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Synthesis of monodisperse oligocarbazoles-functionalized anthracenes with intense blue-emitting

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ABSTRACT

New well-defined monodisperse oligocarbazoles-functionalized anthracenes **An-OCZn** (*n* = 1, 2, 3) have been synthesized through Suzuki cross-coupling reaction of the brominated oligocarbazoles and 9,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene. They show good solubility in organic solvents, including dichloromethane, chloroform, toluene, ethyl acetate, and tetrahydrofuran. It should be noted that, in the case of **An-OCZn**, the formation of the excimer based on anthracene unit is suppressed completely due to the introduction of oligocarbazoles in 9,10-position of anthracene so that an intense blue-emitting has been afforded. In addition, the obtained **An-OCZn** exhibit good electrochemical and thermal stabilities. Thus, the oligocarbazoles-functionalized anthracenes can be a class of promising candidates for novel blue-emitting materials employed in OLEDs or related devices.

In recent years, well-defined monodisperse π-conjugated oligomers have attracted more scientific and technological interests due to their potential applications in solar cells,[1] electrical conductors,[2] filed-effect transistors (FETs),[3] organic light-emitting diodes (OLEDs),[4] and light-harvesting molecular antenna systems.[5] In addition, the design of monodisperse conjugated oligomers is of importance in understanding and predicting the properties of the related polymers.[6] Till now, a great number of functional oligomers have been synthesized, including oligothiophenes,[7] oligopyrroles,[8] oligoanilines,[9] oligofluorenes,[10] and oligophenothiazine.[11] In particular, the oligocarbazoles in different conformations have been prepared as model compounds of polycarbazoles, which have emerged as leading electroluminescent materials due to their strong photoluminescence, high hole mobility, and high thermal stability.[12] For example, Strohriegl and co-workers reported the stepwise synthesis of *N*-alkylcarbazol-3,6-diyl trimers and pentamers by Suzuki coupling reaction.[13] Leclerc and co-workers prepared 2,7-carbazolenevinylene-based oligomers used as active semiconductor layer in OFETs.[14] Song and co-workers synthesized pyrene-centered starburst oligocarbazoles with strong blue emission.[15] Our group has previously reported a series of molecular antennae based on porphyrin or subporphyrin-centered 3,9-linked oligocarbazoles.[16] On the other hand, anthracene unit has been widely used as a building block for conjugated small molecules, oligomers, and polymers with excellent optoelectronic properties on account of its promising light-emitting and charge carrier transport properties.[17] However, the excimer with bathochromic-shifted emission is often detected in some anthracene-based emitting materials.[18] The strategy of the restraint of the excimer formation will be helpful for preparation of novel blue-emitting materials with high fluorescence efficiency. Miller and co-workers have suggested that the formation of excimer can be completely suppressed by the incorporation of 9,10-anthracene into the main chain of polyfluorenes.[19] Kwon and co-workers fabricated deep-blue OLEDs using anthracene derivatives bearing multi-phenyl-based bulky substituents in 9,10-positions as emitters.[20] We have found that the formation of excimers can be suppressed with an increase in the number of fluorece-vinylene units linked in 9,10-positions of anthracene, but the emission from excimer was not quenched completely.[21] In order to obtain novel blue-emitting materials with high fluorescence efficiency, we intended to introduce oligocarbazole units into 9,10-positions of anthracene. As shown in Chart 1 the monodisperse oligocarbazole-functionalized anthracenes **An-OCZn** (*n* = 1, 2, 3) have been synthesized. Notably, the formation of the excimer based on anthracene unit is suppressed completely, and intense blue-emitting has been afforded. Moreover, **An-OCZn** exhibit high electrochemical and thermal stabilities. Therefore, the oligocarbazole-functionalized anthracenes might be used as good candidates for blue-emitting materials with high fluorescent efficiencies employed in OLEDs or related devices with good stability.

The synthetic routes for the monodisperse oligocarbazole-functionalized anthracenes **An-OCZn** (*n* = 1, 2, 3) are sketched in Schemes 1 and 2. The brominated oligocarbazoles **1**, **8**, and compound **3** were firstly synthesized according to the reported

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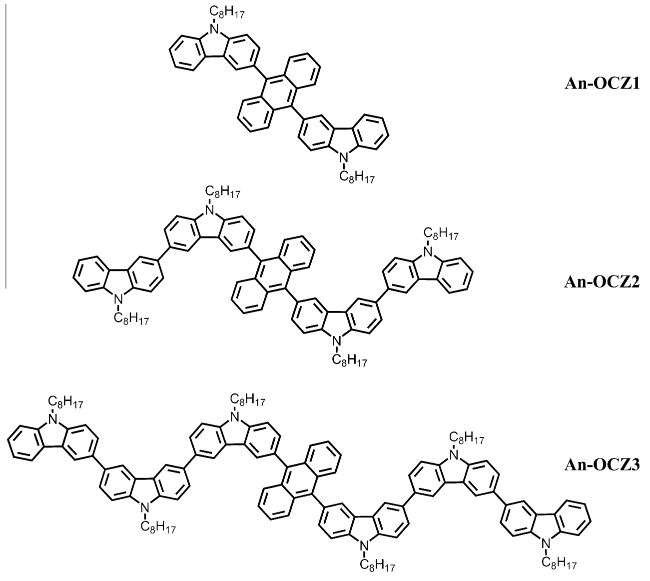
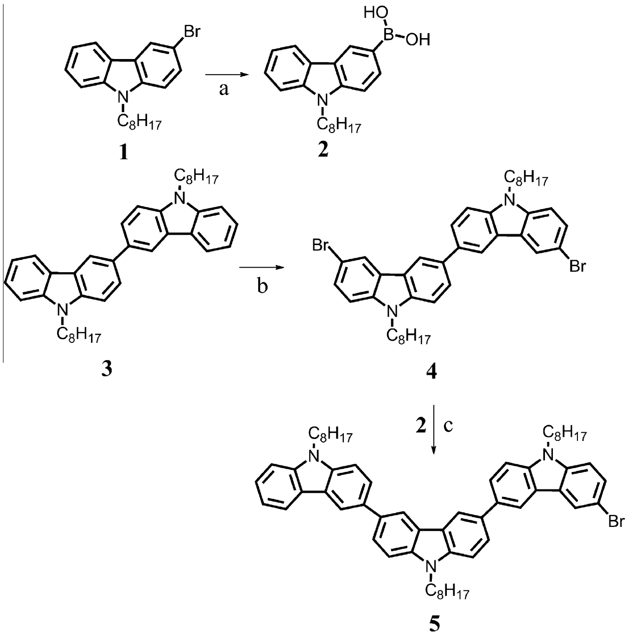


Chart 1. The molecular structures of **An-OCZn**.



(a) 1) n-BuLi, THF, -78 °C; 2) $B(OCH_3)_3$, -78 °C; 3) HCl/H_2O;
(b) NBS, DMF, r.t; (c) $Pd(PPh_3)_4$, K_2CO_3, toluene, H_2O, 85 °C.

Scheme 1. The synthetic route for the brominated oligocarbazole **5**.

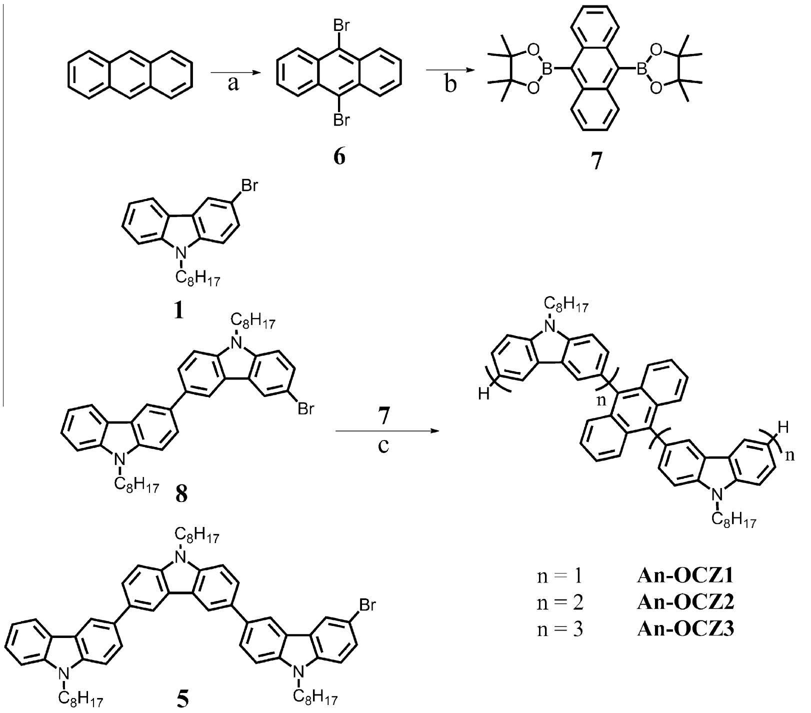
methods.[15,22] The transformation of compound **1** into boronic acid **2** was performed by lithium–bromide exchange at −78 °C, followed by reaction with trimethyl borate at −78 °C and hydrolyzed in hydrochloric acid at room temperature. The bromination reaction of compound **3** afforded compound **4**, which was transformed into the brominated tricarbazole **5** via Suzuki cross-coupling reaction with 1/3 equiv of boronic acid **2** catalyzed by palladium in a yield of 48%. Meanwhile, 9,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene **7** was synthesized by the cross-coupling reaction between bis(pinacolato)diboron and 9,10-dibromoanthracene (**6**), which was obtained via the bromination reaction of anthracene, in the presence of KOAc as a base and $Pd(OAc)_2$ as a catalyst. Finally, the $Pd(PPh_3)_4$-catalyzed Suzuki cross-coupling reactions between compound **7** and excess of the brominated oligocarbazoles **1**, **8,** and **5** afforded the desired oligocarbazole-functionalized anthracenes **An-OCZn** ($n = 1, 2, 3$) in yields of 66%, 62%, and 46%, respectively. All the intermediates and the final products were purified by column chromatography, and the new compounds were characterized with FT-IR, ^1H NMR, ^{13}C NMR, elemental analysis, and MALDI/TOF mass spectroscopy.[27] Due to the introduction of octyl to 9-position of carbazole unit, the obtained monodisperse oligomers were readily dissolved in common organic solvents, including dichloromethane, chloroform, toluene, ethyl acetate, and tetrahydrofuran, which made it possible that **An-OCZn** became solution-processible materials.

The UV–vis absorption and fluorescence emission spectra of **An-OCZn** ($n = 1, 2, 3$) in $CHCl_3$ are shown in Figure 1, and the corresponding photophysical data are summarized in Table 1. The absorption bands assigned to the π–π^* transitions of carbazole or oligocarbazole units appeared at ca. 300 nm,[23] and were similar to those of dicarbazole **3** (see Fig. S1). These absorption bands red-shifted slightly with the increase in the number of carbazole units on account of the extending of π-conjugation, for example, the absorption maximum shifted from 298 nm for **An-OCZ1** to 304 and 310 nm for **An-OCZ2** and **An-OCZ3**, respectively (Table 1). Although the n–π^* transition bands of carbazole or oligocarbazole overlapped with the absorption of anthracene core in the range of 330–370 nm, we could also detect the characteristic vibrational patterns of the isolated anthracene group in **An-OCZn** ($\lambda = 356$, 381 and 401 nm for **An-OCZ1**, $\lambda = 358$, 381 and 401 nm for **An-OCZ2**, $\lambda = 356$, 381 and 401 nm for **An-OCZ3**).[18] On the other hand, we could find from Figure 1b that the compounds **An-OCZn** emitted intense blue light maximized at ca. 450 nm when excited at 365 nm. With the increase in the number of carbazole units, the fluorescent emission bands of **An-OCZ2** and **An-OCZ3** red-shifted to 453 nm from 446 nm for **An-OCZ1** on account of the extending of π-conjugation. It indicated that the conjugation for oligocarbazoles linked by 3,6-position would not be enlarged obviously with the increase in the carbazole units. It should be noted that the excimers with bathochromic-shifted emission were often detected for anthracene derivatives, however, in the case of **An-OCZn**, the formation of excimers was suppressed completely. Compared with our previous result, we can deduce that the suppression effect of carbazole on the formation of excimer of anthracene core is superior than that of fluorene since the formation of excimers is suppressed by fluorene-vinylene units to a certain of extent, not completely.[21] As a result, the oligocarbazoles cored with anthracene might become good candidates for blue-emitting materials.

In general, the fluorescence quantum yields (Φ_F) of the anthracence derivatives not bearing other conjugated units were less than 0.34 against quinine sulfate ($\Phi_F = 0.546$, $\lambda_{ex} = 365$ nm) as a standard.[24] However, when the anthracenes were linked by oligocarbazoles in 9,10-positions, the quantum yields increased significantly, they reached 0.76 for **An-OCZ1**, 0.66 for **An-OCZ2,** and 0.70 for **An-OCZ3** in toluene. The reason for the high fluorescence quantum yields of **An-OCZn** might be that the excitons could be well confined in the low-band gap, highly chromophoric segment (anthracene).[25]

Figure 2 shows the absorption and emission spectra of **An-OCZn** ($n = 1, 2, 3$) in the films obtained via spinning the chloroform solutions (10 mg mL^{-1}) onto quartz slides. In comparison with the ones in solutions, **An-OCZn** showed red-shift of 0–5 nm of the absorption and emission bands. For example, the absorption maximum of **An-OCZ3** in the films red-shifted to 315 nm from 310 nm in the solution, meanwhile, its emission peak red-shifted to 456 nm in the film from 453 nm in the solution, indicating the occurrence of the intermolecular interaction in the solid state.

The electrochemical behaviors of **An-OCZn** ($n = 1, 2, 3$) have been investigated by cyclic voltammetry (CV) using a standard



(a) Br_2, $CHCl_3$, r.t.; (b) bis(pinacolato)diboron, $Pd(OAc)_2$, KOAc, DMF, 80 °C; (c) $Pd(PPh_3)_4$, K_2CO_3, toluene, H_2O, 85 °C.

Scheme 2. Syntheses of oligocarbazoles-functionalized anthracenes **An-OCZn**.

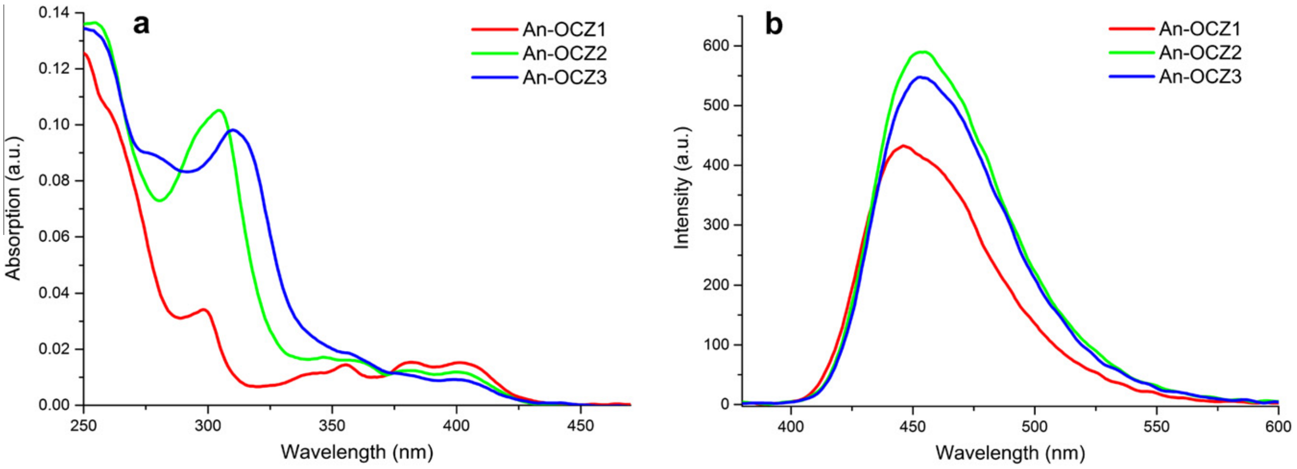


Figure 1. UV–vis absorption (a) and fluorescence emission (b, λ_{ex} = 365 nm) spectra of **An-OCZn** in chloroform (1.0×10^{-6} M).

Table 1
Photophysical and thermal properties of **An-OCZn** (n = 1, 2, 3)

Compounds	Absorption		Photoluminescence[b]		Φ_F[c]	T_m[d] (°C)	T_d[e] (°C)
	Solution[a]	Film	Solution[a]	Film			
An-OCZ1	298, 339, 356, 381, 401	301, 337, 351, 384, 403	446	447	0.76	274	410
An-OCZ2	304, 346, 358, 381, 401	303, 345, 360, 401	453	453	0.66	184	462
An-OCZ3	310, 356, 381, 401	315, 360 (shoulder), 404	453	456	0.70	107	457

[a] Measured in chloroform.
[b] Excited at 365 nm.
[c] The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 (Φ_F = 0.546) as a standard excited at 365 nm.
[d] Obtained from DSC measurement.
[e] Obtained from TGA measurement (temperature at 5% weight loss under nitrogen, 10 °C/min ramp rate).

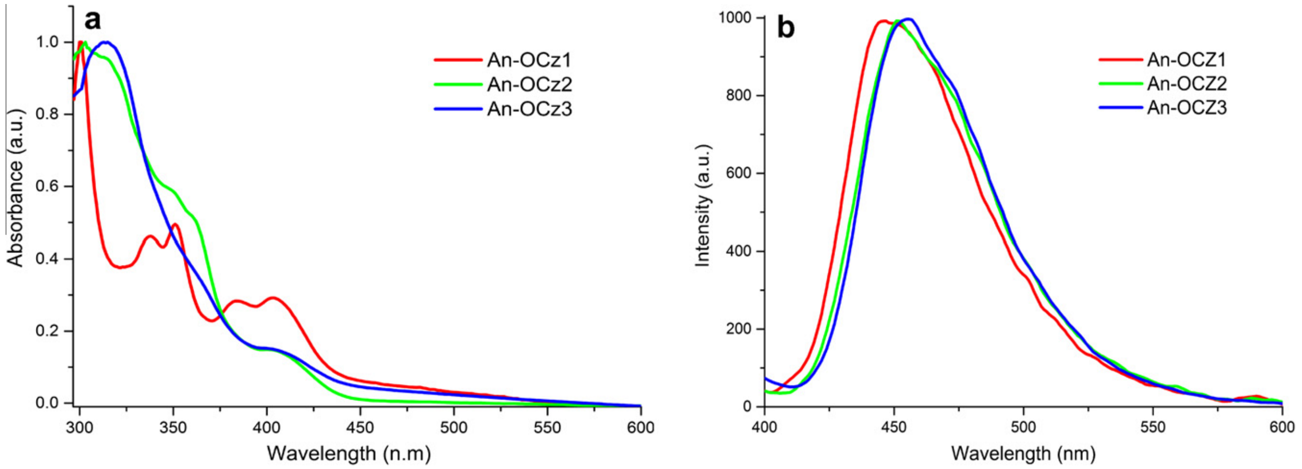


Figure 2. Normalized UV–vis absorption (a) and PL (b, λ_{ex} = 365 nm) spectra of **An-OCZn** in the films.

three-electrode cell and an electrochemical workstation (CHI 604) under N_2 atmosphere. Platinum button is used as the working electrode, a platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and ferrocene is used as a standard. The cyclic voltammetry (CV) diagrams of **An-OCZn** in CH_2Cl_2 in the presence of Bu_4NPF_6 as the supporting electrolyte are shown in Figure 3, and the corresponding electrochemical data listed in Table S1. The redox potential of Fc/Fc^+, which possesses an absolute energy level of −4.8 eV relative to the vacuum level for calibration, is located at 0.36 eV in 0.10 M Bu_4NPF_6/CH_2Cl_2 solution at a scan rate of 100 mV s^{-1}.[26] It was clear that **An-OCZ1** and **An-OCZ2** gave one well-defined reversible redox peak with $E_{1/2}$ (half-wave oxidation potentials) being of 0.98 and 0.78 V. As to **An-OCZ3**, two reversible redox peaks appeared at 0.70 and 0.83 V, and the $E_{1/2}$ for **An-OCZ3** was 0.70 V. Obviously, the oxidation potential decreases with the increase in the number of carbazole units. On the basis of the half-wave oxidation potentials, the highest occupied molecular orbital (HOMO) energy levels can be estimated as −5.42, −5.22, −5.14 eV for **An-OCZ1**, **An-OCZ2,** and **An-OCZ3**, respectively, based on the equation of $E_{HOMO} = -E_{1/2} - 4.44$ eV. It suggested that the electron-donating ability would be enhanced with increasing the length of the oligocarbazole arms. Although we did not observe redox processes in the negative potential region, the lowest unoccupied molecular orbital (LUMO) energy level of the **An-OCZn** could be estimated from the HOMO energy level and energy band gap (E_g) which was calculated from the absorption edge of **An-OCZn**

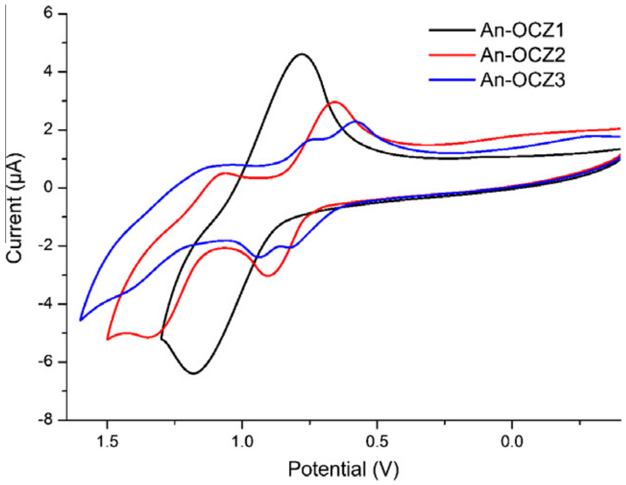


Figure 3. The cyclic voltammograms of **An-OCZn** in CH_2Cl_2.

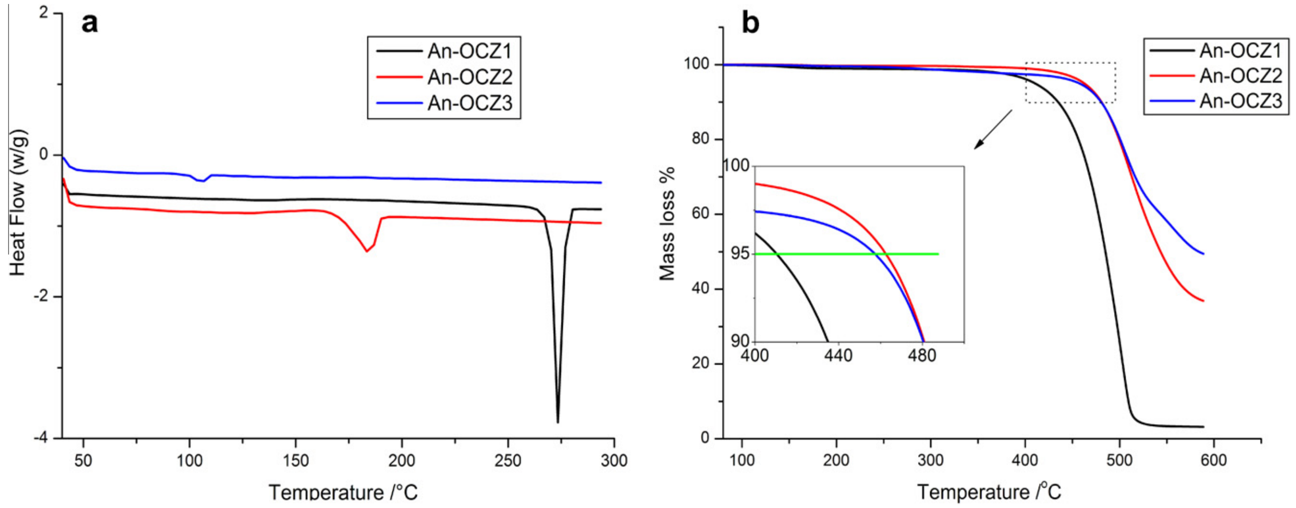


Figure 4. (a) DSC and (b) TGA thermograms of **An-OCZn** under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

($E_{LUMO} = E_{HOMO} + E_g$). The LUMO energy levels were −2.64, −2.35, −2.23 eV for **An-OCZ1**, **An-OCZ2,** and **An-OCZ3**, respectively. Figures S2–S4 showed multiple cyclic voltammograms, which gave very weak shifts (<1 mV) after 10 scan cycles for **An-OCZn**. It indicated that the obtained oligocarbazoles-functionalized anthracenes exhibited excellent electrochemical stability, and could withstand the redox cycles for many times. We deduced that the excellent electrochemical stability for **An-OCZn** might be due to the introduction of substitutes in 3,6-positions of carbazole units, which would restrain the electrochemical polymerizations. Thus, these compounds might become potential candidates applied in electrooptic devices.

Thermal stabilities of these compounds were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in N_2 at a heating rate of 10 °C/min. As shown in Figure 4 and Table 1, **An-OCZn** exhibited high melting points (T_m) in the range of 107–274 °C. Moreover, T_m of **An-OCZn** decreased with the increase in the number of carbazole units. Based on TGA results, we could find that the decomposition temperatures (T_d, corresponding to a 5% weight loss) of **An-OCZn** were in the range of 410–462 °C, indicating much higher thermal stability.

In summary, we have synthesized three new well-defined monodisperse oligocarbazoles-functionalized anthracenes **An-OCZn** ($n = 1, 2, 3$) via Suzuki cross-coupling reaction between the brominated oligocarbazoles and 9,10-bis(4,4,5,5-tetramethyl 1,3,2-dioxaborolan-2-yl)anthracene. It is interesting that the introduction of oligocarbazoles into 9,10-positions of anthracene can prevent the formation of excimers so that **An-OCZn** can emit intense blue light with high fluorescence quantum yields of 0.66–0.76 against quinine sulfate as a standard. On the other hand, the **An-OCZn** showed superior electrochemical and thermal stabilities, which made it possible that the obtained oligomers became good candidates as novel blue-emitting materials employed in OLEDs or related devices with good stability.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.11.099. These data include MOL files and InChiKeys of the most important compounds described in this article.

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27. ***An-OCZ1***: ^{1}H NMR (500 MHz, TMS, $CDCl_3$): δ (ppm) = 8.24 (s, 2H), 8.08 (t, J = 6.5 Hz, 2H), 7.83–7.81 (m, 4H), 7.64 (dd, J = 2.0 Hz, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.52–7.49 (m, 4H), 7.31–7.29 (m, 4H), 7.24–7.22 (m, 2H), 4.44 (t, J = 7.0 Hz, 4H), 2.05–1.99 (m, 4H), 1.45–1.24 (m, 20H), 0.90 (t, J = 6.5 Hz, 6H) (Fig. S14) ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 140.96, 139.89, 137.84, 130.73, 129.41, 129.06, 129.03, 125.87, 124.80, 123.25, 123.21, 122.96, 122.94, 122.77, 120.54, 120.52, 118.96, 108.88, 108.56, 108.53, 43.41, 31.86, 29.72, 29.47, 29.27, 29.18, 27.48, 22.67, 14.13 (Fig. S15). IR (KBr, cm^{-1}): 2930, 2850, 1650, 1490, 1470, 1380, 1150, 1120, 804, 748. Elemental analysis calculated for $C_{54}H_{56}N_2$: C, 88.48; H, 7.70; N, 3.82. Found: C, 88.43; H, 7.69; N, 3.88. MS, m/z: calcd 733.0, found: 732.2 (Fig. S16). Mp >250.0 °C. ***An-OCZ2***: ^{1}H NMR (500 MHz, TMS, $CDCl_3$): δ (ppm) = 8.45–8.42 (m, 4H), 8.37 (s, 2H), 8.17 (d, J = 8.0 Hz, 2H), 7.93–7.83 (m, 6H), 7.84 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.67–7.62 (m, 4H), 7.51–7.46 (m, 4H), 7.44–7.42 (m, 2H), 7.37–7.35 (m, 4H), 7.27–7.23 (m, 2H), 4.52 (t, J = 7.5 Hz, 4H), 4.36–4.33 (m, 4H), 2.13–2.07 (m, 4H), 1.94–1.91 (m, 4H), 1.49–1.27 (m, 40H), 0.94 (t, J = 6.0 Hz, 6H), 0.90–0.86 (m, 6H) (Fig. S17) ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 140.91, 140.36, 140.06, 139.55, 133.58, 133.25, 130.77, 129.48, 129.16, 127.46, 125.78, 125.62, 125.43, 124.83, 123.42, 123.39, 123.22, 123.06, 120.45, 119.09, 119.06, 118.89, 118.72, 109.10, 108.90, 108.74, 108.67, 108.65, 43.56, 43.23, 31.89, 31.81, 29.72, 29.51, 29.41, 29.29, 29.26, 29.19, 29.05, 27.52, 27.36, 22.68, 22.61, 14.14, 14.08 (Fig. S18). IR (KBr, cm^{-1}): 2930, 2850, 1650, 1490, 1470, 1380, 1150, 1120, 804, 748. Elemental analysis calculated for $C_{94}H_{102}N_4$: C, 87.67; H, 7.98; N, 4.35. Found: C, 87.62; H, 8.02; N, 4.41. MS, m/z: calcd 1287.8, found: 1286.2 (Fig. S19). Mp: 184.0–186.0 °C. ***An-OCZ3***: ^{1}H NMR (500 MHz, TMS, $CDCl_3$): δ (ppm) = 8.49–8.36 (m, 10H), 8.18–8.13 (m, 2H), 7.94–7.92 (m, 2H), 7.89–7.77 (m, 10H), 7.68–7.60 (m, 6H), 7.51–7.38 (m, 10H), 7.34–7.31 (m, 4H), 7.23–7.19

(m, 2H), 4.49 (t, *J* = 7.0 Hz, 4H), 4.38–4.29 (m, 6H), 4.18 (t, *J* = 7.0 Hz, 2H), 2.10–2.14 (m, 4H), 1.96–1.88 (m, 6H), 1.82–1.77 (m, 2H), 1.47–1.20 (m, 60H), 0.92–0.89 (m, 6H), 0.88–0.85 (m, 9H), 0.82 (t, *J* = 7.0 Hz, 3H) (Fig. S20) ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 140.91, 140.40, 140.37, 140.07, 140.02, 139.98, 139.55, 137.86, 135.36, 133.58, 133.36, 133.27, 133.22, 130.78, 129.50, 127.47, 125.80, 125.72, 125.69, 125.57, 125.51, 125.48, 124.83, 123.76, 123.70, 123.48, 123.41, 123.27, 123.11, 121.37, 121.28, 120.51, 119.08, 118.99, 118.94, 118.83, 118.70, 118.65, 109.12, 108.99, 108.88, 108.74, 108.66, 43.57, 43.23, 31.89, 31.83, 29.51, 29.43, 29.38, 29.30, 29.27, 29.17, 29.11, 29.07, 27.53, 27.38, 27.31, 22.69, 22.63, 14.14, 14.10 (Fig. S21). IR (KBr, cm^{-1}): 2930, 2850, 1650, 1490, 1470, 1380, 1150, 1120, 804, 748. Elemental analysis calculated for $C_{134}H_{148}N_6$: C, 87.34; H, 8.10; N, 4.56. Found: C, 87.22; H, 8.04; N, 4.63. MS, *m*/*z*: calcd 1842.6, found: 1841.1 (Fig. S22). Mp: 106.0–108.0 °C.