

## Doubly Ortho-linked Quinoxaline/Triarylamine Hybrid as a Bifunctional, Dipolar Electroluminescent Template for Optoelectronic Applications

Chien-Tien Chen,<sup>\*a</sup> Jin-Sheng Lin,<sup>a</sup> Murthy V. R. K. Moturu,<sup>a</sup> Yi-Wen Lin,<sup>a</sup> Wei Yi,<sup>a</sup> Yu-Tai Tao,<sup>\*b</sup>  
and Chin-Hsiung Chien<sup>b</sup>

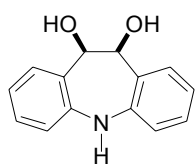
Experimental details of compounds **2a-c**, **2c'** and **3a,b**, UV-Vis, PL, CV spectra, *I-V-L* characteristics and EL spectra of devices, ORTEP drawings and selected crystal data for **2c**, **3a**, and **3b** (12 pages)

### General.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AV500 (500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C), Jeol JVM-EX400 (400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C) or Varian Gemini-2000 (200 MHz <sup>1</sup>H, 50 MHz <sup>13</sup>C) spectrometers in deuteriochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm ( $\delta$ ). Coupling constants, *J*, are reported in Hz. Infrared spectra were recorded on a Perkin-Elmer Paragon-500 FTIR spectrometer. Peaks are reported in units of cm<sup>-1</sup> with the following relative intensities: br (broad), s (strong 67-100 %), m (medium 33-67 %), or w (weak 0-33 %). Mass spectra were recorded on a Finnigan TCQ-700 spectrometer with an ionization voltage of 70 or 20 eV unless otherwise stated. High-resolution mass spectra were measured on JEOL SX-102A spectrometer. Combustion analyses were performed on a Perkin-Elmer 2400-CHN analyzer by the Northern Instrument Center of Taiwan. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT-95S spectrometer. Data are reported in the form *m/e* (intensity relative to base peak). Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light or with phosphomolybdic acid (PMA) and KMnO<sub>4</sub> staining agents. Column (flash) chromatography was performed using 32-63  $\mu$ m silica gel. Solvents for extraction and chromatography were reagent grade. Dichloromethane was dried over CaH<sub>2</sub> before use. THF was dried over Na with benzophenone-ketyl intermediate as indicator. All reactions were run under argon. Absorption spectra (CH<sub>2</sub>Cl<sub>2</sub>) were measured on a HP-8453 Diode Array spectrometer using spectrophotometric grade solvents. Emission spectra (10  $\mu$ M) were measured on an Aminco-Bowman Series 2 luminescence spectrometer upon excitation at

the absorption maxima in the same solvent. Quantum yield measurements were performed by using Coumarin-1<sup>1</sup> (99%, EtOAc) and DCM<sup>2</sup> (65%, CH<sub>3</sub>CN) as standards. X-ray structures were measured on Nonius CAD4 or Bruker Nonius Kappa CCD instrument. Cyclic voltammetry (CV) measurements were carried out in 1.0 mM of substrate in anhydrous degassed solvents containing 0.1 M tetrabutylammonium perchlorate (*n*-Bu<sub>4</sub>NClO<sub>4</sub>) as a supporting electrolyte on a PARC EG&G 273 potentiostat. Platinum electrode was used as a counter electrode and carbon electrode was used as a working electrode and Ag/AgCl as a reference electrode. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-2920 Low-Temperature Difference Scanning Calorimeter. The samples were firstly heated (20 °C/min) to melt and then quenched with liquid nitrogen. T<sub>g</sub>s were recorded by heating (10 °C/min) the cooled samples.

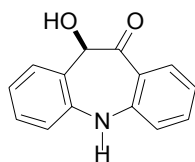
### 10,11-Dihydro-5H-dibenzo[b,f]azepine-10,11-diol<sup>3</sup>



A mixture of iminostilbene (5.01 g, 25.9 mmol), 4-methylmorpholine *N*-oxide (7.53 g, 55.6 mmol, 2.2 equiv), 1,4-diazabicyclo- [2,2,2]octane (DABCO, 0.3 g, 2.7 mmol, 0.1 equiv) and potassium osmate (0.010 g, 0.027 mmol, 0.1 mol%) was

stirred in 50% aqueous acetone (100 mL) at ambient temperature for 24h. After completion of the reaction as evidenced by TLC analysis, the resulting reaction mixture was quenched with saturated aqueous Na<sub>2</sub>SO<sub>3</sub> (30 mL) and stirred for 30 min. The clear solution was concentrated under reduced pressure. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL). The combined organic extracts were washed with water (30 mL), brine (30 mL), dried (MgSO<sub>4</sub>), and evaporated to give 5.42 g (92 %) of the corresponding *cis*-diol as a colorless puffy material which was used directly for next step.

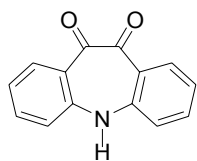
### 11-Hydroxy-5,11-dihydro-dibenzo[b,f]azepin-10-one



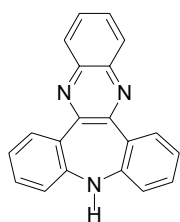
To a solution of diol (10.0 g, 44.0 mmol) in 1,4-dioxane (150 mL) at 15 °C was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 11.0 g, 48.5 mmol, 1.1 equiv) in portions. The resulting mixture was stirred at this temperature for 10 h.

After completion of the reaction as evidenced by TLC analysis, the reaction mixture was filtered and the filtrate was concentrated. The residue was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the mixture was filtered again. Evaporation of the filtrate gave crude  $\alpha$ -hydroxy-ketone, which was re-crystallized from CH<sub>2</sub>Cl<sub>2</sub> to provide 8.42 g (85 %) of the pure  $\alpha$ -hydroxy-ketone as colorless needles.

#### 5H-Dibenzo[b,f]azepine-10,11-dione<sup>4</sup>

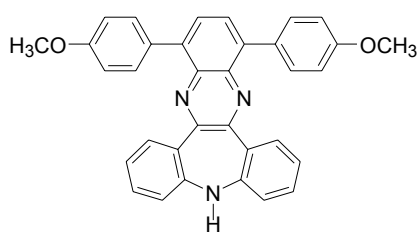


A mixture of  $\alpha$ -hydroxy-ketone (2.7 g, 12.0 mmol), NH<sub>4</sub>NO<sub>3</sub> (0.96 g, 12.0 mmol, 1equiv) and Cu(OAc)<sub>2</sub> (0.12 g, 0.6 mmol, 5 mol%) was heated in 80% aqueous AcOH (40 mL) at 80 °C for 30 min. The reaction mixture was gradually cooled to ambient temperature and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  50 mL). The combined organic layers were washed with water (30 mL), brine (30 mL), dried (MgSO<sub>4</sub>), and evaporated. Purification of the crude residue by column chromatography on silica gel gave diketone as yellow solid, which was further re-crystallized from CH<sub>2</sub>Cl<sub>2</sub> to give 1.472 g (55 %) of the pure product as orange needles: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.40 (s, 1H), 8.61 (d, *J* = 8.8, 2H), 8.21 (d, *J* = 8.8, 2H), 7.75 (dd, *J* = 8.8, 6.8, 2H), 7.60 (dd, *J* = 8.8, 6.8, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  193.4, 149.0, 132.1, 130.3, 129.9, 128.6, 123.5; TLC R<sub>f</sub> 0.37 (EtOAc/hexane, 1/7).



A solution of the diketone (4.0 g, 17.9 mmol), *o*-phenylenediamine (2.7 g, 25.1 mmol, 1.4 equiv) and catalytic amount of *p*-toluenesulfonic acid (*p*-TSA, 17 mg, 0.9 mmol, 5 mol%) in CHCl<sub>3</sub> (50 mL) was heated to reflux for 10 h. The reaction mixture was cooled to ambient temperature and then quenched with saturated aqueous NaHCO<sub>3</sub> (35 mL). The aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2  $\times$  100 mL). The combined organic layers were washed with water (35 mL), brine (30 mL), dried (MgSO<sub>4</sub>), and evaporated. Purification of the crude residue by column chromatography on silica gel gave crude product, which was re-crystallized from CH<sub>2</sub>Cl<sub>2</sub> to provide 4.49 g (85 %) of pure **2a** as yellow needles: m.p. 211 °C (CH<sub>2</sub>Cl<sub>2</sub>, by DSC); T<sub>d</sub> 256 °C; T<sub>g</sub> 57 °C; IR (KBr)  $\nu$  3306 (w), 3059 (w), 1610 (m), 1596 (w), 1516 (m), 1477 (s), 1451 (m), 1365 (m), 1311 (m), 1246 (w), 1221 (w), 1141 (w); <sup>1</sup>H

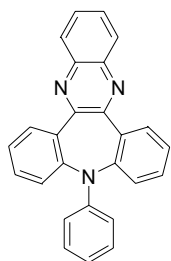
NMR (200 MHz, CDCl<sub>3</sub>) δ 8.18-8.09 (m, 4H), 7.73 (dd, *J* = 6.4, 3.4, 2H), 7.38-7.18 (m, 4H), 6.92 (d, *J* = 7.8, 2H), 5.47 (s, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 152.6, 150.7, 141.7, 132.0, 130.8, 129.8, 129.7, 129.3, 124.2, 119.8; MS (20 eV) 295 (M<sup>+</sup>, 100), 75 (39), 62 (14), 52 (18), 50 (48); TLC R<sub>f</sub> 0.35 (EtOAc/hexane, 1/8); HR-MS calcd for C<sub>20</sub>H<sub>13</sub>N<sub>3</sub>: 295.1109, found: 295.1109; Anal. Calcd for C<sub>20</sub>H<sub>13</sub>N<sub>3</sub>: C, 81.34, H, 4.44, N, 14.23. Found: C, 81.22, H, 4.59, N, 14.03.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (dd, *J* = 7.8, 1.4, 2H), 7.82 (s, 1H), 7.81 (d, *J* = 6.8, 4H), 7.28 (td, *J* = 6.9, 1.4, 2H), 7.12 (t, *J* = 7.5, 2H), 7.06 (d, *J* = 4.9, 4H), 6.86 (d, *J* = 7.2, 2H), 5.41 (s, 1H), 3.91 (s, 6H); <sup>13</sup>C NMR (10 MHz, CDCl<sub>3</sub>) δ 158.9, 150.6, 149.9,

139.2, 138.6, 132.0, 131.7, 130.7, 130.2, 129.5, 129.2, 123.6, 119.3, 113.1, 55.0; MS (70 eV) 507 (M<sup>+</sup>, 100), 254 (18), 216 (10); TLC R<sub>f</sub> 0.35 (EtOAc/hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1/15/2).

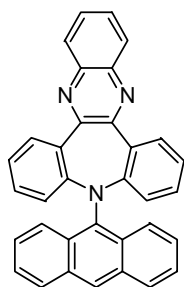
### Representative procedure for the preparation of **2b-c**, **2c'**, and **3a,b**



To a solution of Q-H-**2a** (295 mg, 1.0 mmol), *t*-BuONa (288 mg, 3.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (11.6 mg, 1 mol%) in dry toluene (15 mL) was added P(*t*-Bu)<sub>3</sub> (0.03 M in toluene, 1 mL, 3 mol%) and iodobenzene (224 mg, 1.1 mmol, 1.1 equiv). The resulting mixture was refluxed for 8h in argon atmosphere until complete

consumption of **2a** as evidenced by TLC analysis. The reaction mixture was then cooled to ambient temperature and quenched with saturated aqueous NaHCO<sub>3</sub> (20 mL). The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 25 mL). The combined organic extracts were washed sequentially with water (15 mL) and brine (10 mL), dried (MgSO<sub>4</sub>), and concentrated to give crude product-**2b**, which was purified by column chromatography on silica gel (EtOAc/ hexane, 1/10) afford the pure compound-**2b** in 87% yield as yellow solid: m.p. 213-214 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane, by DSC); T<sub>d</sub> 273 °C; T<sub>g</sub> 86 °C; IR (KBr) ν 3066 (w), 1591 (m), 1498 (s), 1452 (m), 1350 (m), 1317 (m), 1283 (w), 1062 (w), 1020 (w); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (dd, *J* = 7.8, 1.2, 2H), 8.18 (dd, *J* = 6.4, 3.4, 2H), 7.78 (d, *J* = 6.4, 3.4, 2H), 7.65 (dd, *J* = 7.8, 1.6, 2H), 7.62 (td, *J* =

7.8, 1.4, 2H), 7.53 (td,  $J = 7.8, 1.6$ , 2H), 6.96 (dd,  $J = 8.8, 7.4$ , 2H), 6.60 (t,  $J = 7.4$ , 1H), 6.58 (d,  $J = 8.8$ , 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 147.4, 146.5, 141.5, 137.4, 132.6, 131.2, 130.1, 129.3, 129.1, 128.8, 127.8, 118.2, 112.0; MS (70 eV) 371 ( $\text{M}^+$ , 100), 268 (10), 255 (20), 185 (10), 77 (10); TLC  $R_f$  0.37 (EtOAc/hexane, 1/10); HR-MS calcd for  $\text{C}_{26}\text{H}_{17}\text{N}_3$ : 371.1417, found: 371.1426; Anal. Calcd for  $\text{C}_{26}\text{H}_{17}\text{N}_3$ : C, 84.07, H, 4.61, N, 11.31. Found: C, 83.86, H, 4.58, N, 11.20.



Data for **2c** (yellowish solid): m.p. 273 °C ( $\text{CH}_2\text{Cl}_2$ , by DSC);  $T_d$  350 °C;  $T_g$  154 °C;

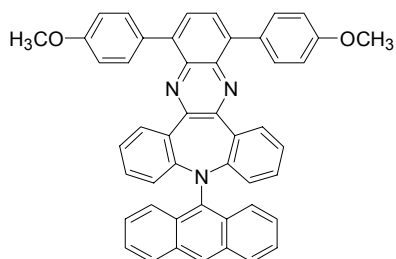
IR (KBr)  $\nu$  3054 (w), 1485 (m), 1449 (m), 1352 (m), 1312 (m), 788 (m), 754 (s), 741

(s), 730 (s);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s, 1H), 8.23-8.15 (m, 6H), 8.05 (d,  $J$

= 8.5, 2H), 7.80 (dd,  $J = 6.3, 3.4$ , 2H), 7.43 (t,  $J = 6.8$ , 2H), 7.31 (t,  $J = 8.0$ , 2H), 7.16

(t,  $J = 6.9$ , 2H), 7.09 (bd,  $J = 7.7$ , 2H), 7.03 (td,  $J = 6.8, 1.6$ , 2H);  $^{13}\text{C}$  NMR (50 MHz,

$\text{CDCl}_3$ )  $\delta$  153.8, 152.0, 142.2, 136.7, 132.6, 132.4, 132.3, 131.4, 130.0, 129.9, 129.5, 129.0, 128.2, 126.8, 125.5, 125.5, 124.3, 122.6; MS (70 eV) 471 ( $\text{M}^+$ , 100), 293 (5), 234 (38), 190 (10); TLC  $R_f$  0.4 (EtOAc/hexane, 1/9); HR-MS calcd for  $\text{C}_{34}\text{H}_{21}\text{N}_3$ : 471.1735, found 471.1748; Anal. Calcd for  $\text{C}_{34}\text{H}_{21}\text{N}_3$ : C, 86.60, H, 4.49, N, 8.91. Found: C, 86.48, H, 4.42, N, 8.92.



Data for **2c'** (yellowish solid): m.p. 324 °C ( $\text{CH}_2\text{Cl}_2$ , by DSC);  $T_d$

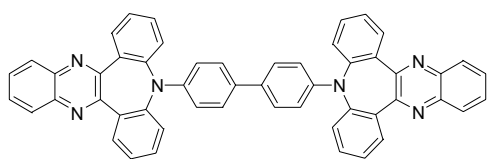
464 °C;  $T_g$  159 °C; IR (KBr)  $\nu$  3054 (w), 1485 (m), 1449 (m), 1352

(m), 1312 (m), 788 (m), 754 (s), 741 (s), 730 (s);  $^1\text{H}$  NMR (400 MHz,

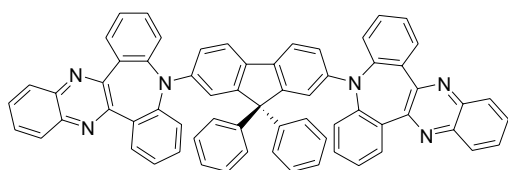
$\text{CDCl}_3$ )  $\delta$  8.52 (s, 1H), 8.27 (d,  $J = 8.7$ , 2H), 8.10 (dd,  $J = 7.8, 3.0$ ,

2H), 8.04 (d,  $J = 8.4$ , 2H), 7.89 (s, 2H), 7.88 (dd,  $J = 6.6, 2.3$ , 4H),

7.43 (t,  $J = 7.6$ , 2H), 7.36 (t,  $J = 7.6$ , 2H), 7.08-7.03 (m, 8H), 6.95 (t,  $J = 8.3$ , 2H), 3.88 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 152.0, 151.6, 140.0, 138.9, 137.1, 133.0, 132.3, 132.0, 131.5, 131.0, 129.8, 129.6, 128.9, 128.0, 126.8, 125.6, 125.4, 124.0, 122.6, 113.5, 55.3; MS (70 eV) 683 ( $\text{M}^+$ , 100), 342 (96), 190 (20), 176 (16); TLC  $R_f$  0.3 (EtOAc/hexane, 1/12); Anal. Calcd for  $\text{C}_{48}\text{H}_{33}\text{N}_3\text{O}_2$ : C, 84.31, H, 4.86, N, 6.15. Found: C, 84.43, H, 4.80, N, 6.17.



Data for **3a** (yellow solid): m.p. 448-449 °C (CHCl<sub>3</sub>/hexane, by DSC); T<sub>d</sub> 467 °C; T<sub>g</sub> 202 °C; IR (KBr)  $\nu$  3051 (m), 1630 (m), 1493 (m), 1443 (s), 1367 (m), 1306 (s), 1253 (m), 1203 (m), 1159 (m); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (dd, *J* = 7.7, 1.3, 4H), 8.15 (dd, *J* = 6.4, 3.4, 4H), 7.73 (dd, *J* = 6.5, 3.4, 4H), 7.63 (dd, *J* = 7.8, 1.3, 4H), 7.59 (td, *J* = 7.0, 1.6, 4H), 7.50 (td, *J* = 7.6, 1.6, 4H), 7.00 (d, *J* = 7.2, 4H), 6.56 (d, *J* = 8.8, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.9, 147.4, 146.5, 141.5, 137.4, 132.6, 131.2, 130.1, 129.3, 129.1, 128.8, 127.8, 118.2; 112.1; MS (70 eV) 740 (M<sup>+</sup>, 43), 447 (11), 370 (18), 294 (80), 255 (100), 152 (13), 76 (12); TLC R<sub>f</sub> 0.31 (CHCl<sub>3</sub>/hexane, 1/3); HR-MS calcd for C<sub>52</sub>H<sub>32</sub>N<sub>6</sub>: 740.2683, found: 740.2685; Anal. Calcd for C<sub>52</sub>H<sub>32</sub>N<sub>6</sub>: C, 84.30, H, 4.35, N, 11.34. Found: C, 84.22, H, 4.39, N, 11.34.

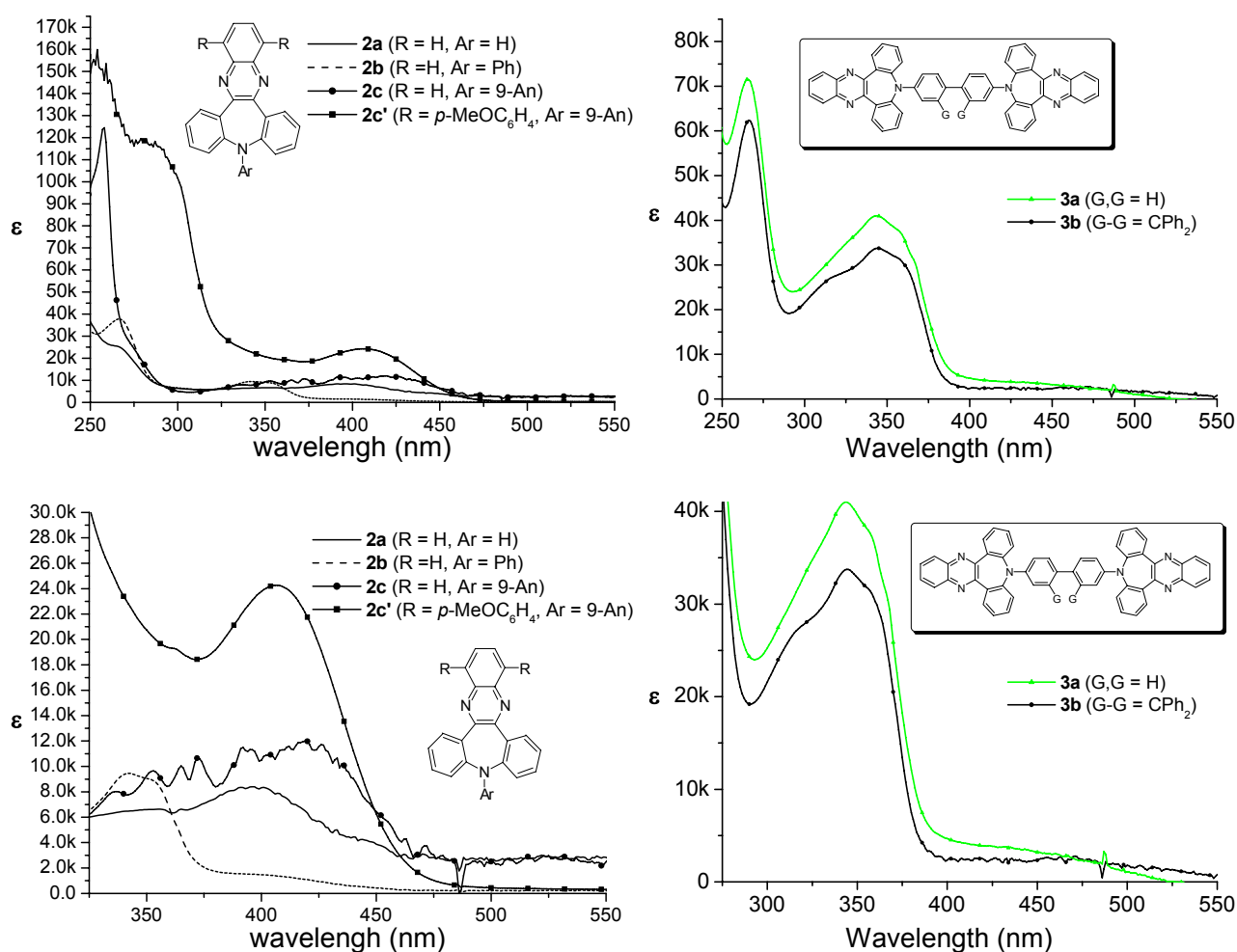


Data for **3b** (yellowish orange solid): m.p. 393 °C (CHCl<sub>3</sub>/hexane, by DSC); T<sub>d</sub> 470 °C; T<sub>g</sub> 294 °C; IR (KBr)  $\nu$  3461 (w), 3047 (w), 1599 (m), 1490 (m), 1470 (s), 1454 (s), 1349 (m), 1312 (m), 1281 (m), 761 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19-8.15 (m, 4H), 8.12-8.10 (m, 4H), 7.79-7.75 (m, 4H), 7.49-7.41 (m, 12H), 7.10 (d, *J* = 7.6, 4H), 7.00 (t, *J* = 7.6, 4H), 6.71 (bd, *J* = 7.2, 4H), 6.60 (d, *J* = 2.4, 2H), 6.53 (dd, *J* = 8.8, 2.4, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 150.5, 146.6, 145.7, 145.4, 141.0, 136.5, 132.0, 130.8, 130.4, 129.7, 129.0, 127.8, 127.5, 127.5, 127.0, 125.7, 118.7, 111.8, 110.3, 62.8; MS (20 eV) 904 (M<sup>+</sup>, 50), 611 (30), 452 (100), 294 (40); TLC R<sub>f</sub> 0.65 (CHCl<sub>3</sub>/hexane, 3/7); HR-MS calcd for C<sub>65</sub>H<sub>40</sub>N<sub>6</sub>: 904.3309, found 904.3304; Anal. Calcd for C<sub>65</sub>H<sub>40</sub>N<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub>: C, 80.07, H, 4.28, N, 8.49. Found: C, 80.08, H, 4.35, N, 8.29.

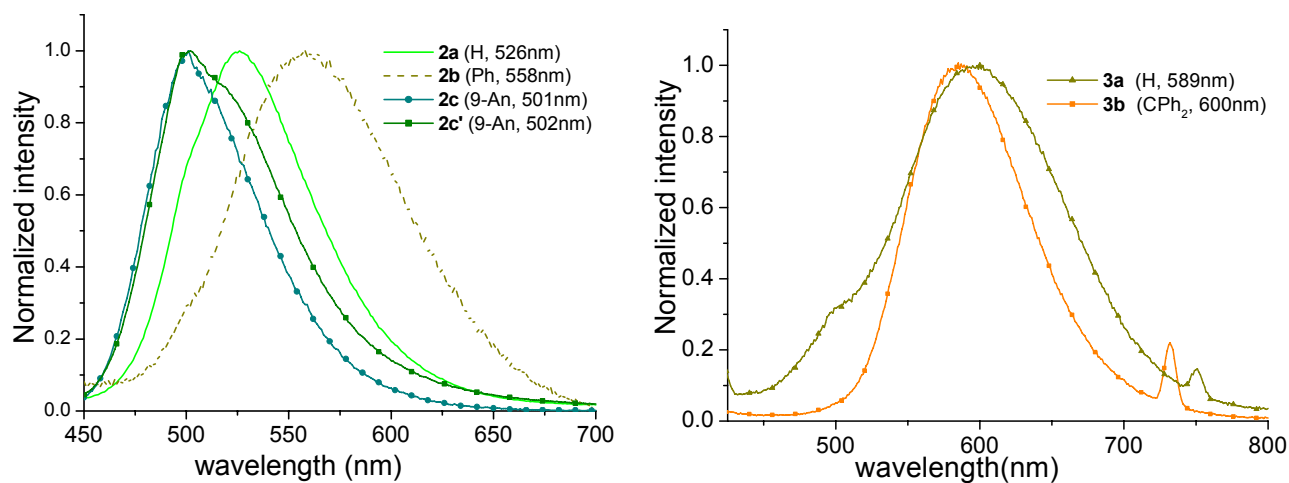
## Device fabrication

Pre-patterned ITO substrates with effective individual device area of 3.14 mm<sup>2</sup> were cleaned by sonication in a detergent solution for 3 min and then washed with large amount of doubly distilled water. Further sonication in deionized water and ethanol for 3 min respectively was done before blowing dry with a stream of nitrogen. The ITO substrates were then treated with oxygen plasma for

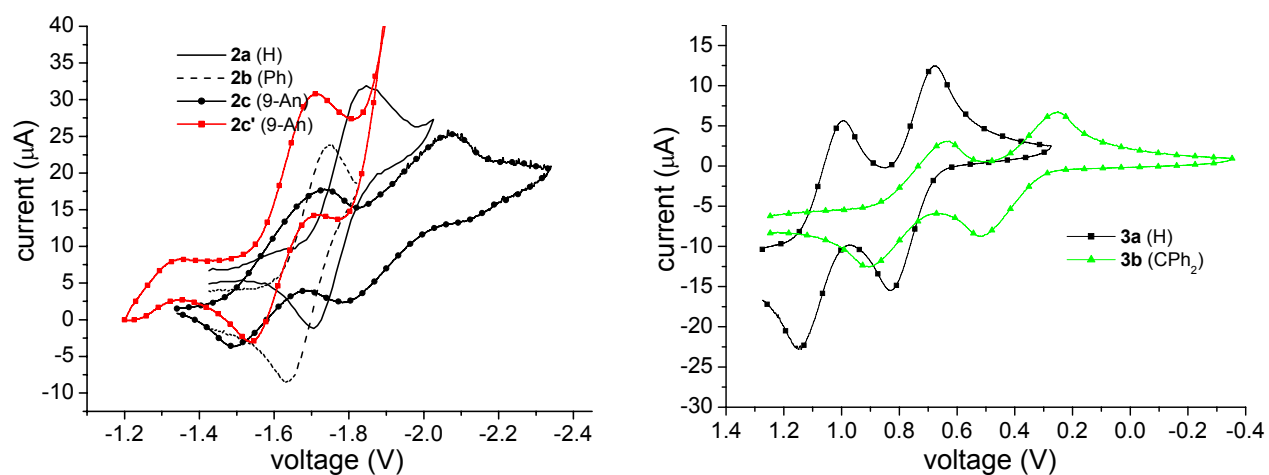
three minutes before loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of  $\sim 0.2$  nm/s under a pressure of  $\sim 2 \times 10^{-5}$  torr in an Ulvac Cryogenic deposition system. The first kind of typical devices were constructed with 40 nm of BPAPF as the hole-transporting layer (HTL), 40 nm of Q family derivative as the electron -transporting layer (ETL) as well as emission layer. The second kind of typical devices were comprised of 40 nm Q family derivative as the HTL and 40nm Alq<sub>3</sub> or TPBI as the ETL. An alloy of magnesium and silver (ca. 10:1, 50 nm) was deposited as the cathode, which was capped with 100 nm of silver. The current-voltage-luminance was measured in ambient with a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with 818ST silicon photodiode.



**Fig. S1.** UV overlays of Q-Ar **2a-c**, **2c'** and Q-spacer-Q **3a,b** series (all in CH<sub>2</sub>Cl<sub>2</sub>): (top) full spectra; (bottom) expanded plots.

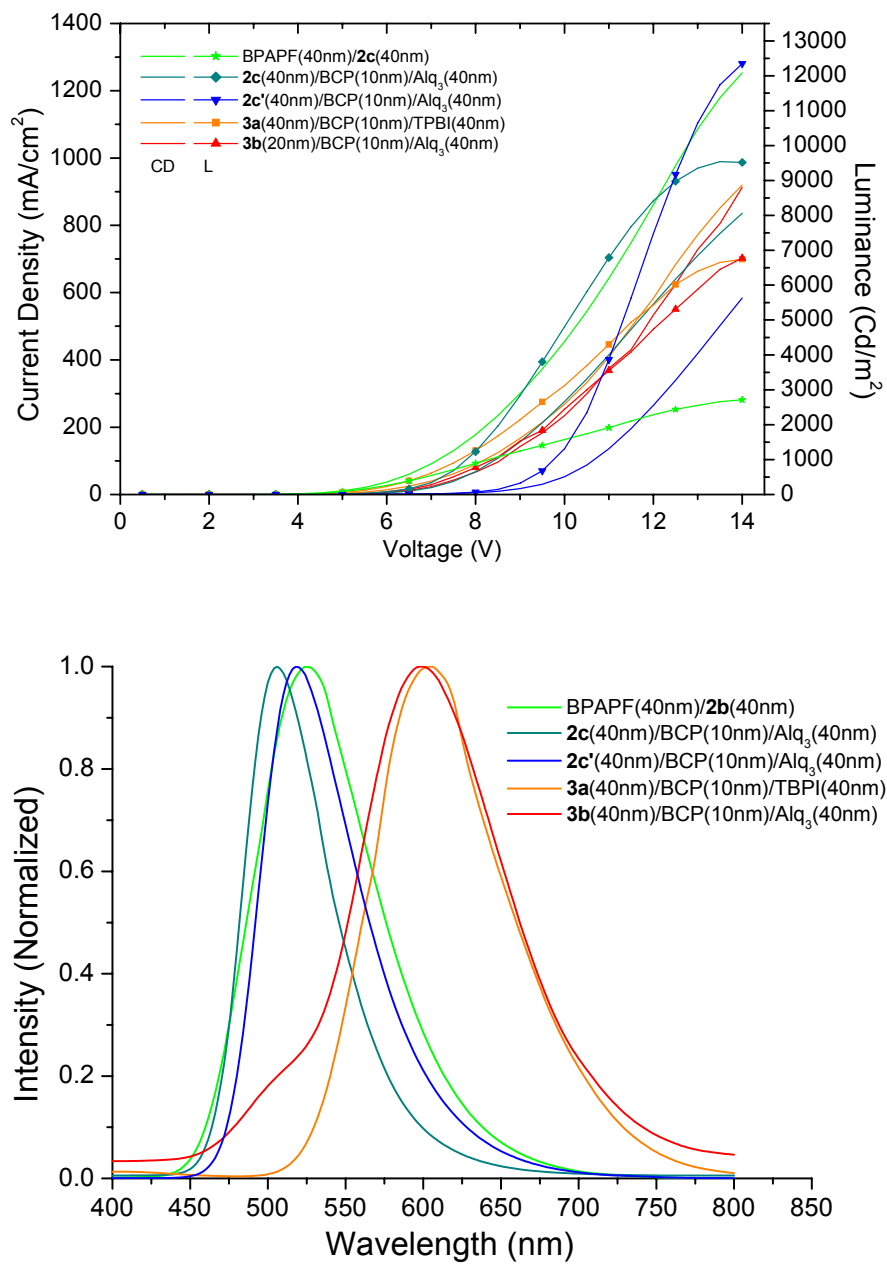


**Fig. S2.** Emission overlays of Q-Ar **2a-c**, **2c'** (CH<sub>2</sub>Cl<sub>2</sub>) and Q-spacer-Q **3a,b** (toluene) series

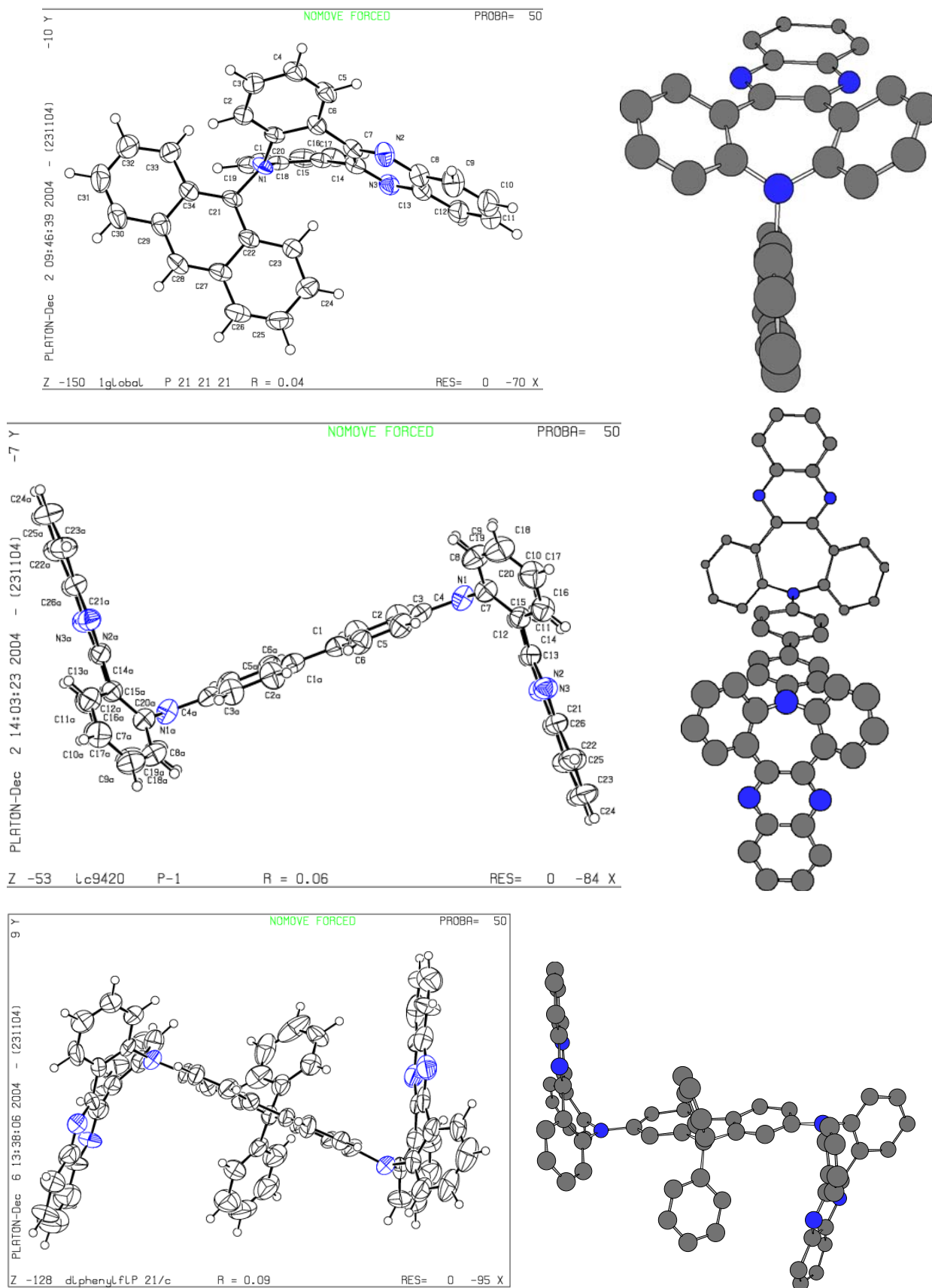


**Fig. S3.** Cyclic voltammogram overlays for **2a-c**, **2c'** (**2c** in THF) and **3a,b** in CHCl<sub>3</sub>

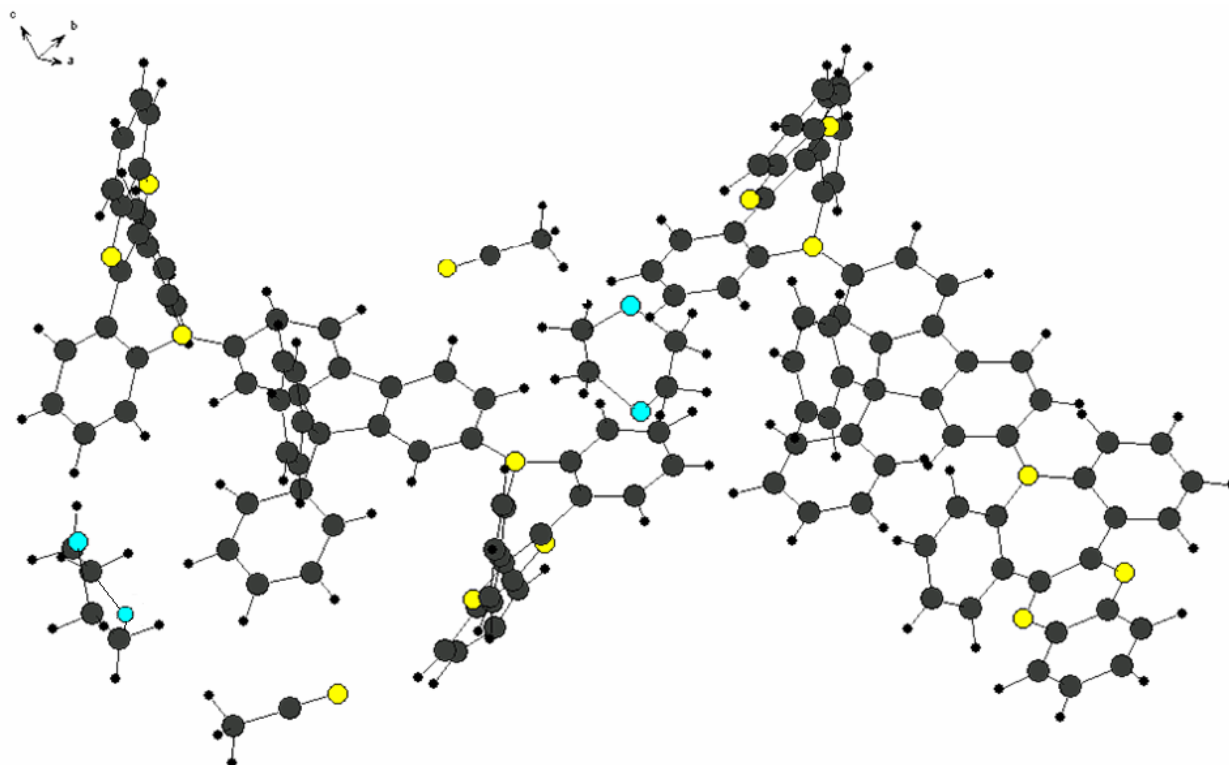




**Fig. S4** The current-voltage-luminance (*I-V-L*) characteristics and electroluminescence spectra of devices in Table 2.



**Fig. S5.** Chem 3D presentations and ORTEP drawings for the X-ray crystal structures of **2c**, **3a**, and **3b** (solvent molecules were removed for clarity for **3b**).



**Fig. S6.** Diamond presentation of for the X-ray crystal structure of **3b** with CH<sub>3</sub>CN and 1,4-dioxane (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) trapped in crystal lattice.

**Selected crystal data for 2c, 3a, and 3b:**

(a) Crystal data for **2c**: C<sub>34</sub>H<sub>21</sub>N<sub>3</sub>,  $M = 471.54$ , orthorhombic, space group P 21 21 21,  $a = 11.012(4)$ ,  $b = 14.223(6)$ ,  $c = 15.175(7)$  Å,  $U = 2376.7(17)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.318$  g cm<sup>-3</sup>,  $\mu = 0.078$  mm<sup>-1</sup>,  $F(000) = 984.0$ ,  $T = 293$  K, wavelength 0.70930 Å, crystal size 0.65 × 0.55 × 0.35 mm,  $\theta_{\max} 24.92^\circ$ , 25013 reflections measured, final R [ $I > 2\sigma(I)$ ] = 0.0389, CCDC 271946;

(b) Crystal for **3a**: C<sub>52</sub>H<sub>32</sub>N<sub>6</sub>,  $M = 740.84$ , triclinic, space group P -1,  $a = 8.654(4)$ ,  $b = 8.868(5)$ ,  $c = 14.316(9)$  Å,  $\alpha = 86.745(3)^\circ$ ,  $\beta = 82.838(3)^\circ$ ,  $\gamma = 61.349(3)^\circ$ ,  $U = 956.61(9)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.286$  g cm<sup>-3</sup>,  $\mu = 0.077$  mm<sup>-1</sup>,  $F(000) = 386.0$ ,  $T = 295$  K, wavelength 0.71073 Å, crystal size 0.40 × 0.20 × 0.15 mm,  $\theta_{\max} 25.03^\circ$ , 13258 reflections measured, final R [ $I > 2\sigma(I)$ ] = 0.0602, CCDC 271944; (c)

Crystal data for **3b**: C<sub>71</sub>H<sub>51</sub>N<sub>7</sub>O<sub>2</sub>,  $M = 1034.22$ , monoclinic, space group P 21/c,  $a = 10.655(2)$ ,  $b = 23.169(4)$ ,  $c = 24.861(4)$  Å,  $U = 6128.9(16)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.121$  g cm<sup>-3</sup>,  $\mu = 0.070$  mm<sup>-1</sup>,  $F(000) = 2168.0$ ,  $T = 293$  K, wavelength 0.70930 Å, crystal size 0.40 × 0.10 × 0.10 mm,  $\theta_{\max} 25.00^\circ$ , 32085 reflections measured, final R [ $I > 2\sigma(I)$ ] = 0.0920, CCDC 271945.

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