Shortwave infrared organic phototransistors with improved performance via

conjugated polymer blends and metal reflector gate architecture

Danbi Kim,^{1,2} Hyemi Han¹, Changsoon Choi⁴, Jeong Ho Cho², Jae-hoon Han^{4*}, and Jung Ah

Lim^{1,3,5*}

- ¹ Electronic and Hybrid Materials Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
- ² Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea
- ³ Division of Nano and Information Technology, KIST School, University of Science and Technology (UST), Seoul 02792, Republic of Korea
- ⁴ Center for Quantum Technology, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
- ⁵ Department of Materials Science and Engineering, YU-KIST Institute, Yonsei University, Seoul 03722, Republic of Korea

* Correspondence and request for materials should be addressed to J. Han, J. A. Lim

(E-mail: hanjh@kist.re.kr, jalim@kist.re.kr)

Supporting Notes 1. A 100 mL one-neck round-bottom flask with stirring bar was degassed and charged with Ar gas gas repeatedly, and then transferred to a glove box filled with highpurity N2 gas. 2Br-BBT (0.3 g), 2Sn-TT (0.2 g), P(o-tolyl) (80 mg), and Pd2(dba)3 (20 mg) was added to the mixture, lastly. After anhydrous toluene (20 mL) solvent were added to the flask, and the resultant mixture was stirred at room temperature until it became homogeneous (~30 min). The resultant red-brown solution was vigorously stirred at 100 °C for 72 h. The reaction mixture was allowed to cool to room temperature. Next, chlorobenzene were injected into the mixture using a syringe. The remaining Pd catalysts and insoluble components were purified by a vacuum filtration system with a paper filter (pore size = 1 μ m). The filtrate was concentrated and poured into stirring MeOH (~300 mL), after which the mixture was stirred overnight. The precipitated product was purified by sequential filtration and washed with MeOH, then dried under vacuum to obtain a red-brown solid.



Scheme S1. Synthesis scheme for the BBTTT polymer via stille coupling reactions using palladium-catalyzed system in anhydrous toluene solvent.



Figure S1. For analysis properties of BBTTT polymer, Photoemission spectroscopy (PES) (a) and thermogravimetric analysis (TGA) (b) was performed.

Supporting Notes 2. A 100 mL one-neck round-bottom flask with stirring bar was degassed and charged with Ar gas gas repeatedly, and then transferred to a glove box filled with highpurity N2 gas. 2Br-DPP (0.2 g), 2Sn-TT (0.09 g), P(o-tolyl) (5 mg), and Pd2(dba)3 (4 mg) was added to the mixture, lastly. After chlorobenzene (20 mL) solvent were added to the flask, and the resultant mixture was stirred at room temperature until it became homogeneous (~30 min). The resultant green solution was vigorously stirred at 130 °C for 72 h. The reaction mixture was allowed to cool to room temperature. Next, chlorobenzene were injected into the mixture using a syringe. The remaining Pd catalysts and insoluble components were purified by a vacuum filtration system with a paper filter (pore size = 1 μ m). The filtrate was concentrated and poured into stirring MeOH (~300 mL), after which the mixture was stirred overnight. The precipitated product was purified by sequential filtration and washed with MeOH, then dried under vacuum to obtain a green-brown solid.



Scheme S2. Synthesis scheme for the DPPTT polymer via stille coupling reactions using palladium-catalyzed system in chlorobenzene solvent.



Figure S2. For analysis properties of DPPTT polymer, Photoemission spectroscopy (PES) (a) and thermogravimetric analysis (TGA) (b) was performed.



Figure S3. Transfer curve (a) and output curve (b) of BT based phototransistors under vacuum condition.



Figure S4. Difference of absorbance with varying BT blend ratios.



Figure S5. The transfer (at V_{DS} = -80 V) and output curve of the DT based phototransistors.



Figure S6. The transfer curve of the blend-based organic phototransistors at V_{DS} = -80 V.



Figure S7. The output curve ($V_{GS} = 0 \sim -80$ V, step = -20 V) of 30% BT (a) 50% BT based phototransistors (d) under 1310 nm light with a light intensity of 16.8 mW/cm². *R* of 30% BT (b) and 50% BT based phototransistors (e) are calculated as a function of V_{GS} at $V_{DS} = -80$ V under 1310 nm light irradiation. *R* of the 30% BT (c) and 50% BT based phototransistors (f) are plotted as a function of light intensity according to the V_{GS}.



Figure S8. Refractive index (n) and extinction coefficient (k) of 70% BT films measured by ellipsometry.

Supporting Notes 3. A finite-difference time-domain (FDTD) simulation was carried out using a COMSOL Multiphysics with a wave optics module. The 2D schematics and parameters of FDTD simulation were shown in Fig. S9. The perpect matching layers and periodic boundary conditions were set the end of simulation region for each axis to prevent the reflection from the simulation edge. The plain wave port where its wavelength was swept from 400 nm to 1600 nm was set far enough from the sample surface to gerentee the zero evanescent field. The input light power was 1 W. To calculate the transmission (T) and reflection (R), Poynting vectors (ewfd.Poavy in COMSOL; only belong y-axis) at each monitor were integrated. To evaluate the absorption (A) in each layer, resistive losses (ewfd.Qrh in COMSOL) in the lossy layer were integrated. Each value was nomarlized by the power of input light. The thicknesses of Al₂O₃ and gold layers were swept from 10 nm to 100 nm to evaluate the thickness dependence on T, R, and A. In the case of metal layer, we deposited titanium on the top or bottom of gold layer to improve its adhesion during the FET process; thus, the metal layer was consisting of Ti/Au/Ti structure.

PML		Layers	Thickness (um)	Used Model in COMSOL
	R	/Parameters		
Air	integration	Air	2	Air (Peck and Reeder 1972)
	Plain wave port Absorption integration	Organics	0.035	Measured by ellipsometry
+ Organics		Al ₂ O ₃	0.01 to 0.1	Al2O3 (Aluminium sesquioxide, Sapphire, Alumina) (Boidin et al. 2016: Thin film)
		Metal/Tungsten*	0.01	W (Tungsten) (Werner et al. 2009)
Al ₂ O ₃ Metal	Absorption	Metal/Gold*	0.01 to 0.1	Au (Gold) (Babar and Weaver 2015)
		SiO ₂ **	0.3	Fused silica (fused quartz) (Malitson 1965)
Si	← Periodic boundary ← T fintegration	Si	2	Si (Silicon) (Li 1980)
		W	0.01	
		Wavelength	0.4 to 1.6	
PML				
w		*Metal layer is consi	sting of tungsten/gc	old/tungsten to improve its adhesion.



*Metal layer is consisting of tungsten/gold/tungsten to improve its adhesion. **SiO₂ is used for organic FET without metal reflector.

Figure S9. The 2D schematics and parameters for optical simulation using COMSOL Multiphysics.



Figure S10. Absorbance of 70% BT active layers as a function of eMR-gate thickness.



Figure S11. Noise spectral density of (a) BT-based phototransistors, (b) conventional phototransistor based on 70% BT blend film, and (c) 70% BT blend-based phototransistors with eMR-gates.



Figure S12. (a) Transfer characteristics of BT-based phototransistor measured under ambient condition after 24 hours of storage. (b) Photoresponses of the 70% BT blend-phototransistors under various light intensities at a V_{DS} =-20 V after 96 hours of ambient storage. (c) The photocurrent (I_{ph} = I_{light} - I_{dark}) of 70% BT blend-phototransistors measured at weak (0.01 mW/cm2) and strong (1 mW/cm2) light intensities during ambient storage.