Supporting Information for

Polymerization of Acrylates Based on n-Type Organic Semiconductors using Cu(0)-RDRP

By Christopher M. Tonge, Ethan R. Sauvé, Nathan R. Paisley, Jordan E. Heyes and Zachary M. Hudson*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, V6T 1Z1.

Tel: +1-604-822-3266; *Fax:* +1-604-822-2847; *e-mail: zhudson@chem.ubc.ca.*

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Experimental Details

Synthetic Procedures

General NaBH₄ Reduction (A):

Modified from a previously reported procedure.¹ Pure aldehyde-functionalized compound (1.0 mmol) was added to a round-bottom flask and dissolved in CH_2Cl_2 . Once all starting material was dissolved, one part EtOH was added for every three parts CH_2Cl_2 . Solid NaBH₄ (1.2 mmol) was then added to the solution and the reaction was monitored by TLC. When no starting material remained by TLC (approximately 16 h) the reaction was quenched by addition of water followed by extraction using CH_2Cl_2 (3 x 50 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. The crude residue was then purified on a short silica column.

General Acrylation (B):²

The desired alcohol-functionalized compound and a magnetic stir bar were added to a flamedried round-bottom flask (1.0 mmol) which was evacuated and backfilled three times with N₂. CH₂Cl₂ (10 mL) and triethylamine (1.3 mmol) were then added to the round bottom flask and stirred until all solid had dissolved. The reaction flask was cooled to 0 °C in an ice bath for 30 minutes, then acryloyl chloride (1.2 mmol) was added to the reaction mixture dropwise over 10 minutes. The reaction was then protected from light using foil and allowed to stir in the ice bath for 24 h. The reaction was quenched by addition of water and extracted with CH₂Cl₂ (3 x 50 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo* without added heat. The crude residue was purified on a short silica column, taking care to elute the product as quickly as possible to avoid decomposition on silica.



2-(4-bromophenyl)-4,6-di-*p*-tolyl-1,3,5-triazine (1a)

Prepared according to modified literature procedure.³ All steps were performed under a nitrogen atmosphere in flame-dried glassware. First, p-bromobenzoyl chloride (5.5 g, 25 mmol, 1 eq.) was combined with p-tolunitrile (5.9 g, 50 mmol, 2 eq.) and a magnetic stir bar in a three neck 100 mL round-bottom flask equipped with a reflux condenser. The flask was evacuated and backfilled three times with nitrogen followed by the addition of freshly distilled CH₂Cl₂ (50 mL). Once completely dissolved, the reaction mixture was allowed to cool for 30 minutes in an ice bath. SbCl₅ (7.5 g, 3.2 mL, 25 mmol, 1 eq.) was weighed into an addition funnel in a nitrogen atmosphere glovebox. CAUTION: SbCl₅ is highly corrosive and should be handled with extreme care. Once measured, the SbCl₅ was removed from the glovebox and added dropwise to the reaction mixture at 0 °C, then the reaction was removed from the ice bath and stirred for one hour at 20 °C. Following this, the reaction was heated to reflux for 8 hours. After this reflux was complete, the reaction was filtered through a glass microfiber filter under a nitrogen atmosphere and washed with dry, degassed CH₂Cl₂. The resulting yellow solid was removed from the filter and dried in vacuo. Once dry, this intermediate was cooled to 0 °C in an ice bath and converted to the final product by slow addition of 150 mL of 28% NH₃ in water under air while stirring. Once addition is complete, the mixture was stirred for 1 hour. The resulting aqueous slurry was then vacuum filtered, collected, and purified by Soxhlet extraction for 48 hours using chloroform. Once complete, the product was collected by precipitation from the concentrated chloroform solution by the addition of methanol followed by filtration. Yield 9.05 g, 87%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.79 (dd, *J* = 8.0, 1.7 Hz, 2H), 8.73 – 8.67 (m, 4H), 7.66 – 7.53 (m, 2H), 7.46 – 7.35 (m, 4H), 2.51 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.56, 170.56, 143.16, 135.42, 133.42, 131.81, 130.42, 129.39, 128.94, 127.22, 21.77 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{23}H_{18}N_3^{79}Br]^{+\bullet}$, 415.06841; found, 415.06859; difference: – 0.4 ppm.



4'-(4,6-di-*p*-tolyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (1b)

Prepared according to modified literature procedure, using **1a** and 4-formylphenyl boronic acid.⁴ To a 500 mL three neck round bottom flask was added **1a** (1.0 g, 2.4 mmol, 1 eq.), 4-formylphenyl boronic acid (0.432 g, 2.9 mmol, 1.2 eq.), and Pd(PPh₃)₄ (0.140 g, 0.12 mmol, 0.05 eq.). The flask was then evacuated and backfilled with N₂ three times. In a separate 250 mL round bottom flask, 120 mL of toluene and 50 mL of EtOH were mixed and sparged with nitrogen gas for 30 minutes. Similarly, 70 mL of 2N Na₂CO₃ in water was sparged in a third 100 mL round bottom flask. First, the organics were cannula transferred to the 500 mL three neck flask, followed by the aqueous base solution. The reaction was then heated to reflux overnight. The reaction was then quenched by opening to atmosphere, then extracted to EtOAc. The organic layer was washed three times with 150 mL portions of distilled water, dried on MgSO₄, and concentrated *in vacuo*. The crude residue was purified on silica using hexane and CH₂Cl₂. Yield 0.90 g, 85%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.08 (s, 1H), 8.81 (d, J = 8.4 Hz, 2H), 8.65 (d, J = 8.2 Hz, 4H), 7.98 (d, J = 8.2 Hz, 2H), 7.81 (dd, J = 16.4, 8.3 Hz, 4H), 7.36 (d, J = 8.0 Hz, 4H), 2.48 (s, 6H) ppm.

¹³C (101 MHz, Chloroform-*d*): δ 191.86, 171.52, 170.81, 146.32, 143.22, 143.11, 136.53, 135.60, 133.54, 130.33, 129.54, 129.40, 128.96, 127.82, 127.47, 21.78 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{30}H_{23}N_3O]^{+\bullet}$, 441.18344; found, 441.18411; difference: 1.5 ppm.



(4'-(4,6-di-*p*-tolyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-4-yl)methanol (1c)

Prepared according to general reaction A using **1b** as starting material. Purified on silica using 2% MeOH in CH₂Cl₂. Yield 99%.

¹**H** NMR (400 MHz, Chloroform-*d*): δ 8.85 (d, *J* = 8.4 Hz, 2H), 8.70 (d, *J* = 8.2 Hz, 4H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.35 (m, 5H), 4.81 (d, *J* = 6.0 Hz, 2H), 2.51 (s, 6H), 1.72 (t, *J* = 6.0 Hz, 1H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.52, 171.15, 144.57, 143.02, 140.63, 139.86, 135.47, 133.68, 129.45, 129.40, 128.96, 127.54, 127.47, 127.20, 65.10, 21.77 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{30}H_{25}N_3O]^{+\bullet}$, 443.19976; found, 443.19969; difference: 0.2 ppm.



(4'-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-4-yl)methyl acrylate (1)

Prepared as general reaction B using 1c as starting material. Purified on silica using CH_2Cl_2 . Yield 93%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.86 (d, *J* = 8.4 Hz, 2H), 8.75 – 8.67 (m, 4H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 4H), 6.51 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.23 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.91 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.31 (s, 2H), 2.51 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.52, 171.12, 166.06, 144.38, 143.03, 140.51, 135.61, 133.67, 131.27, 129.47, 129.40, 128.97, 128.86, 128.30, 127.49, 127.26, 66.06, 21.78 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{33}H_{27}N_3O_2]^{+\bullet}$, 497.21033; found, 497.20999; difference: 0.7 ppm.



(4-(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (2c)

Prepared according to a literature procedure.⁵ Purified on silica using 4:1 CH₂Cl₂:EtOAc. Yield 89%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.16 – 8.04 (m, 4H), 7.57 (dd, *J* = 8.2, 6.0 Hz, 4H), 4.82 (s, 2H), 1.40 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 162.13, 155.39, 145.09, 127.24, 127.02, 126.77, 126.07, 122.96, 121.05, 64.53, 35.11, 31.14 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{19}H_{20}N_2O_2]^{+\bullet}$, 308.15248; found, 308.15203; difference: 1.5 ppm.



4-(5-(4-(*tert*-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate (2)

Prepared as general reaction B using 2c as starting material. Purified on silica using CH_2Cl_2 with 2% ethyl acetate. Yield 73%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.21 – 8.12 (m, 2H), 8.13 – 8.06 (m, 2H), 7.58 (dd, J = 8.2, 5.3 Hz, 4H), 6.52 (dd, J = 17.3, 1.4 Hz, 1H), 6.24 (dd, J = 17.3, 10.4 Hz, 1H), 5.93 (dd, J = 10.5, 1.4 Hz, 1H), 5.31 (s, 2H), 1.41 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 165.84, 164.01 155.43, 139.60, 131.56, 128.54, 128.04, 127.13, 126.81, 126.09, 123.88, 121.06, 65.57, 35.13, 31.14 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{22}H_{22}N_2O_3]^{+\bullet}$, 362.16304; found, 362.16257; difference: 0.5 ppm.



4-(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)benzaldehyde (3a)

Prepared according to modified literature procedure.⁶ A Teflon-capped, 20 mL vial equipped with a magnetic stir bar was charged with **8** (180 mg, 0.927 mmol, 1 eq.), K_3PO_4 (984 mg, 4.63 mmol, 5 eq.), and 15 mL DMF. The reaction was sealed and heated to 150 °C with stirring. 4-fluorobenzaldehyde (0.2 mL, 1.85 mmol, 2 eq.) was then added and the reaction was stirred overnight. Ethyl acetate (20 mL) was added and the organic layer was washed with water (4 x 50 mL), dried over MgSO₄, and concentrated *in vacuo*. The crude residue was purified on a silica column (1:3 ethyl acetate/hexane) to afford **9** as a white solid. Yield 201 mg (72%).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.10 (s, 1H), 8.08 – 7.99 (m, 2H), 7.93 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.60 – 7.46 (m, 4H), 7.45 – 7.29 (m, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 190.83, 152.28, 143.21, 142.13, 136.44, 135.72, 131.14, 129.82, 129.53, 128.55, 128.18, 127.83, 123.83, 123.52, 120.22, 110.17 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{20}H_{14}N_2O]^{+\bullet}$, 298.11061; found, 298.10998; difference: 2.1 ppm.



(4-(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)phenyl)methanol (3b)

Prepared according to general reaction A using **3a** as starting material. Purified on silica using EtOAc. Yield 96%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.91 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.56 – 7.44 (m, 2H), 7.41 – 7.24 (m, 8H), 4.84 (d, *J* = 5.5 Hz, 2H), 2.20 (t, *J* = 5.8 Hz, 1H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 152.39, 142.78, 141.63, 137.15, 135.98, 129.80, 129.53, 129.49, 128.36, 128.15, 127.40, 123.43, 123.10, 119.77, 110.50, 64.37 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{20}H_{16}N_2O]^{+\bullet}$, 300.12626; found, 300.12586; difference: 1.3 ppm.



4-(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)benzyl acrylate (3)

Prepared according to general reaction B using 3b as starting material. Purified on silica using CH₂Cl₂. Yield 88%.

¹**H NMR (400 MHz, Methylene Chloride**-*d*₂): δ 7.88 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.67 – 7.53 (m, 4H), 7.48 – 7.33 (m, 6H), 7.37 – 7.27 (m, 2H), 6.53 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.27 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.95 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.34 (s, 2H) ppm.

¹³C NMR (101 MHz, Methylene Chloride-*d*₂): δ 166.11, 152.70, 143.59, 137.73, 137.23, 137.08, 131.55, 130.57, 129.85, 129.77, 129.70, 128.66, 128.53, 127.91, 123.64, 123.22, 120.06, 110.80, 65.75 ppm.

HRMS (EI) m/z: $[M^{+\bullet}]$ calcd for $[C_{23}H_{18}N_2O_2]^{+\bullet}$, 354.13683; found, 354.13622; difference: 1.7 ppm.



Bis(4-(2-phenyl-1H-benzo[d]imidazol-1-yl)benzyl acrylate) copper(II) bromide (CuBr₂(3)₂)

CuBr₂ (16 mg, 0.07 mmol, 0.5 eq.) and **11** (50 mg, 0.14 mmol, 1 eq.) were added to a 2 mL vial equipped with a magnetic stir bar. 0.2 mL of NMP was added, resulting in the immediate formation of a dark brown solution and the reaction was stirred overnight. To isolate compound **3c**, 1 mL of benzene was added to the mixture, stirring was turned off and the NMP/benzene solution of **3c** was layered with approximately 2 mL of hexane. After 24 hours dark brown crystals suitable for X-ray crystallography were obtained. Yield 46 mg (70%). **3c** is paramagnetic and not suitable for analysis by ¹H or ¹³C NMR spectroscopy.

HRMS (ESI) m/z: $[M-2Br]^{+\bullet}$ calcd for $[C_{46}H_{36}N_4O_4{}^{63}Cu]^{+\bullet}$, 771.2033; found, 771.2029; difference: -0.5 ppm.

Additional Figures:



Figure S1 Normalized absorbance (solid) and photoluminescence (PL, dashed) for monomers **1** (a), **2** (b), **3** (c) at 1 x 10⁻⁵ M in CH₂Cl₂.



Figure S2 Kinetic study of the synthesis by Cu(0)-RDRP of $\mathbf{1}_{10k}$ (a), $\mathbf{2}_{10k}$ (b), $\mathbf{3}_{10k}$ (c) in NMP: $\ln([M_0]/[M])$ vs. time plot. At high conversion, the rate becomes non-linear with respect to [M].



Figure S4 ¹H NMR spectrum of 2 in CDCl₃.



Figure S6 ¹H NMR spectrum of $\mathbf{1}_{10k}$ in CD₂Cl₂. * = THF.



Figure S7 ¹H NMR spectrum of 2_{10k} in CD₂Cl₂. * = THF.



Figure S8 ¹H NMR spectrum of 3_{10k} in CD₂Cl₂. * = THF



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



Figure S10 Calculated HOMO and LUMO diagrams for the *sec*-butyl analog of 2.



Figure S11 Calculated HOMO and LUMO diagrams for the *sec*-butyl analog of 3.



Figure S12 Thermogravimetric analysis of polymer 1_{10k} (a, 7.79 mg), 2_{10k} (b, 4.20 mg), and 3_{10k} (c, 2.55 mg), run at 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen from 25 to 800 °C.



Figure S13 DSC traces of polymers 1_{10k} (a), 2_{10k} (b), and 3_{10k} (c), 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 S14 Cyclic voltammograms of polymers 1_{10k} , 2_{10k} , and 3_{10k} relative to $\text{FeCp}_2^{0/+}$, recorded at a rate of 50 mV s⁻¹ in THF containing 2 mg mL⁻¹ of analyte and 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.⁷

X-Ray Crystallography Details

Experimental. Single brown plate-shaped crystals of $CuBr_2(3)_2$ were recrystallized from a benzene solution of $\text{CuBr}_2(3)_2$ layered with hexane. A suitable crystal (0.44×0.22×0.09) mm³ was selected and mounted on a mylar loop with oil on a Bruker APEX II area detector diffractometer. The crystal was kept at T = 90(2) K during data collection. Data were measured using wand ϕ scans of 0.5° per frame for 20 s using MoK_a radiation (TRIUMPH monochromator, sealed X-ray tube, 50kV, 30mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution achieved was Θ = 28.299°. Cell parameters were retrieved using the **SAINT** (Bruker, V8.34A, after 2013) software and refined using SAINT (Bruker, V8.34A, after 2013) on 9961 reflections, 40 % of the observed reflections. Data reduction was performed using the SAINT (Bruker, V8.34A, after 2013) software which corrects for Lorentz polarisation. The final completeness is 99.80 % out to 28.299° in Θ A multi-scan absorption correction was performed using SADABS-2014/5 (Bruker, 2014/5) was used for absorption correction. $wR_2(int)$ was 0.0646 before and 0.0453 after correction. The ratio of minimum to maximum transmission is 0.7657. The $\lambda/2$ correction factor is 0.00150. The absorption coefficient μ of this material is 2.091 mm⁻¹ at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.634 and 0.828. Using Olex2,⁸ the structure was solved with the XT⁹ structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of XL¹⁰ using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Additional crystallographic data can be found in Table S1.

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Formula	$C_{58}H_{48}Br_2CuN_4O_4$
$D_{calc.}$ / g cm ⁻³	1.449
μ/mm^{-1}	2.091
Formula Weight	1088.36
Colour	brown
Shape	plate
Size/mm ³	0.44×0.22×0.09
T/K	90(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	16.4411(18)
$b/{ m \AA}$	8.8490(10)
$c/{ m \AA}$	18.948(2)
$lpha/^{\circ}$	90
$eta\!/^\circ$	115.172(2)
$\gamma/^{\circ}$	90
$V/Å^3$	2495.0(5)
Ζ	2
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK_{lpha}
Θ_{min}/\degree	2.375
$\Theta_{max}/°$	28.299
Measured Refl.	25174
Independent Refl.	6173
Reflections Used	4845
R_{int}	0.0462
Parameters	372
Restraints	313
Largest Peak	1.535
Deepest Hole	-1.293
GooF	1.107
wR_2 (all data)	0.1264
wR_2	0.1164
R_1 (all data)	0.0811
R_1	0.0585

Table S1 Crystallography data for solid-state structure of compound CuBr₂(3)₂.

References

- 1 X. Yu, Z. Ci, T. Liu, X. Feng, C. Wang, T. Ma and M. Bao, *Dye. Pigment.*, 2014, **102**, 126–132.
- 2 Q. Xiao, Q. He, J. Li and J. Wang, Org. Lett., 2015, 17, 6090–6093.
- 3 H. Tanaka, K. Shizu, H. Nakanotani and C. Adachi, *J. Phys. Chem. C*, 2014, **118**, 15985–15994.
- 4 W.-H. Huang, W.-L. Jia and S. Wang, *Can. J. Chem.*, 2006, **84**, 477–485.
- 5 Z. Li, W. Chen, J. J. Hale, C. L. Lynch, S. G. Mills, R. Hajdu, C. A. Keohane, M. J.

Rosenbach, J. A. Milligan, G. J. Shei, G. Chrebet, S. A. Parent, J. Bergstrom, D. Card, M. Forrest, E. J. Quackenbush, L. A. Wickham, H. Vargas, R. M. Evans, H. Rosen and S. Mandala, *J. Med. Chem.*, 2005, **48**, 6169–6173.

- 6 F. Diness and D. P. Fairlie, Angew. Chemie Int. Ed., 2012, 51, 8012–8016.
- 7 J. R. Aranzaes, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288–299.
- 8 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 9 G. M. Sheldrick, Acta Crystallogr. Sect. A Found. Crystallogr., 2015, 71, 3–8.
- 10 G. M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem., 2015, 71, 3–8.