Supporting Information

Synthesis and Colour Tuning of Highly Efficient Fluorescent 9,10-Disubstituted-2,3,6,7-tetraphenylanthracene

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General Information.

All other reagents were used as received from commercial sources, unless otherwise stated. Unless otherwise noted, all experiments were carried out under N\textsubscript{2} atmosphere in oven-dried glassware using standard syringe, cannula and septa apparatus. Tetrahydrofuran, Toluene and hexane were dried with sodium and distilled before use. CH\textsubscript{2}Cl\textsubscript{2} were dried over CaH\textsubscript{2} and distilled before use. All the \textsuperscript{1}H NMR and \textsuperscript{13}C NMR were recorded in CDCl\textsubscript{3} solution unless otherwise stated. Coupling constants (\(J\) values) are given in Hertz (Hz) and chemical shifts are expressed in parts per million (ppm). Substrate was prepared from the corresponding readily available 4,6-dibromoisophthalaldehyde after several steps. UV-Vis and PL spectra in diluted dichloromethane solution (10\textsuperscript{-5} M) were recorded using a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Quantum yield was measured with reference to Coumarin-I (\(\Phi_f = 0.99\))\textsuperscript{1}. The wavelength at the intersection point of the two absorption spectra between the sample and the standard was taken as the excitation wavelength for PL spectra and determining quantum yields. The HOMO energy level of the studied compound was calculated from the oxidation potential (\(E^{1/2}\)) obtained from the cyclic voltammetry (CV) measurement with Pt wire as counter electrode, glassy carbon electrode as working electrode. The potentials were measured against an Ag/Ag\textsuperscript{+} (Ag/0.01 M AgNO\textsubscript{3}) reference electrode. The final results were calibrated with the ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) couple. Under the assumption that the
energy level of ferrocene/ferrocenium is 4.8 eV below vacuum, the HOMO energy levels of 2c and 4a-4g were determined from the equation: 4.8 eV + E¹/² (versus Fc/Fc⁺).

Device fabrication and characterization.

The EL devices with a configuration of ITO/TCTA (50 nm)/4a (3%) in DMPPP (30 nm)/BCP (10 nm)/TPBI(30 nm)/LiF(1 nm)/Al (100 nm) were fabricated by sequential thermal evaporation onto a clean glass precoated with a layer of indium tin oxide having a sheet resistance of 25 ohm/square. The effective area of the emitting diode is 9.00 mm². Current, voltage and light intensity measurements were recorded simultaneously using a Keithley 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photodiode. EL spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. All the measurements were carried out at room temperature in the air.

A. Representative Synthetic procedures:

(I) Synthesis of 2,3,6,7-tetraphenylanthracene 2c

![Scheme S1](image-url)
(a) 4,6-Bis((4-tert-butylphenyl)ethynyl)isophthalaldehyde:

Nitrogen was bubbled through a mixture of THF (80 mL) and triethylamine (80 mL) for 30 min, and to this solution was added 4,6-dibromoisophthalaldehyde (5 g, 17.1 mmol), CuI (0.326 g, 1.71 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.602 g, 0.86 mmol), and 1-tert-butyl-4-ethynylbenzene (6.23 g, 39.4 mmol). The resulting solution was stirred at 80 °C for 8 h before it was cooled to room temperature. Solvent was removed under reduced pressure, and the solution was filtered through a short silica bed with ethyl acetate/hexane (1:1 volume ratio). After concentration in vacuo, the crude material was eluted through a silica column with ethyl acetate/hexane (5/95) to afford the desired product (4.74 g, 62%) as a yellow solid.

(b) Synthetic procedure for 2,3,6,7-tetraphenylanthracene (2c).

A mixture of compound 1c (6.5 g, 22.4 mmol), Cu(OTf)$_2$ (0.081 g, 0.22 mmol) and CF$_2$HCO$_2$H (1.1 g, 11.2 mmol) in 1,2-dichloroethane (240 mL) was stirred for 10 min at 100 °C under Ar atmosphere. To this mixture was added a 1,2-dichloroethane (10 ml) solution of 4,6-bis((4-tert-butylphenyl)ethynyl)isophthalaldehyde (1.0 g, 2.2 mmol) drop-wise over a period of 2 h, and the mixture was stirred for additional 3 h. The solution was cooled to room temperature before it was treated with saturated NaHCO$_3$ aqueous solution. The organic layer was extracted with dichloromethane, dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was eluted through a silica column using dichloromethane/hexane as an eluent, giving 2c (0.87 g) in a 55%
yield.

![Scheme S2](image)

(e) 9,10-Dibromo-2,3,6,7-tetrakis(4-tert-butylphenyl)anthracene (3).

A dichloromethane (70 mL) solution of 2c (0.5 g, 0.71 mmol) was cooled to 0 °C, and to this solution was added dropwise a dichloromethane solution (2 ml) of Br₂ (0.25 g, 1.56 mmol) for a period of 5 min. The mixture was stirred for 0.5 h in dark. A saturated aqueous solution of Na₂SO₃ was added, and the resulting mixture was extracted with dichloromethane, dried over MgSO₄, and concentrated under reduced pressure. The residues were eluted with CHCl₃/hexane (5/95) through a silica column to afford compound 3 (0.495 g, 81%) as a yellow solid.

![Scheme S3](image)

(c) Synthetic procedure for compound (4a):

The 3,5-di-tert-butylphenylboronic acid (0.108 g, 0.46 mmol), compound 3 (0.1 g, 0.12 mmol), Pd(Ph₃P)₄ (0.007 g, 0.06 mmol) and K₂CO₃ (0.064 g, 0.46 mmol) were dissolved in a mixing solvent of toluene (8 mL), ethanol (3 mL) and water (6 mL); the resulting mixture
was then heated to 80 °C for 8 h. The solution was cooled to room
temperature, extracted with dichloromethane, dried over MgSO₄ and
concentrated under reduced pressure. The residues were eluted through a
silica column to afford compound 4a (0.095 g, 76%).

(d) Synthetic procedure for compound (4c):

Compound 3 (0.10 g, 0.12 mmol), Pd(Ph₃P)₄ (0.007 g, 0.06 mmol) and
CuI (0.003 g, 0.12 mmol) were dissolved in a solution of THF (7 ml) and
triethylamine (7 ml), and the mixture was stirred for 5 min. To this
mixture was added (triisopropylsilyl)acetylene (0.064 g, 0.35 mmol)
drop-wise under nitrogen atmosphere, and the resulting solution was
heated to 80 °C for 8 h. The resulting solution was cooled to room
temperature, and the solvent was removed under reduced pressure. The
residues were eluted through a silica column to give compound 4c (0.093
g, 75%).
(e) Synthetic procedure for compound (4e):

A mixture of compound 3 (0.10 g, 0.12 mmol), diphenylamine (0.081 g, 0.48 mmol), sodium tert-butoxide (0.097 g, 0.48 mmol), Pd$_2$(dba)$_3$ (0.01 g, 0.01 mmol) and P(t-Bu)$_3$ (0.005 g, 0.02 mmol) in dry toluene (15 ml) were stirred under nitrogen atmosphere at 100 °C for 12 h. The resulting solution was cooled to room temperature, and extracted with dichloromethane. The extract was dried over MgSO$_4$, concentrated under reduced pressure, and purified by a silica column to afford 4e (0.055 g, 46%).

Reference:

B. Electrochemical experiments for 2c, 4a-4g

Measurement:

Figure 1. Cyclic voltammetry of 2c with ferrocene

Figure 2. Cyclic voltammetry of 4a with ferrocene
Figure 3. Cyclic voltammetry of 4b with ferrocene

Figure 4. Cyclic voltammetry of 4c with ferrocene
Figure 5. Cyclic voltammetry of 4d with ferrocene

Figure 6. Cyclic voltammetry of 4e with ferrocene
Figure 7. Cyclic voltammetry of 4f with ferrocene

Figure 8. Cyclic voltammetry of 4g without ferrocene
C. EL performance of the device using compound 4a as dopant (ITO/TCTA (50 nm)/4a (3%) in DMPPP (30 nm)/BCP (10 nm)/TPBI(30 nm)/LiF(1 nm)/Al).
Figure 11. External Quantum Efficiency of compound 4a over various Current Density

D. Spectral data for key compounds:

Spectral data for compound:

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\text{solid; IR (neat, cm}^{-1}) : 2780 (w), 2170 (w), 1705 (s), 1390(s), 1375 (m), 1372 (s); ^1H NMR (400 MHz, CDCl}_3): \delta 10.59 (s, 2 H), 8.45 (s, 1 H), 7.88 (s, 1H), 7.51 (m, 4H), 7.42 (m, 4H), 1.33 (s, 18H); ^13C NMR (100 MHz, CDCl}_3): \delta 189.9, 153.3, 137.6, 134.34, 131.7, 131.1, 127.1, 125.6, 118.5, 100.9, 83.6, 34.9, 31.0; HRMS calcd for C\textsubscript{32}H\textsubscript{30}O\textsubscript{2}: 446.2246,
found 446.2241. Anal. calcd for C_{32}H_{30}O_{2}: C 86.06; H 6.77. Found: C 85.93; H 7.02.

**Spectral data for compound (2a):**

![Diagram of 2a](image)

solid; IR (neat, cm^{-1}): 3058(s), 1658 (s), 1492 (s); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 8.48 (s, 2 H), 8.05 (s, 4 H), 7.26 (m, 20H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 141.4, 139.0, 131.4, 129.9, 129.6, 127.9, 126.6, 126.0 ; HRMS calcd for C_{38}H_{26}: 482.2035, found 482.2058. Anal. calcd for C_{38}H_{26}: C 94.57; H 5.43. found: C 94.12; H 5.71.

**Spectral data for compound (2b):**

![Diagram of 2b](image)

solid; IR (neat, cm^{-1}): 3120(s), 2989 (s), 1570 (m), 1450 (s), 1380(m), 1280 (s); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 8.40 (s, 2 H), 7.97(s, 4H), 7.18 (d, J= 6.8, 8.8 Hz, 8 H), 6.81 (d, J= 8.8 Hz, 8H), 3.80 (s, 12H); \textsuperscript{13}C NMR (150 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \delta 158.9, 139.1, 134.3, 131.7, 131.3, 129.4, 125.8, 113.7, 55.5; HRMS calcd for C_{42}H_{34}O_{4}: 602.2457, found 602.2454. Anal. calcd for C_{42}H_{34}O_{4}: C 83.70; H 5.69. found: C 83.38; H 5.84.

**Spectral data for compound (2c):**
solid; IR (neat, cm^-1): 3280 (s), 2989 (s), 1650(m), 1395 (m), 1372 (s); ^1H NMR (600 MHz, CDCl_3): δ 8.42 (s, 2 H), 8.03 (s, 4H), 7.26 (m, 8H), 7.19 (m, 8H), 1.30 (s, 36H); ^13C NMR (150 MHz, CDCl_3): δ 149.4, 139.0, 138.5, 131.3, 129.5, 129.3, 125.7, 124.6, 34.4, 31.3 ; HRMS calcd for C_{54}H_{58}: 706.4539, found 706.4540. Anal. calcd for C_{54}H_{58}: C 91.73; H 8.27. found: C 91.38; H 8.42.

Spectral data for compound (3):

solid; IR (neat, cm^-1): 3290 (s), 2979 (s), 1460(s), 1394(m), 1371 (s), 706 (m); ^1H NMR (400 MHz, CDCl_3): δ 8.58 (s, 4H), 7.29 (d, J = 8.8 Hz, 8H), 7.22 (d, J = 8.8 Hz, 8H), 1.32 (s, 36H); ^13C NMR (100 MHz, CDCl_3/CS_2): δ 149.8, 140.9, 137.6, 130.4, 129.5, 124.8, 122.8, 34.3, 31.3 ; MALDITOF-MS calcd for C_{54}H_{56}Br_2: 862.2749, found m/z = 864.831. Anal. calcd for C_{54}H_{56}Br_2: C 74.99; H 6.53. Found: C 74.58; H 6.62.

Spectral data for compound (4a):
solid; IR (neat, cm\(^{-1}\)): 3280 (s), 2970(s), 1673 (s), 1310(s), 1395 (m), 1371 (s); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.91. (s, 4H), 7.56 (s, 2H), 7.54 (s, 4H), 7.20 (d, \(J= 8.4\) Hz, 8H), 7.09 (d, \(J= 8.4\) Hz, 8H), 1.46 (s, 36H), 1.27 (s, 36H); \(^13\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 151.1, 150.0, 139.3, 138.7, 138.2, 137.7, 129.9, 129.3, 127.0, 125.1, 121.6, 35.4, 34.8, 31.9, 31.5 ;MALDITOF-MS calcd for C\(_{82}\)H\(_{98}\) : 1082.7669, found m/z = 1082.531. Anal. calcd for C\(_{82}\)H\(_{98}\): C, 90.88; H, 9.12. Found: C, 90.81; H, 9.08.

**Spectral data for compound (4b) :**

solid; IR (neat, cm\(^{-1}\)): 3238 (s), 2989 (s), 1393 (m), 1370(s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.06-8.04 (m, 4H), 7.99-7.97 (m, 2H), 7.94-7.91 (m, 2H), 7.76 (d, \(J=0.4\) Hz, 4H), 7.71-7.69 (m, 2H), 7.58-7.55 (m, 4H), 7.07 (m, 8H), 6.93 (m, 8H), 1.20 (s, 36H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.2, 138.8, 138.5, 136.9, 136.5, 133.6, 132.9, 130.3, 129.9, 129.6, 129.5, 128.3, 128.2, 127.94, 127.90, 126.2, 126.1, 124.5, 34.3, 31.3 ; MALDITOF-MS calcd for C\(_{74}\)H\(_{70}\): 958.5478, found m/z = 958.133. Anal. calcd for C\(_{74}\)H\(_{70}\): C, 92.65; H, 7.35. Found: C, 92.60; H, 7.38.
Spectral data for compound (4c):

\[
\begin{align*}
\text{solid; IR (neat, cm}^{-1}) & : 3240 \text{ (s)}, 2940\text{(s)}, 2890 \text{ (m)}, 2130\text{(w)}, 1385\text{(s),} \\
1370\text{(s)}; & \quad ^1\text{H NMR (400 MHz, CDCl}_3) : \delta 8.69 \text{ (s, 4H)}, 7.27 \text{ (s, 16H)}, 1.33 \\
\text{(s, 36H), 1.23 \text{ (m, 42H); ^13C NMR (100 MHz, CDCl}_3) : \delta 149.6, 139.9,} \\
138.2, 132.0, 129.6, 129.0, 124.7, 118.0, 104.9, 103.6, 34.5, 31.4, 18.9, \\
11.5 \text{ ; MALDITOF-MS calcd for C}_{76}\text{H}_{98}\text{Si}_2 : 1066.7207, \text{ found m/z =} \\
1066.605. \text{ Anal. calcd for C}_{76}\text{H}_{98}\text{Si}_2: C, 85.49; H, 9.25. \text{ Found: C, 85.00;} \\
H, 9.40. 
\end{align*}
\]

Spectral data for compound (4d):

\[
\begin{align*}
\text{solid; IR (neat, cm}^{-1}) & : 3280 \text{ (s)}, 2960\text{(s)}, 2845 \text{ (m), 2090(w), 1396(m),} \\
1370\text{(s)}; & \quad ^1\text{H NMR (400 MHz, CDCl}_3) : \delta 8.74 \text{ (s, 4H)}, 7.56 \text{ (d, } J = 1.6\text{Hz,} \\
4\text{H), 7.44 \text{ (d, } J = 1.6\text{Hz, 2H), 7.29 \text{ (s, 16H) 1.36 \text{ (s, 36H), 1.31 \text{ (s, 36H);} } \\
^13\text{C NMR (100 MHz, CDCl}_3) : \delta 151.0, 149.7, 140.1, 138.6, 131.8, 129.7,} \\
128.8, 126.1, 124.8, 123.2, 122.7, 118.0, 104.1, 86.0, 34.9, 34.5, 31.4; \text{ MALDITOF-MS calcd for C}_{86}\text{H}_{98}: 1130.7669, \text{ found m/z =} \quad 1130.592. 
\end{align*}
\]
Anal. calcd for C$_{86}$H$_{98}$: C, 91.27; H, 8.73. Found: C, 91.01; H, 8.75.

**Spectral data for compound (4e):**

solid; IR (neat, cm$^{-1}$): 3230 (s), 2900(s), 2840 (m), 1560(s), 1397(m), 1370(s), 1243 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.20 (s, 4H), 7.26-7.16(m, 16H), 7.10 (d, $J = 8.4$ Hz, 8H), 6.95 (t, $J = 7.2$ Hz, 4H), 6.70 (d, $J = 8.4$ Hz, 8H), 1.25 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.5, 148.1, 139.7, 138.1, 130.9, 129.5, 129.3, 126.4, 124.5, 121.4, 120.9, 34.4, 31.3; MALDITOF-MS calcd for C$_{78}$H$_{76}$N$_2$: 1040.6009, found m/z = 1040.528. Anal. calcd for C$_{78}$H$_{76}$N$_2$: C, 89.95; H, 7.36; N, 2.69. Found: C, 89.63; H, 7.28; N, 2.80.

**Spectral data for compound (4f):**

solid; IR (neat, cm$^{-1}$): 3238 (s), 2910 (m), 1396(m), 1370(s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (s, 4H), 7.25 (d, $J = 8$ Hz, 8H), 7.09 (d, $J = 8.4$ Hz, 8H), 7.06 (d, $J = 8.4$Hz, 8H), 6.71 (d, $J = 8$ Hz, 8H), 1.33 (s, 36H), 1.24 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.4, 146.1, 143.8, 139.2, 138.2, 137.4, 130.7, 129.6, 126.9, 126.1, 124.4, 120.5, 34.4, 34.3, 31.6, 31.4; MALDITOF-MS calcd for C$_{94}$H$_{108}$N$_2$: 1264.8513, found m/z
= 1264.727. Anal. calcd for C_{94}H_{108}N_{2}: C, 89.19; H, 8.60; N, 2.21. Found: 
C, 88.72; H, 8.73; N, 2.34.

**Spectral data for compound (4g):**

solid; IR (neat, cm⁻¹): 3200 (s), 2910 (s), 2860 (m), 1397 (m), 1372 (s);

¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 4H), 7.11 (d,  J=8.4, 8H), 7.06 
(d,  J = 9.2 Hz, 8H), 6.81(d,  J = 6.4 Hz, 8H), 6.79 (d,  J = 6.8Hz, 8H), 
3.77(s, 12H), 1.25 (s, 36H) ; ¹³C NMR (100 MHz, CDCl₃): δ 154.0, 
149.4, 142.4, 139.5, 138.2, 137.3, 131.0, 129.6, 126.6, 124.5, 121.8, 
114.7, 55.7, 34.4, 31.4; MALDITOF-MS calcd for C₈₂H₇₄N₂O₄: 
1160.6431, found m/z = 1160.451. Anal. calcd for C₈₂H₇₄N₂O₄: C, 84.79; 
H, 7.29; N, 2.41. Found: C, 84.57. H, 7.38; N, 2.29.

**E. NMR spectral- data for key compounds:**