Full Paper

Aryl-Substituted Boron Subphthalocyanines and their Application in Organic Photovoltaics

Catherine Bonnier,^{A,D} David S. Josey,^{A,D} and Timothy P. Bender^{A,B,C,E}

^ADepartment of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada M5S 3E5.

^BDepartment of Materials Science and Engineering, University of Toronto,

184 College Street, Toronto, Ontario, Canada M5S 3E4.

^CDepartment of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario, Canada M5S 3H6.

^DThese authors contributed equally to preparing the contents of this paper.

^ECorresponding author. Email: tim.bender@utoronto.ca

A family of five axial aryl-substituted boron subphthalocyanine (BsubPc) derivatives bearing a hydrido, methyl, methoxy, phenyl, or fluoro substituent at the *para* position of the aryl were synthesised from Br-BsubPc and the corresponding aryl Grignard reagent in moderate yields. The physicochemical characterisation of these derivatives gave similar absorption, photoluminescence, and cyclic voltammetry profiles and photoluminescence quantum yields, indicating that the nature of the substituent at the *para* position does not influence the basic photophysical properties of this generic class of BsubPcs. Conversely, the solid-state structural arrangement obtained from single crystals is highly dependent on the *para* substituent; for the non-polar hydrido, methyl, and phenyl substituents, only concave isoindole π interactions are present. Substitution for the polar methoxy or fluoro ligand affords one-dimensional ribbons formed by convex π interactions, where these ribbons further interact through concave isoindole π interactions with the adjacent ribbon, creating an extended two-dimensional π network. On incorporation of the hydrido, methyl, and fluoro derivatives. Both, however, were significantly outperformed by the hydrido derivative. The uniqueness of the hydrido derivative is only realised once incorporated into OPVs as it shares the same basic physical properties as the other derivatives. Given these findings, we identify the hydrido derivative as the aryl-BsubPc with the most promise for future work in OPVs.

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Introduction

The quest to replace inorganic semiconductors with low-cost, stable, and efficient organic electronic materials remains recurrent. Devices such as organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs) require the use of an organic semiconductor material to act as a chromophore to absorb the solar radiation and generate a photocurrent or as a fluorophore to emit light, respectively. In this search, organic molecules possessing an extended aromatic system are of interest due to their appropriate absorption profiles and high luminescence properties.

Of all the extended π systems reported, boron subphthalocyanine (BsubPc) derivatives are promising candidates due to their strong absorption in the visible region, narrow photoluminescence,^[1] low tendency to aggregate owing to their unusual bowl shape,^[2] and their retention of macrocyclic geometry upon accepting or donating electrons.^[3] Owing to the extensive use of Cl-BsubPc and the achievement of high performance in OPV^[4–9] and OLED^[10–12] devices, the derivatization of the ligand at the axial position has become an attractive methodology to synthesise BsubPcs with higher device performance.^[1] It has been shown that the nature of the axial ligand on the BsubPc has an insignificant influence on the absorption and emission profiles in solution, however, their solution electrochemistry and solid-state behaviour were shown to be highly ligand-dependent.^[13–15]

To the best of our knowledge, only two types of BsubPcs bearing an axial hydrocarbyl moiety have been reported in the literature (i.e. a direct carbon-boron bond): phenyl-[16-18] and phenylalkynyl-substituted derivatives.^[19] Despite the presence of several synthetic methods describing the preparation of phenyl-BsubPc, this compound has lacked in-depth characterisation. Conversely, Ziessel et al. reported the synthesis and solidstate, physicochemical, and electrochemical characterisation of a series of arylethynyl-substituted BsubPcs.^[19a] These derivatives exhibited interesting stacking patterns in the solid state owing to intermolecular concave–concave isoindole and aryl–aryl π interactions, and their electrochemical behaviour was remarkable; most derivatives exhibited reversible oxidation and reduction processes and in addition, a second reduction was observed, albeit irreversible. The generation and observation of the BsubPc dianion under mild electrochemical conditions is scarce, thus



Scheme 1. Synthesis of aryl-BsubPcs **3a–e**, where R = H, CH_3 , C_6H_5 , and F respectively. Conditions: (i) THF, reflux, 16 h; (ii) (a) Ar-MgBr where Ar = 2,4,6-trifluorophenyl or pentafluorophenyl or (b) observed as side product under conditions (i).

suggesting that the lifetime of ethynyl-BsubPcs as n-type materials could be enhanced based on cyclic voltammetry experiments.^[20] In order to expand the library of hydrocarbyl-BsubPcs, we herein report the synthesis and extended characterisation of aryl-substituted BsubPcs bearing a hydrido, methyl, methoxy, phenyl, or fluoro substituent at the *para* position of the aryl ligand. Integration of a subset of these materials into organic photovoltaics devices is also presented. The presence of a variety of substituents at this position will provide insight on the factors influencing the properties of aryl-BsubPcs.

Results and Discussion

Synthesis

Previously reported syntheses of axial-substituted hydrocarbyl-BsubPc derivatives either involve the reaction between an appropriate hydrocarbylboron derivative with phthalimide^[16,17,22] or an axial substitution between X-BsubPc (X = Cl, trifluoromethanesulfonate) with the corresponding lithium or Grignard reagent.^[18,19a,19b,23] The latter methodology is attractive due to its versatility, the milder conditions requirements, and the higher conversion rates. For this study however, we chose Br-BsubPc as the starting material due to the ease of its synthesis and higher reactivity when compared with Cl-BsubPc.^[13]

Upon refluxing a suspension of Br-BsubPc and aryl Grignard reagent in THF, a subtle colour change from purple to magenta– red along with the disappearance of the Br-BsubPc suspension occurred. After purification of the crude by column chromatography and recrystallization from a mixture of CH₂Cl₂ and hexanes, aryl-BsubPcs **3a–e** were obtained as red–bronze crystalline materials in 17–38 % yield (Scheme 1). However, this method failed at preparing higher fluorinated aryl derivatives such as 2,4,6-trifluorophenyl- and pentafluorophenyl-substituted BsubPcs. Instead, a different BsubPc species was observed, which was also present in every crude reaction mixture in various proportions; this by-product was identified by multinuclear NMR spectroscopy and mass spectrometry as being 4-bromobutoxy-BsubPc **4**,^[24] and its presence can account for the mediocre yields of aryl-BsubPcs obtained.

Absorption and Emission Spectroscopy

The UV-visible spectra of aryl-BsubPc derivatives were obtained in CH_2Cl_2 and plotted against the molar extinction



Fig. 1. UV-Visible (solid lines) and photoluminescence (normalized, dashed lines) spectra of **3a–e** measured in CH₂Cl₂. Excitation wavelength = 566 nm.

coefficient (Fig. 1). All traces showed the usual features attributed to BsubPcs: an absorption maximum at 566 nm, corresponding to the Q band, in addition to a Soret band centred at 309 nm (Table 1). All maxima are at the same wavelength, confirming that these transitions are BsubPc-centred and that the nature of the axial aryl substituent is non-influential in the position of the transition. The molar extinction coefficient of the Q band is relatively unaffected by the electron density of the aryl group, whereas the Soret band experienced a hypochromic shift when a substituent other than hydrogen is present. Most derivatives are lacking transitions associated with the aryl moiety, with the exception of 3d which exhibits an absorption at 254 nm due to the presence of an additional isolated phenyl ring (Fig. S3, Supplementary Material).

All aryl-BsubPc derivatives exhibited moderate photoluminescence upon excitation at 566 nm in deoxygenated CH_2Cl_2 solution. A maximum at ~586 nm was observed with a quantum yield efficiency of ~0.39 (Table 1). These values are very similar to the phenoxy-dodecafluoroBsubPc standard,^[20] suggesting that the nature of the axial substituent has no effect on the photoluminescence in the absence of more complex phenomenon (i.e. Förster resonance energy transfer (FRET)). Indeed, one could have anticipated a larger Stokes shift in **3d**

Compound	Q band		Sor	et band	Photoluminescence	
	λ_{\max} [nm]	$\epsilon [\text{M}^{-1} \text{cm}^{-1}]$	λ_{\max} [nm]	$\varepsilon [\mathrm{M}^{-1} \mathrm{cm}^{-1}]$	λ_{\max} [nm]	$\varphi^{ m B}_{ m PL}$
3a	566	95700	309	76000	590	0.39 ± 0.01
3b	566	88000	310	53700	587	0.39 ± 0.02
3c	566	97900	309	59300	583	0.39 ± 0.01
3d	566	83500	309	52500	587	0.38 ± 0.01
3e	566	91900	310	57500	583	0.39 ± 0.02

Table 1. Absorbance and photoluminescence (PL) data of aryl-BsubPcs 3a-e^A

^ARecorded in CH₂Cl₂.

^BMeasured in deoxygenated CH₂Cl₂ using phenoxy-dodecafluoroBsubPc as the standard ($\varphi_{PL} = 0.40$)^[20] according to the methodology previously described.^[21]

Table 2.	Electrochemical	data	of aryl-BsubPc 3a-e ^A
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	BsubPc ^{•+} /BsubPc [V]	BsubPc/BsubPc ^{•-} [V]	$BsubPc^{\bullet-}/BsubPc^{2-}$ $[V]^B$	HOMO $[eV]^C$	LUMO [eV] ^C
3a	+1.11	-1.06	-1.50	-5.7	-3.7
3b	+1.10	-1.06	-1.58	-5.6	-3.7
3c	+1.10	-1.04	-1.56	-5.7	-3.7
3d	+1.10	-1.05	-1.58	-5.7	-3.7
3e	+1.12	-1.04	-1.51	-5.7	-3.7

^ARecorded at 100 mV s⁻¹ in deoxygenated CH₂Cl₂ containing 0.1 M [nBu_4N]⁺[PF₆]⁻ as supporting electrolyte and 1 mM of analyte and calibrated with FeCp*₂ as internal standard ($E_{1/2} = -0.012$ V versus Ag/AgCl).^[27]

^BDetermined by differential pulse voltammetry.

^CCalculated at the onset assuming an energy value for vacuum at -4.7 eV (versus saturated calomel electrode (SCE))^[29] or -4.655 eV versus Ag/AgCl.

if the biphenyl substituent was involved in the excited state, owing to the drastic change in dihedral angle between the two phenyl moieties from $\sim 35^{\circ}$ to 0° (see below).^[25] The absence of variation in the absorption and photoluminescence data within the aryl-BsubPc series and with phenoxy-BsubPcs suggests that all the orbitals involved in the processes observed are localised on the rigid BsubPc macrocyle.^[26]

Electrochemistry

All aryl-BsubPc derivatives were subjected to cyclic voltammetry analysis in CH₂Cl₂ using 0.1 M [*n*Bu₄N]⁺[PF₆]⁻ as the supporting electrolyte; the potential scale was calibrated using FeCp*₂ as the internal standard ($E_{1/2} = -0.012$ V versus Ag/AgCl).^[27] Computational studies have shown that the B–X_{axial} bond exhibits the greatest length variation upon oxidation (shorter) or reduction (longer);^[28] therefore, the reversibility of an electrochemical process can be related to the strength of that bond.

All derivatives possessed similar voltammograms: one reversible oxidation at $\sim +1.10$ V, one reversible reduction centred near -1.05 V, and one quasi-reversible reduction at approximately -1.55 V (Table 2, Fig. 2). The formation of the aryl-BsubPc radical cation is ~ 20 mV more anodic than that of alkynyl-BsubPcs, whereas the generation of the radical anion occurs at similar potentials. The behaviour of aryl-BsubPcs towards their oxidation and first reduction processes is very similar to that of their phenoxy derivatives. In **3a** and **3b**, these processes occur at a similar potential compared with phenoxy and 4-methylphenoxy-BsubPc.^[26] Voltammogramms of compounds **3a** and **3c**-e are illustrated in Figs S1–S4 (Supplementary Material).

The presence of a second reduction process, associated with the formation of $aryl-BsubPc^{2-,[19a]}$ was found to be



Fig. 2. Cyclic voltammogramm of 3b (representative) recorded at 100 mV s^{-1} in deoxygenated CH₂Cl₂ containing $[nBu_4N]^+[PF_6]^-$ as supporting electrolyte.

quasi-reversible ($i_{anode}/i_{cathode} < 1$, Table S1, Supplementary Material). The presence of a substituent other than hydrogen at the *para* position on the aryl ligand decreases the reversibility of this electrochemical process. Electrochemically generated dianions of perhydrogenated BsubPc have only been reported with arylethynyl axial ligands,^[19a] suggesting that BsubPc derivatives bearing a hydrocarbyl ligand at the axial position exhibit greater structural stability when reduced. In addition to this feature, the energy level of the HOMO and LUMO calculated using the electrochemical potential of the oxidation and first reduction events versus vacuum (Table 2) fall within those of CBP (4,4'-N,N'-dicarbazole-biphenyl) and TPBi (1,3,5-tris (*N*-phenylbenzimidazole-2-yl)benzene), two host materials

used in OLED fabrication, suggesting that they would be suitable candidates as n-type materials.^[30]

X-Ray Crystallography

Suitable crystals of most aryl-BsubPcs were grown by train sublimation in order to best mimic the packing occurring in solid thin films.^[14] Unfortunately, crystals of **3d** obtained by sublimation did not diffract; instead, layering hexanes on top of a saturated CH_2Cl_2 solution afforded X-ray quality crystals. Owing to the fact that all the electronic processes described above are localised on the BsubPc moiety (see above), macrocycle intermolecular interactions are believed to be crucial for optimal electronic communication in a device.^[31]

The structure of phenyl-BsubPc has been previously reported, ^[16,17,18,32] and these unit cell parameters were similar to those measured for the crystals of **3a** obtained by sublimation, indicating identical packing patterns. Most aryl-BsubPc derivatives, including **3a**, crystallized in the *Pbca* space group, except for **3d** (*C*2/*c*). Due to the presence of the larger *para*-phenyl substituent, **3d** is the only derivative possessing enough void space in its unit cell to potentially accommodate solvent molecules. The presence of a methyl or phenyl substituent at the *para* position of the aryl ligand did not alter the packing of the BsubPc unit. In fact, **3a**, **3b**, and **3d** possess a pair of centrosymmetric π - π interactions between concave isoindoles moieties of ~3.7 Å along the *a*-axis (Fig. 3, Table 3). In contrast to the aryl fragment that is definitely sheltered from any intermolecular interaction in **3a**, the tolyl moiety of **3b** is



Fig. 3. (a) Thermal ellipsoid diagram (35 % probability) and (b) packing structure of **3b**, showing the concave isoindole π interactions. Hydrogen atoms were omitted for clarity purposes. Centroids are illustrated in red.

involved in weak (\sim 4 Å) C–H edge-to-face interactions with a neighbouring BsubPc unit.

The two axial aryl moieties of **3d** bisect with a dihedral angle of $\sim 35^{\circ}$. The presence of the larger biphenyl group at the axial position of the BsubPc probably accounts for the presence of biphenyl edge-to-face C–H–centroid interactions of 3.52 and 3.83 Å, which probably results from packing constraints (Fig. 4).

The presence of an electronegative heteroatom at the *para* position of the aryl ligand in 3c and 3e induces profound changes to the solid-state packing of BsubPcs. These structures are dominated by convex-convex edge-to-face isoindole N to isoindole centroid(s) interactions (Fig. 5a), which generate one-dimensional ribbons along the *a*-axis (Fig. 5b,c). These ribbons are connected to each other by the means of a pair of centrosymmetric π - π interactions between concave isoindoles moieties along the b-axis (Fig. 5c), forming a two-dimensional π network. Clearly, the presence of an electronegative heteroatom is responsible for the formation of ribbons as these interactions are not observed in 3a or 3b. It can be noticed that the interactions responsible for the formation of the twodimensional π network are shorter in the case of **3e** (Table 3), suggesting that the electronegativity of the heteroatom at the para position of the aryl is proportional to the strength of the π network.

The presence of extended inter-unit cell π interactions has been proven to be an effective feature yielding high charge carrier mobilities,^[31] and suggests that **3c** and **3e** would be promising n-type organic electronic material candidates. Subtle electronic or steric changes of the *para* substituent of the aryl ligand were found to have a profound effect on the packing pattern of crystals obtained by sublimation. This effect is not observed with analogous *para*-halophenoxy-BsubPcs.^[33] This observation suggests that aryl-BsubPcs would be interesting candidates for further crystal engineering studies.

OPV Device Integration

Three of the aryl-BsubPcs, i.e. phenyl-BsubPc (**3a**), 4-tolyl-BsubPc (**3b**), and 4-fluorophenyl-BsubPc (**3e**), were selected to be examined further in OPVs as electron donors and electron acceptors. These three aryl-BsubPcs were selected for the following reasons: (1) **3a**, **3b**, and **3e** all have robust reduction electrochemistry; (2) **3a** and **3b** have similar solid state arrangements; (3) **3a** and **3b** differ in the presence of a mild electron-donating group (CH₃) in the *para* position of the aryl

	3a ^A	3b	3c	3d	3e
CCDC deposition number/reference	YOKMUG, YOKMUG01, YOKMUG02, YOKMUG03	1415357	1415358	1415359	1415360
Bowl depth [Å] ^B	~2.50	2.386	2.653	2.728	2.575
Cg–Cg isoindole concave distance [Å]	~ 3.70	3.7321(8)	3.4516(8)	3.5972(8)	3.4153(8)
B–B concave distance [Å]	~ 8.50	8.202	8.672	8.510	8.891
B–B convex distance [Å]			7.506		7.466
N–Cg ribbon distance [Å]			3.417		3.276
			3.654		3.495
Aryl–BsubPc distance [Å]			3.536		3.507
			3.676		3.946

^AAverage metrical parameters of all four structures reported (see above).

^BBowl depth is calculated between a centroid formed by the six outmost carbon atoms constituting the BsubPc macrocycle and the boron centre.



Fig. 4. (a) Thermal ellipsoid diagram (35% probability) and (b) packing structure of **3d**, showing the concave isoindole and the biphenyl edge-to-face C–H–centroid interactions. Hydrogen atoms were omitted for clarity purposes. Centroids are illustrated in red.



Fig. 5. Packing structure of **3e** displaying (a) the interactions generating ribbons, the ribbon–ribbon interactions along the (b) *a*-axis (middle left) and (c) *b*-axis, and (d) the concave centrosymmetric isoindole interaction between ribbons. Each ribbon is represented by a different colour. Thermal ellipsoids were generated with 35% probability. Hydrogen atoms were omitted for clarity purposes. Centroids are illustrated in red.



Fig. 6. (a) Current density versus voltage characteristics of phenyl-BsubPc, 4-tolyl-BsubPc, 4-fluorophenyl-BsubPc/fullerene (C₆₀) devices. Shading indicates +/- one standard deviation. (b) Measured (EQE) spectra of phenyl-BsubPc, 4-tolyl-BsubPc, 4-fluorophenyl-BsubPc/C₆₀ devices. Shading indicates +/- one standard deviation.

moiety; and (4) 3e has a very different solid state arrangement and has a mild electron-withdrawing group (F) in the *para* position of the aryl moiety.

To investigate these aryl-BsubPcs as both electron donors and acceptors, six sets of OPV devices were fabricated. The first three sets were made by pairing each aryl-BsubPc with C₆₀ to scope their potential as electron-donating materials within the following device configuration: indium-tin oxide (ITO)/poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS)/aryl-BsubPc (10 nm)/fullerene (C₆₀; 30 nm)/bathocuproine (BCP; 10 nm)/silver (Ag; 80 nm). The device thicknesses were selected to be close to those used for a previously published Cl⁻BsubPc/C₆₀ device by Sullivan et al.^[34] The other three sets were made by pairing each aryl-BsubPc with sexithiophene



Fig. 7. (a) Current density versus voltage characteristics of sexithiophene (α -6T)/phenyl-BsubPc, 4-tolyl-BsubPc, 4-fluorophenyl-BsubPc devices. Shading indicates +/- one standard deviation. (b) Measured EQE spectra of α -6T/phenyl-BsubPc, 4-tolyl-BsubPc, 4-fluorophenyl-BsubPc devices. Shading indicates +/- one standard deviation.

(α -6T) to evaluate their potential as electron acceptors within the following device configuration: ITO/PEDOT:PSS/ α -6T (55 nm)/aryl-BsubPc (20 nm)/BCP (10 nm)/Ag (80 nm), following our previously published method for screening BsubPcs as acceptors.^[35] Current density–voltage (*J*–*V*) characteristics (Figs 6a and 7a) and characteristic parameters (Table 4) were measured under 100 mW cm⁻² of simulated solar illumination. External quantum efficiency (EQE) measurements are shown in Figs 6b and 7b.

As an electron donor material paired with C_{60} , phenyl-BsubPc (**3a**) outperforms 4-tolyl-BsubPc (**3b**) and 4-fluoro-BsubPc (**3e**). With only a slightly higher open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}), when compared with those of the other derivatives, the main increase in power

Device	$V_{\rm OC}$ [V]	$J_{\rm SC} [{ m mA} { m cm}^{-2}]$	FF	PCE [%]
Phenyl-BsubPc (3a)/C ₆₀	1.00 (0.003)	4.90 (0.17)	0.65 (0.01)	3.18 (0.12)
4-Tolyl-BsubPc $(3b)/C_{60}$	0.94 (0.004)	4.62 (0.08)	0.62 (0.01)	2.70 (0.06)
4-Fluorophenyl-BsubPc $(3e)/C_{60}$	0.98 (0.003)	4.38 (0.15)	0.62 (0.03)	2.66 (0.05)
α -6T/Phenyl-BsubPc (3a)	1.24 (0.004)	4.67 (0.22)	0.50 (0.02)	2.89 (0.14)
α -6T/4-Tolyl-BsubPc (3b)	1.25 (0.002)	3.33 (0.11)	0.45 (0.01)	1.87 (0.05)
α -6T/4-Fluorophenyl-BsubPc (3e)	1.16 (0.003)	3.03 (0.14)	0.47 (0.02)	1.64 (0.06)

Table 4. Average parameters of all devices

The standard deviation is indicated in brackets next to each parameter. At least eight devices were tested to determine these values

conversion efficiency (PCE) comes from a higher fill factor (FF = 0.65). This device matches the FF of the Cl-BsubPc/C₆₀ device reported by Sullivan et al. and almost matches their 3.29 % PCE.^[34] The EQE spectra (Fig. 6b) show that the contribution to the photocurrent from the BsubPc region (~550 nm to ~650 nm) is highest for the phenyl-BsubPc device and lowest for the fluoro-phenyl-BsubPc device, although only by a slight margin, as consistent with the small differences observed in $J_{\rm SC}$ s.

As an electron acceptor material paired with α -6T, all of the aryl-BsubPcs generate very high V_{OC} s, with 1.25 V from the 4-tolyl-BsubPc device representing the highest reported $V_{\rm OC}$ for any single-junction OPV to date using a BsubPc as the acceptor, with one exception of an OPV fabricated by Sullivan et al.; the latter device uses BsubPcs as both an electron donor and electron acceptor in an 'all BsubPc OPV'.^[6] Overall, phenyl-BsubPc once again outperforms the other two aryl-BsubPcs, this time by a wider margin. A higher FF is again measured for the phenyl-BsubPc-containing device, and this time a significant increase in J_{SC} is also observed. The α -6T/phenyl-BsubPc device produces a higher J_{SC} (corresponding to an increase of more than 35%) than either of the other two devices, with most of this difference coming from a significantly higher contribution to the photocurrent in the BsubPc region (Fig. 7b). However, the PCE of α -6T/ phenyl-BsubPc falls short of that of our previously reported α -6T/Cl-BsubPc device.^[35]

The differences in the measured $J_{\rm SC}$ could be due to differences in exciton diffusion lengths or dissociation rates of the corresponding aryl-BsubPcs.^[36] Considering the aryl-BsubPc thickness when applied as an acceptor layer is double the thickness when applied as a donor layer, it is expected that the effect of different exciton diffusion lengths within the aryl-BsubPcs would be exaggerated for the acceptor devices.^[36] This could explain why the acceptor devices have significantly different $J_{\rm SC}$ s, whereas the donor devices all have similar $J_{\rm SC}$ s. If true, the corresponding $J_{\rm SC}$ s from the devices using aryl-BsubPcs as electron acceptors suggest that phenyl-BsubPc may have the longest exciton diffusion length, whereas 4-tolyl-BsubPc and 4-fluorophenyl-BsubPc may have similar and relatively shorter exciton diffusion lengths.^[36]

The electrochemical data outlined showed that the HOMO and LUMO levels of all the studied aryl-BsubPcs are the same. Hence, in both the donor and acceptor cases, the small changes in $V_{\rm OC}$ (less than 10%) are unlikely to be due to differences in the HOMO–LUMO gap at the interface.^[37] Therefore, the small changes are likely due to subtle differences in carrier recombination or dielectric effects.^[38] The improvement in FF for the phenyl-BsubPc devices suggests better charge balance, possibly due to a better charge carrier mobility or better charge carrier

extraction.^[39] It may be possible to improve the FF of the 4-tolyl- and 4-fluorophenyl-BsubPc devices through rigorous optimization, but for the purposes of this study, we adhere to the rapid screening method outlined previously^[35] to determine which aryl-BsubPcs hold the most promise as electron-accepting and/or electron-donating materials in OPVs. Based on our results, we can conclude that phenyl-BsubPc (**3a**) shows the most promise, and interestingly enough, it is also the easiest of the group to synthesise.

Conclusion

A novel family of BsubPcs bearing various aryl ligands at the axial position of boron were synthesised and characterised by absorption and photoluminescence spectroscopy, X-ray crystallography, and cyclic voltammetry.

The similar absorption and photoluminescence properties measured for all derivatives agree with the frontier orbitals being localised on the BsubPc macrocycle.

The electrochemical generation of BsubPcs radical anions and cations occurred at similar potentials, and their behaviour was reversible under our conditions. Interestingly, the formation of BsubPcs dianion was observed, but was quasireversible, suggesting that aryl-BsubPcs are stable under cathodic conditions.

Contrarily to the properties described above, the solid-state structure of these derivatives depends on the nature of the substituent at the *para* position. Derivatives bearing an electronegative heteroatom displayed ribbons formed by edge-to-face isoindole N and C–H aryl π interactions. Centrosymmetric π – π interactions between concave isoindoles moieties, which are present in the structure of all derivatives, connect ribbons into an extended two-dimensional π network. Due to the interesting properties of **3e**, we are currently investigating the behaviour of other fluoro- and perfluoroaryl-BsubPcs.

By immediately integrating **3a**, **3b**, and **3e** in OPV devices, we have demonstrated their dual functionality as electron donors and electron acceptors, and identified the aryl-BsubPc with the most promise in future OPVs. Derivative **3a** exhibits better performance across the board when compared with the other derivatives. The higher performance is hypothesised to be mainly due to a longer exciton diffusion length. As all derivatives have the same basic physical properties, including electrochemical behaviour, and **3a** and **3b** share the same solid-state arrangement, the distinction of **3a** was only found once incorporated into OPVs. Combined with the additional advantage of having the easiest synthesis when compared with the other derivatives, we feel that **3a** has significant potential for further investigation in different and/or more rigorously optimized OPV architectures.

Experimental

General Considerations

CH₂Cl₂ and THF solvents were purchased from Caledon Laboratory Ltd (Caledon, Ontario, Canada); THF was dried and purified by passing through activated alumina. Phenylmagnesium bromide (1.0 M in THF), 4-bromobiphenyl, Mg turnings, I₂, and BCP (99.6%) were purchased from Sigma-Aldrich and used as received. PEDOT:PSS (Heraeus, Clevois P VP AI 4083), Ag (R.D. Mathis, 99.999%), and silver paint (PELCO, Conductive Silver 187) were purchased and used as received. α -6T (Sigma-Aldrich) and C₆₀ (SES Research, 99.5%) were purchased and purified once by train sublimation before use. Column chromatography was carried out on Silicycle Silica 60 silica gel (particle size 40-63 µm) and thin layer chromatography was performed on silica gel 60 coated with $F_{254 \text{ nm}}$. All NMR spectra were recorded in CDCl₃ (purchased from Cambridge Isotope Laboratories Inc. and used as is) on a Bruker Advance III 400 MHz spectrometer operating at 400 MHz (¹H), 128 MHz (¹¹B), 100 MHz (¹³C), and 376 MHz (¹⁹F) at 25°C. Chemical shifts are reported in ppm relative to the residual solvent signal (¹H and ¹³C), BF₃·OEt₂ (¹¹B, 0 ppm) and C₆F₆ $(^{19}F, 0 ppm)$ standards.

UV-Visible spectra were obtained using a PerkinElmer Lambda 25 spectrophotometer operating in double-beam mode with a slit width of 1 nm. Fluorescence spectra were obtained using a PerkinElmer LS55 spectrophotometer. Electrochemical studies were performed at 100 mV s⁻¹ using a Bioanalytical Systems C3 workstation with a three-electrode cell, consisting of a Pt wire auxiliary electrode, an Ag/AgCl reference electrode, and a glassy carbon disc (1 mm) working electrode. Solutions comprised 1 mM test compound and 0.1 M $[nBu_4N]^+[PF_6]^-$ as the supporting electrolyte in deoxygenated CH₂Cl₂. All $E_{1/2}$ values were referenced internally to Cp*₂Fe $(E_{1/2} = -0.012 \text{ V in CH}_2\text{Cl}_2 \text{ versus Ag/AgCl}).^{[27]}$ X-ray crystallographic analyses were performed on suitable crystals mounted on a Kappa CCD system.

Br-BsubPc (1),^[13] 4-tolylmagnesium bromide (2b),^[40] 4-methoxyphenylmagnesium bromide (2c),^[40] and 4-fluorophenylmagnesium bromide (2e)^[41] were synthesised according to literature procedures.

Synthesis

Preparation of 4-Biphenylmagnesium Bromide (2d)

Under an atmosphere of Ar, Mg turnings (1.2 equiv.) and a crystal of I_2 were dissolved in anhydrous THF, and the mixture was warmed at 35°C. 4-Bromobiphenyl (1 equiv.), dissolved in a minimum amount of anhydrous THF, was added dropwise, and the resulting mixture was stirred at 35°C for 5 h.

General Preparation of Aryl-BsubPc (3a–e)

In a 500-mL three-neck flask, equipped with a condenser and an argon inlet, the corresponding aryl magnesium bromide reagent (2.0 equiv.) was added dropwise to a suspension of Br-BsubPc (2.44 g, 5.1 mmol, 1.0 equiv.) in anhydrous THF (400 mL). The mixture was refluxed under an atmosphere of argon for 16 h and after being cooled to room temperature, the excess aryl magnesium bromide reagent was quenched with methanol (MeOH). Volatiles were removed via rotary evaporation, and the crude material was purified through column chromatography using CH_2Cl_2 as the eluent and further purified by recrystallization from a mixture of CH_2Cl_2 /hexanes and/or train sublimation, affording red–bronze solids. *Phenyl-BsubPc (3a)*: 35 % yield. Spectroscopic characterisation agrees with the literature.^[18] $\delta_{\rm H}$ (CDCl₃, 400 MHz) 8.86 (6H, m), 7.89 (6H, m), 6.72 (1H, tt, ${}^{3}J_{\rm HH}$ 7.4, ${}^{4}J_{\rm HH}$ 1.3), 6.59 (2H, m), 5.45 (2H, d, ${}^{3}J_{\rm HH}$ 7.7).

4-Tolyl-BsubPc (**3b**): 37 % yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 8.84 (6H, m), 7.87 (6H, m), 6.42 (2H, d, ${}^{3}J_{\rm HH}$ 7.8), 5.36 (2H, d), 1.90 (3H, s). $\delta_{\rm C}$ (CDCl₃, 100 MHz) 151.0, 137.4, 131.0, 129.7, 128.6, 127.9, 122.15, 21.0; *C*-BsubPc signal was not observed. $\delta_{\rm B}$ (CDCl₃, 128 MHz) -15.8 (s). *m/z* (high-resolution mass spectrometry direct analysis in real time (HRMS DART)) 487.18315; $[{}^{12}{\rm C}_{31}^{1}{\rm H}_{20}^{11}{\rm B}^{14}{\rm N_{6}}]^{+}$ requires 487.18425.

4-Methoxyphenyl-BsubPc (3c): 38% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz) 8.85 (6H, m), 7.88 (6H, m), 6.14 (2H, d, ${}^{3}J_{\rm HH}$ 8.6), 5.39 (2H, d), 3.43 (3H, s). $\delta_{\rm C}$ (CDCl₃, 100 MHz) 159.2, 150.9, 131.0, 129.9, 129.7, 122.1, 112.8, 54.9; *C*-BsubPc signal was not observed. $\delta_{\rm B}$ (CDCl₃, 128 MHz) – 15.9 (s). *m/z* (HRMS DART) 503.17780; $[{}^{12}C_{31}^{1}H_{20}^{11}B^{14}N_{6}^{16}O]^{+}$ requires 503.17916.

 $\begin{array}{l} \textit{4-Biphenyl-BsubPc} \ (\textit{3d}): 17 \ \% \ yield. \ \delta_{H} \ (CDCl_{3}, 400 \ MHz) \\ 8.87 \ (6H, m), 7.90 \ (6H, m), 7.19 \ (5H, m), 6.82 \ (2H, d, \ ^{3}J_{HH} \ 8.1), \\ 5.54 \ (3H, d). \ \delta_{C} \ (CDCl_{3}, 100 \ MHz) \ 151.0, 141.0, 140.6, 131.0, \\ 129.8, 129.1, 128.6, 127.1, 127.0, 126.0, 122.2; \ \textit{C-BsubPc signal} \\ was not \ observed. \ \delta_{B} \ (CDCl_{3,128} \ MHz) \ -15.8 \ (s). \ \textit{m/z} \ (HRMS \ DART) \ 549.19858; \ [\ ^{12}C_{36}^{1}H_{22}^{1B} \ ^{14}N_{6}]^{+} \ requires \ 549.19990. \end{array}$

4-Fluorophenyl-BsubPc (3e): 24 % yield. $\delta_{\rm H}$ (CDCl₃400 MHz) 8.85 (6H, m), 7.89 (6H, m), 6.27 (2H, dd, ${}^{3}J_{\rm HF}$ 8.9, ${}^{3}J_{\rm HH}$ 8.3), 5.40 (2H, dd, ${}^{4}J_{\rm HF}$ 5.9). $\delta_{\rm C}$ (CDCl₃, 100 MHz) 162.5 (d, ${}^{1}J_{\rm CF}$ 245), 151.0, 131.0, 130.4 (d, ${}^{3}J_{\rm CF}$ 7.5), 129.8, 122.2, 114.1 (d, ${}^{2}J_{\rm CF}$ 20); C-BsubPc signal was not observed. $\delta_{\rm B}$ (CDCl₃, 128 MHz) -16.0 (s). $\delta_{\rm F}$ (CDCl₃, 376 MHz) -114.03 (s). *m/z* (HRMS DART) 491.15917; [${}^{12}{\rm C}_{30}^{1}{\rm H}_{17}^{1}{\rm B}^{19}{\rm F}^{14}{\rm N}_{\rm 6}$]⁺ requires 491.15918.

OPV Fabrication

OPV device fabrication and characterisation was performed according to a previously described method.^[35] OPV devices were fabricated on 25 mm by 25 mm glass substrates coated with ITO, with a sheet resistance of 15 Ω per square (Thin Film Devices, Inc.). The ITO was pre-patterned, leaving 8 mm from one side as uncoated glass. Substrates were cleaned by successive sonication processes in detergent and solvents, followed by 5 min of atmospheric plasma treatment. PEDOT:PSS was spincoated onto the substrates at 500 rpm for 10 s, followed by 4000 rpm for 30 s. Substrates were baked on a hot plate at 110°C for 10 min, and then transferred into a nitrogen atmosphere glove box (O₂ < 10 ppm, H₂O < 10 ppm).

All subsequent device layers were thermally evaporated at $\sim 1.0 \text{ Å s}^{-1}$ and a working pressure of $\sim 1 \times 10^{-7}$ torr for organic layers and $\sim 1 \times 10^{-6}$ torr for Ag. Silver electrodes were evaporated to a thickness of 80 nm through a shadow mask, defining 0.2 cm² as the active area for each device. A transfer back to the glove box was required between BCP and Ag layers to change the shadow masks.

OPV Characterisation

The layer thickness and deposition rates of the evaporated films were monitored using a quartz crystal microbalance calibrated against films deposited on glass, and also measured with a KLA-Tencor P16+ surface profilometer. To enhance the electrical contact during testing, silver paint was applied to the ITO and metal electrode contact points, and left to dry for 20 min. Devices were kept in the nitrogen-filled glove box throughout testing. Voltage sweeps of the devices were performed under

full illumination by a 300 W Xe arc lamp (Oriel) with an AM 1.5G filter, and the corresponding currents were measured with a Keithley 2401 low voltage source meter. Light intensity was calibrated to 100 mW cm⁻² with reference to a calibrated silicon photodetector. Wavelengths scans at 10 nm intervals were performed using an in-line CornerstoneTM 260 1/4 m monochromator, and the corresponding currents were measured using a Newport 2936-R optical power meter and converted to external quantum efficiencies using a reference wavelength scan of a calibrated silicon photodetector.

Supplementary Material

NMR spectra, cyclic voltammograms, X-ray information tables, and *ORTEP* diagrams of **3c** and **3e** are available on the Journal's website.

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