Benzofuran Trimers for Organic Electroluminescence

Sally Anderson,* Peter N. Taylor, and Geraldine L. B. Verschoor[a]

Abstract: Four linear benzofuran trimers have been prepared by a two-stage synthetic procedure. They were tested as materials for organic electroluminescence (OEL). Precursor phenylene ethynylene oligomers were formed in the first stage, then after removal of the phenolic hydroxyl protecting groups, a base was used to promote the cyclization of *ortho*-hydroxy phenylene ethynylenes to benzofurans. Both acetate esters and *tert*-butyl carbonates were employed as protecting groups. *tert*-Butyl and *n*-hexyl substituents on the benzofurans were used to modulate solubility, aggregation, and film-forming properties; two *tert*-butyl groups prevented aggregation in the solid state, thus maintaining emission in the blue region of the visible spectrum. The OEL characteristics of the *tert*-butyl-substituted benzofuran trimer were explored, and blue emission was observed. The two-stage synthetic procedure employed for the preparation of these benzofuran trimers may be applied to a wide variety of benzofuran oligomer and polymer targets.

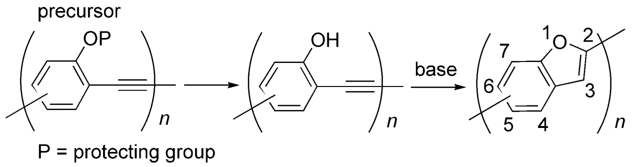
Keywords: benzofuran • chromophores • luminescence • oligomerization • organic electroluminescence

Introduction

Organic electroluminescence (OEL) is an emerging display technology allowing the manufacture of efficient, low-voltage multicolor displays.[1] In an OEL display, thin films of organic materials are sandwiched between electrodes. When an electric field is applied, holes are injected from the anode and electrons from the cathode. The holes and electrons combine to form excited states which may decay back to the ground state with the emission of light. Full-color OEL displays that use evaporated organic materials may be achieved in the following ways: 1) By generating an array of red-, green-, and blue-emitting subpixels from different OEL materials by using shadow mask technology.[2] 2) Using white-emitting organic materials and then generating red, green, and blue subpixels with absorption filters.[3] 3) Making an array of blue-emitting pixels and then with external emissive filters generating red and green subpixels.[4] 4) By evaporating red-, green-, and blue-emitting materials on top of one another interleaved with transparent electrodes to form a stacked device.[5]

Blue-emitting materials[6] can be used in a number of ways: they may be used directly for blue emission, as matrices in which to dope fluorescent dyes for energy-transfer to generate green and red light, or as a light source for emissive filters external to the OEL device. We have been exploring various chromophores for blue OEL, and herein we describe our investigations into the benzofuran chromophore. The benzofuran chromophore appealed to us as a material for OEL for the following reasons: it has high photoluminescence (PL) quantum efficiencies in solution,[7] it may be sublimed without chemical degradation, it emits light in the blue/UV region of the visible spectrum and is, therefore, an ideal chromophore for full-color generation using one of the methods outlined above. A detailed study of the OEL of this chromophore has not been carried out,[8] and the synthetic method employed for the preparation of these materials is very general and may be applied to a wide variety of benzofuran oligomer and polymer targets. We have prepared benzofuran trimers to investigate the suitability of the benzofuran chromophore for OEL.

These molecules are members of a new class of conjugated oligomers and polymers for OEL (Scheme 1). 2,6-Linked oligomers are through-conjugated (Scheme 2a), whereas



Scheme 1. Generalized reaction scheme for benzofuran oligomer/polymer formation.

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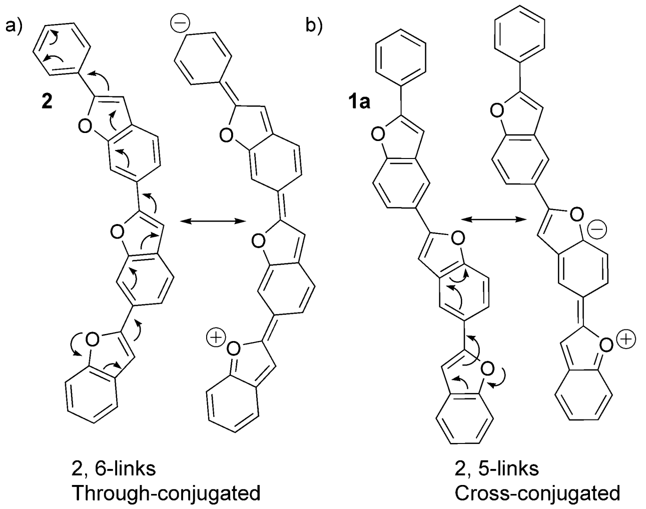
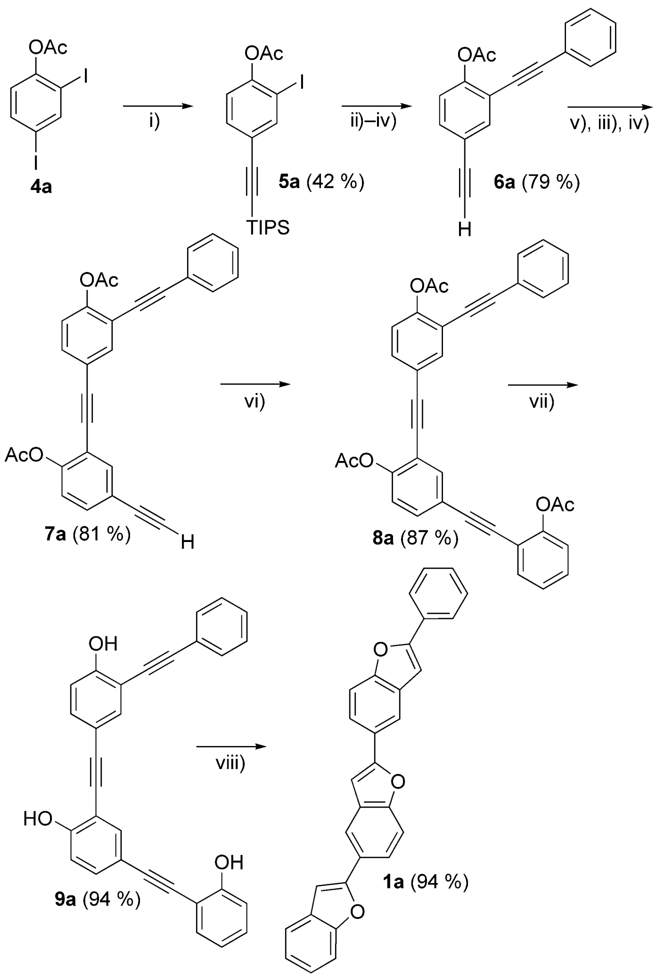


Scheme 2. Resonance forms for a) 2,6-linked benzofurans, b) 2,5-linked benzofurans.



Scheme 3. Synthesis of unsubstituted linear benzofuran trimer **1a** with acetate ester protecting groups. i) $TIPSC_2H$, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; ii) PhC_2H, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; iii) TBAF, CH_2Cl_2; iv) CH_2Cl_2, Et_3N, DMAP, AcCl; v) **5a**, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; vi) acetic acid 2-iodophenyl ester, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; vii) NaOH, MeOH, THF, RT; viii) NaOH, MeOH, reflux.

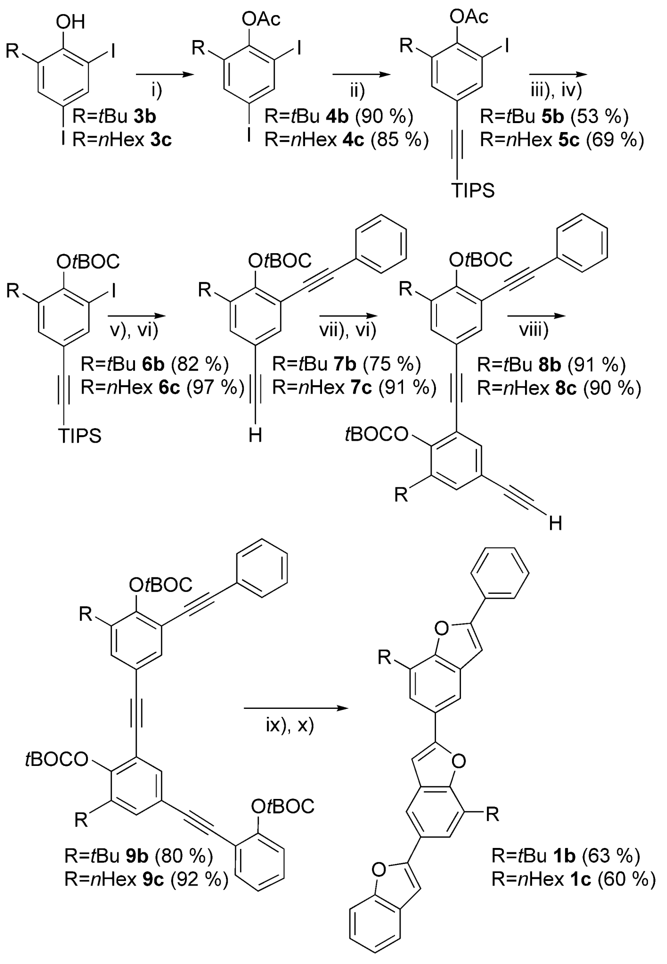
2,5-linked oligomers are cross-conjugated (Scheme 2b). The degree of conjugation influences the emission color: better electronic delocalization leads to emission at a longer wavelength. We chose trimers, rather than other oligomers, as our first synthetic targets to facilitate sublimation and to minimize recrystallization in thin films.

The benzofuran trimers were synthesized in two stages: the first stage generates a soluble oligomeric phenylene ethynylene precursor with protected phenolic hydroxyl groups located *ortho* to the alkynes. In the second stage, each of the phenolic hydroxyl groups is deprotected and then cyclized to generate the corresponding benzofurans. We refer to this second stage as the "zipping" procedure.[9] "Zipping" was found to be most easily carried out in a basic solution. This two-stage synthetic procedure has a further potential advantage: the phenylene ethynylene chains may be prepared with the aid of a polymer support, for example the Merrifield resin, facilitating the preparation of combinatorial sequence libraries.[10] This type of two-stage synthesis is reminiscent of the methods used by, for example, Swager and Tovar to make ladder polymers.[11]

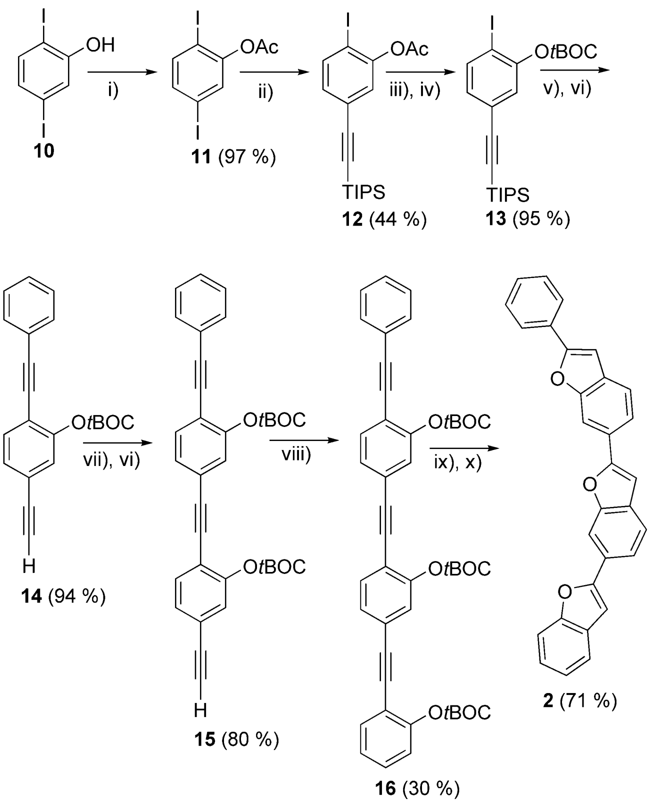
Results and Discussion

Synthesis: We prepared benzofuran linear trimers **1a–c** and **2**[12] (as outlined in Schemes 3–5). We employed a modified literature procedure[13] to couple one equivalent of triisopropylsilyl acetylene ($TIPSC_2H$) to aryl diiodides **4a–c** and **11** by using palladium catalysis. In the case of the conversion of **4b** to **5b**, ^1H NMR spectroscopy of the crude coupling reaction mixture showed 17% disubstitution, 62% monosubstitution (**5b**), and 21% starting material (**4b**). No signals from monosubstitution of the iodine adjacent to the protected phenol group were observed, suggesting that a reaction at the less hindered iodine is strongly favored over a reaction adjacent to the protected phenol until the first iodine has already been displaced. Similar results were obtained for the other analogues. To prevent "zipping" occurring simultaneously with phenylene ethynylene oligomer growth, the phenolic hydroxyl groups were protected. Compound **1a** was prepared with acetate ester protecting groups, while **1b** was prepared by two routes: the first employed only acetate esters and the second (outlined in Scheme 4) used both acetate esters and *tert*-butyl carbonate protecting groups. We found that acetate esters proved best for the purification of **5a–c** and **12**, and *tert*-butyl carbonates for the remainder of the syntheses. *tert*-Butyl carbonates remained intact when tetrabutyl ammonium fluoride (TBAF) was used to remove triisopropylsilyl (TIPS) groups, whereas acetate esters underwent partial hydrolysis. Oligomerization proceeded smoothly yielding an end-capped phenylene ethynylene trimer; the *tert*-butyl carbonate phenol protecting groups were then removed thermally for **9b,c** and **16**, and the acetate esters from **9a** by using sodium hydroxide in methanol.

Once the triphenol was formed it was simply "zipped" to the corresponding benzofuran trimer by refluxing overnight in methanolic sodium hydroxide (Scheme 5). The benzofuran trimers formed as white precipitates that were collected



Scheme 4. Syntheses of *tert*-butyl- and *n*-hexyl-substituted linear benzofuran trimers **1b** and **1c**. i) AcCl, DMAP, Et_3N, CH_2Cl_2; ii) $TIPSC_2H$, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; iii) NaOH, MeOH, THF, RT; iv) di-*tert*-butyl dicarbonate, DMAP, [18]crown-6, K_2CO_3, THF; v) PhC_2H, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; vi) TBAF, CH_2Cl_2; vii) **6b** or **6c**, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; viii) Carbonic acid *tert*-butyl ester 2-iodophenyl ester, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; ix) 180 °C, 30 min, 0.03 mbar; x) NaOH, MeOH, reflux.



Scheme 5. Synthesis of through-conjugated linear benzofuran trimer **2**. i) AcCl, DMAP, Et_3N, CH_2Cl_2; ii) $TIPSC_2H$, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; iii) NaOH, MeOH, THF, RT; iv) di-*tert*-butyl dicarbonate, DMAP, [18]crown-6, K_2CO_3, THF; v) PhC_2H, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; vi) TBAF, CH_2Cl_2; vii) **13**, $Pd(OAc)_2$, CuI, PPh_3, Et_3N; viii) carbonic acid *tert*-butyl ester 2-iodophenyl ester, $Pd(OAc)_2$, CuI, PPh_3, Et_3N, pyridine; ix) 180 °C, 30 min, 0.03 mbar; x) NaOH, MeOH, reflux.

by centrifugation, washed carefully with methanol, and then sublimed under reduced pressure (0.02 mbar, 200 °C). Benzofuran trimers **1a–c** and **2** were significantly less soluble than the corresponding precursor end-capped phenylene ethynylene trimers **9a–c** and **16**. The deprotection and "zipping" reactions were very efficient. Where the reaction procedure was optimized (e.g. **1a**), yields in excess of 90% were obtained for the "zipping" reaction. We believe that the lower yields for **1b**, **1c**, and **2** reflect the unoptimized nature of the thermal removal of *tert*-butyl carbonate protecting groups. Very pure benzofuran trimers may be prepared provided the precursor phenylene ethynylenes have been purified carefully. Since the *tert*-butyl-carbonate-protected phenylene ethynylene precursors are soluble, purification is readily achieved by flash column chromatography and recrystallization. Side chains and geometries were varied to modulate the solubility, film forming properties, intermolecular aggregation, and emission color: benzofuran trimers **1a** (cross-conjugated, no substituents), **1b** (cross-conjugated, *tert*-butyl substituents), **1c** (cross-conjugated, *n*-hexyl substituents), and **2** (through-conjugated, no substituents). The benzofuran trimers were all purified by sublimation before their photophysical and electrolumininescence properties were explored.

PL and absorption in solution: PL and absorption spectra were measured in solution in CH_2Cl_2. The extinction coefficients and PL quantum efficiencies were found to be similar for benzofuran trimers **1a–c** (see Table 1 and the Experi-

Table 1. Summary of photoluminescence (PL) data for benzofuran trimers **1a–c** and **2**. Solution measurements were carried out in nitrogen-saturated CH_2Cl_2 at room temperature. Thin films were prepared by thermal evaporation onto fused silica at 10^{-7} mbar. The normal substrate position for evaporation is about 40 cm from the evaporation source; the close position is about 20 cm from the source.

	$\lambda_{\max PL}$	Φ_{PL}
1a (solution)	362, 378	0.94
1a (thin film, normal position)	455, 484	–
1a (thin film, close to source)	390, 411, 455, 484	
1a (crystal from methanol)	390, 411	–
1b (solution)	362, 387	0.93
1b (thin film, normal position)	390, 448, 477	–
1b (thin film, close to source)	390, 428, 478	–
1c (solution)	362, 378	0.93
2 (solution)	410, 435, 463	0.80

mental Section for details). This was not surprising since the molecules contain the same chromophore. The absorption and PL spectra for **1a** and **2** are compared in Figure 1. As expected, the absorption and emission spectra of **2** are red-shifted by about 50 nm compared to those of **1a–c**, since **2** is through-conjugated and **1a–c** cross-conjugated.

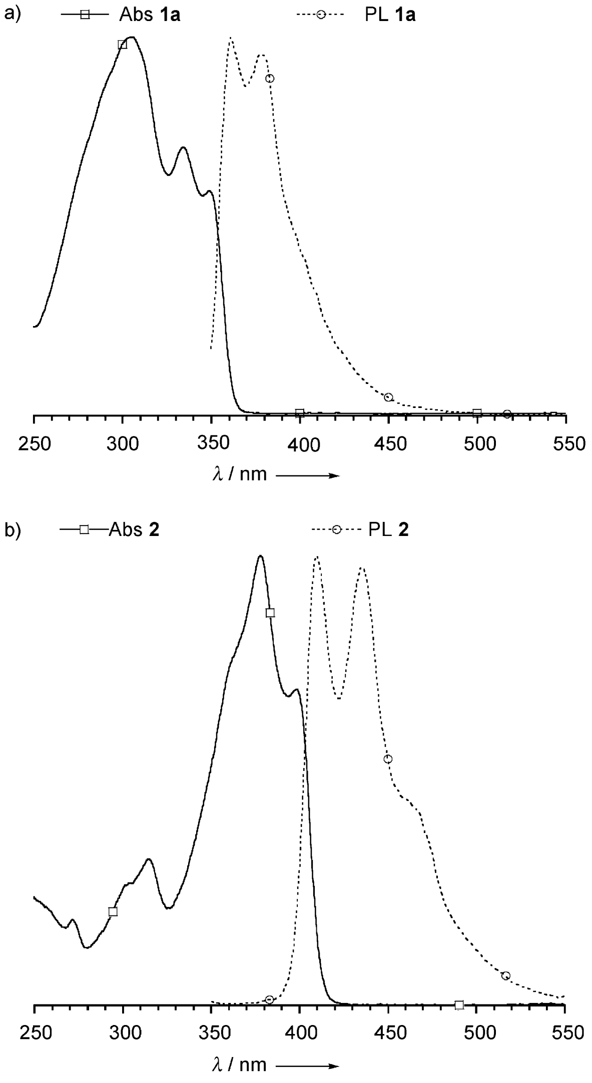


Figure 1. Normalized PL and absorption (abs) spectra in CH_2Cl_2 for a) cross-conjugated benzofuran trimer **1a**, and b) through-conjugated benzofuran trimer **2**.

PL and absorption in the solid state: The film-forming properties of the benzofuran trimers were explored by evaporating a series of films onto fused silica substrates at 10^{-7} mbar. The substrates were positioned between 20 and 40 cm from the evaporation source, the rate of evaporation for the substrate 40 cm from the source (the normal position to fabricate an OEL device) was between 0.1 and 0.3 nms^{-1}. After evaporation the films were analyzed by PL spectroscopy. The PL spectra from thin films of the unsubstituted linear benzofuran trimer **1a** are illustrated in Figure 2a (see Table 1 for a summary of the thin-film PL characteristics). As the substrate was moved further away from the evaporation source, the longer wavelength components became more dominant, and the peaks at about 380 nm disappeared. These results were compared with PL spectra carried out in solution (see Figure 1) and PL spectra from crystalline material, obtained by crystallization from methanol (dotted line Figure 2a), pressed onto fused silica. Interestingly, the crystalline material pressed on to fused silica showed a main peak at about 380 nm, but no peaks stretching out to 500 nm as in the sublimed thin films. The chemical integrity of the sublimed films and the crystalline material was checked by dissolving each of the samples in chloroform

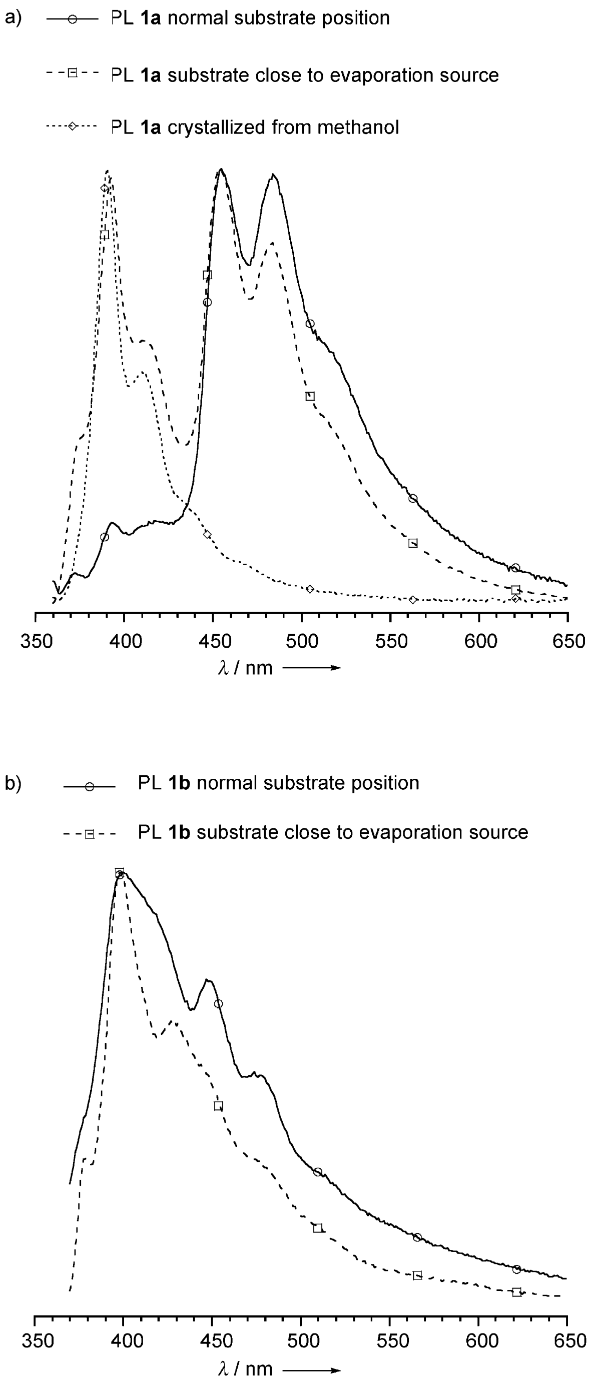


Figure 2. PL from evaporated thin films of benzofuran trimer a) **1a** and b) **1b**.

and recording the PL and absorption spectra. These spectra were found to be completely superimposable, confirming that any differences in PL of the films corresponded to different packing arrangements of the molecules and not to different chemical compositions. We believe that the PL spectra become broader and red-shifted as the distance between the evaporation source and the substrate was increased because the further away the substrate the lower the evaporation rate when the molecules hit the substrate. A slower evaporation rate results in a more ordered crystalline film.

The PL properties of the *tert*-butyl linear trimer **1b** were then explored in a similar way. Figure 2b shows the PL spectra for thin films evaporated onto fused silica positioned in the same places in the evaporation chamber as for the unsubstituted trimer **1a**. The solid line shows the PL spectrum for the substrate in the normal position, and the dashed line the substrate close to the evaporation source. The blue component at about 380 nm was strong in both spectra, and, although the longer wavelength components were more pronounced when the substrate was further away from the evaporation source, the differences in the spectra were very small compared to those observed with the unsubstituted linear benzofuran trimer **1a**. Presumably, the two *tert*-butyl groups help to prevent aggregation of the chromophores, and hence reduce crystallization in thin films at any substrate position. As might be expected, *n*-hexyl substituents on the benzofuran trimer do not disaggregate the chromophores as well as the *tert*-butyl groups; the PL spectra of thin films of **1c** are broad with a strong emission out to 500 nm. The conjugated linear trimer **2** showed emission to longer wavelengths consistent with its increased conjugation and aggregation in the thin film.

Electroluminescence results: Trimer **1b** was found to show good blue PL over a range of thin-film forming conditions, and it was thus our first choice for incorporation into two simple test organic light emitting diodes (OLEDs). Two OLED configurations were tested: i) simple single-layer OLEDs were prepared by subliming **1b** onto indium tin oxide (ITO) coated with poly(3,4-ethylene dioxythiophene) doped with poly(4-styrene sulfonate) (PEDOT·PSS).[14] To generate the cathode, lithium fluoride followed by aluminum were evaporated, the OLED structure may be abbreviated as follows: ITO/PEDOT·PSS/**1b**(120 nm)/LiF(7 nm)/Al. ii) The second type of OLED prepared contained a thin film of an oxadiazole (OXD 7)[15] evaporated on top of **1b** to improve the injection of electrons into the benzofuran layer from the LiF/Al cathode. This resulted in the OLED structure ITO/PEDOT·PSS/**1b**(60 nm)/OXD 7(50 nm)/LiF(1.7 nm)/Al (we refer to this OLED as the bilayer device). In both OLED structures emission was observed from **1b**, although the EL spectrum from the OLED containing **1b** and OXD 7 was broader than the emission from the single-layer OLED (Figure 3). Interestingly, the PL spectrum of **1b** evaporated onto PEDOT·PSS (Figure 3, solid line) showed a very narrow emission compared to the emission from the thin film evaporated onto fused silica (Figure 2b, solid line). We have observed a narrower emission from thin films evaporated onto PEDOT·PSS for a number of materials and presume that PEDOT·PSS inhibits crystallization.

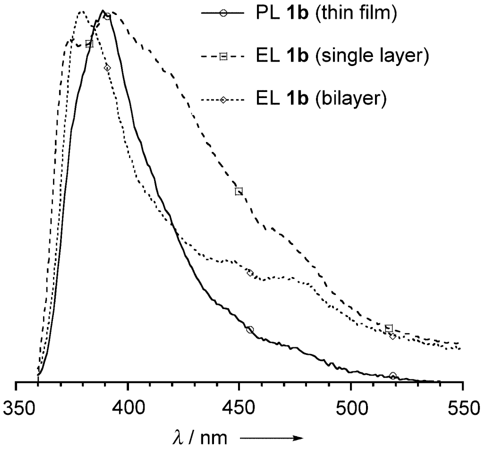


Figure 3. PL and electroluminescence (EL) for single-layer OLED (ITO/PEDOT·PSS/**1b**(120 nm)/LiF (7 nm)/Al), and bilayer OLED (ITO/PEDOT·PSS/**1b**(60 nm)/OXD 7(50 nm)/LiF (1.7 nm)/Al).

In the single-layer OLED a brightness of 3.3 cdm^{-2} was achieved at 3.1 mA and 20 V, whereas when the efficient electron-transport and hole-blocking layer OXD 7 was incorporated between the benzofuran and the cathode a maximum efficiency of 0.23 lmW^{-1} was obtained at 33 cdm^{-2}, 11 V and 0.17 mA. Unfortunately, the efficiency of the bilayer OLED dropped substantially as the voltage was increased, so that at 100 cdm^{-2} the efficiency was only 0.05 lmW^{-1}.

The current density/voltage and luminance/voltage curves for the bilayer OLED are illustrated in Figure 4, and the band structure for this OLED is outlined in Figure 5. The ionization potential measured for **1b** was 5.4 eV (evaporated thin film, Riken Keiki), suggesting that reasonable hole injection from the PEDOT·PSS anode should be possible. The HOMO energy (5.4 eV) was taken as the ionization potential, and the LUMO energy calculated from the HOMO and

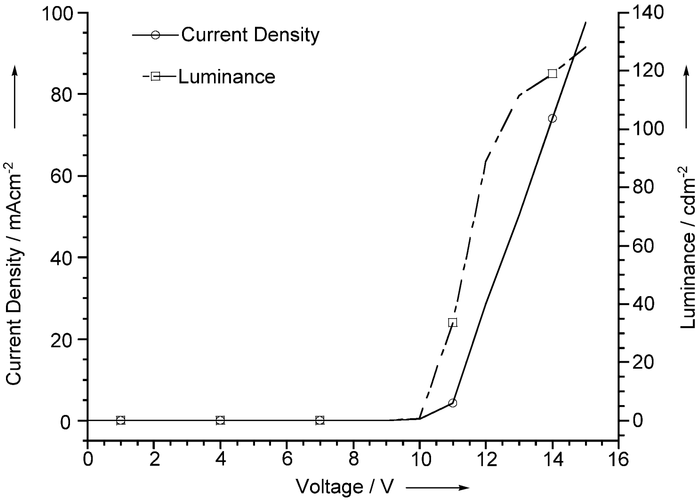


Figure 4. Current/voltage and luminance/voltage curves for the bilayer device (ITO/PEDOT.PSS/**1b**(60 nm)/OXD 7 (50 nm)/LiF(1.7 nm)/Al).

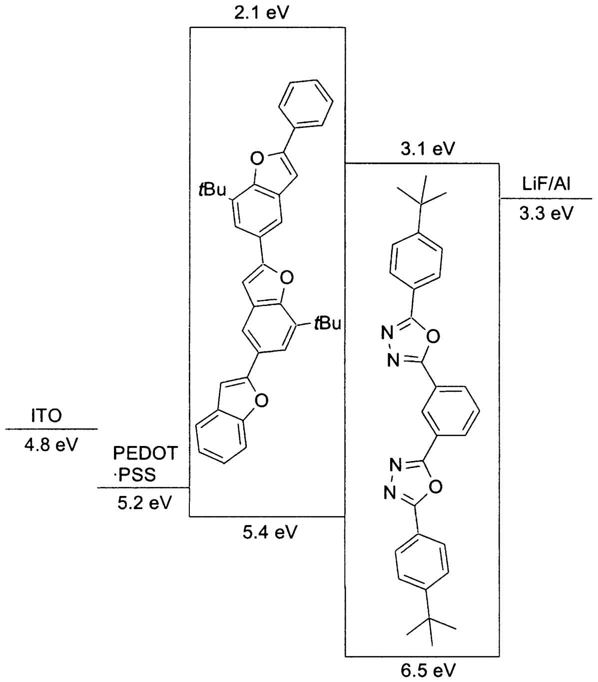


Figure 5. Band structure for the bilayer device (ITO/PEDOT·PSS/**1b**(60 nm)/OXD 7(50 nm)/LiF (1.7 nm)/Al).

the lowest energy absorption edge of the UV/Vis absorption spectra.

The ionization potential for OXD 7 (6.5 eV)[16] indicates that it acts as a hole-blocking layer, thus it is less favorable for holes to enter the OXD 7 layer and so recombination and emission are more likely to take place in **1b**. Disappointingly, on driving the single-layer and bilayer OLEDs, the blue/UV emission became whiter, suggesting that emission was being observed from a molecular aggregate. The initial color of the device was blue/violet, ($x = 0.15$ and $y = 0.02$), in the CIE (Commission Internationale de L'Eclairage) chromaticity coordinates.

Conclusions

We have explored the synthesis of a series of benzofuran trimers by means of a two-stage approach: oligomerization to a protected phenylene ethynylene oligomer followed by a "zipping" step to generate benzofurans. This synthesis proved very efficient and could easily be extended to prepare a library of benzofuran oligomers and a variety of polymers. Compounds **1a–c** and **2** were readily sublimed to generate thin films. The PL of these thin films showed that, for benzofuran trimers **1a**, **1c**, and **2**, the film morphology is very dependent on the evaporation conditions. Since the film morphology of *tert*-butyl-substituted linear benzofuran trimer **1b** seemed more consistent over a range of evaporation conditions, we chose to investigate its OEL properties. OEL was observed from **1b** in both single-layer and bilayer OLEDs, initially in the UV/blue region of the visible spectrum and then as the OLEDs were driven the emission spectra became increasingly whitish blue, suggesting that emission was now coming from an aggregate. Initial OEL results from **1b** were disappointing. We are now focusing on the optimization of materials for improved color stability and lifetime.[17]

Experimental Section

Unless otherwise stated, the starting materials were purchased commercially and used without further purification. Flash column chromatography was performed with Merck silica gel 60 μm (230–400 mesh). Dry triethylamine was obtained by distillation from calcium hydride under nitrogen. Mass spectrometry was carried out at the University of Southampton. Elemental analyses were carried out at The Inorganic Chemical Laboratory, Oxford University. Nuclear magnetic resonance (NMR) spectra in $CDCl_3$ were recorded on a Bruker DPX300. Overlapping signals in ^{13}C NMR spectra (determined by integration comparison of similar environments) are denoted with an asterisk. Melting points are uncorrected and were measured by differential scanning calorimetry (DSC). Absorption spectra were measured on a Shimadzu 2401 PC spectrophotometer; solution measurements were carried out in CH_2Cl_2. Solution PL measurements were recorded on a Perkin-Elmer LS50B spectrophotometer. The PL quantum yields (Φ_{PL}) in CH_2Cl_2 were measured by comparison with anthracene in ethanol (0.27)[18] in air.

5a:[13] Acetic acid 2,4-diiodophenyl ester[13] (10 g, 2.58×10^{-2} mol), palladium(II) acetate (116 mg, 5.2×10^{-4} mol), copper(I) iodide (50 mg, 2.6×10^{-4} mol), and triphenylphosphine (262 mg, 1.0×10^{-3} mol) were dissolved in triethylamine (60 mL), and the mixture was degassed with two freeze–thaw cycles with nitrogen saturation. Triisopropylsilylacetylene (4.7 g, 5.8 mL, 2.6×10^{-2} mol) was then added with a syringe, and the mixture was degassed by boiling under reduced pressure and then flushing with nitrogen. After stirring at room temperature for three days, hexanes were added, and the triethylamine hydrogen iodide removed by filtration through celite. The filtrate was evaporated and then chromatographed on silica (hexanes containing 0.25 % diethyl ether) to yield **5a** as a white solid (4.68 g, 42 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, ^4J(H,H) = 2 Hz, 1H), 7.46 (dd, ^4J(H,H) = 2, ^3J(H,H) = 8 Hz, 1H), 7.03 (d, ^3J(H,H) = 8 Hz, 1H), 2.36 (s, 3H), 1.13 ppm (s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.75, 151.55, 142.88, 133.48, 123.65, 123.01, 104.77, 92.82, 90.52, 21.61, 19.06, 11.66 ppm; MS (GC EIMS): *m*/*z*: 442 $[M]^+$, 339 $[M-\mathrm{Ac}]^+$.

6a: Aryl iodide **5a** (2.4 g, 5×10^{-3} mol), palladium(II) acetate (24 mg, 1.1×10^{-4} mol), copper(I) iodide (10 mg, 5.4×10^{-5} mol), and triphenylphosphine (57 mg, 2.2×10^{-4} mol) were dissolved in triethylamine (20 mL) and the resulting mixture was degassed with two freeze–thaw cycles with nitrogen saturation. Phenylacetylene (665 mg, 715 μL, 6.5×10^{-3} mol) was added with a syringe, and the resulting solution was degassed by boiling under reduced pressure and saturating with nitrogen. The reaction mixture was heated to 70 °C for 6 h before filtering through celite. The celite was washed with hexanes, and the solvent was evaporated. Chromatography (silica, CH_2Cl_2/hexanes 1:3) gave a colorless oil (2.16 g, 96 %), which was then taken on to the next step without further purification or characterization. To a solution of the triisopropylsilyl (TIPS)-protected acetylene (2.0 g, 4.8×10^{-3} mol) dissolved in CH_2Cl_2, was added tetrabutylammonium fluoride (TBAF) (1 M in THF, 4.8 mL, 4.8×10^{-3} mol). The reaction was complete after stirring at room temperature for 15 min, and was quenched by the addition of calcium chloride and brine. The product was extracted with CH_2Cl_2, the organic fractions were dried over $MgSO_4$, and then the solvent was evaporated. A reacylation step was then carried out because some of the acetate-protecting groups were lost during the TBAF TIPS deprotection reaction. To a mixture of crude **6a**, dissolved in dry CH_2Cl_2 (50 mL), triethylamine (1.0 mL, 0.73 g, 7.2×10^{-3} mol), and 4-(dimethylamino)pyridine (DMAP) (41 mg, 3.7×10^{-4} mol), was slowly added acetyl chloride (0.6 g, 0.5 mL, 6.4×10^{-3} mol). The resulting mixture was left to stir overnight and then quenched by washing with ammonium chloride solution (100 mL, 10 % solution) followed by $NaHCO_3$ (100 mL, 5 % solution). The organic fractions were dried over $MgSO_4$, and the solvent was evaporated. Chromatography (silica, CH_2Cl_2/hexanes 1:1) yielded (0.99 g, 79 %) of **6a** as a cream-colored crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, ^4J(H,H) = 2 Hz, 1 H), 7.52–7.44 (m, 3 H), 7.40–7.34 (m, 3 H), 7.10 (d, ^3J(H,H) = 8 Hz, 1 H), 3.09 (s, 1 H), 2.37 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.02, 152.00, 136.97, 133.44, 132.03, 129.26, 128.88, 122.98*, 120.66, 118.30, 95.28, 83.70, 82.43, 78.35, 21.27 ppm; MS (GC EIMS): *m*/*z*: 260 [*M*]$^+$, 218 [*M*−Ac]$^+$.

7a: See the preparation of **6a** for experimental details. Quantities used: **6a** (0.9 g, 3.5×10^{-3} mol), aryl iodide **5a** (1.5 g, 3.5×10^{-3} mol), palladium(II) acetate (16 mg, 6.9×10^{-5} mol), copper(I) iodide (7 mg, 3.5×10^{-5} mol), triphenylphosphine (36 mg, 1.4×10^{-4} mol), triethylamine (10 mL). Chromatography (silica, CH_2Cl_2/hexanes 1:1) gave a white solid (1.79 g, 90 %), which was then taken on to the next step without further purification or characterization. TIPS deprotection: TIPS-protected product (1.6 g, 2.8×10^{-3} mol in CH_2Cl_2 80 mL), TBAF (1 M in THF, 2.8 mL, 2.8×10^{-3} mol). Reacylation: Dry CH_2Cl_2 (80 mL), triethylamine (1.3 mL, 0.93 g, 9.2×10^{-3} mol), DMAP (51 mg, 4.5×10^{-4} mol), acetyl chloride (0.72 g, 0.66 mL, 9.2×10^{-3} mol). Chromatography (silica, CH_2Cl_2/hexanes 1:1) yielded **7a** as a cream-colored crystalline solid (0.94 g, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.68 (m, 2 H), 7.53–7.43 (m, 4 H), 7.40–7.34 (m, 3 H), 7.13 (d, ^3J(H,H) = 9 Hz, 1 H), 7.11 (d, ^3J(H,H) = 9 Hz, 1 H), 3.09 (s, 1 H), 2.384 (s, 3 H), 2.378 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.05, 168.98, 152.01*, 137.05, 136.34, 133.70, 132.90, 132.03, 129.29, 128.89, 123.13, 123.03, 122.94, 121.12, 120.70, 118.47, 117.90, 95.41, 93.49, 84.29, 83.68, 82.33, 78.41, 21.32, 21.29 ppm; MS (GC EIMS): *m*/*z*: 418 [*M*]$^+$, 376 [*M*−Ac]$^+$, 334 [*M*−2 Ac]$^+$.

8a: See the preparation of **6a** for the experimental details of palladium(0)-catalyzed coupling. Aryl acetylene **7a** (0.9 g, 2×10^{-3} mol), acetic acid 2-iodophenyl ester (0.53 g, 0.31 mL, 2×10^{-3} mol), palladium(II) acetate (20 mg, 9×10^{-5} mol), copper(I) iodide (9 mg, 4.5×10^{-5} mol), triphenylphosphine (47 mg, 1.8×10^{-4} mol), triethylamine (12 mL, freshly distilled over CaH_2). Chromatography (silica, CH_2Cl_2/hexanes 3:1) gave a white solid **8a**, which was recrystallized from chloroform with layered addition of hexanes to yield a white solid (0.98 g, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.68 (m, 2 H), 7.59–7.55 (m, 1 H), 7.53–7.45 (m, 4 H), 7.42–7.35 (m, 4 H), 7.28–7.22 (m, 1 H), 7.16–7.12 (m, 3 H), 2.38 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.33, 169.06*, 152.01, 151.97, 151.84, 136.36, 133.51, 133.14, 132.92, 132.04, 130.21, 129.30, 128.89, 126.42, 123.14, 122.94, 122.77, 121.52, 121.13, 118.48, 117.99, 117.40, 95.42, 93.53, 92.74, 85.36, 84.36, 83.67, 21.37, 21.34, 21.30 ppm; MS (APCI$^+$ MS): *m*/*z*: 553 [*M*]$^+$, 513 [*M*−Ac]$^+$, 469 [*M*−2 Ac]$^+$.

1a: Triacetate **8a** (0.9 g, 1.6×10^{-3} mol) was dissolved in THF (45 mL). To this solution was added methanolic sodium hydroxide (0.2 g, 5×10^{-3} mol, dissolved in 4.5 mL methanol). The resultant mixture was then left to stir overnight. The reaction mixture was neutralized with dilute hydrochloric acid and then poured into ether. The ether layer was washed with water, dried over $MgSO_4$, and the solvent was evaporated. The resultant solid was recrystallized from CH_2Cl_2 with layered addition of hexanes to yield **9a** (650 mg, 94 %). The triphenol **9a** was then converted to the benzofuran trimer **1a** without further characterization or purification. Triphenol **9a** (500 mg, 1.2×10^{-3} mol) and sodium hydroxide (0.14 g, 3.5×10^{-3} mol) were dissolved in methanol (100 mL). The mixture was degassed and then left to reflux overnight. The resultant white precipitate was collected by centrifugation to yield **1a** as a white crystalline solid (470 mg, 94 %). M.p. 312 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, ^4J(H,H) = 1.4 Hz, 1 H), 8.12 (d, ^4J(H,H) = 1.7 Hz, 1 H), 7.92–7.85 (m, 2 H), 7.85–7.75 (m, 2 H), 7.62–7.31 (m, 8 H), 7.32–7.20 (m, 1 H), 7.10 (s, 1 H), 7.07 (s, 1 H), 7.03 ppm (s, 1 H); the material was too insoluble for ^{13}C NMR; MS (EIMS): *m*/*z*: 426 [*M*]$^+$; elemental analysis calcd (%) for $C_{30}H_{18}O_3$ (426.48): C 84.48, H 4.26; found: C 84.57, H 4.31; $\lambda_{\max abs}[\log\varepsilon]$ = 305[4.82], 335[4.67], 349[4.60] nm; $\lambda_{\max PL}$ 362, 378 nm; Φ_{PL} 0.94.

3b:[19] Triethylamine (23.3 mL, 16.9 g, 0.167 mol) was added to a solution of 2-*tert*-butylphenol (10 g, 10.22 mL, 0.067 mol) in CH_2Cl_2 (600 mL) at 0 °C under nitrogen. After slow addition of a solution of iodine monochloride (21.76 g, 0.134 mol) in CH_2Cl_2 (200 mL), the dark mixture was stirred for 3.5 h at 0 °C and then quenched by addition of glacial acetic acid (7.0 mL), saturated aqueous sodium thiosulfate solution (300 mL), and water (1000 mL). The separated aqueous layer was extracted with ethyl acetate (2×500 mL), the combined organic layers were washed with brine (2×600 mL), dried ($MgSO_4$), and the solvent was evaporated. The dried product was chromatographed (silica, CH_2Cl_2/hexane 1:1) gave **3b**, (23.35 g, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, ^4J(H,H) = 2 Hz, 1 H), 7.47 (d, ^4J(H,H) = 2 Hz, 1 H), 5.51 (s, 1 H), 1.36 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.17, 143.41, 139.63, 137.11, 90.47, 83.54, 36.01, 29.52 ppm; MS (GC EIMS): *m*/*z*: 402 [*M*]$^+$.

4b: Acetyl chloride (2.34 g, 2.12 mL, 2.98×10^{-2} mol) was added dropwise to a solution of triethylamine (3.02 g, 4.16 mL, 2.98×10^{-2} mol), **3b** (10 g, 0.025 mol), and DMAP (167 mg, 1.49×10^{-3} mol) in CH_2Cl_2 (190 mL) at 0 °C. The mixture was stirred for 1 h, washed with aqueous NH_4Cl (500 mL, 10 % solution) and aqueous $Na(CO_3)_2$ (500 mL, 5 % solution). The organic layer was dried ($MgSO_4$) and evaporated. The crude product was chromatographed (silica, CH_2Cl_2/hexane 1:3) and then recrystallized from a minimum volume of hot ethanol to yield a white crystalline solid **4b** (9.9 g, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, ^4J(H,H) = 2 Hz, 1 H), 7.64 (d, ^4J(H,H) = 2 Hz, 1 H), 2.38 (s, 3 H), 1.30 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.73, 150.33, 146.07, 145.65, 137.44, 95.97, 91.88, 35.68, 30.68, 22.73 ppm; MS (EIMS): *m*/*z*: 444 [*M*]$^+$, 402 [*M*−Ac]$^+$.

5b: Aryl iodide **4b** (7.8 g, 1.76×10^{-2} mol), palladium(II) acetate (90 mg, 4.0×10^{-4} mol), copper(I) iodide (38 mg, 2.0×10^{-4}), and triphenylphosphine (210 mg, 8.0×10^{-4} mol) were dissolved in triethylamine (50 mL), and the mixture was degassed with two freeze–thaw cycles with nitrogen saturation. Triisopropylsilylacetylene (3.2 g, 3.9 mL, 1.8×10^{-2} mol) was added with a syringe and the mixture was degassed by boiling under reduced pressure and then flushing with nitrogen. After stirring the mixture for 3 d at room temperature, hexanes were added and the triethylamine hydrogen iodide was removed by filtration through celite. The filtrate was evaporated and then chromatographed (silica, hexanes containing 2.5 % ethyl acetate) to yield **5b** as a white solid (4.68 g, 53 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, ^4J(H,H) = 2 Hz, 1 H), 7.45 (d, ^4J(H,H) = 2 Hz, 1 H), 2.38 (s, 3 H), 1.32 (s, 9 H), 1.12 ppm (s, 21 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.85, 150.34, 143.76, 141.30, 131.86, 123.29, 105.38, 94.25, 92.06, 35.55, 30.66, 22.72, 19.07, 11.67 ppm; MS (EIMS): *m*/*z*: 498 [*M*]$^+$, 456 [*M*−Ac]$^+$.

6b: NaOH (0.56 g, 1.4×10^{-2} mol) was dissolved in methanol (2 mL) and added to TIPS-protected acetylene **5b** (7 g, 1.4×10^{-2} mol) dissolved in THF (100 mL). The reaction mixture was left to stir overnight. Further NaOH (0.56 g, 1.4×10^{-2} mol in methanol (2 mL)) was then added because thin-layer chromatography revealed a partial reaction. When the reaction was complete, the base was neutralized with HCl (10 % aqueous). The mixture was then thoroughly extracted with diethyl ether. The organic fractions were dried over $MgSO_4$, and then evaporated. The phenol was collected as a colorless oil and carefully dried and then added to potassium carbonate (2.93 g, 2.2×10^{-2} mol), DMAP (catalytic amount), and [18]crown-6 (catalytic amount). THF (85 mL, dry and oxygen-free) was then added with a syringe followed by di-*tert*-butyl dicarbonate (3.52 g, 3.7 mL, 1.61×10^{-2} mol). The reaction was then left to stir until no starting material was observed by TLC (1 h). The reaction was quenched by the addition of brine and the resulting mixture extracted with diethyl ether. The organic fractions were then dried over $MgSO_4$ and evaporated. The pale yellow oil was chromatographed (silica, CH_2Cl_2/hexanes 1:3) to yield **6b** as a colorless oil (7.3 g, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, ^4J(H,H) = 2 Hz, 1 H), 7.43 (d, ^4J(H,H) = 2 Hz, 1 H), 1.57 (s, 9 H), 1.34 (s, 9 H), 1.12 ppm (s, 21 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.36, 150.17, 143.82, 141.30, 131.79, 123.20, 105.45, 94.23, 91.96, 84.54, 35.64, 30.57, 28.19, 19.08, 11.68 ppm; MS (CI MS): *m*/*z*: 574 [*M*+NH_4]$^+$.

7b: Aryl iodide **6b** (1.9 g, 3.42×10^{-3} mol), palladium(II) acetate (15.4 mg, 6.8×10^{-5} mol), copper(I) iodide (6.5 mg, 3.4×10^{-5} mol), and triphenylphosphine (36 mg, 1.4×10^{-4} mol) were dissolved in triethylamine (20 mL), and the resulting mixture was degassed with two freeze–thaw cycles with nitrogen saturation. Phenylacetylene (384 mg, 413 μL, 3.8×10^{-3} mol) was added with a syringe and the resulting solution was degassed by boiling under reduced pressure and saturating with nitrogen. The reaction mixture was heated to 70 °C for 6 h, before filtering through celite. The celite was washed with hexanes and then the solvent was evaporated. Chromatography (silica, CH_2Cl_2/hexanes 1:3) gave a colorless oil (1.77 g, 98 %), which was taken on to the next step without further purification or characterization. This oil (1.5 g, 2.83×10^{-3} mol) was dissolved in CH_2Cl_2, and TBAF (1 M in THF, 3.11 mL, 3.11×10^{-3} mol) was added. After stirring for 15 min at room temperature, the reaction was quenched by the addition of calcium chloride and brine. The product was extracted with CH_2Cl_2, the organic fractions were dried over $MgSO_4$, and the solvent was evaporated. Chromatography (silica, CH_2Cl_2/hexanes 1:1) yielded **7b** as a thick colorless oil (0.82 g, 77 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, ^4J(H,H) = 2 Hz, 1 H), 7.54–7.51 (m, 2 H), 7.49 (d, ^4J(H,H) = 2 Hz, 1 H), 7.36–7.32 (m, 3 H), 3.06 (s, 1 H), 1.54 (s, 9 H), 1.38 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.24, 150.96, 142.88, 134.77, 132.13, 131.77, 129.02, 128.69, 123.21, 119.95, 119.88, 95.02, 84.31, 84.21, 83.14, 77.59, 35.23, 30.49, 28.03 ppm; MS (CI MS): m/z: 392 $[M+NH_4]^+$, 292 $[M+NH_4-t\mathrm{BOC}]^+$, 275 $[M-t\mathrm{BOC}]^+$.

8b: See the preparation of **7b** for experimental details. Quantities used: **6b** (1.16 g, 2.1×10^{-3} mol), **7b** (0.78 g, 2.1×10^{-3} mol), palladium(II) acetate (9.4 mg, 4.2×10^{-5} mol), copper(I) iodide (4 mg, 2.1×10^{-5} mol), triphenylphosphine (22 mg, 8.4×10^{-5} mol), triethylamine (15 mL). Chromatography (silica, CH_2Cl_2/hexanes 1:1) gave a colorless oil, which was dissolved in CH_2Cl_2 (50 mL), and TBAF (2.1 mL, 1 M in THF, 2.1×10^{-3} mol) was added. The reaction was quenched by the addition of calcium chloride and brine, the product was extracted with CH_2Cl_2, the organic fractions were dried over $MgSO_4$, and then the solvent was evaporated. Chromatography (silica, CH_2Cl_2/hexanes 1:1) yielded **8b** as a pale yellow oil (1.29 g, 91 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.49 (m, 6 H), 7.36–7.33 (m, 3 H), 3.06 (s, 1 H), 1.48 (s, 9 H), 1.46 (s, 9 H), 1.39 (s, 9 H), 1.38 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.27, 151.09, 150.98, 150.89, 142.93, 142.86, 134.77, 134.49, 132.11, 131.93, 131.20, 129.02, 128.71, 123.24, 120.65, 120.01, 119.87, 119.66, 95.02, 94.08, 84.37, 84.34, 84.21*, 83.08, 77.67, 35.31, 35.25, 30.55, 30.49, 28.08, 28.03 ppm; MS (CI MS): m/z: 664 $[M+NH_4]^+$, 564 $[M+NH_4-t\mathrm{BOC}]^+$, 464 $[M+NH_4\text{-}2t\mathrm{BOC}]^+$.

9b: See the preparation of **7b** for experimental details. Quantities used were as follows: carbonic acid *tert*-butyl ester 2-iodophenyl ester (0.54 g, 1.7×10^{-3} mol), **8b** (1.1 g, 1.7×10^{-3} mol), palladium(II) acetate (7.6 mg, 3.4×10^{-5} mol), copper(I) iodide (3.2 mg, 1.7×10^{-5} mol), triphenylphosphine (17.9 mg, 6.8×10^{-5} mol), triethylamine (10 mL). Chromatography (silica, CH_2Cl_2/hexanes 1:1) gave **9b** as a white foam (1.14 g, 80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.51 (m, 7 H), 7.40–7.34 (m, 4 H), 7.27–7.19 (m, 2 H), 1.54 (s, 9 H), 1.49 (s, 9 H), 1.46 (s, 9 H), 1.39 ppm (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.10, 151.78, 151.08, 151.04, 150.96, 150.92, 142.90, 142.88, 134.45*, 133.43, 132.11, 131.29, 131.20, 130.08, 129.03, 128.71, 126.43, 123.25, 122.50, 120.92, 120.71, 119.89, 119.66, 117.79, 95.01, 94.04, 93.89, 84.49*, 84.38, 84.31, 84.25, 84.22, 35.30*, 30.55*, 28.12, 28.09, 28.04 ppm; MS (CI MS): m/z: 857 $[M+NH_4]^+$, 756 $[M+NH_4-t\mathrm{BOC}]^+$, 656 $[M+NH_4-2t\mathrm{BOC}]^+$.

1b: Compound **9b** (300 mg, 3.57×10^{-4} mol) was heated to 180 °C under reduced pressure (0.02 mbar) until no further evolution of gas was observed. The resultant yellow glass was dissolved in methanol (50 mL) and NaOH (0.051 g, 1.28×10^{-3} mol) was added. The resultant mixture was refluxed overnight to produced a precipitate which was collected by centrifugation and washed with methanol (3×50 mL). The white solid was dried under reduced pressure (0.02 mbar, 70 °C). Yield of **1b** (120 mg, 63 %); m.p. 214 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, ^4J(H,H) = 1.7 Hz, 1 H), 7.96 (d, ^4J(H,H) = 1.6 Hz, 1 H), 7.92–7.89 (m, 2 H), 7.74 (d, ^4J(H,H) = 1.6 Hz, 1 H), 7.70 (d, ^4J(H,H) = 1.6 Hz, 1 H), 7.61–7.21 (m, 7 H), 7.11 (s, 1 H), 7.04 (s, 1 H), 7.02 (s, 1 H), 1.67 (s, 3 H), 1.66 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.50, 157.35, 156.43, 155.25, 153.77, 153.66, 135.56, 135.32, 130.93, 130.77, 130.68, 130.00, 129.31*, 129.12, 125.94, 125.31, 124.19, 123.25, 121.06, 119.11, 118.73, 115.95, 115.90, 111.51, 101.79, 100.73, 100.68, 34.98, 34.93, 30.42, 30.31 ppm; MS (EIMS): m/z: 538 $[M]^+$; elemental analysis calcd (%) for $C_{38}H_{34}O_3$ (426.48): C 84.72, H 6.37; found: C 84.69, H 6.27; $\lambda_{\text{max abs}}[\log\varepsilon] = 307$ [4.88], 334 [4.71], 349[4.63] nm; $\lambda_{\text{max PL}}$ 362, 378 nm; Φ_{PL} 0.93.

Carbonic acid *tert*-butyl ester 2-iodophenyl ester: Di-*tert*-butyl dicarbonate (5.4 g, 2.5×10^{-2} mol) was added to a mixture of 2-iodophenol (5 g, 2.3×10^{-2} mol), potassium carbonate (4.5 g, 3.4×10^{-2} mol), DMAP (catalytic amount), and [18]crown-6 (catalytic amount) in THF (130 mL). After stirring for 1 h at room temperature, the reaction appeared to be complete by TLC. The reaction was quenched by the addition of brine, and the resulting mixture was extracted with diethyl ether. The organic fractions were then dried over $MgSO_4$ and evaporated. The pale yellow oil was chromatographed (silica, CH_2Cl_2/hexanes 1:3) to yield a colorless oil (6.9 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (dd, ^4J(H,H) = 1, ^3J(H,H) = 8 Hz, 1 H), 7.36 (ddd, ^4J(H,H) = 1, ^3J(H,H) = 8, ^3J(H,H) = 8 Hz, 1 H), 7.17 (dd, ^4J(H,H) = 1, ^3J(H,H) = 8 Hz, 1 H), 6.97 (ddd, ^4J(H,H) = 1, ^3J(H,H) = 8, ^3J(H,H) = 8 Hz, 1 H), 1.58 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.77, 151.36, 139.87, 129.94, 128.09, 123.25, 91.03, 84.58, 23.31 ppm; MS (CIMS): m/z: 338 $[M+NH_4]^+$.

3c:[20] 1-*n*-Hexyl-2-methoxybenzene (11 g, 5.7×10^{-2} mol) was dissolved in CH_2Cl_2 (200 mL) and the mixture was degassed by boiling under reduced pressure and then saturating with nitrogen twice. Boron tribromide (21.5 g, 8.6×10^{-2} mol) was then added carefully with a syringe, and the mixture was left to stir under nitrogen. When the reaction was complete, the excess boron tribromide was quenched with methanol, and then water. The aqueous layer was neutralized with NaOH and then extracted with CH_2Cl_2. The CH_2Cl_2 fractions were combined, and the solvent was evaporated to yield a pale brown oil, which was taken on to the next step without further purification. To 2-*n*-hexylphenol (10 g, 5.6×10^{-2} mol) and triethylamine (19.5 mL, 14.2 g, 0.14 mol) in CH_2Cl_2 (500 mL) at 0 °C under nitrogen was added a solution of iodine monochloride (18.2 g, 0.11 mol) in CH_2Cl_2 (150 mL). The dark mixture was stirred for 3.5 h at 0 °C and then quenched by the addition of glacial acetic acid (6 mL), saturated aqueous sodium thiosulfate solution (250 mL), and water (800 mL). The separated aqueous layer was extracted with ethyl acetate (2×400 mL), the combined organic layers were washed with brine (2×500 mL), dried ($MgSO_4$), and the solvent was evaporated. The dried product was chromatographed (silica, CH_2Cl_2/hexanes 1:3) to yield the white crystalline solid **3c** (17.3 g, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, ^4J(H,H) = 2 Hz, 1 H), 7.36 (d, ^4J(H,H) = 2 Hz, 1 H), 5.27 (s, 1 H), 2.7–2.5 (m, 2 H), 1,6–1.5 (m, 2 H), 1.4–1.2 (m, 6 H), 1.0–0.8 ppm (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.03, 143.00, 139.59, 132.53, 87.82, 83.32, 32.06, 31.47, 29.76, 29.50, 23.00, 14.54 ppm; MS (GC EIMS): m/z: 430 $[M]^+$.

4c: See the preparation of **4b** for experimental details. Quantities used: Acetyl chloride (3.28 g, 3.0 mL, 4.2×10^{-2} mol), triethylamine (4.22 g, 5.82 mL, 4.18×10^{-2} mol), **3c** (15 g, 3.5×10^{-2} mol), dimethylaminopryridine (234 mg, 2.08×10^{-3} mol), CH_2Cl_2 (250 mL) at 0 °C. The crude product was chromatographed (silica, CH_2Cl_2/hexanes 1:1) and then recrystallized from a minimum volume of hot ethanol to yield **4c** (15.89 g, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, ^4J(H,H) = 2 Hz, 1 H), 7.51 (d, ^4J(H,H) = 2 Hz, 1 H), 2.5–2.4 (m, 2 H), 2.37 (s, 3 H), 1.6–1.4 (m, 2 H), 1.3 (br s, 6 H), 0.9–0.8 ppm (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.49, 150.09, 144.82, 139.45, 139.13, 93.36, 91.65, 31.90, 31.34, 29.88, 29.43, 22.92, 21.50, 14.47 ppm; MS (GC EIMS): m/z: 472 $[M]^+$, 430 $[M-\mathrm{Ac}]^+$.

5c: See the preparation of **5b** for experimental details. Quantities used: **4c** (7 g, 1.48×10^{-2} mol), palladium(II) acetate (67 mg, 3.0×10^{-4} mol), copper(I) iodide (28 mg, 1.5×10^{-4}), triphenylphosphine (156 mg, 5.9×10^{-4} mol), triethylamine (40 mL, freshly distilled over CaH_2), triisopropylsilylacetylene (2.7 g, 3.3 mL, 1.5×10^{-2} mol). The crude product mixture was chromatographed (silica, hexanes containing 2.5 % ethyl acetate) to yield **5c** as a white solid (5.4 g, 69 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, ^4J(H,H) = 2 Hz, 1 H), 7.29 (d, ^4J(H,H) = 2 Hz, 1 H), 2.5–2.4 (m, 2 H), 2.37 (s, 3 H), 1.6–1.5 (m, 2 H), 1.4–1.2 (m, 6 H), 1.12 (s, 21 H), 0.9–0.8 ppm (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.57, 150.07, 140.52, 136.80, 134.10, 123.69, 105.13, 92.20, 91.65, 31.92, 31.52, 29.97, 29.50, 22.94, 21.52, 19.05, 14.46, 11.66 ppm; MS (EIMS): m/z: 526 $[M]^+$, 483 $[M-\mathrm{Ac}]^+$.

6c: See the preparation of **6b** for experimental details. Quantities used: NaOH (0.38 g, 9.5×10^{-3} mol) in methanol (10 mL), **5c** (5 g, 9.5×10^{-3} mol), THF (100 mL). *tert*-Butyl carbonate formation: potassium carbonate (1.88 g, 1.36×10^{-2} mol), DMAP (catalytic amount), [18]crown-6 (catalytic amount), THF (50 mL, dry and oxygen free), di-*tert*-butyl dicarbonate (2.28 g, 2.4 mL, 1.04×10^{-2} mol). The crude reaction mixture was chromatographed (silica, CH_2Cl_2/hexanes 1:3) to yield **6c** as a colorless oil (5.4 g, 97 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, ^4J(H,H) = 2 Hz, 1 H), 7.28 (d, ^4J(H,H) = 2 Hz, 1 H), 2.55–2.49 (m, 2 H), 1.57 (s, 9 H), 1.57–1.52 (m, 2 H), 1.37–1.25 (m, 6 H), 1.11 (s, 21 H), 0.91–0.85 ppm (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.61, 149.89, 140.56, 136.90, 134.23, 123.58, 105.13, 92.15, 91.69, 84.56, 31.95, 31.39, 30.09, 29.53, 28.09, 22.94, 19.06, 14.51, 11.65 ppm; MS (CIMS): m/z: 602 $[M+NH_4]^+$, 485 $[M-t\mathrm{BOC}]^+$.

7c: See the preparation of **7b** for experimental details. Quantities used for the palladium-catalyzed coupling: **6c** (2.0 g, 3.42×10^{-3} mol), palladium(II) acetate (15.4 mg, 6.8×10^{-5} mol), copper(I) iodide (6.5 mg, $3.4\times$

10^{-5} mol), triphenylphosphine (36 mg, 1.4×10^{-4} mol), triethylamine (20 mL, freshly distilled over CaH_2), phenylacetylene (384 mg, 413 µL, 3.8×10^{-3} mol). For the TIPS deprotection: dichloromethane (100 mL), TBAF (1 M in THF, 3.42 mL, 3.42×10^{-3} mol). The crude reaction mixture was chromatographed (silica, CH_2Cl_2/hexanes 1:1) to yield **7c** as a thick colorless oil (1.25 g, 91%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.6–7.4 (m, 3H), 7.4–7.3 (m, 4H), 3.06 (s, 1H), 2.56 (t, ^3J(H,H) = 7.6 Hz, 2H), 1.65–1.5 (m, 2H), 1.49 (s, 9H), 1.2–1.4 (m, 6H), 0.89 ppm (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.17, 150.54, 136.29, 134.45, 134.28, 132.10, 129.05, 128.71, 123.20, 120.30, 118.64, 95.02, 84.22, 83.96, 82.80, 77.78, 32.00, 30.44, 30.05, 29.43, 27.99, 22.93, 14.49 ppm; MS (CIMS): *m*/*z*: 420 $[M+NH_4]^+$, 320 $[M+NH_4-t\mathrm{BOC}]^+$.

8c: See the preparation of **8b** for experimental details. Quantities used: **6c** (1.82 g, 3.1×10^{-3} mol), arylacetylene **7c** (1.25 g, 3.1×10^{-3} mol), palladium(II) acetate (13.9 mg, 6.2×10^{-5} mol), copper(I) iodide (6 mg, 3.1×10^{-5} mol), triphenylphosphine (33 mg, 1.2×10^{-4} mol), triethylamine (20 mL, freshly distilled over CaH_2). For the TIPS deprotection: CH_2Cl_2 (125 mL) and TBAF (3.1 mL, 1 M in THF, 3.1×10^{-3} mol). Chromatography of the crude reaction mixture (silica, CH_2Cl_2/hexanes 1:1) yielded **8c** as a pale yellow viscous oil (1.96 g, 90%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.55 (m, 1H), 7.55–7.45 (m, 3H), 7.40–7.30 (m, 5H), 3.06 (s, 1H), 2.50–2.64 (m, 4H), 1.65–1.45 (m, 4H), 1.40–1.25 (m, 12H), 0.95–0.80 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.19, 151.14, 150.58, 150.40, 136.37, 136.29, 134.46, 134.39, 134.10, 133.72, 132.09, 129.05, 128.73, 123.23, 120.97, 120.35, 118.66, 118.39, 95.01, 93.79, 84.35, 84.23, 84.18, 83.99, 82.74, 77.63, 32.03, 32.00, 30.51, 30.44, 30.11, 30.05, 29.46, 29.43, 28.03, 28.00, 22.93*, 14.52* ppm.

9c: See the preparation of **9b** for experimental details. Carbonic acid *tert*-butyl ester 2-iodophenyl ester (0.89 g, 2.8×10^{-3} mol), **8c** (2.0 g, 2.8×10^{-3} mol), palladium(II) acetate (12.5 mg, 5.6×10^{-5} mol), copper(I) iodide (5.3 mg, 2.8×10^{-5} mol), triphenylphosphine (29.3 mg, 1.1×10^{-4} mol) triethylamine (16 mL, freshly distilled over CaH_2). The crude reaction mixture was chromatographed (silica, CH_2Cl_2/hexanes 1:1) to yield **9c** as a white foam (2.3 g, 92%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.45 (m, 5H), 7.40–7.30 (m, 6H), 7.30–7.15 (m, 2H), 2.58 (m, 4H), 1.70–1.45 (m, 4H), 1.56 (s, 9H), 1.52 (s, 9H), 1.50 (s, 9H), 1.45–1.25 (m, 12H), 0.85–0.95 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.14, 151.78, 151.19, 151.16, 150.39, 150.37, 136.33, 136.30, 134.06, 134.03, 133.86, 133.71, 133.37, 132.09, 131.98, 130.09, 129.05, 128.73, 126.42, 123.24, 122.51, 121.25, 121.02, 118.68, 118.39, 117.78, 95.01, 93.73, 93.69, 84.69, 84.30*, 84.25, 84.22, 84.01, 32.03*, 30.51*, 30.11, 30.10, 29.46, 28.11, 28.05, 28.00, 22.92*, 14.50* ppm; MS (APCI): *m*/*z*: 794 $[\mathrm{M}-t\mathrm{BOC}]^+$, 695 $[M-2t\mathrm{BOC}]^+$, 595 $[M-3t\mathrm{BOC}]^+$.

1c: See the preparation of **1b** for experimental details. Quantities used: **9c** (1.35 g, 1.51×10^{-3} mol). For the cyclization: methanol (50 mL) and NaOH (0.23 g, 1.51×10^{-3} mol). Yield of **1c** (0.52 g, 60%); m.p. 107°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.89 (m, 4H), 7.62–7.46 (m, 6H), 7.39 (tt, 1H), 7.31–7.21 (m, 2H), 7.10 (s, 1H), 7.04 (s, 1H), 7.01 (s, 1H), 3.05 (m, 4H), 1.89 (m, 4H), 1.54–1.37 (m, 12H), 0.95–0.89 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.64, 157.31, 156.83, 155.20, 154.37, 154.24, 130.79, 130.04, 129.96, 129.76, 129.24, 129.11, 127.30, 127.10, 126.15, 126.09, 125.35, 124.17, 123.22, 122.20, 121.80, 121.03, 115.57, 115.33, 111.44, 102.08, 101.11, 100.64, 32.11, 32.10, 30.37, 30.34, 30.21*, 29.62*, 23.05*, 14.58, 14.55 ppm; MS (MALDI MS): *m*/*z*: 594 $[M]^+$; elemental analysis calcd (%) for $C_{42}H_{42}O_3$ (594.84): C 84.80, H 7.13; found: C 84.32, H 7.28; $\lambda_{\mathrm{max\,abs}}[\log\varepsilon]=309[4.88]$, 334[4.69],348[4.59] nm; $\lambda_{\mathrm{max\,PL}}$ 362, 378 nm; Φ_{PL} 0.93.

11: Acetyl chloride (2.7 g, 2.5 mL, 3.5×10^{-2} mol) was added dropwise to a solution of triethylamine (3.5 g, 4.8 mL, 3.5×10^{-2} mol), **10**[21] (10 g, 2.9×10^{-2} mol) and dimethylaminopryridine (234 mg, 2.08×10^{-3} mol) in CH_2Cl_2 (220 mL) at 0°C. The mixture was stirred for 1 h, and then washed with aqueous ammonium chloride (500 mL, 10% solution) and aqueous sodium bicarbonate (500 mL, 5% solution). The organic layer was dried ($MgSO_4$) and evaporated. The crude product was chromatographed (silica, hexane containing 5% ethyl acetate) and then recrystallised from a minimum volume of hot hexane to yield **11** (10.9 g, 97%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, ^3J(H,H) = 8 Hz, 1H), 7.43 (d, ^4J(H,H) = 2 Hz, 1H), 7.30 (dd, ^4J(H,H) = 2, ^3J(H,H) 8 Hz, 1H) , 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.66, 152.11, 140.87, 137.17, 132.50, 93.61, 90.76, 21.56 ppm; MS (GC EI MS): *m*/*z*: 388 $[M]^+$, 345 $[M-\mathrm{Ac}]^+$.

12: See the preparation of **5b** for the general procedure. Quantities used: acetic acid 2-iodo-5-methylphenyl ester (10 g, 2.58×10^{-2} mol), palladium(II) acetate (116 mg, 5.2×10^{-4} mol), copper(I) iodide (50 mg, 2.6×10^{-4} mol), triphenylphosphine (262 mg, 1.0×10^{-3} mol), triethylamine (60 mL), and triisopropylsilylacetylene (4.7 g, 5.78 mL, 2.58×10^{-2} mol). Chromatography (silica, 5% ethyl acetate/hexanes) yielded **12** as a white solid (5 g, 44%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.2 (d, ^3J(H,H) = 8 Hz, 1H), 7.18 (d, ^4J(H,H) = 2 Hz, 1H), 7.06 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H) 1.12 ppm (s, 21H); MS (GC EI MS): *m*/*z*: 442 $[M]^+$, 399 $[M-\mathrm{Ac}]^+$.

13: See the preparation of **6b** for experimental details. Quantities used for acetate deprotection: NaOH (0.45 g, 1.1×10^{-2} mol, in methanol 2 mL), **12** (5 g, 1.1×10^{-2} mol, in THF 75 mL). Quantities used for *t*-butyl carbonate formation: THF (65 mL), potassium carbonate (2.45 g, 1.8×10^{-2} mol), DMAP (catalytic amount), 18-crown-6 (catalytic amount), di-*tert*-butyl dicarbonate (2.84 g, 1.3×10^{-2} mol). Chromatography (silica, CH_2Cl_2/hexanes 1:3) gave a waxy solid that was recrystallized from pentane to yield **13** (5.36 g, 95%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, ^3J(H,H) = 8 Hz, 1H), 7.26 (d, ^4J(H,H) = 2 Hz, 1H), 7.07 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H), 1.59 (s, 9H), 1.12 ppm (s, 21H); MS (ES^+ MS): *m*/*z*: 523 $[M+\mathrm{Na}]^+$, 539 $[M+\mathrm{K}]^+$, 555 $[M+\mathrm{Na}+\mathrm{MeOH}]^+$.

14: See the preparation of **7b** for experimental details. Quantities used for the coupling reaction: **13** (2.5 g, 5.0×10^{-3} mol), palladium(II) acetate (22.2 mg, 1.0×10^{-4} mol), copper(I) iodide (9.5 mg, 5.0×10^{-5} mol), triphenylphosphine (53 mg, 2.0×10^{-4} mol), triethylamine (25 mL), phenylacetylene (572 mg, 615 µL, 5.6×10^{-3} mol). The product was chromatographed (silica, CH_2Cl_2/hexanes 1:3). TIPS deprotection: CH_2Cl_2 (100 mL) TBAF (1 M in THF, 4.7 mL, 4.7×10^{-3} mol). Chromatography (silica, CH_2Cl_2/hexanes 2:1) followed by recrystallization from pentane yielded **14** as a pale yellow waxy solid (1.4 g, 94%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 3H), 7.39–7.33 (m, 4H), 7.32 (d, ^4J(H,H) = 2, 1H), 3.20 (s, 1H), 1.52 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.52, 151.22, 133.00, 131.91, 129.90, 129.00, 128.56, 125.87, 123.44, 122.89, 118.69, 96.49, 84.30, 83.81, 82.52, 79.85, 27.84 ppm; MS (ES^+ MS): *m*/*z*: 341 $[M+\mathrm{Na}]^+$.

15: See the preparation of **8b** for experimental details. Quantities used: **14** (2.2 g, 4.4×10^{-3} mol), **13** (1.4 g, 4.4×10^{-3} mol), palladium(II) acetate (19.1 mg, 9.0×10^{-5} mol), copper(I) iodide (8.3 mg, 4.3×10^{-5} mol), triphenylphosphine (45 mg, 1.7×10^{-4} mol), triethylamine (25 mL). Chromatography (silica, CH_2Cl_2/hexanes 1:2) yielded the TIPS-protected acetylene. TIPS deprotection: CH_2Cl_2 (100 mL) and TBAF (1 M in THF, 3.54 mL, 3.54×10^{-3} mol). Chromatography (silica, CH_2Cl_2/hexanes 1:1) followed by recrystallization from pentane yielded **15** as a waxy solid (1.9 g, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.57 (m, 4H), 7.41–7.32 (m, 7H), 3.22 (s, 1H), 1.53 ppm (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.66*, 151.64, 151.20, 133.06, 133.00, 131.92, 129.95, 129.37, 129.03, 128.59, 125.95, 125.43, 123.95, 123.94, 122.92, 118.55, 118.14, 96.72, 95.11, 86.29, 84.50, 84.28, 83.95, 82.45, 80.14, 27.85* ppm; MS (ES^+ MS): *m*/*z*: 557 $[M+\mathrm{Na}]^+$.

16: See the preparation of **9b** for experimental details. Quantities used: Carbonic acid *tert*-butyl ester 2-iodophenyl ester (1.25 g, 3.91×10^{-3} mol), **15** (1.9 g, 3.55×10^{-3} mol), palladium(II) acetate (17.8 mg, 8.0×10^{-5} mol), copper(I) iodide (7.6 mg, 4×10^{-5} mol), triphenylphosphine (42 mg, 1.6×10^{-4} mol), triethylamine (10 mL), pyridine (10 mL, freshly distilled over CaH_2). The reaction mixture was stirred at 70°C overnight. Chromatography (silica, CH_2Cl_2/hexanes 3:1) gave a mixture of the product and a significant impurity which could be removed by repeated recrystallization from chloroform/hexane. **16** was obtained as a bright yellow solid (750 mg, 30%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.50 (m, 5H), 7.45–7.34 (m, 8H), 7.24–7.18 (m, 2H), 1.52 ppm (s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.99, 151.74, 151.63, 151.52, 151.17*, 133.20, 133.04, 132.97, 131.90, 130.22, 129.35*, 129.01, 128.57, 126.25, 125.42, 125.39, 124.80, 123.99, 122.89, 122.34, 118.49, 117.66, 117.27, 96.70, 95.13, 93.28, 87.04, 86.49, 84.40, 84.26, 84.14, 83.95, 27.86, 27.83* ppm; MS (ES^+ MS): *m*/*z*: 749 $[M+\mathrm{Na}]^+$.

2: Compound **16** (250 mg, 3.44×10^{-4} mol) was heated to 180°C under reduced pressure (0.02 mbar) until no further evolution of gas was observed. The resultant yellow glass was dissolved in methanol (35 mL) containing NaOH (0.042 g, 1.03×10^{-3} mol), the resultant mixture was refluxed overnight to produce a precipitate that was collected by centrifugation. It was then washed with methanol (3×50 mL). The yellow solid was sublimed (0.05 mbar, 250 °C). Yield of **2** (103 mg, 71 %); m.p. 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09–8.06 (m, 2H), 7.93–7.91 (m, 2H), 7.81–7.79 (m, 2H), 7.68–7.40 (m, 8H), 7.33–7.25 (m, 1H), 7.10 (s, 1H), 7.09 ppm (m, 2H); MS (ES$^+$ MS): m/z: 875[2M+Na]$^+$, 1301[3M+Na]$^+$; analysis calcd (%) for $C_{30}H_{18}O_3$ (426.48): C 84.48, H 4.26; found C 84.57, H 4.31; $\lambda_{\max abs}[\log\varepsilon] = 378[4.81]$, 399[4.65] nm; $\lambda_{\max PL}$ 410, 435, 463 nm; Φ_{PL} 0.80.

Photophysical experiments: Thin films of the benzofuran trimers were prepared by evaporation at 10^{-7} mbar onto fused silica. Solid-state PL spectra were measured with an Edinburgh Instruments FS900 CDT spectrofluorimeter.

OLED fabrication: ITO (indium tin oxide) on glass with a sheet resistivity of 20 Ω/square was obtained from Merck; it was cleaned by sonication in Decon, followed by 2 % NaOH solution, then it was washed with deionized water and dried from isopropanol. The ITO on glass was then patterned by etching into 2 mm-wide strips, and then cleaned again, before depositing any organic layers. The metal cathodes (2 mm strips) were evaporated normal to the ITO strips, thus defining 2 mm × 2 mm pixels. The luminance/current/voltage characteristics were measured by a Topcon BM-7 luminance meter and a current/voltage measuring unit (Keithley SM 4236) under nitrogen. Electroluminescence spectra were measured with an Edinburgh Instruments FS900 CDT spectrofluorimeter.

*Single-layer OLED ITO/PEDOT·PSS/**1b**(120 nm)/LiF(7 nm)/Al*: PEDOT·PSS (BaytronP, Bayer) was spin coated onto ITO-glass. The resulting film was heated to 110 °C for 30 min under nitrogen, resulting in a film about 50 nm thick. **1b** was then evaporated at a rate of about 0.2 nm s^{-1} onto the PEDOT.PSS at 10^{-7} mbar, followed by the LiF Al cathode in a Pfeiffer PLS evaporator.

*Bilayer OLED ITO/PEDOT.PSS/**1b**(60 nm)/OXD 7(50 nm)/LiF(1.7 nm)/Al*: In this device OXD 7 was evaporated on top of **1b**.

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