Palladacycle-Catalyzed Triple Suzuki Coupling Strategy for the Synthesis of Anthracene-Based OLED Emitters

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Supporting Information

ABSTRACT: The development of the site-selective Suzuki–Miyaura cross-coupling of dibromoanthracene as an efficient strategy toward organic light emitting diodes (OLEDs) is disclosed in this article. An unprecedented step-economic palladacycle-promoted triple Suzuki coupling protocol allowed the synthesis of three new OLED emitters and could prove to be a useful general strategy for researchers working in this field. Characterization of the synthesized molecules by UV–vis spectroscopy and thermogravimetric analysis–differential scanning calorimetry followed by density functional theory studies of the different properties strongly confirms the derivatives possess more significant hole mobility character than electron transfer capability.

1. INTRODUCTION

Transition-metal catalyzed reactions have in recent decades emerged as an efficient method for the installation of C–C bonds in a wide variety of substrates. Their applications range from synthesizing simple biaryls to complex natural products and functional molecules such as organic light emitting diodes (OLEDs). Amongst others, palladium has played a special role in revolutionizing the way catalytic reactions have been performed in the past few decades. Excellent functional group tolerance, milder reaction conditions, and the ability to activate rather inert bonds. These qualities of palladacyclic complexes has contributed to the enhancement of nucleophilicity leading to efficient insertion into a variety of rather inert bonds. These qualities of palladacyclic complexes have proved especially useful in catalyzing synthetic processes such as the selective reduction of alkenes, alkynes, and/or nitroalkanes. However, the most noteworthy application comes in the form of their utilization as catalysts in cross-coupling reactions for the installation of C–C bonds in substrates of wide-ranging complexity.

In spite of all this success, the true potential of palladacyclic complexes has yet to be realized and recent developments in this field of research (with applications in anticancer studies, liquid crystalline material synthesis, and others) are a testament of their growing importance. One such area that has yet to experience the impact of palladacycles is the development of functional material synthesis (OLEDs, semiconductors, etc.). For the development of OLEDs and related molecules, palladium-catalysis has played a major role with Suzuki–Miyaura cross-coupling reactions as the key step. This is commonly achieved by the incorporation of organic molecules that can enhance the thermal stability and lifetime of the fabricated OLEDs. The same is true for the improvement of
Besides the common occurrence of substructures such as p-terphenyls, carbazoles, triphenylamines, etc. in OLED frameworks, anthracene, with its unique blend of properties, has attracted the most attention. To date, the catalytic processes employed for the incorporation of the anthracenyl structural motif into the OLED framework involve several low-yielding synthetic steps with tedious work-up procedures. Recently, our group has disclosed an efficient route for obtaining differently substituted anthracenes using a novel N-heterocyclic carbene ligand system in combination with Pd(OAc)$_2$ via Suzuki–Miyaura cross-coupling reactions. However, although the route provides easy access to substituted anthracenes, the involvement of several synthetic and purification steps needs to be addressed in order to develop a more sustainable approach to such molecules.

Table 1. Screening Study for Selective Arylation of 9,10-Dibromoanthracene$^{a,b,c}$

| s. no. | Pd-catalyst/precursor | catalyst (mol %) | base | solvent (mL) | temp. ($^\circ$C) | time (h) | mono (3a) | di (3a') |
|-------|----------------------|-----------------|------|-------------|-----------------|---------|-----------|----------|
| 1     | Pd(OAc)$_2$          | 5.0             | K$_2$CO$_3$ (aq) | tetrahydrofuran (THF) | 80              | 12      | 22        | 38       |
| 2     | PdCl$_2$             | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 20        | 20       |
| 3     | [Pd(PPh)$_3$)$_2$]   | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 39        | 51       |
| 4     | Pd(OAc)$_2$ + 1,10 phenanthroline | 5.0 | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 50        | 35       |
| 5     | Pd(OAc)$_2$ + S1Pr   | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 35        | 41       |
| 6     | Pd(OAc)$_2$ + XPhos  | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 41        | 53       |
| 7     | XPhos PdG1           | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 15        | 81       |
| 8     | XPhos PdG2           | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 19        | 77       |
| 9     | XPhos PdG1           | 5.0             | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 52        | 41$^d$ |
| 10    | [Pd(Phbz)(mal)(PPh)$_3$] | 5.0 | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 70        | 30       |
| 11    | [Pd(Phbz)(OAc)(PPh)$_3$] | 5.0 | K$_2$CO$_3$ (aq) | THF            | 80              | 12      | 43        | 37       |

| s. no. | Pd-catalyst/precursor | catalyst (mol %) | base | solvent (mL) | temp. ($^\circ$C) | time (h) | mono (3a) | di (3a') |
|-------|----------------------|-----------------|------|-------------|-----------------|---------|-----------|----------|
| 12    | [Pd(Phbz)(mal)(PPh)$_3$] | 2.5 | K$_2$CO$_3$ (aq) | THF       | 80              | 12      | 70        | 30       |
| 13    | [Pd(Phbz)(mal)(PPh)$_3$] | 1.0 | K$_2$CO$_3$ (aq) | THF       | 80              | 12      | 70        | 30       |
| 14    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_2$CO$_3$ (aq) | THF       | 80              | 12      | 80        | 20       |
| 15    | [Pd(Phbz)(OAc)(PPh)$_3$] | 0.5 | K$_2$CO$_3$ (aq) | THF       | 80              | 12      | 58        | 32       |
| 16    | XPhos PdG1           | 0.5             | K$_2$CO$_3$ (aq) | THF       | 80              | 12      | 28        | 68       |
| 17    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.1 | K$_2$CO$_3$ (aq) | THF       | 80              | 12      | 72        | 08       |

| s. no. | Pd-catalyst/precursor | catalyst (mol %) | base | solvent (mL) | temp. ($^\circ$C) | time (h) | mono (3a) | di (3a') |
|-------|----------------------|-----------------|------|-------------|-----------------|---------|-----------|----------|
| 18    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | KOH            | THF       | 80              | 12      | 47        | 43       |
| 19    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | Et$_3$N        | THF       | 80              | 12      | 26        | 24       |
| 20    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_3$PO$_4$    | THF       | 80              | 12      | 54        | 36       |
| 21    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | Cs$_2$CO$_3$   | THF       | 80              | 12      | 72        | 23       |
| 22    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_2$CO$_3$    | THF       | 80              | 12      | 51        | 21$^c$   |
| 23    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_2$CO$_3$    | THF       | 80              | 12      | 66        | 29$^f$   |

| s. no. | Pd-catalyst/precursor | catalyst (mol %) | base | solvent (mL) | temp. ($^\circ$C) | time (h) | mono (3a) | di (3a') |
|-------|----------------------|-----------------|------|-------------|-----------------|---------|-----------|----------|
| 24    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_2$CO$_3$ (aq) | THF   | 120            | 12      | 50        | 50       |
| 25    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_2$CO$_3$ (aq) | THF   | 60             | 12      | 90        | 10       |
| 26    | [Pd(Phbz)(mal)(PPh)$_3$] | 0.5 | K$_2$CO$_3$ (aq) | THF   | 32             | 12      | 48        | 02       |

$^a$1.0 mmol of 1a, 1.5 mmol of boronic acid, base (2.0 mmol). $^b$Isolated yield. $^c$Bold font highlights catalytic activity. $^d$Rather than 9,10-dibromoanthracene, 9,10-dichloroanthracene was used. $^e$Instead of 1.5 mmol K$_2$CO$_3$, 1.0 mmol was used. $^f$Instead of 1.5 mmol K$_2$CO$_3$, 1.2 mmol was used.
With this in mind, herein we report a largely improved synthetic protocol for accessing differently substituted anthracenes with promising thermal stability and photophysical properties. This was achieved via the employment of palladacyclic complexes enabling the site-selective (preferential) Suzuki–Miyaura arylation of dibromoanthracenes in a one-pot sequential manner. Notably, a unique and unprecedented one-pot sequential triple Suzuki–Miyaura arylation protocol was made possible allowing for the development of potential OLEDs with greater structural complexity.

2. RESULTS AND DISCUSSION

At the outset of our studies we investigated the possibility of the selective monoarylation of 9,10-dibromoanthracene using different palladium catalyst systems (summarized in Table 1). Initially, the employment of general palladium(II) precursors such as Pd(OAc)$_2$ and PdCl$_2$ showed poor reactivity and selectivity toward monoarylation (entries 1 and 2, Table 1). The commonly applicable Pd(0) source, Pd(PPh$_3$)$_4$, brought about a slight improvement in the overall conversion but provided poor selectivity (entry 3, Table 1). In situ generated Pd(II) species via the addition of commercially available σ-donor ligands such as 1,10-phenanthroline, SIPr, and XPhos, provided similar results with a loss of selectivity (entries 4–6, Table 1). To test the effect of complexed XPhos Pd complexes on the catalytic process, XPhos PdG1 and XPhos PdG2 were employed. Although improved reactivity was observed, the selectivity was poor with the diarylated product obtained in higher amounts than that of the monoarylated product (entries 7–9, Table 1).

We next turned our attention to the palladacyclic complexes of the formula [Pd(Phbz)(X)(PPh$_3$)]$^{2c}$ (X = maleimide IA, OAc IB), which were recently introduced by us as efficient catalysts for the homocoupling of aryl boronic acids under aerobic conditions. It was observed that subtle variation in the electronic properties (maleimide acting as a better σ-acceptor than OAc) led to a dramatic improvement in the overall conversion as well as selectivity for the monoarylated product (entries 7 and 8, Table 1). Palladacycle IA outperformed other catalytic systems with an overall conversion of 100% and appreciable selectivity for monoarylation. Catalysis experiments performed on catalyst IA revealed that activity was retained even at 0.5 mol % catalyst concentration and a slight improvement in selectivity was observed. Any further reduction led to a reduction in reactivity. Base screening was next undertaken with stronger bases such as KOH showing better conversions but at the expense of selectivity. Similar observations were made for other bases such as Et$_3$N and K$_3$PO$_4$. In the case of Cs$_2$CO$_3$, though, comparable reactivity and selectivity was achieved.

However, the more expensive nature of the base made the process less attractive and therefore the use of K$_3$CO$_3$ with slightly better selectivity was chosen for further development. To further enhance the selectivity toward monoarylation, varied temperature studies were performed. At elevated temperatures, rapid conversion to the product was followed by a loss in selectivity with both mono- and diarylated products obtained in equal amounts. Optimimum conditions for monoselectivity were eventually made possible by a reduction in reaction temperature to 60 °C. Any further reduction in temperature led to less than satisfactory yields.

Having developed a selective protocol for obtaining the monoarylated anthracene, we decided to synthesize differently substituted anthracenes allowing for further modification. Another reason for synthetic development is related to the identification of potential candidates exhibiting good emissive properties as starting points for obtaining OLED-type molecules. The catalytic reactions were carried out at 60 °C using the palladacycle IA in THF as solvent using 2 M K$_2$CO$_3$ as the base employing different aryl boronic acids. Electronic and steric effects play a major role in obtaining the desired monoarylated products selectively with benzofuran-2-boronic acid providing the best results.

The synthesized molecules were further subjected to UV analysis to determine their respective absorption wavelengths. Introduction of different groups on the anthracenyl moiety brings about a bathochromic shift (relative to the primary molecule, i.e., 9,10-dibromoanthracene) in wavelength. A maximum in enhancement was observed when the benzofuran moiety was installed on the anthracene substructure using the developed protocol. Yet, a variety of other moieties also provided a decent enhancement in absorbance values. The examples highlighted in Scheme 1 can thus serve as indicators to the reader for further exploitation toward the quest for the development of excellent OLED materials.

The synthesized products were generally obtained as a crystalline powder after column chromatographic purification and in one of the cases (2c), it was even possible to obtain a single-crystal X-ray structure; the crystal having been grown from a dichloromethane/hexane solvent mixture (Figure 1). It was observed that the torsion angle between the anthracene and the phenyl ring is 108.2°, the angle between the phenyl and naphthalene ring is 82.7°, and consequently the angle between anthracene and the naphthalene rings is 25.6°. No coplanarity whatsoever was observed in the crystal structure. As the three planar aromatic moieties are not coplanar, it can be concluded that the molecule does not represent a fully delocalized π-system in its crystalline form, but this may change in solution or in its noncrystalline solid form. An activation of rotations around the torsion angles by light, for instance, can be envisioned.

With the development of an efficient protocol permitting the site-selective arylation of dibromoanthracene, we turned our attention to the problem that is commonly associated with the synthesis of OLED materials, that is, sustainability of synthesis. Current routes for the synthesis of OLED-type materials suffer from the usage of higher concentrations of the metal catalyst and the necessity of several synthetic and purification steps making the process commercially less attractive. With the aim of providing a sustainable solution to this problem, we decided to explore the idea of performing the selective arylation followed by a second arylation via a palladium-catalyzed one-pot sequential protocol, which could furnish differently substituted anthracenes of varying complexity. This would provide researchers with a useful handle for fine-tuning the electronic and fluorescence properties of the molecules through judicious choice of the arylation groups.

Our earlier study identified monoarylation using benzofuran-2-boronic acid as particularly facile and also providing the highest absorbance value compared to those of the others. It was therefore decided to perform the first catalytic arylation in the one-pot sequence with benzofuran-2-boronic acid as the coupling partner followed by the introduction of other aryl boronic acids to furnish an array of diversely substituted anthracenes (Schemes 2 and 3). From Scheme 2 it can be seen that in most cases a good yield of the cross-coupled product
was obtained over two reaction steps without isolation of the monoarylated intermediates.

The employment of electronically different aryl boronic acids resulted in the formation of diarylated anthracenes exhibiting promising fluorescence properties, as is evident from the absorbance wavelengths obtained for the respective molecules (see Section 3.1). With the success of the one-pot sequential double Suzuki−Miyaura cross-coupling of 9,10-dibromoanthracene, we envisaged a unique triple one-pot coupling process involving the employment of three different aryl boronic acids as an efficient synthetic strategy to obtain OLED-type

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**Scheme 1. Synthesis of Monoarylated Anthracenes**

\[ \text{Br} \quad \text{B(OH)}_2 \quad \text{[Pd(Ph3P)2]} \quad \text{K}_2\text{CO}_3 \quad \text{THF/H}_2\text{O} \quad \text{Br} \quad \text{R} \]

1.0 mmol of 1a, catalyst IA (0.5 mol %), 1.5 mmol of aryl boronic acid, K₂CO₃ (2.0 mmol), 60 °C, 12 h in THF (2.0 mL)/H₂O (2.0 mL). Isolated yield.

**Scheme 2. Sequential One-Pot Synthesis of Diversely Substituted Anthracene-Based Emitters**

**Sequential one-pot synthesis**

\[ \text{Br} \quad \text{B(OH)}_2 \quad \text{[Pd(Ph3P)2]} \quad \text{K}_2\text{CO}_3 \quad \text{THF/H}_2\text{O} \quad \text{Br} \quad \text{R} \]

Part I: 1.0 mmol of 1a, catalyst IA (0.5 mol %), 1.5 mmol of aryl boronic acid, K₂CO₃ (2.0 mmol), 60 °C, 12 h in THF (2.0 mL)/H₂O (2.0 mL); Part II: 1.5 mmol of aryl boronic acid, K₂CO₃ (2.0 mmol), 80 °C, 12 h. Isolated yield.

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**Figure 1.** Molecular structure of 2c obtained from X-ray structural analysis. The ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity.
molecules directly without isolation of any intermediates. The initial coupling was performed with benzofuran-2-boronic acid, followed by the employment of 4-chlorophenyl boronic acid, which provided us with a handle for further modification. These two processes were catalyzed by the palladacyclic complex IA. However, the next activation involving C−Cl bond cleavage followed by coupling could only be achieved with the incorporation of an electron-rich XPhos ligand into the catalytic system.

Without the need for isolation of any of the intermediates, synthesizing OLED-type molecules could be made much easier by the employment of such a step-economic methodology. These two processes were catalyzed by the palladacyclic complex IA. However, the next activation involving C−Cl bond cleavage followed by coupling could only be achieved with the incorporation of an electron-rich XPhos ligand into the catalytic system.

Without the need for isolation of any of the intermediates, synthesizing OLED-type molecules could be made much easier by the employment of such a step-economic methodology. It was also observed that in comparison to the general methods employed for the synthesis of OLED-type molecules, only a very low concentration of palladium catalyst was required. Sustainability in catalytic processes leading to molecules of such relevance could thus be achieved via these types of one-pot sequential procedures.

### 3. PHOTOPHYSICAL AND THERMAL ANALYSIS

The above methodology provides a step-economic alternative to the known synthetic procedures that involve tedious work-up procedures, lower product formation, and multiple purification steps. During the initial screenings a few of the synthesized molecules, namely 4a–c, were found to exhibit promising UV absorbance in CH2Cl2 as solvent, thus warranting further investigation into their photophysical and thermal properties.

#### 3.1. Photophysical Properties

The unprecedented triple Suzuki coupling protocol resulted in the formation of three molecules comprising the anthracenyl substructure and extended conjugation. The absorbance and emission spectra of 4a–c were recorded in CH2Cl2. For the emission spectral analysis, the excitation wavelength was kept fixed at 400 nm. Substituting the anthracene structural motif in the 9,10 position with different functionalities had a pronounced effect on the photophysical properties of the resulting molecules (see Figure 2). This is evident from the shift in the emission wavelengths well above 500 nm for 4a and 4c (564 and 503 nm, respectively).

#### 3.2. Thermal Properties

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are useful tools for analyzing the thermal stability of compounds. In recent years, both analytical tools have been applied to

![Scheme 3. Novel Sequential One-Pot Triple Suzuki Coupling](image)

“Part I: 1.0 mmol of 1a, catalyst IA (0.5 mol %), 1.5 mmol of aryl boronic acid, K2CO3 (2.0 mmol), 60 °C, 12 h in THF (2.0 mL)/H2O (2.0 mL); Part II: 1.5 mmol of aryl boronic acid, K2CO3 (2.0 mmol), 80 °C, 12 h; Part III: XPhos (1.0 mol %), 1.5 mmol of aryl boronic acid, K2CO3 (2.0 mmol), 80 °C, 12.0 h. Isolated yield.

![Figure 2. (A) Absorbance spectra for 4a–c; (B) emission spectra for 4a–c recorded in CH2Cl2 at 25 °C. The concentration of solutions was 1 × 10−6 M.](image)
molecules with possible OLED applications because thermal stability, naturally, is a prerequisite in this respect. Consequently, we first subjected the synthesized molecules 4a−c to TGA in the temperature range of 33−600 °C under a N₂ atmosphere by heating at a rate of 10 °C/min (Figure 4). The anthracene-based molecules 4a−c show high thermal stabilities with decomposition temperatures (Tₐ) ranging from 280 to 410 °C. Higher values of decomposition temperatures observed for 4a−c could be directly related to the extent of substitution on anthracene. The intrinsically amorphous characteristics of the synthesized compounds were further confirmed by DSC, which provided the individual melting temperatures. For compounds 4a, 4b, and 4c, the melting temperature (Tₘ) was found to be 320, 230, and 280 °C, respectively. These comparatively high values of Tₐ and Tₘ are apparently due to the one extra phenyl ring and larger molecular size of the synthesized molecules compared to that of their disubstituted analogs (3a−f).

4. DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS

4.1. Geometries. The effect of substituents on the geometry of the anthracene core is already well documented.²³−²⁵ It has been shown that the dihedral angle between anthracene and its substituents affects the extent of conjugation in the molecule irrespective of the nature of the substituent. Selected geometrical parameters of 4a, 4b, and 4c are given in Table 2 and the optimized geometries and labeling schemes of the models are depicted in Figure 5. The dihedral angles between the anthracene core and its two substituents for 4a are Φ1 = 58.7° and Φ2 = 89.2° for the benzofuran and phenyl rings, respectively (Table 2). The increased dihedral angle for the phenyl ring is due to the repulsion between its two ortho hydrogens and anthracene whereas benzofuran only bears one ortho hydrogen. Hence, the near perpendicularity between the anthracene moiety and the phenyl ring prohibits an extended π-electron conjugation retaining the individuality of each fragment.

The structural distinction of 4a, 4b, and 4c, is based on the biphenyl, benzofuran, and triphenyl amine moieties bound to the para position of the bridging phenyl ring. These substituents have little effect on the dihedral angle between the anthracene core and phenyl ring (85.4 and 79.5° for 4b and 4c, respectively) and nearly no effect on the dihedral angle between benzofuran and the anthracene core (ranging from 58.4 to 58.7°).

Major structural differences are, however, evident in the dihedral angle Φ3, that is, the angle between the bridging phenyl ring and the varied para substituents distinct in each molecule (−36.9, 0.3, and −35.4° in 4a, 4b, and 4c, respectively).

The comparably small differences in the dihedral angles Φ1 and Φ2 do not result in any significant changes in the conjugation of the neutral geometry of the anthracene core. Here, the bond length alternation (BLA) is almost zero in the central benzene ring whereas in the remaining two benzene rings it is about 0.06 Å only. Interestingly, the variance in BLA of the anthracene core is even reduced to about 0.03 Å in both the cation and anion geometries of 4a and 4b and to 0.04 and...
0.03 Å for the cation and anion of 4c, respectively, supporting a stronger conjugation upon oxidation or reduction in these derivatives. Notably, the varied substituents have only a negligible effect on the oxidized or reduced geometries of all derivatives compared to those of each other.

### 4.2. Frontier Molecular Orbitals.

From the data summarized in Table 3, the electron density dependence on the substituent side groups can be derived. The apparent structural near perpendicularity of the substituent side groups with respect to the anthracene core is well reflected by the appearance of the frontier molecular orbitals. Derivatives 4a and 4b are quite similar in their electronic density distribution in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which are localized predominately within the anthracene core. In contrast, the strong donor triphenyl amine group of 4c contributes very strongly to the HOMO whereas the LUMO is still centered at the anthracene core. Hence, the LUMO levels are almost unperturbed at −1.84, −1.87, and −1.82 eV, respectively, for 4a, 4b, and 4c. The predominance of the triphenyl amine

| geometry parameter<sup>b</sup> | 4a          | 4b          | 4c          |
|-------------------------------|-------------|-------------|-------------|
| 1                             | 1.421       | 1.407       | 1.405       |
| 2                             | 1.368       | 1.380       | 1.382       |
| 3                             | 1.433       | 1.423       | 1.425       |
| 4                             | 1.411       | 1.428       | 1.436       |
| 5                             | 1.412       | 1.429       | 1.437       |
| 6                             | 1.433       | 1.423       | 1.425       |
| 7                             | 1.369       | 1.379       | 1.381       |
| 8                             | 1.421       | 1.406       | 1.405       |
| 9                             | 1.369       | 1.381       | 1.382       |
| 10                            | 1.432       | 1.421       | 1.424       |
| 11                            | 1.417       | 1.436       | 1.438       |
| 12                            | 1.417       | 1.436       | 1.438       |
| 13                            | 1.433       | 1.421       | 1.424       |
| 14                            | 1.369       | 1.382       | 1.382       |
| 15                            | 1.447       | 1.440       | 1.447       |
| 16                            | 1.445       | 1.444       | 1.446       |
| 17                            | 1.474       | 1.449       | 1.452       |
| 18                            | 1.498       | 1.477       | 1.475       |
| Φ1                            | 58.7        | 41.0        | 45.6        |
| Φ2                            | 89.2        | 120.1       | 53.4        |
| Φ3                            | −36.9       | −31.2       | −26.2       |

<sup>a</sup>Bond lengths are in angstrom and dihedral angles are in degree. <sup>b</sup>Geometry parameter labels are according to Figure 4.
substituent in 4c results in a HOMO level of −4.98 eV, whereas for 4a and 4b, it is located at about −5.2 eV. Thus, the HOMO−LUMO gaps (HLGs) differ with 3.17 eV for 4c and about 3.3 eV for 4a and 4b. This can also be attributed to the relatively smaller adiabatic electron affinity (EA) value of 5.86 eV for 4c, though the adiabatic ionization potential (IP) values are not very different for all derivatives.

4.3. Absorption and Reorganization Energies. For a deeper insight into the electron transition character of all of the derivatives, the excitation energies and reorganization energies for hole and electron mobility were calculated (see Table 3). In general, a good agreement between experimental and calculated excitation energies was found within the accepted limit of 0.1 eV for time-dependent density functional theory (TDDFT). The electronic excitation is strongly dominated by the HOMO−LUMO transition for which the electron density distribution was discussed in the previous section. A localized electron rearrangement within the anthracene core is observed during transitions in 4a and 4b whereas a significant shift of electron density from the triphenyl amine to the anthracene core was found for 4c.

In addition, the electron/hole transport parameters, namely the reorganization energies (\( \lambda^+ \) and \( \lambda^- \)), were calculated. From smaller reorganization energies, greater charge mobilities can be anticipated. Notably, the reorganization energies for hole mobility are always smaller than those for electron mobility by 0.026, 0.055, and 0.105 eV for 4a, 4b, and 4c, respectively (Table 3). This increased charge mobility can be attributed to the considerable geometrical changes and HOMO levels in 4a, 4b, and 4c. All derivatives possess superior hole mobility than electron transfer capability.

5. CONCLUSIONS
The development of a unique synthetic methodology for obtaining novel OLED-type emitters in a single-pot multistep procedure has been achieved via a palladacycle-catalyzed triple Suzuki coupling protocol. The procedure allows the synthesis of three new OLED-type emitters, 4a–c, that were found to exhibit interesting photophysical properties. These molecules were characterized by different characterization techniques, and molecule 4a exhibited promising absorption and emission values. TGA of these molecules also suggested high thermal stability, which will be useful for OLED applications. Theoretical calculations (DFT) performed on these molecules provided details on the geometry, HOMO−LUMO energies, as well as the reorganization energies. On the basis of these findings, it could be concluded that the hole mobility of the synthesized molecules 4a–c is far more superior than the electron transfer, which makes these compounds excellent candidates for efficient OLED emitters.

6. EXPERIMENTAL SECTION
6.1. General Remarks. All catalytic reactions were conducted under an inert atmosphere of N\(_2\) on a Schlenk line. Thin-layer chromatography (TLC) analysis was performed on aluminum backed silica gel plates and compounds were visualized by UV light (254 nm), phosphomolybdic acid solution (5% in EtOH), or 1% ninhydrin in EtOH. Aryl boronic acids and other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be \( >95\% \) pure as determined by \(^1\)H NMR. NMR data (\(^1\)H, \(^13\)C) were recorded on a 400 MHz spectrometer. Chemical shifts are reported in parts per million downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz). UV studies were performed in dichloromethane as solvent at a concentration of \( 1 \times 10^{-6} \) M.

6.1.1. X-ray Structural Analysis. A suitable single crystal of 2c was mounted on a thin glass fiber coated with paraffin oil. X-ray single-crystal structural data were collected at low temperature (170 K) using a STOE IPDS 2T diffractometer equipped with a normal-focus, 2.4 kW, sealed-tube X-ray source.
Table 4. Crystal Data and Structure Refinement Parameters for 2c

| empirical formula | C_{30}H_{19}Br |
|-------------------|-----------------|
| formula weight    | 459.36          |
| temperature       | 170(2) K        |
| wavelength        | 0.71073 Å       |
| crystal system, space group | monoclinic, P2₁/c |
| unit cell dimensions | a = 15.892(3) Å  |
| volume            | b = 7.5837(15) Å |
| Z                 | c = 17.555(4) Å |
| calculated density | β = 90.64(3)°   |
| absorption coefficient | 2115.6(7) Å² |
| F(000)            | 4              |
| crystal size      | 1.442 g/cm³    |
| theta range for data collection | 1.958 mm⁻¹ |
| limiting indices  | 936            |
| reflections collected/unique | 0.439 x 0.366 x 0.361 mm³ |
| completeness to θ = 25.242 | 2.320–27.185° |
| max. and min. transmission | =−20 h ≤ 20 ≤ k ≤ 9 – 22 ≤ l ≤ 22 |
| refinement method | 17 977/4614 [R(int) = 0.0741] |
| data/restraints/parameters | 99.9% |
| goodness-of-fit on F² | 0.9591 and 0.7581 |
| R indices (all data) | 0.366 mm³ |
| largest diff. peak and hole | 0.0961 |

*R₁ = \sum |F$_{o}$| − |F$_{c}$|/\sum |F$_{o}$|, $R_{p}$ = \left(\sum [w(F$_{c}$)² − F$_{o}$²)²]/\sum [w(F$_{c}$)²]²\right)^{1/2}.

with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The program X-Area was used for integration of the diffraction profiles; numerical absorption correction was made with the programs X-shape and X-red; all from STOE 2010. The structure was solved by SHELX-2014 and refined by full-matrix least-squares methods using SHELXL-2013. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.2 Ueq of their pivot atoms. All calculations were carried out using SHELX-2013 and the WinGX GUI, ver2013.2. The crystallographic data are summarized in Table 4.

The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC) 12 Union Road, Cambridge CB2 1EZ, U.K. These data can be obtained free of charge quoting the depository number CCDC 1544200 by e-mail (deposits@ccdc.cam.ac.uk) or their web interface (http://www.ccdc.cam.ac.uk).

6.2. Computational Methodology. All calculations in this study were carried out using the Gaussian 09 program. The ground state neutral optimized geometries were obtained at the B3LYP/6-31G(d,p) level of theory. Second order analytical gradients were verified to assure the obtained geometries were global minima on the respective potential energy surfaces. In order to get a deeper insight into the absorption spectra, electronic transitions were studied using TDDFT methodology at the same level of theory. Upon ionization, the cationic and anionic geometries were fully optimized at the UB3LYP/6-31G(d) level and the resulting geometries were verified with all positive eigen values in the frequency calculation. Using the ground state neutral and ionized geometries, the total reorganization energies with respect to hole or electron transfer were calculated. The reorganization energy for hole transport ($\lambda^+$) is the sum of the stabilization energies from losing an electron from the cationic potential energy surface and upon regaining this electron on a neutral potential energy surface. Similarly, electron transport reorganization energy ($\lambda^-$) is obtained with respect to the addition of an electron and loosing this added electron to/from anionic and neutral potential energy surfaces, respectively. The IPs and EAs were also calculated by using cationic and anionic optimized geometries, respectively.

6.3. Synthetic Procedures and Characterization Data. Synthetic procedures and characterization data have been provided herewith. For 1H and 13C NMR spectra and single-crystal structure data for 2c, please refer to supporting information file.

6.4. Representative Procedure for Site-Selective Suzuki–Miyaura Monoarylation. A mixture of catalyst (0.5 mol %) and aryl bromide (1 mmol) was placed in 2 mL of dry THF–deionized (DI) water (1:1) and stirred for 5–10 min followed by the addition of potassium carbonate (2.0 mmol) and aryl boronic acid (1.5 mmol). The resultant solution was then stirred at 60 °C for 12 h. After completion, the reaction mass was extracted with dichloromethane and evaporated. The crude solid obtained was purified by column chromatography using petrol ether.

6.4.1. 2a: 9-Bromo-10-phenylanthracene. Yield = 90%, green solid; 1H NMR (400 MHz, CDCl₃) δ 8.6 (t, J = 10.7 Hz, 2H), 7.6 (t, J = 7.9 Hz, 2H), 7.6–7.5 (m, 5H), 7.4–7.3 (m, 4H). 13C NMR (400 MHz, CDCl₃) δ 138.3, 137.7, 131.2, 131.1, 130.9, 130.1, 128.4, 127.8, 127.7, 127.3, 127.4, 126.9, 126.5, 125.5, 124.8, 124.8, 122.6. Electrospay ionisation mass spectrometry (ESI MS) (m/z): 334 (M⁺ + H⁺). Anal. Calcd (%) for C₂₀H₁₃Br: C, 72.09; H, 3.92. Found: C, 72.19; H, 3.92.

6.4.2. 2b: 9-Bromo-10-(naphthalen-2-yl)anthracene. Yield = 70%, green solid; 1H NMR (400 MHz, CDCl₃) δ 8.6 (d, J = 8.9 Hz, 2H), 8.0 (dd, J = 14.6, 8.3 Hz, 2H), 7.8 (d, J = 6.4 Hz, 2H), 7.7–7.5 (m, 6H), 7.5 (d, J = 8.2 Hz, 1H), 7.3–7.3 (m, 2H). 13C NMR (400 MHz, CDCl₃) δ 137.5, 135.8, 133.2, 132.7, 131.1, 130.2, 129.1, 128.1, 127.9, 127.8, 127.4, 126.9, 126.5, 125.6, 125.6, 122.8. ESI MS (m/z): 384.
(M' + H'). Anal. Calcld (%) for \( \text{C}_{22}\text{H}_{13}\text{BrO} \): C, 70.79; H, 3.51. Found: C, 71.32; H, 3.62.

6.4.10. 2j: 9-Bromo-10-(4-methoxyphenyl)anthracene. Yield = 80%, white solid; \( \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.5 (d, \( J = 8.9 \text{ Hz}, 2\text{H} \)), 7.6 (d, \( J = 8.7 \text{ Hz}, 2\text{H} \)), 7.6–7.5 (m, 2H), 7.4–7.2 (m, 4H), 7.1 (d, \( J = 8.7 \text{ Hz}, 2\text{H} \)), 3.9 (s, 3H). \( \text{Cl} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 159.1, 137.5, 132.1, 131.3, 130.2, 127.7, 127.4, 126.8, 126.4, 125.4, 124.7, 113.8, 55.3. ESI MS (m/z): 364 (M' + H'). Anal. Calcld (%) for \( \text{C}_{31}\text{H}_{18}\text{BrO} \): C, 69.44; H, 4.16. Found: C, 69.54; H, 4.07.

6.5. Representative Procedure for One-Pot Tandem Double Suzuki–Miyaura Aylation. A mixture of ary bromide (1.0 mmol) and catalyst (0.5 mol %) was placed in a Schlenk tube containing 2 mL of dry THF and DI water (1:1) under a nitrogen atmosphere and the resultant solution was stirred for 5–10 min. To this reaction mixture was added potassium carbonate (2.0 mmol) and ary boronic acid (1.5 mmol). The resultant mixture was then stirred at 60 °C for 12 h. On completion of the reaction (confirmed by TLC), a second ary boronic acid (1.5 mmol) was added to the same reaction solution followed by potassium carbonate (2.0 mmol). The resultant reaction mass was stirred for 12 h at 80 °C. The reaction mass was allowed to cool to r.t. and was extracted with dichloromethane, dried over Na\(_2\)SO\(_4\), and evaporated. The crude solid thus obtained was further purified by column chromatography using petrol ether.

6.5.1. 3a: 2-(10-(4-Naphthalen-1-yl)anthracen-9-yI)benzofuran. Yield = 70%, dark yellow solid; \( \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.0 (d, \( J = 8.7 \text{ Hz}, 2\text{H} \)), 7.8 (d, \( J = 7.5 \text{ Hz}, 2\text{H} \)), 7.8–7.7 (m, 6H), 7.6 (d, \( J = 7.8 \text{ Hz}, 1\text{H} \)), 7.5 (t, \( J = 7.6 \text{ Hz}, 4\text{H} \)), 7.4–7.3 (m, 8H), 7.1 (s, 1H). \( \text{Cl} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 155.4, 153.1, 140.1, 139.8, 139.5, 137.5, 133.9, 131.6, 131.3, 130.1, 129.9, 128.8, 128.3, 127.8, 127.2, 127.1, 126.2, 126.1, 126.0, 125.8, 125.4, 125.3, 125.1, 124.3, 124.0, 121.0, 111.5, 109.2. ESI MS (m/z): 497 (M' + H'). Anal. Calcld (%) for \( \text{C}_{33}\text{H}_{18}\text{BrO} \): C, 91.86; H, 4.87. Found: C, 91.91; H, 4.78.

6.5.2. 3b: 2-(10-(4-Naphthalen-2-yl)anthracen-9-yI)benzofuran. Yield = 75%, dark green solid; \( \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.2 (s, 1H), 8.0 (d, \( J = 18.0 \text{ Hz}, 6\text{H} \)), 7.9 (d, \( J = 8.3 \text{ Hz}, 2\text{H} \)), 7.8 (d, \( J = 8.6 \text{ Hz}, 3\text{H} \)), 7.6 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.6–7.5 (m, 4H), 7.4–7.3 (m, 6H), 7.1 (s, 1H). \( \text{Cl} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 155.4, 153.1, 140.1, 139.8, 139.5, 137.5, 133.9, 131.6, 131.3, 130.1, 129.9, 128.8, 128.3, 127.8, 127.2, 127.1, 126.2, 126.0, 125.8, 125.4, 125.3, 125.1, 124.3, 124.0, 121.0, 111.5, 109.2. ESI MS (m/z): 497 (M' + H'). Anal. Calcld (%) for \( \text{C}_{33}\text{H}_{18}\text{BrO} \): C, 91.91; H, 4.87. Found: C, 91.84; H, 4.78.

6.5.3. 3c: 2-(10-(Naphthalene-2-yl)anthracen-9-yl)benzofuran. Yield = 75%, dark green solid; \( \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.0 (d, \( J = 8.4 \text{ Hz}, 1\text{H} \)), 8.0 (d, \( J = 8.7 \text{ Hz}, 3\text{H} \)), 7.9–7.8 (m, 2H), 7.7 (t, \( J = 7.3 \text{ Hz}, 1\text{H} \)), 7.6–7.5 (m, 6H), 7.1 (s, 1H). \( \text{Cl} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 155.4, 153.1, 139.6, 131.6, 133.2, 132.7, 131.2, 130.3, 129.0, 128.8, 128.0, 127.8, 127.2, 126.5, 126.3, 126.1, 125.3, 125.2, 124.3, 123.0, 121.0, 111.5, 109.2. ESI MS (m/z): 421 (M' + H'). Anal. Calcld (%) for \( \text{C}_{33}\text{H}_{18}\text{BrO} \): C, 91.40; H, 4.79. Found: C, 91.51; H, 4.79.

6.5.4. 3d: 2-(10-(1,1'-Biphenyl)-4-yl)benzofuran. Yield = 80%, dark green solid; \( \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.0 (d, \( J = 8.2 \text{ Hz}, 2\text{H} \)), 7.8–7.7 (m, 7H), 7.6 (d, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 7.5 (t, \( J = 7.6 \text{ Hz}, 4\text{H} \)), 7.4–7.3 (m, 7H), 7.1 (s, 1H). \( \text{Cl} \) NMR (101
MH2, CD2Cl2) δ 157.1, 153.1, 150.3, 145.3, 137.5, 132.4, 131.2, 130.0, 129.8, 128.7, 127.0, 126.1, 126.1, 125.3, 124.3, 123.6, 123.0, 121.0, 119.3, 118.4, 111.5, 109.2. ESI MS (m/z): 447 (M+ + H+). Anal. Calcd (%) for C38H24O: C, 91.45; H, 4.97. Found: C, 91.37; H, 4.81.

6.5. 5e: 2-(10-(4-Phenoxyphenyl)anthracen-9-yl)-benzofuran. Yield = 78%, dark green solid; 1H NMR (400 MHz, CDCl3) δ 8.0 (d, J = 8.7 Hz, 1H), 7.8–7.7 (m, 5H), 7.6–7.5 (m, 4H), 7.4–7.3 (m, 6H), 7.3–7.2 (m, 4H), 7.2 (ddd, J = 9.7, 7.6, 1.5 Hz, 6H), 7.1 (s, 1H), 7.1 (d, J = 0.9 Hz, 1H), 7.1–7.0 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 155.3, 153.1, 147.6, 147.3, 139.9, 139.6, 137.0, 134.4, 131.5, 131.2, 129.8, 129.2, 128.8, 127.7, 127.1, 126.5, 126.1, 125.2, 124.4, 123.3, 123.8, 123.0, 121.0, 111.5, 109.2. ESI MS (m/z): 613 (M+ + H+). Anal. Calcd (%) for C34H22O2: C, 91.37; H, 4.81. Found: C, 90.02; H, 5.09, N, 2.28. Found: C, 90.11; H, 5.26, N, 2.16.

■ ASSOCIATED CONTENT
3 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00725.

NMR spectra’s; single crystal structure data for 2c (PDF) Crystallographic data (CIF)

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