.3	1.2

[a] In DMSO solution, ref. 40. [b] Ref. 41.

that having 3,5-bis(^{t}Bu)aryl groups in both the α and β-positions is close to the steric crowding limit for successful synthesis of 1,3,8,10,15,17,22,24-octaarylphthalocyanines.

In conclusion, we report 4-(Bpin)- and 3,5-bis(Bpin) phthalonitrile (**1** and **2**, respectively), synthesized by Ir-catalysed C–H mono- and unpredicted bis-borylation of phthalonitrile, as potential divergent intermediates for phthalocyanine chemistry. As a first demonstration of the utility of **2**, we synthesized a series of 3,5-substituted phthalonitrile derivatives bearing bulky aryl groups that subsequently undergo regioselective cyclization to afford a series C_{4h} 1,3,8,10,15,17,22,24-octaarylphthalocyanines, **6–10**, as confirmed by NMR spectroscopy and by SC-XRD for **6**, **7** and **9**. The high symmetry of these non-aggregating Pc derivatives was further confirmed by UV-visible absorption spectroscopy. We are currently investigating the use of **1** in preparing phthalonitrile derivatives, as well as exploring methods to differentiate the two Bpin groups of **2** to facilitate the synthesis of multifunctional phthalocyanines with controlled symmetry. The rapid functionalization of phthalonitrile reported herein may also find use in the preparation of near-infrared azaBODIPY dyes, potentially further extending its usefulness.[42,43]

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Conflicts of interest

There are no conflicts to declare.

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