Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Synthetic procedure

2-methylbenzo[b]thiophene (2)

A 300 ml four necked flask was charged with **1** (13.4 g, 100 mmol) in 100 ml of dry THF and cooled to -78 °C. *n*-BuLi in hexane (66 ml, 105 mmol) was added slowly and the mixture was stirred for 15 min, followed by adding MeI (14.9 g, 105 mmol) at that temperature. The solution was kept at -78 °C for additional 30 min. The resulting mixture was quenched by water and was extracted with ether washed and concentrated to afford 2-methylbenzo[b]thiophene **2** as colorless liquid (14.5 g, 100 mmol, >99 %).

3-iodo-2-methylbenzo[b]thiophene (3)

A 100 ml of four neck flask was charged with H_2SO_4(1.5 ml), AcOH(50 ml), H_2O(10 ml), $HIO_4 \cdot 2H_2O$(2.28 g, 10 mmol), I_2(5.08 g, 20 mmol) and 2-methylbenzo[b]thiophene(7.41 g, 50.0 mmol). Then, reaction mixture was stirred at 65 °C for 5 h. The reaction mixture was Neutralized with 10 M KOH aq., then, under base condition, was treated with $Na_2S_2O_3 \cdot 5H_2O$. The resulting solution was extracted

with ether. The organic layer was dried over anhydrous magnesium sulfate, filterd and concentrated. The residue was purified with silica gel column chromatography (hexane) to afford 3-iodo-2-methylbenzo[b]thiophene (, 73%) as pale red liquid. ^{1}H-NMR (CD_3CN, 300MHz) 8.09-8.05(m, 2H), 7.79-7.74(m, 2H), 7.64-7.57(m, 2H), 7.56-7.50(m, 3H), 7.28-7.20(m, 4H), 2.14(s, 6H) ^{13}C-NMR ($(CD_3)_2CO$, 75 MHz) 168.0, 149.5, 141.3, 140.5, 140.3, 140.2, 138.7(2), 138.6(6), 134.5, 131.3, 130.1, 128.7, 128.3, 127.2, 125.6, 125.2, 125.0, 124.8, 123.8, 123.7, 122.9, 122.8, 122.6, 15.0, 14.9. EI-HRMS(m/z) $[M]^+$ calcd. for C27H19NS3, 453.07, found, 453.0685. Anal. Calcd. for $C_{27}H_{19}NS_3$: C, 71.49; H, 4.22; N, 3.09. Found: C, 71.36; H, 4.13; N, 3.05.

4,4,5,5-tetramethyl-2-(2-methylbenzo[b]thiophen-3-yl)-1,3,2-dioxaborolane (5)

A 300 ml four necked flask was charged with **3** (5.48 g, 20.0 mmol) in 100 ml of dry THF and cooled to -78 °C. *n*-BuLi in hexane (15 ml, 24.0 mmol) was added slowly and the mixture was stirred for 30 min, followed by adding 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.9 ml, 24 mmol) at that temperature. The solution was kept at -78 °C for additional 30 min. The resulting mixture was quenched by water and was extracted with ether washed and concentrated.

The crude product was purified by recrystallization to afford 4,4,5,5-tetramethyl-2-(2-methylbenzo[b]thiophen-3-yl)-1,3,2-dioxaborolane **5** as colorless crystals (1.7 g, 6.20 mmol, 31 %).

2-(benzo[b]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)

A 100 ml four necked flask was charged with **4** (8.14 g, 38.2 mmol) in 100 ml of dry THF and cooled to -78 °C. *n*-BuLi in hexane (25 ml, 40.0 mmol) was added slowly and the mixture was stirred for 15 min, followed by adding 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.7 ml, 40 mmol) at that temperature. The solution was kept at -78 °C for additional 30 min. The resulting mixture was quenched by water and was extracted with ether washed and concentrated. The crude product was purified by recrystallization to afford 4,4,5,5-tetramethyl-2-(2-methylbenzo[b]thiophen-3-yl)-1,3,2-dioxaborolane as colorless crystals (2.1 g, 8.1 mmol, 20%) ^{1}H-NMR ($CDCl_3$, 300MHz) 8.38-8.35(m, 1H), 8.07(s, 1H), 7.90-7.87(m, 1H), 7.43-7.30(m, 2H), 1.38(s, 12H).

4,5-bis(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (TA-1)

A 100 ml of four neck flask was charged with **5** (576 mg, 2.1 mmol), **7** (319 mg, 1.0 mmol), PPh_3 (131 mg, 0.5 mmol), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) and K_3PO_4 in water / dioxane (2M, 30 ml). Then, reaction mixture was stirred at 110 °C under Ar atmosphere for 9 h. The reaction mixture was extracted with ether purified with silica gel column chromatography (hexane / AcOEt = 20: 1) and further purified with the HPLC with C18 / silica gel-column to afford **TA-1** (160mg, 35 %). ^{1}H-NMR (CD_3CN, 300MHz) 8.09-8.05(m, 2H), 7.79-7.74(m, 2H), 7.64-7.57(m, 2H), 7.56-7.50(m, 3H), 7.28-7.20(m, 4H), 2.14(s, 6H) ^{13}C-NMR ($(CD_3)_2CO$, 75 MHz) 168.0, 149.5, 141.3, 140.5, 140.3, 140.2, 138.7(2), 138.6(6), 134.5, 131.3, 130.1, 128.7, 128.3, 127.2, 125.6, 125.2, 125.0, 124.8, 123.8, 123.7, 122.9, 122.8, 122.6, 15.0, 14.9. EI-HRMS(m/z) $[M]^+$ calcd. for C27H19NS3, 453.07, found, 453.0685. Anal. Calcd. for $C_{27}H_{19}NS_3$: C, 71.49; H, 4.22; N, 3.09. Found: C, 71.36; H, 4.13; N, 3.05.

4,5-di(benzo[b]thiophen-3-yl)-2-phenylthiazole(TA-2)

A 100 ml of four neck flask was charged with **6** (832 mg, 1.95 mmol), **7** (303 mg, 0.95 mmol), PPh_3 (124 mg, 0.5 mmol), $Pd(PPh_3)_4$ (225 mg, 0.20 mmol) and K_3PO_4 in water / dioxane (2M, 30 ml). Then, reaction mixture was stirred at 110 °C under Ar atmosphere for 12 h. The reaction mixture was extracted with ether purified with silica gel column

chromatography (hexane / AcOEt = 15: 1) and further purified with the HPLC with C18 / silica gel-column to afford **TA-1** (80 mg, 20 %). ^{1}H-NMR (CD_3CN, 300MHz) 8.84-8.82(m, 1H), 8.24(s, 1H), 8.13-8.10(m, 1H), 8.00-7.96(m, 1H), 7.89-7.83(m, 2H), 7.65(s, 1H), 7.51-7.43(m, 3H), 7.35-7.26(m, 4H), 7.18-7.12(m, 1H), EI-HRMS (m/z) $[M]^+$ calcd. for C25H15NS3, 425.0367, found, 425.0364.

Complete reference for Gaussian calculation

19.(a) Gaussian 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.;

Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004. (b) GaussView, Version 4.1, Dennington II, Roy; Keith, Todd; and Millam, John; Semichem, Inc., Shawnee Mission, KS, 2007.

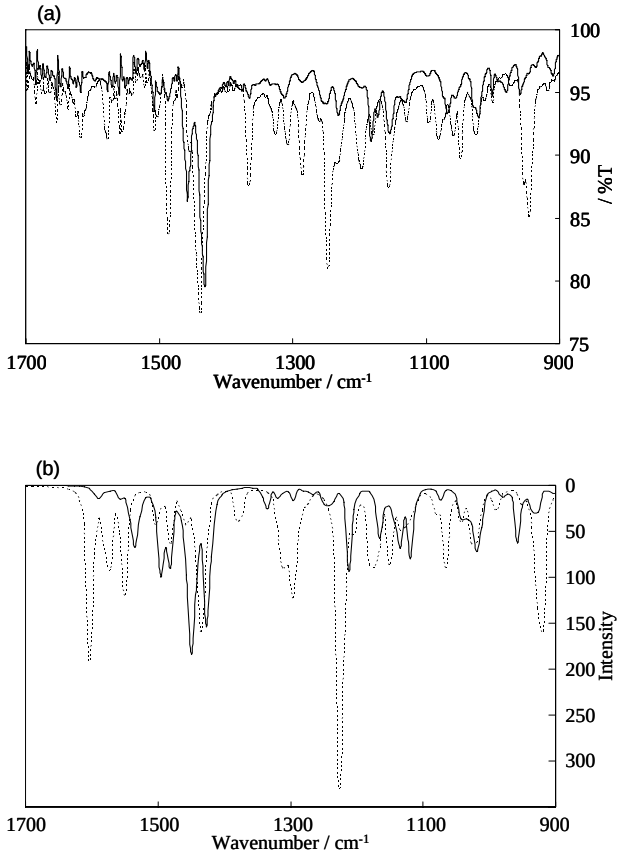
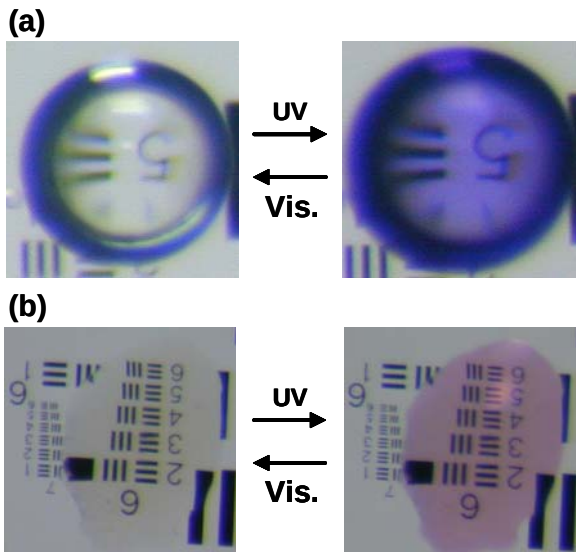


Figure S1. Observed infrared spectra (a) of open-ring isomer TA-1a (—) and closed-form isomer TA-1b (···) of bulk amorphous state, and DFT calculated spectra (b) of TA-1a(—) and closed-form isomer TA-1b(···).

Figure S2. Photo-induced coloration of (a) TA-1 and of (b)TA-2 in bulk amorphous phase.



X-ray crystallographic analyses of TA-1.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{27}H_{19}NS_3$
Formula Weight	453.63
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.28 X 0.24 X 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 300.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm

Lattice Parameters	a = 10.7209(5) Å
	b = 10.8452(5) Å
	c = 11.2030(5) Å
	α = 79.6997(14) ^{o}
	β = 74.6185(15) ^{o}
	γ = 63.0804(11) ^{o}
	V = 1117.21(9) Å^{3}
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.348 g/cm^{3}
F_{000}	472.00
μ(MoKα)	3.468 cm^{-1}
B. Intensity Measurements	
Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å)
	graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	55 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0^{o}
Exposure Rate	180.0 sec./^{o}
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0^{o}

Exposure Rate	180.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.8^{o}
No. of Reflections Measured	Total: 11079
	Unique: 5056 (R_{int} = 0.032)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.734 - 0.933)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	$1/[0.0006Fo^2+1.0000\sigma(Fo^2)]/(4Fo^2)$
$2\theta_{max}$ cutoff	54.8^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	3627
No. Variables	299
Reflection/Parameter Ratio	12.13
Residuals: R1 (I>2.00σ(I))	0.0306
Residuals: wR2 (I>2.00σ(I))	0.0770
Goodness of Fit Indicator	1.005
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.24 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.22 $e^-/Å^3$

Supplementary Material (ESI) for Journal of Materials Chemistry

Formation of surface relief grating

Experimental condition

Thin film

Concentration of 1 mg / ml chloroform solution containing TA-1 were dropped on the quartz plate, and the plates were spun by 500 rpm for 10 seconds, and then by 5000 rpm for 20seconds.

Light source

500W Super-high-pressure UV Lamp, Optical Modulex SX-UID 501HUVQ (USHIO) + Filter UG 11 (USHIO)

Procedure

The thin film was irradiated with UV light containing 313nm and 365 nm with a mask of 200 lines/mm（Edmund Industrial Optics）glass plate.

AFM

JSTM-4200D (JEOL) with a micro cantilever (OMCL-AC160TS-C2, OLYMPUS)

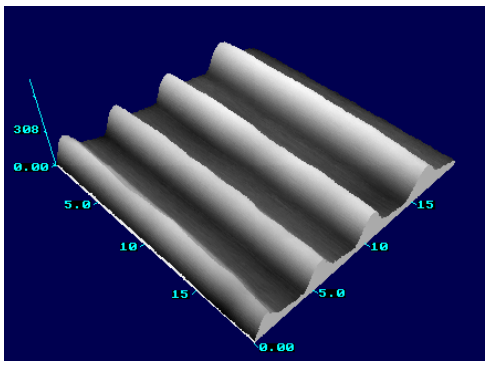


Fig. S-1. AFM image of the surface of the amorphous film of TA-1 after