Supporting Information

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CONTENTS
1. General methods and materials ................................................................. S1-S2
2. Experimental section ................................................................................ S3-S5
3. $^1$H and $^{13}$C NMR spectra ................................................................. S6-S10
4. Cyclic voltammograms ........................................................................... S11-S12
5. X-ray crystal structures .......................................................................... S12-S13
6. References .................................................................................................. S14

General methods and materials
All commercial reagents were used as received. Et$_3$N was re-distilled before use. Para substituted phenyl acetylenes were synthesized according to the previously reported procedure. Unless otherwise specified, all reactions were run in oven-dried glassware. Reactions were monitored by thin layer chromatography on silica G TLC plates (Sorbent Technologies No. 1634126). Purifications were performed by column chromatography on silica gel (Sorbent Technologies, 40-63 µm particle size) or neutral alumina (Sorbent Technologies, 32-63 µm particle size). $^1$H- and $^{13}$C-NMR spectra were measured on a Bruker Avance 400 MHz instrument. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA 30071. Cyclic voltammetry was performed on a CH-instruments 6017E model with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in dry acetonitrile using a glassy carbon as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode with a scan rate of 100 mV/sec. The HOMO and LUMO energy values were calculated from the onset of the first oxidation and reduction potentials from the equations $E_{\text{HOMO}}$ (eV) = - [$E_{\text{ox onset}}$ - $E_{1/2}$ (Fc/Fc$^+$) + 4.8] and $E_{\text{LUMO}}$ (eV) = - [$E_{\text{red onset}}$ - $E_{1/2}$ (Fc/Fc$^+$) + 4.8],

S1
where $E_{1/2}$ (Fc/Fc$^+$) was the cell correction. Melting points were obtained using a melting point apparatus, upper temperature limit 400 °C. UV-vis spectra were recorded on a Cary 5000 UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. Fluorescence and UV-vis measurements were taken in CHCl$_3$. Optical bandgap was calculated from wavelength corresponding to the energy absorption onset from the intersection of the leading edge tangent with the $x$-axis. Quantum yield measurements were performed in dilute CHCl$_3$ solutions with absorbance ranging from 0.01 to 0.04. Quinine sulfate was used as the reference. The excitation wavelength of 313 nm was used to obtain the fluorescence spectra for each solution ranging from 320 to 600 nm. The fluorescence intensity (area of the fluorescence spectrum) was then calculated and recorded. Quantum yields were calculated using following equation:

$$\phi_s = \phi_r \left( \frac{A_r F_s}{A_s F_r} \right) \left( \frac{n_s^2}{n_r^2} \right).$$

$\phi_r$ is 0.51, $A_s$ and $A_r$ are absorbances of the sample and reference solutions, respectively at the same excitation wavelength, $F_s$ and $F_r$ are the corresponding relative integrated fluorescence intensities, $n$ is the refractive index [CHCl$_3$ ($n_s = 1.445$) and 1 N H$_2$SO$_4$ ($n_r = 1.339$) were used]. Crystallographic data are collected in Table S1. A Bruker Ultra diffractometer equipped with a mini rotating-anode Mo source and microfocus optics was used for data collection with one-second, one-degree width images. Direct methods were used for structure solution and all non-hydrogen atoms were refined with anisotropic thermal parameters and without restraint. Hydrogen atoms were included as idealized contributions. All software was contained in the current packages of SHELX software as provided by the Bruker Corporation (Madison, WI).
Experimental Section:

**Synthesis of 2a:** In a 8 mL reaction vial, compound 1 (50 mg, 0.123 mmol) was taken and under an argon atmosphere Pd(PPh₃)₄ (7.0 mg, 5 mol%), CuI (0.57 mg, 0.003 mmol), Et₃N (2 mL) and 4-tert-butylphenylacetylene (50.61 mg, 0.32 mmol) were added and sealed. The reaction vial was heated to 80 °C for a period of 16 h. After 16 h the solvent was evaporated. The resulting residue was purified by column chromatography using alumina column using Hexane/EtOAc (98:2) to afford the yellow solid in 87 %.³ Mp 190–192 °C. ¹H NMR (400 MHz, Chloroform-δ) δ 7.62 – 7.48 (m, 4H), 7.46 – 7.37 (m, 5H), 4.55 (s, 3H), 4.05 (d, J = 0.8 Hz, 6H), 3.92 (s, 3H), 1.34 (d, J = 1.2 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 162.26, 154.80, 152.17, 150.14, 134.52, 131.60, 130.98, 128.94, 125.67, 125.53, 124.55, 120.41, 120.38, 111.08, 110.65, 103.50, 100.07, 98.85, 82.96, 82.47, 61.90, 61.82, 51.83, 35.01, 34.99, 33.73, 31.32, 31.30. Elemental Anal. Calcd. for C₃₇H₃₉NO₄: C, 79.12; H, 7.00; N, 2.49. Found: C, 78.68; H, 7.02; N, 2.54.

**Synthesis of compound 2b:** This compound was prepared using the procedure reported for 2a (yellow solid, 42% yield). Mp 196–198 °C ¹H NMR (400 MHz, Chloroform-δ) δ 7.55 – 7.39 (m, 5H), 6.74 – 6.65 (m, 4H), 4.56 (s, 3H), 4.04 (d, J = 1.0 Hz, 6H), 3.91 (s, 3H), 3.02 (d, J = 0.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 162.26, 154.24, 150.30, 150.26, 149.56, 134.80, 134.52, 131.60, 130.98, 128.94, 125.67, 125.53, 124.55, 120.41, 120.38, 111.08, 110.65, 103.50, 100.07, 98.85, 82.96, 82.47, 61.90, 61.82, 51.83, 35.01, 34.99, 33.73, 31.32, 31.30. Elemental Anal. Calcd. for C₃₇H₃₉NO₄: C, 79.12; H, 7.00; N, 2.49. Found: C, 78.68; H, 7.02; N, 2.54.
Synthesis of compound 2c: This compound was prepared using the procedure reported for 2a (yellow solid, 99 % yield). Mp 129–131 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.67 – 7.50 (m, 4H), 7.41 (s, 1H), 7.15 – 7.04 (m, 4H), 4.54 (s, 3H), 4.05 (d, $J = 2.7$ Hz, 6H), 3.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.99, 162.05, 161.48, 154.73, 150.08, 134.33, 133.69, 133.61, 133.05, 132.97, 129.01, 124.36, 119.34, 116.03, 115.86, 115.81, 115.64, 110.84, 110.37, 103.20, 98.68, 97.42, 83.09, 82.61, 61.80, 61.72, 51.77, 33.61. Elemental Anal. Calcd. for C$_{29}$H$_{21}$F$_2$NO$_4$ 0.15Et$_2$O: C, 71.59; H, 4.57; N, 2.82. Found: C, 71.66; H, 4.92; N, 2.71.

Synthesis of compound 2d: This compound was prepared using the procedure reported for 2a (yellowish-orange solid, 57 % yield). Mp 150–152 °C $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.74 – 7.61 (m, 8H), 7.40 (s, 1H), 4.54 (s, 3H), 4.05 (d, $J = 3.9$ Hz, 6H), 3.94 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.89, 155.05, 150.49, 134.72, 132.29, 132.21, 132.15, 129.48, 127.96, 127.87, 124.41, 118.47, 118.38, 111.99, 111.91, 110.90, 110.18, 103.20, 98.20, 96.92, 87.64, 87.26, 61.95, 61.88, 51.93, 33.70. Elemental Anal. Calcd. for C$_{31}$H$_{21}$N$_3$O$_4$ 0.5CHCl$_3$: C, 67.66; H, 3.88; N, 7.51. Found: C, 67.70; H, 4.10; N, 7.65.
Synthesis of compound 2e: This compound was prepared using the procedure reported for 2a (orange solid, 56 % yield). Mp 248–250 °C

$^1$H NMR (400 MHz, Chloroform-$d$) δ 8.32 – 8.23 (m, 4H), 7.82 – 7.74 (m, 2H), 7.75 – 7.67 (m, 2H), 7.42 (s, 1H), 4.56 (s, 3H), 4.07 (d, $J = 4.5$ Hz, 6H), 3.95 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.85, 155.13, 150.58, 147.26, 134.20, 132.43, 131.75, 129.90, 129.80, 129.57, 124.43, 123.90, 123.75, 110.96, 110.16, 103.23, 98.06, 96.75, 88.52, 88.15, 61.98, 61.91, 51.94, 33.71. Elemental Anal. Calcd. for C$_{29}$H$_{21}$N$_3$O$_8$: C, 64.56; H, 3.92; N, 7.79. Found: C, 64.39; H, 3.88; N, 7.88
$^{1}H$ NMR 2a:

$^{13}C$ NMR 2a:
$^1$H NMR 2b:

$^{13}$C NMR 2b:
$^1$H NMR 2e:

$^{13}$C NMR 2e:
Fig. S1 Cyclic voltammogram of 2a

Fig. S2 Cyclic voltammogram of 2b

Fig. S3 Cyclic voltammogram of 2c

Fig. S4 Cyclic voltammogram of 2d
Fig. S5 Cyclic voltammogram of 2e

Fig. S6 X-ray crystal structure of compound 2a
Fig. S7 X-ray crystal structure of compound 2c

Fig. S8 X-ray crystal structure of compound 2e
References: