

**Supplementary Information for *Chem. Commun.***

**Self-assembled zinc(II) Schiff base polymers for applications in polymer light-emitting devices**

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Synthetic procedures and physical data of the polymers and monomers as well as fabrication procedures for the PLEDs are presented.

### **Procedure for device fabrication and characterizations**

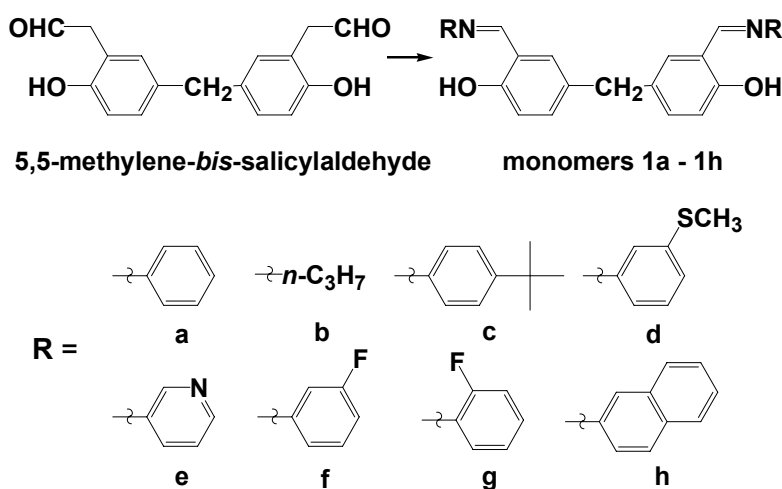
The electroluminescent (EL) devices were prepared on patterned indium-tin-oxide (ITO) glass with a sheet resistance of  $20 \Omega / \square$ . The device configurations were ITO / PEDOT : PSS (3,4-polyethylenedioxythiophene : polystyrenesulfonate, 30 nm) / **2c** (device **A**) or **2g** (device **B**, 30 – 50 nm) / BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 20 nm) / Alq<sub>3</sub> (tris(8-quinolinonato)aluminium, 20 nm) / LiF (0.5 nm) / Al (200 nm). PEDOT:PSS was spun onto the ITO glass using standard spin-coating method. This is followed by thermal vacuum deposition of BCP, Alq<sub>3</sub> and the LiF / Al electrode sequentially under a vacuum of  $1 \times 10^{-6}$  torr. The performance of the devices was examined using Photoresearch PR-650 in air without encapsulation. The current-voltage characteristics were studied using a Keithley 2400 sourcemeter.

### **Physical characterizations of the polymers**

Positive electron impact (EI) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a DRX270 or DRX300 Bruker FT-NMR spectrometers, with chemical shifts (in ppm) determined relative to tetramethylsilane. UV/Vis spectra were recorded on a PerkinElmer Lambda 900 UV/Vis spectrophotometer. Emission spectra were obtained on a SPEX Fluorolog-3 fluorescence spectrophotometer. Luminescence quantum yields were measured according to a previously reported method (L. O. Pålsson and A. P. Monkman, *Adv. Mater.* 2002, **14**, 757), with an estimated error of  $\pm 15$  %. The thickness of the films was measured using Veeco Dektak-3ST Surface Profilometer. The decomposition temperature was determined using a PerkinElmer TGA7 under nitrogen atmosphere with a heating rate of 20 °C / min. Atomic Force Microscopy (AFM) measurement

was performed with a Digital Instruments Nanoscope IIIA. The topographic image was obtained under ambient conditions using the tapping mode.

The 5,5-methylene-*bis*-salicylaldehyde for preparation of monomers was synthesized according to modified procedures based on that in literature (R. I. Kureshy, N. H. Khan, S. H. R. Abdi, S. T. Patel and R. V. Jasra, *Tetrahedron: Asymmetry*, 2001, **12**, 433).



**Scheme S1.** Syntheses of monomers **1a – 1h**.

### **Syntheses of monomers 1a – 1h**

The synthesis of **1a** is described as a typical example. Other monomers were prepared in a similar manner. A solution of aniline (0.002 mol) and 5,5-methylene-*bis*-salicylaldehyde (0.002 mol) in dichloromethane was refluxed for 24 hours. After cooling, the precipitate was washed with cold ethanol and dried under vacuum to give the product as a solid. Yield: 75 %. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ [ppm] = 13.12 (s, 2H), 8.56 (s, 2H), 7.41 (td, *J* = 6.59, 1.65 Hz, 4H), 7.29-7.24 (m, 8H), 7.18 (dd, *J* = 10.13, 5.13 Hz, 2H), 6.98 (d, *J* = 8.64 Hz, 2H), 3.93 (s, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ [ppm] = 162.54, 159.60, 148.49, 133.77, 132.09, 131.60, 129.36, 126.86, 121.12, 119.05, 117.39, 39.74. EIMS: *m/e* 406.1684; C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> requires *m/e* 406.1681.

**[1b]**: Yield: 70 %.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 13.51 (s, 2H), 8.26 (s, 2H), 7.11 (dd,  $J$  = 8.24, 2.43 Hz, 2H), 6.99 (d,  $J$  = 1.89 Hz, 2H), 6.87 (d,  $J$  = 8.64 Hz, 2H), 3.86 (s, 2H), 3.53 (td,  $J$  = 5.94, 1.08 Hz, 4H), 1.70 (sextet,  $J$  = 7.46 Hz, 4H), 0.96 (t,  $J$  = 7.29 Hz, 6H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 164.43, 159.69, 132.54, 131.04, 130.92, 118.56, 116.99, 61.21, 39.75, 23.99, 11.62. HREIMS:  $m/e$  338.1996;  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$  requires  $m/e$  338.1994.

**[1c]**: Yield: 80%.  $^1\text{H}$  NMR (270 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  [ppm] = 13.05 (s, 2H), 8.91 (s, 2H), 7.47-7.44 (m, 6H), 7.35-7.27 (m, 6H), 6.91 (d,  $J$  = 8.64 Hz, 2H), 3.91 (s, 2H), 1.29 (s, 18H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 161.78, 159.62, 150.21, 145.80, 133.59, 132.01, 131.59, 126.30, 120.79, 119.20, 117.37, 39.81, 34.62, 31.38. EIMS:  $m/e$  518.2925;  $\text{C}_{35}\text{H}_{38}\text{N}_2\text{O}_2$  requires  $m/e$  518.2933.

**[1d]**: Yield: 69%.  $^1\text{H}$  NMR (270 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  [ppm] = 12.75 (s, 2H), 8.92 (s, 2H), 7.49 (s, 2H), 7.39-7.26 (m, 6H), 7.15 (t,  $J$  = 7.36 Hz, 4H), 6.91 (d,  $J$  = 8.37 Hz, 2H), 3.90 (s, 2H), 2.51 (s, 6H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 162.96, 159.65, 149.12, 140.09, 133.97, 132.19, 131.66, 129.64, 124.77, 119.08, 118.98, 117.66, 117.46, 39.76, 15.73. EIMS:  $m/e$  498.1433;  $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$  requires  $m/e$  498.1436.

**[1e]**: Yield: 67%.  $^1\text{H}$  NMR (270 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  [ppm] = 12.37 (s, 2H), 8.95 (s, 2H), 8.59 (d,  $J$  = 2.70 Hz, 2H), 8.47 (dd,  $J$  = 4.59, 1.35 Hz, 2H), 7.85-7.80 (m, 2H), 7.52 (d,  $J$  = 1.89 Hz, 2H), 7.49-7.44 (m, 2H), 7.32 (dd,  $J$  = 8.64, 2.43 Hz, 2H), 6.93 (d,  $J$  = 8.10 Hz, 2H), 3.92 (s, 2H). HREIMS:  $m/e$  408.1596 ;  $\text{C}_{25}\text{H}_{20}\text{N}_4\text{O}_2$  requires  $m/e$  408.1586.

**[1f]**: Yield: 78%.  $^1\text{H}$  NMR (270 MHz, DMSO- $d_6$ ):  $\delta$  [ppm] = 12.53 (s, 2H), 8.92 (s, 2H), 7.51-7.43 (m, 4H), 7.33 (t,  $J$  = 1.98 Hz), 7.31-7.28 (m, 2H), 7.23 (dd,  $J$  = 7.02, 1.62 Hz, 2H), 7.13 (td,  $J$  = 8.51, 1.89 Hz, 2H), 6.93 (d,  $J$  = 8.37 Hz, 2H), 3.92 (s, 2H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 163.48, 159.63, 150.34, 134.20, 132.30, 131.70, 130.61, 130.49, 118.79, 117.51, 117.11, 117.07, 113.76, 113.47, 108.43, 108.13, 39.69. EIMS:  $m/e$  442.1492;  $\text{C}_{27}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_2$  requires  $m/e$  442.1493.

**[1g]**: Yield: 80%.  $^1\text{H}$  NMR (270 MHz, DMSO- $d_6$ ):  $\delta$  [ppm] = 12.81 (s, 2H), 9.00 (s, 2H), 7.59-7.52 (m, 4H), 7.35-7.27 (m, 8H), 6.94 (d,  $J$  = 8.4 Hz), 3.93 (s, 2H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 164.44, 159.79, 156.99, 154.43, 134.18, 132.23, 131.57, 127.84, 127.77, 124.62, 124.58, 121.35, 119.00, 117.56, 116.62, 116.42, 39.66. EIMS:  $m/e$  442.1492;  $\text{C}_{27}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_2$  requires  $m/e$  442.1493.

**[1h]**: Yield: 64%.  $^1\text{H}$  NMR (270 MHz, DMSO- $d_6$ ):  $\delta$  [ppm] = 12.89 (s, 2H), 8.99 (s, 2H), 8.15 (t,  $J$  = 3.51 Hz, 2H), 7.98 (t,  $J$  = 4.59 Hz, 2H), 7.87 (d,  $J$  = 8.37 Hz, 2H), 7.64 (m, 8H), 7.43-7.36 (m, 4H), 7.00 (d,  $J$  = 8.10 Hz, 2H), 3.97 (s, 2H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 163.48, 159.72, 146.21, 133.96, 134.01, 132.19, 131.74, 128.20, 127.87, 126.88, 126.63, 126.44, 125.87, 123.18, 119.36, 117.47, 113.92, 39.78. EIMS:  $m/e$  506.1990;  $\text{C}_{35}\text{H}_{26}\text{N}_2\text{O}_2$  requires  $m/e$  506.1994.

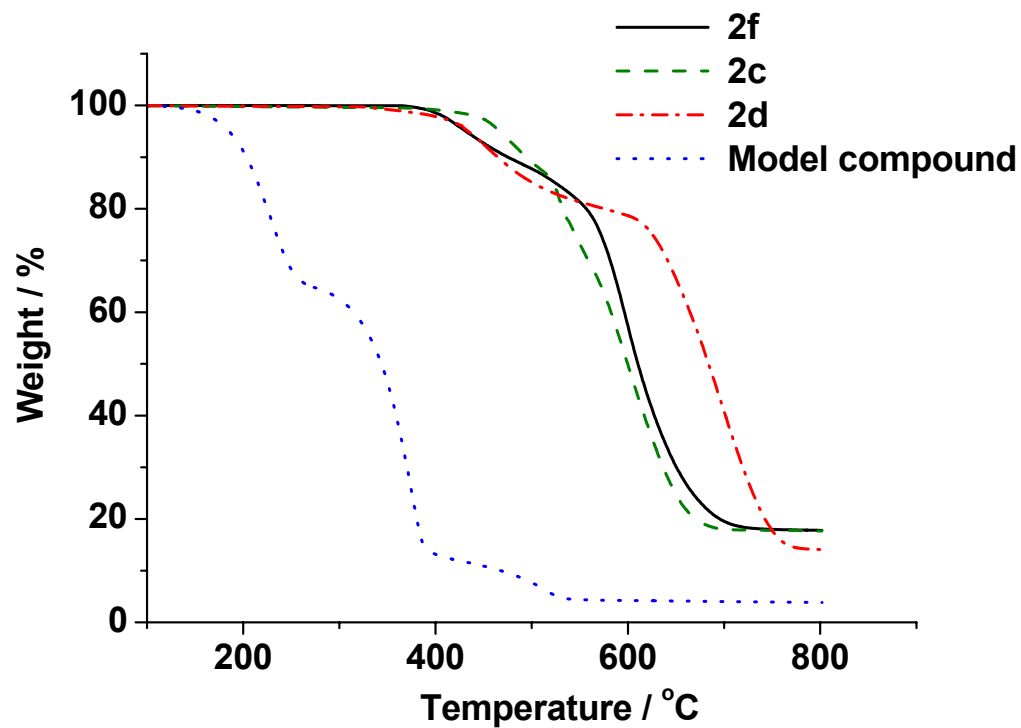
### **Syntheses of polymers 2a – 2h**

The synthesis of **2a** is described as a typical example. Other polymers were prepared in a similar manner. A solution of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.1 mmol) in DMF (5 mL) was added dropwise to another solution of salicylaldehyde monomer **1a** (0.1 mmol) in DMF (5 mL). The mixture was heated at 100 °C under nitrogen atmosphere for 24 hours. Upon cooling to room temperature, the resulting solution was poured into methanol. The precipitate obtained was purified by repeated precipitations using DMF and methanol. The polymer product was dried under vacuum at 80 °C for 24 hours. Yield: 79%.

**Table S1.** Properties of the Zn(II) Schiff base polymers.

	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2e</b>	<b>2f</b>	<b>2g</b>	<b>2h</b>
$\lambda_{\max, \text{abs}} \text{ (nm)}/$	315(34.6)	282 (20.7)	291 (24.3)	304 (27.2)	286 (57.7)	305 (54.3)	284 (34.6)	280 (44.6)
$a \text{ (} 10^4 \times \text{dm}^3$	351 (23.1)	325 (28.7)	311 (26.5)	319 (26.0)	352 (24.1)	322 (47.4)	309 (32.3)	358 (48.3)
$\text{g}^{-1} \text{cm}^{-1})^e$	408 (12.0)	378 (11.0)	413 (18.1)	351 (30.1)	425 (11.4)	345 (41.2)	324 (30.1)	
							352 (26.0)	
							427 (3.5)	
$\lambda_{\max, \text{PL sol}} \text{ (nm)}/\Phi$								
$\text{PLsol}^{b,d}$	508/0.06	458/0.09	501/0.15	534 <sup>f</sup>	518/0.02	516/0.34	514/0.20	562 <sup>f</sup>
$\lambda_{\max, \text{PL film}} \text{ (nm)}/\Phi$	538/0.13	509/0.04	536/0.13	/	534/0.07	538/0.15	538/0.19	/
$\text{PL film}^{c,d}$								
<b>Yield (%)</b>	79	82	75	69	73	85	83	71
<b>T<sub>d</sub> (°C)</b>	450	420	453	429	441	404	389	461
<b>M<sub>n</sub><sup>a</sup></b>	13580	19500	16660	16570	/	20440	19720	/

<sup>a</sup> Number-average molecular weight of polymers determined using GPC (Polystyrene as standard). <sup>b</sup> Concentration at  $1 \times 10^{-5} \text{ mol dm}^{-3}$  in DMF. <sup>c</sup> The thickness of films was  $\sim 30\text{--}50 \text{ nm}$ . <sup>d</sup> Excitation wavelength was at 350 nm. <sup>e</sup> Absorption coefficient ( $a_{\max}$ ) is expressed in  $10^4 \times \text{g}^{-1} \text{dm}^3 \text{cm}^{-1}$ . <sup>f</sup> PL quantum yield less than 0.01.



**Fig. S1.** Thermograms of the Zn Schiff base polymers 2c, 2d, 2f and the model compound.