Supporting Information for

Cu(0)-RDRP as an Efficient and Low-Cost Synthetic Route to Blue-Emissive Polymers for OLEDs

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Experimental Details

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images were obtained using an Asylum Instruments Cypher S AFM system in tapping mode at scan rates of 0.44 Hz. Samples were prepared by spincoating solutions of polymer or small molecule blends onto freshly cleaved mica at 2000 rpm for 30 s at concentrations of 10 mg mL⁻¹. For best results, 2:1 chloroform/chlorobenzene was used as the solvent for solutions. Samples were placed in a vacuum oven (60 °C) for at least 2 h before images were obtained using Mikromasch HQ:NSC14/No Al probes, with typical resonance frequency f = 160 kHz and spring constant k = 5 N/m.

Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5 -2 mg mL^{-1} using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array and right-angle and low angle light scattering detectors. Calibration of interdetector distances was performed using a polystyrene standard from Malvern Inc. Refractive index increments (dn/dc) were determined using 100% mass recovery methods from Malvern

OMNISEC software version 10.2 with each polymer sample being run at least five times to ensure reproducibility of the calculated refractive index increment.

Thermal Analysis

Thermal degradation studies were performed using a NETZSCH TG 209F1 Libra instrument. Samples were placed in an Al₂O₃ crucible and heated at a rate of 10 °C min⁻¹ from 25 to 800 °C under a flow of nitrogen (50 mL min⁻¹). Glass transition temperatures were determined using differential scanning calorimetry (DSC) on a NETZSCH DSC 214 Polyma instrument. The polymer samples were placed in an aluminum pan and heated from 25 to 200 °C at 10 °C min⁻¹ under a flow of nitrogen for 3 heating/cooling cycles.

Electrochemical Methods

Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in 1,2-difluorobenzene);¹ counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene. Experiments were run at a scan rate of 50 mV s⁻¹ in dry degassed electrolyte solution with ~4 mg mL⁻¹ of analyte. The HOMO level was found by referencing the oxidation peak to ferrocene and using the known HOMO of ferrocene (-4.80 eV) to calculate HOMO of **P1** and of the **tBuODA** monomer in **P4**. The LUMO level was calculated by subtracting the optical energy bandgap (Eg) from the HOMO value determined above. Eg was determined from the low-energy UV-absorption band edge.

Density Functional Theory

Calculations were performed using the Gaussian 09 software package.² Ground state geometries and energies were calculated at the B3LYP/6-31+g(d) level of theory. To simulate electronic properties of these polymeric materials, analogous versions of each monomer were calculated in which the vinyl end group of the acrylate functionality was replaced with a *sec*-butyl group to more closely mimic the structure of the corresponding polymer chain. If this approximation is not made, the LUMO lies on the acrylate moiety in all cases.

Ultraviolet Photoelectron Spectroscopy (UPS)

ITO-coated glass substrates were cleaned in an ultrasonic bath using soap, deionized water, acetone, and methanol, and then were treated with ultraviolet ozone for 15 min. Then, the polymer emissive layer in chlorobenzene (5-30 mg mL–1) was spin-cast on ITO at 3000 r.p.m. for 45 s, and annealed at 100 °C for 10 min in a nitrogen-filled glovebox. The sample was then transferred *in situ* to a PHI 5500 photoemission analysis chamber for UPS measurement (He I α , 21.22 eV) under a base pressure of approximately 10⁻⁹ torr.

General Procedure for Free Radical Polymerization

Polymers were prepared by free radical polymerization to compare to those generated by Cu(0)-RDRP following a procedure adapted from Fosong Wang and coworkers.³ To a 4 mL tefloncapped vial under a nitrogen atmosphere was added host monomer (135 mg, 0.41 mmol, 47.5 eq.), **tBuODA** dopant monomer (15 mg, 0.02 mmol, 2.6 eq.), 50 μ L of a solution of azobisisobutyronitrile (AIBN) in THF (1.25 mg, 7.64 μ mol, 1 eq. C_{AIBN} = 25 mg ml⁻¹), and 450 μ L of THF. Prior to polymerization, THF was prepared by distillation from sodium and AIBN was prepared by recrystallization from uninhibited diethyl ether. The polymerization was allowed to run for 18 hours (approx. 95% conversion) followed by precipitation into water to quench the polymerization. Preparatory SEC purification in THF to remove residual monomer and other small molecule impurities was then performed on Bio-Rad Bio Beads SX-1 resin.

Additional Figures:



Figure S1: Normalized absorbance (dashed) and photoluminescence (PL, solid) for host monomer (a) and **tBuODA** (b) at 1 x 10⁻⁵ M in toluene.



Figure S2: Normalized absorbance (dashed) and photoluminescence (PL, solid) for **P1** (a), **P2** (b), **P3** (c), **P4** (d) at 0.01 mg mL⁻¹ in toluene.



Figure S3: Normalized photoluminescence of films of P1 (a), P2 (b), P3 (c), P4 (d) spin-cast from 2:1 chlorobenzene/chloroform on a 1 in. x 1 in. glass slide.



Figure S4: Size exclusion chromatography data for P1-P4, refractive index trace shown.



Figure S5: Thermogravimetric analysis of polymer **P1** (**a**, 4.81 mg), **P2** (**b**, 2.58 mg), **P3** (**c**, 1.91 mg), **P4** (**d**, 4.01 mg), run at a rate of 10 °C min-1 under a 50 mL min⁻¹ flow of nitrogen from 25 to 800 °C.



Figure S6: DSC traces of polymers **P1** (a), **P2** (b), **P3** (c), and **P4** (d), run at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen. Three consecutive heating and cooling cycles were performed, the second is shown above.



Figure S7: ¹H NMR spectrum of tBuODA in CDCl₃.



Figure S8: ¹H NMR spectrum of P2 (used for device testing) in CDCl₃.



Figure S9: Calculated HOMO and LUMO diagrams for the *sec*-butyl analogue of 1.



Figure S10: EQE vs. current density for four devices prepared from 5, 10, 20, and 30 mg mL⁻¹ solutions.



Figure S11: Fluorescence decay of polymers P1 (a), P2 (b), P3 (c) and P4 (d) at 1×10^{-5} M in toluene sparged with nitrogen for 5 minutes prior to measurement. Green trace = decay, grey trace = scattering standard, red trace = fit line generated using Horiba DAS6 software.



Figure S12: Cyclic voltammograms of polymers **P1** and **P4** relative to FeCp₂^{0/+}, recorded at a rate of 50 mV s⁻¹ in difluorobenzene containing 4 mg mL⁻¹ of analyte and 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.¹



Figure S13: UPS data of polymer films measured with He I α (21.22 eV) under a base pressure below 10^{-9} torr.



Figure S14: Photo of aggregation induced emission samples including 100% THF. Color change from 100% THF to 90% THF is due to solvatochromic shift due to the polarity change upon water addition.



Figure S15: Enlarged photo of working polymer-based device.



Figure S16: ¹H NMR spectra of a 10% **tBuODA** doped polymerization prior to SEC polymerization (red trace) showing less than 5% residual monomer and post SEC polymerization (black trace) showing complete removal of residual monomer and other small molecule impurities.



Figure S17: SEC traces of a polymer prepared by Cu(0)-RDRP, doped with 10% **tBuODA** prior to preparatory SEC purification (**a**) and post purification and precipitation (**b**).



Figure S18: SEC traces of a polymer prepared by free radical polymerization (**a**) doped with 10% w/w **tBuODA** prior to SEC purification and (**b**) post purification and precipitation demonstrating the significantly broadened dispersity and reduced degree of molecular weight control for uncontrolled polymerizations.



Figure S19: Cyclic voltammetry of P2 (a) and a 10% tBuODA doped polymer generated by uncontrolled radical polymerization (b) relative to $FeCp_2^{0/+}$, recorded at a rate of 100 mV s⁻¹ in difluorobenzene containing 4 mg mL⁻¹ of analyte and 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.¹

Table S1: Targeted doping concentrations of **tBuODA** monomer in **P1** to **P4** compared to doping concentration observed by ¹H NMR

Entry	Target doping conc. ^a	Doping conc. ^{b,c}	Doping conc. ^{a,c}
P1	0	0	0
P2	10%	5.6%	10.6%
P3	17.5%	9.1%	16.8%
P4	25%	14.0%	24.8%

a: by mass percent, b: by mole percent, c: measured via ¹H NMR

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