

## Electron injection barrier reduction for organic light-emitting devices by quinacridone derivatives

Toan V. Pho,<sup>a</sup> Andres Garcia,<sup>a</sup> Peter Zalar,<sup>a</sup> Thuc-Quyen Nguyen<sup>a</sup> and Fred Wudl<sup>a\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, USA.

E-mail: [wudl@chem.ucsb.edu](mailto:wudl@chem.ucsb.edu)

**Electronic Supplementary Information (ESI) available:** Synthesis details, OLED fabrication and characterization, UV/vis and fluorescence spectra, and cyclic voltammograms.

**General.** Quinacridone (TCI America) was used as received. All other chemicals were purchased from Aldrich and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE500 spectrometer and referenced to tetramethylsilane (TMS). Electrochemical measurements were performed with a Princeton Applied Research Potentiostat/Gavanostat model263A. The electrochemical measurements were carried out in DMF solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, with a platinum disc, platinum wire, and silver wire as the working, counter, and pseudo-reference electrodes, respectively. Ferrocene was used as an internal standard. X-ray crystallographic analysis was carried out on a Bruker 3-axis platform diffractometer.

Solution spectroscopic measurements were performed using 10 mm quartz cuvettes on either water or methanol solutions of the quinacridone derivatives at concentrations of 1x10<sup>-3</sup>% w/v (g/ml) obtained by serial dilution of higher concentrated stock solutions (0.1% w/v).

Solution photoluminescence quantum yields measurements were carried using solutions of fluorescein in basic water (pH 12) as a reference. For solid state spectroscopic measurements 2% w/v 50:50 water:methanol (v:v) solution of the quinacridone derivatives were spun coat onto quartz substrates at 1,000 rpm for 60 seconds. Solid state photoluminescence quantum yield measurements were performed using an integrated sphere. Solution and solid state UV-vis absorption spectra were recorded on a Shimadzu UV-2401 PC diode array spectrometer while fluorescence was measured by using a PTI Quantum Master fluorometer.

Organic light-emitting diodes (OLEDs) were prepared on ITO substrates that were previous cleaned by successive rinsing and ultrasonic treatment in water, acetone, isopropyl alcohol and then drying with N<sub>2</sub> gas and several hours in an oven. The substrates were treated with UV/O<sub>3</sub> prior to polymer deposition. OLED devices with ITO/PEDOT:PSS/MEH-PPV/EIL/Al architecture were fabricated by first spin coating a ~ 100 nm hole injection film of PEDOT:PSS (Baytron P 4083, Bayer AG.) onto a clean ITO-coated glass followed by drying at 150 °C for ~ 1 hour before spin coating (1,500 rpm) 60 nm of a MEH-PPV emissive layer from a 0.5 % w/v toluene solution. The EIL was then spin coated from a 0.05% w/v 30:70 (v:v) water:methanol solution at 5,000 rpm. The films were then dried under a 10<sup>-6</sup> torr vacuum for 12 hours before thermal evaporation of Al cathode electrodes also at a pressure of 10<sup>-6</sup> torr. Reference devices ITO/PEDOT:PSS/MEH-PPV/Ba/Al without an electron injection barrier were also fabricated for comparison. All fabrication and testing were performed inside a N<sub>2</sub> atmosphere glove box.

### **Ph<sub>4</sub>P<sup>+</sup>QPSO<sub>3</sub><sup>-</sup> (2)**

NaH (2.8 g, 70 mmol, 60% dispersion in mineral oil) was added in portions to a suspension of quinacridone (4.0 g, 13 mmol) in DMF (500 mL) at 0 °C. The blue mixture was stirred for 30 minutes at room temperature. 1,3-propanesultone (6.3 g, 4.5 mL, 52 mmol) was added, and the reaction was stirred at 80 °C overnight. MeOH was added to quench the residual NaH, followed by the addition of Et<sub>2</sub>O to precipitate the red sodium propyl sulfonate. The solid was filtered and washed with ether. The solid was then dissolved in water, and Ph<sub>4</sub>PCl (12.0 g, 32 mmol) was added. The mixture was extracted with DCM (3x), and the combined organic extracts were dried over MgSO<sub>4</sub> and concentrated in *vacuo*. The red solid was then recrystallized from DCM/acetone to afford **2** (11.8 g, 10 mmol, 75%) as red crystals.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.72 (s, 2H), 8.43 (d, *J* = 7.9 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.84 (t, *J* = 7.8 Hz, 8H), 7.73-7.67 (m, 18H), 7.55 (m, 16H), 7.20 (t, *J* = 7.5 Hz, 2H), 4.77 (br s, 4H), 2.93 (t, *J* = 6.4 Hz, 4H), 2.34 (p, *J* = 7.5 Hz, 4H).

<sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 178.20, 143.01, 136.10, 135.20, 134.90, 131.02, 127.66, 126.72, 121.35, 120.95, 118.30, 117.58, 116.51, 113.70, 48.79, 46.05, 23.52.

MS (ESI) *m/z*: 277 (M-2Ph<sub>4</sub>P)<sup>2-</sup>.

### **Na<sup>+</sup>QPSO<sub>3</sub><sup>-</sup> (3)**

A solution of NaI (0.3 g, 2.0 mmol) in acetone (75 mL) was added to a suspension of **2** (1.0 g, 0.80 mmol) in acetone (300 mL). The mixture was stirred for 45 minutes at room temperature, resulting in a red precipitate that was filtered and washed with acetone. Yield 99%.

$^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  8.65 (s, 2H), 8.36 (d,  $J$  = 7.8 Hz, 2H), 8.01 (d,  $J$  = 8.8 Hz, 2H), 7.81 (t,  $J$  = 7.7 Hz, 2H), 7.28 (t,  $J$  = 7.4 Hz, 2H), 4.73 (br, 4H), 2.77 (t,  $J$  = 6.9 Hz, 4H), 2.20 (p,  $J$  = 7.6 Hz, 4H).

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  176.68, 141.95, 135.10, 134.85, 126.86, 125.58, 120.85, 120.19, 115.90, 113.10, 48.15, 44.77, 22.91.

MS (ESI)  $m/z$ : 277 (M-2Na) $^{2-}$ , 577 (M-Na) $^-$ .

#### ***N,N'*-di(6-bromohexyl)quinacridone (4)**

NaH (4.32 g, 108 mmol, 60% dispersion in mineral oil) was added in portions to a suspension of quinacridone (15.0 g, 48 mmol) in DMF (500 mL) at 0 °C. The blue mixture was then stirred for 30 minutes at room temperature. Et<sub>4</sub>NBr (1.0 g, 4.8 mmol) and 1,6-dibromohexane (176 g, 110 mL, 720 mmol) was added, and the reaction was stirred at 80 °C overnight. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl and extracted with DCM (3x). The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated in *vacuo*. Hexane was added to precipitate a red solid, which was filtered and washed with additional hexane. The solid was purified by silica gel chromatography (2% MeOH/DCM) to afford **4** (13.5 g, 21 mmol, 44%) as a red/orange solid.

$^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.65 (s, 2H), 8.51 (d,  $J$  = 7.9 Hz, 2H), 7.70 (t,  $J$  = 7.6 Hz, 2H), 7.44 (d,  $J$  = 8.6 Hz, 2H), 7.23 (t,  $J$  = 7.6 Hz, 2H), 4.46 (t,  $J$  = 7.0 Hz, 4H), 3.46 (t,  $J$  = 6.6 Hz, 4H), 2.00-1.94 (m, 8H), 1.64 (m, 8H).

$^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  178.11, 142.26, 135.72, 134.76, 128.21, 126.32, 121.21, 121.04, 114.67, 113.52, 46.26, 33.84, 32.85, 28.15, 27.13, 26.39.

MS (ESI)  $m/z$ : 659 (M+Na) $^+$ .

### **Ph<sub>4</sub>P<sup>+</sup>QHSO<sub>3</sub><sup>-</sup> (5)**

A solution of Na<sub>2</sub>SO<sub>3</sub> (1.18 g, 9.6 mmol) in H<sub>2</sub>O (20 mL) was added to a mixture of **3** (1.0 g, 1.6 mmol) in EtOH (20 mL). The mixture was refluxed for two days. Additional Na<sub>2</sub>SO<sub>3</sub> (0.59 g, 4.8 mmol) and H<sub>2</sub>O (20 mL) were added, and the mixture was refluxed for another two days. Ph<sub>4</sub>PCl (2.40 g, 6.4 mmol) and H<sub>2</sub>O (50 mL) were added, and the mixture was extracted with DCM (3x). The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated in *vacuo*. The residue was recrystallized from hot acetone to give **5** (1.5 g, 1.1 mmol, 73%) as red crystals.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.65 (s, 2H), 8.42 (d, *J* = 7.8 Hz, 2H), 7.89 (t, *J* = 7.4 Hz, 8H), 7.73 (m, 18H), 7.61 (t, *J* = 8.1 Hz, 16H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 4.45 (t, *J* = 7.4 Hz, 4H), 2.71 (t, *J* = 7.7 Hz, 4H), 1.96 (br, 4H), 1.81 (p, *J* = 6.7 Hz, 4H), 1.61 (p, *J* = 6.7 Hz, 4H), 1.55 (p, *J* = 6.7 Hz, 4H).

<sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 178.17, 142.86, 136.31, 135.17, 135.03, 131.19, 128.20, 126.84, 121.62, 121.15, 118.48, 117.77, 115.53, 113.82, 52.31, 46.89, 29.35, 27.50, 27.37, 26.07.

MS (ESI) *m/z*: 319 (M-2Ph<sub>4</sub>P)<sup>2-</sup>, 977 (M-Ph<sub>4</sub>P)<sup>-</sup>.

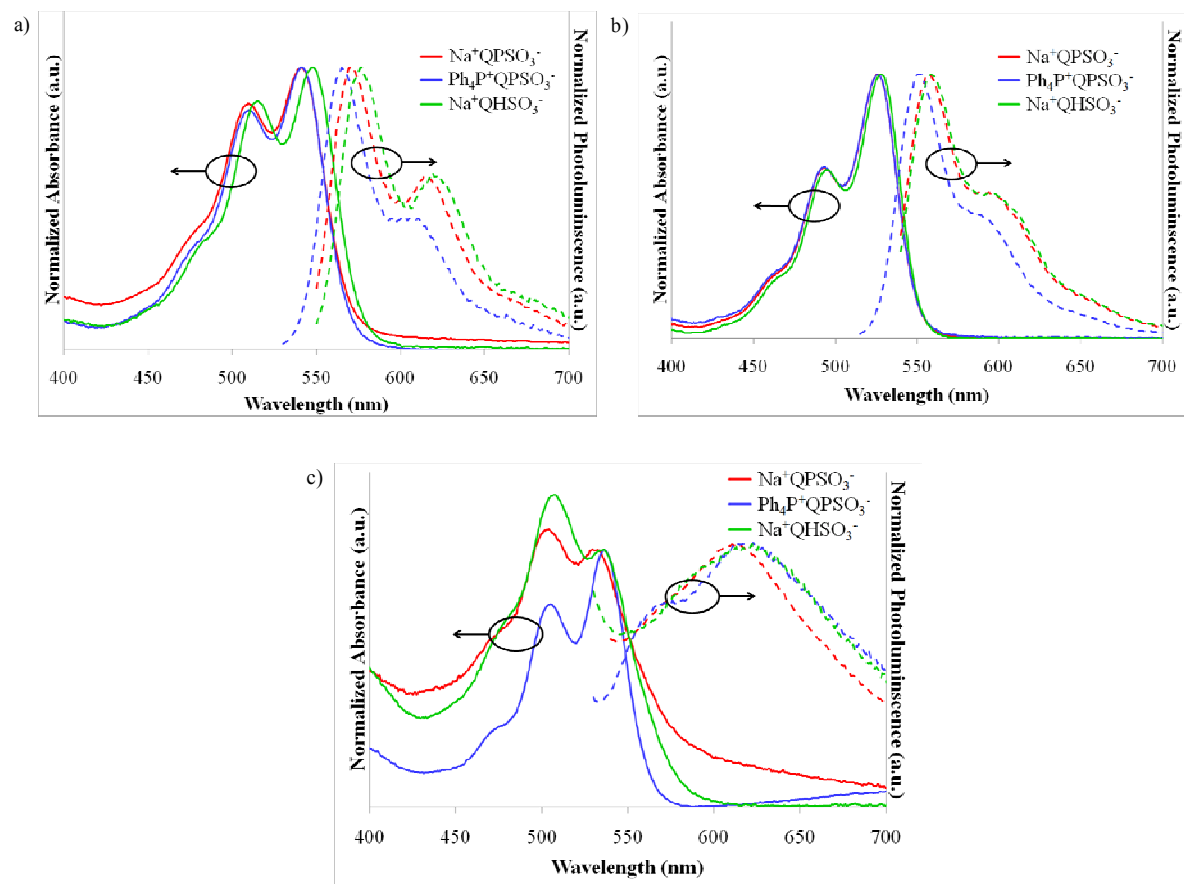
### **Na<sup>+</sup>QHSO<sub>3</sub><sup>-</sup> (6)**

**6** was prepared according to the above procedure for **3**. Yield 99%.

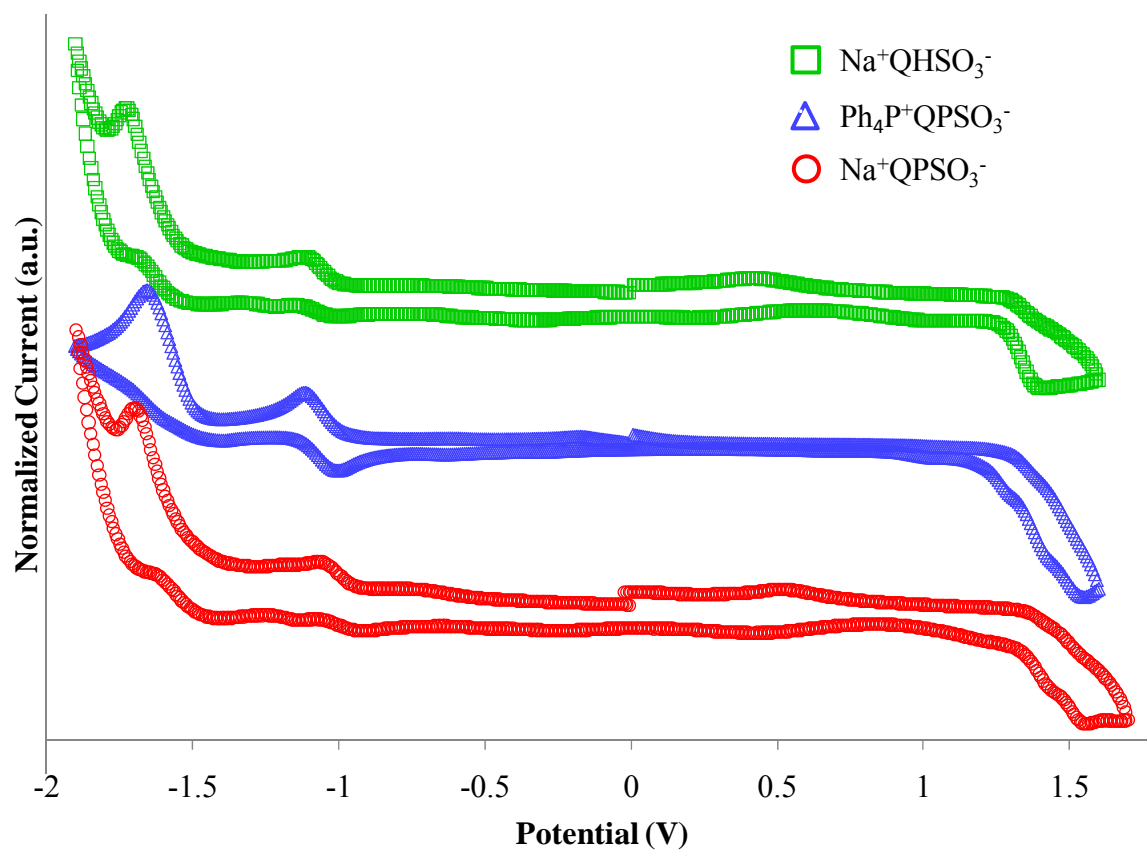
<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 8.65 (s, 2H), 8.38 (d, *J* = 7.8 Hz, 2H), 7.87-7.85 (m, 4H), 7.32 (t, *J* = 7.0 Hz, 2H), 4.54 (t, *J* = 6.8 Hz, 4H), 2.44 (t, *J* = 7.1 Hz, 4H), 1.88 (br, 4H), 1.63 (p, *J* = 7.0 Hz, 4H), 1.56 (p, *J* = 6.2 Hz, 4H), 1.48 (p, *J* = 6.6 Hz, 4H).

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ 176.68, 141.95, 135.20, 135.03, 127.04, 125.70, 120.94, 120.32, 115.68, 113.11, 51.43, 45.56, 28.26, 26.56, 26.16, 25.27.

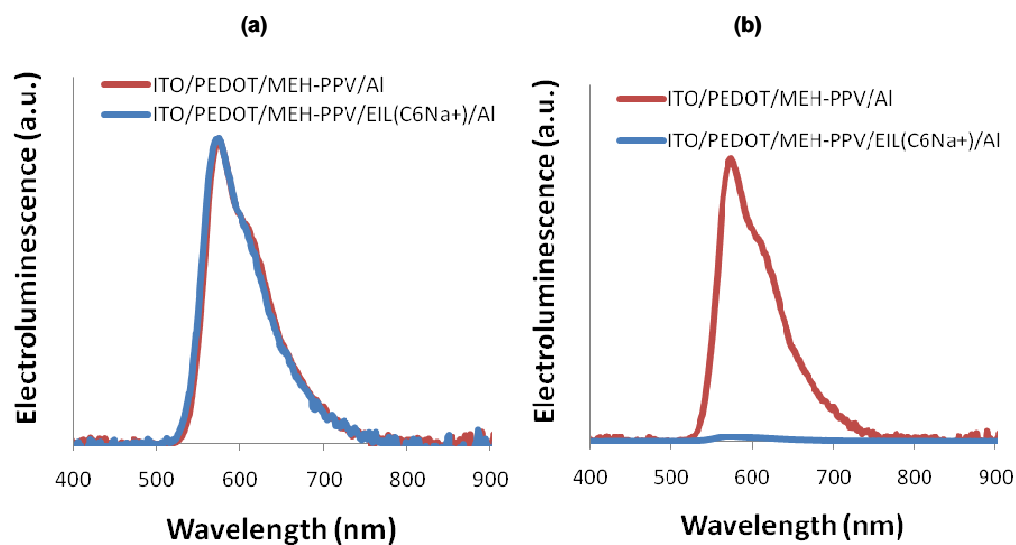
MS (ESI) *m/z*: 319 (M-2Na)<sup>2-</sup>, 661 (M-Na)<sup>-</sup>.



**Figure S1.** UV/vis and photoluminescence spectra of quinacridone derivatives in a)  $\text{H}_2\text{O}$  b) MeOH c) the solid state.



**Figure S2.** Cyclic voltammograms of quinacridone salts vs.  $\text{Ag}/\text{Ag}^+$



**Figure S3.** a) Normalized electroluminescence (EL) spectra of the devices with and without the EIL. b) EL spectrum (red) of ITO/PEDOT:PSS/MEH-PPV/Al without correction lenses and EL spectrum (blue) of ITO/PEDOT:PSS/MEH-PPV/EIL/Al with correction lenses.