

Supporting Information

Water-soluble 1,2,4-Triazole with Diethylene Glycol Monoethyl Ether Groups: Synthesis, Characterization and Application as Electron Injection Layer for PLEDs

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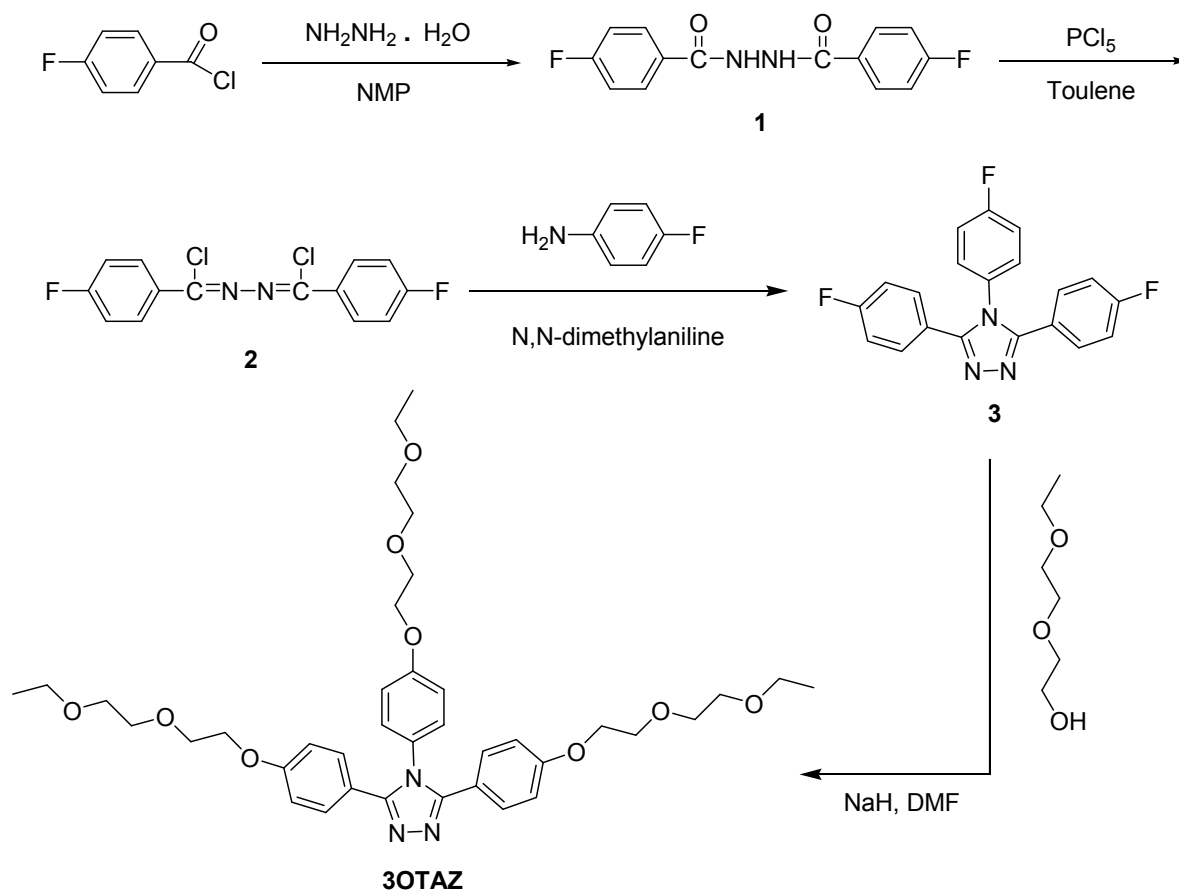
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1,2-Bis(4-fluorobenzoyl)hydrazine (1).¹

To a two-neck glass reactor were added with 4-bromobenzoyl chloride (3.24 g, 20.5 mmol), hydrazine monohydrate (0.51 g, 10.25 mmol), and 20 ml of N-methylpyrrolidone (NMP). The mixture was stirred at room temperature for 6 h, poured into a large amount of distilled water. The appearing precipitates were collected by filtration and recrystallized from DMSO and water to afford **1** (80 %). mp > 240 °C. ¹H NMR (DMSO-d₆, ppm): δ 10.55 (s, 2H, N-H), 8.02~7.98 (m, 4H, Ar-H), 7.39~7.35 (t, 4H, Ar-H). FTIR (KBr pellet, cm⁻¹): ν 3207 (-CONH-). Anal. Calcd.(%) for C₁₄H₁₀F₂N₂O₂: C, 60.87% ; H, 3.65% ; N, 10.14%. Found: C, 61.08%; H, 3.59% ; N, 10.06%.

1,2-Bis((4-fluorophenyl)chloromethylene)hydrazine (2).¹

The mixture of **1** (1.09 g, 3.94 mmol), phosphorus pentachloride (1.87 g, 9.0 mmol), and 30 ml of toluene was stirred at 120 °C for 3 h under nitrogen atmosphere. After stripping off toluene under vacuum, the solid residue was washed twice with deionized water, dried *in vacuo*, and then recrystallized from ethanol to afford **2** (85 %). mp: 131 °C. ¹H NMR (DMSO-d₆, ppm): δ 8.13~8.10 (m, 4H, Ar-H), 7.44~7.39 (m, 4H, Ar-H). FTIR (KBr pellet, cm⁻¹): ν 1593 (-N=N-). Anal. Calcd.(%) for C₁₄H₈Cl₁₂F₂N₂: C, 53.70% ; H, 2.58% ; N, 8.95%. Found: C, 53.83% ; H, 2.55% ; N, 8.90%.



Scheme 1. Synthetic procedures of **3OTAZ**.

3,4,5-tris(4-fluorophenyl)-4H-1,2,4-triazole (3).¹

Mixture of **2** (0.58 g, 2.01 mmol), 4-fluoroaniline (0.66 g, 5.98 mmol), and 10 ml of *N,N*-dimethylaniline was stirred at 135 °C for 12 h under nitrogen atmosphere. After adding aqueous solution of HCl (100 ml, 2 N), the mixture was stirred for additional 30 minutes. The precipitated solid was collected by filtration, dried *in vacuo*, and recrystallized from DMSO and water to afford **3** (74%). mp: 225~226 °C. ¹H NMR (DMSO-*d*₆, ppm): δ 7.53~7.49 (m, 2H, Ar-H), 7.45~7.41 (m, 4H, Ar-H), 7.34~7.30 (m, 2H, Ar-H), 7.26~7.21 (m, 4H, Ar-H). FTIR (KBr pellet, cm⁻¹): ν 1607 (C=N). Anal. Calcd.(%) for C₂₀H₁₂F₃N₃: C, 68.37% ; H, 3.44% ; N, 11.96%. Found: C, 68.34%; H, 3.48% ; N, 11.95%.

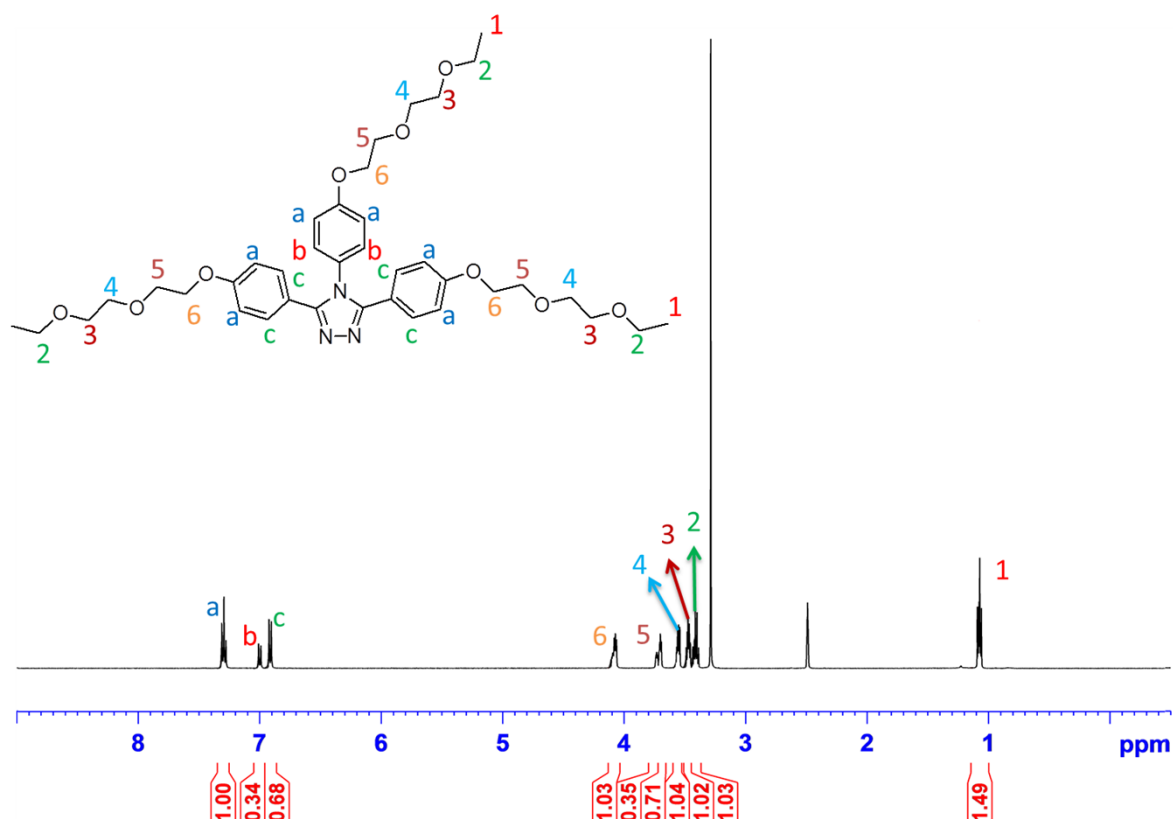


Figure S1. ¹H NMR spectrum of compound **3OTAZ**.

The chemical shifts at 7.31~6.91 ppm are assigned to the protons on the aromatic parts of **3OTAZ** (Figure S1 in SI). The ratio of peak area among the chemical shifts at 7.31~7.28 ppm, 7.00 ppm and 6.91 ppm was about 1:0.34:0.68 which is acceptable compared to theoretical ratio (3:1:2). And the chemical shift at 1.07 ppm is attributed to the characteristic protons on the terminal methyl group of alkyl chain. The complex and multiple chemical shifts around 4.10~3.38 ppm are the signals of the protons belonging to ether groups (C-O-C) parts of **3OTAZ**. Due to the complexity of the spectrum, the assignment of individual protons has been assisted by the two dimensional COSY and NOESY spectra (Figure S2 and Figure S3 in SI).

The homonuclear correlation spectroscopy (COSY) is used to identify spins which are coupled to each other. The COSY spectrum gives information about pairs of protons that are

J-coupled. This usually indicates that the protons are on adjacent carbons, e.g., 3-bonds away. The NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum signals proton-proton through space interactions via NOE which gives information about pairs of protons that are close in space ($< 5 \text{ \AA}$ apart).

As demonstrated in COSY spectrum (Figure S2 in SI), there is an off-diagonal J-coupling signal between 1.07 ppm and 3.44~3.39 ppm. The 1.07 ppm is known to be the protons of position 1 (terminal CH_3) which assigns the peaks in 3.44~3.39 ppm to the protons of position 2 ($-\text{CH}_2-\text{CH}_3$). In NOESY spectrum (Figure S3 in SI), there is also an off-diagonal coupling between 3.44~3.39 ppm (position 2) and 3.49~3.46 ppm, leading to the assignment of 3.49~3.46 ppm as protons of position 3. From another off-diagonal coupling between 3.49~3.46 ppm (position 3) and 3.58~3.54 ppm, the 3.58~3.54 ppm can be assigned to the protons in position 4 (Figure S2 in SI). The chemical shifts at 4.10~4.06 ppm can be attributed to the protons of position 6 due to their proximity to the triazole part. As shown in Figure S2 (SI), the off-diagonal coupling is observed between 4.10~4.06 ppm (position 6) and 3.74~3.69 ppm, confirming that 3.74~3.69 ppm are ascribed to position 5 protons. The protons at positions 2, 3, 4, 5 and 6 can be further confirmed by the peak area of ^1H NMR. As discussed above, by detailed analysis of ^1H -NMR, COSY and NOESY spectra, the protons of **3OTAZ** have been assigned completely.

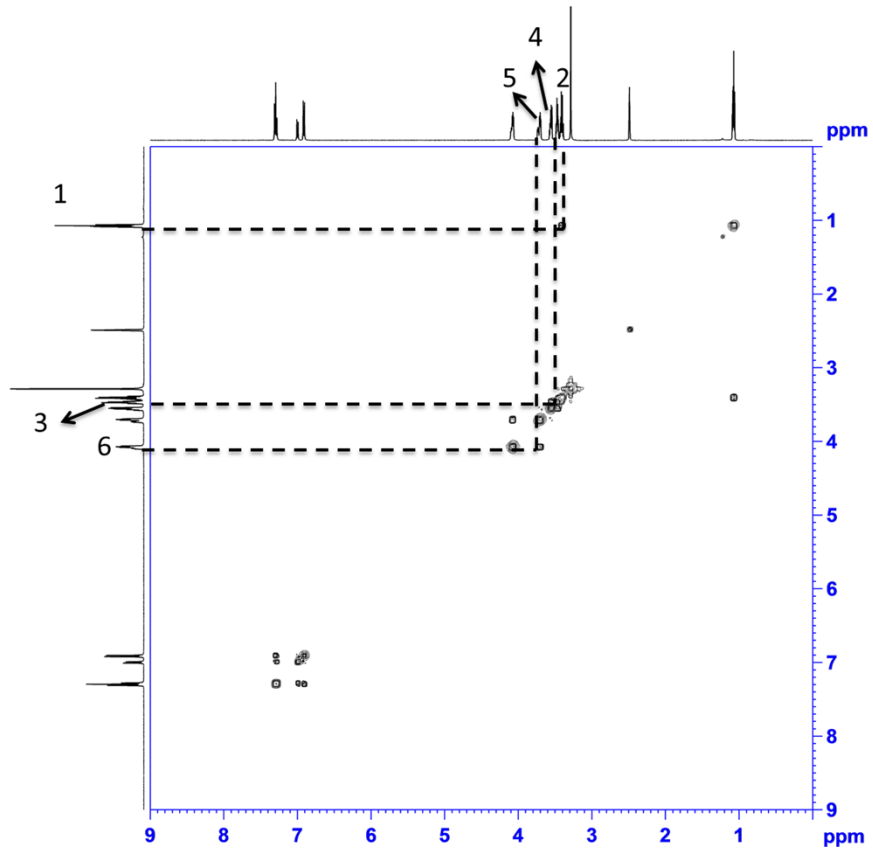


Figure
COSY
of

S2. The
spectrum
3OTAZ.

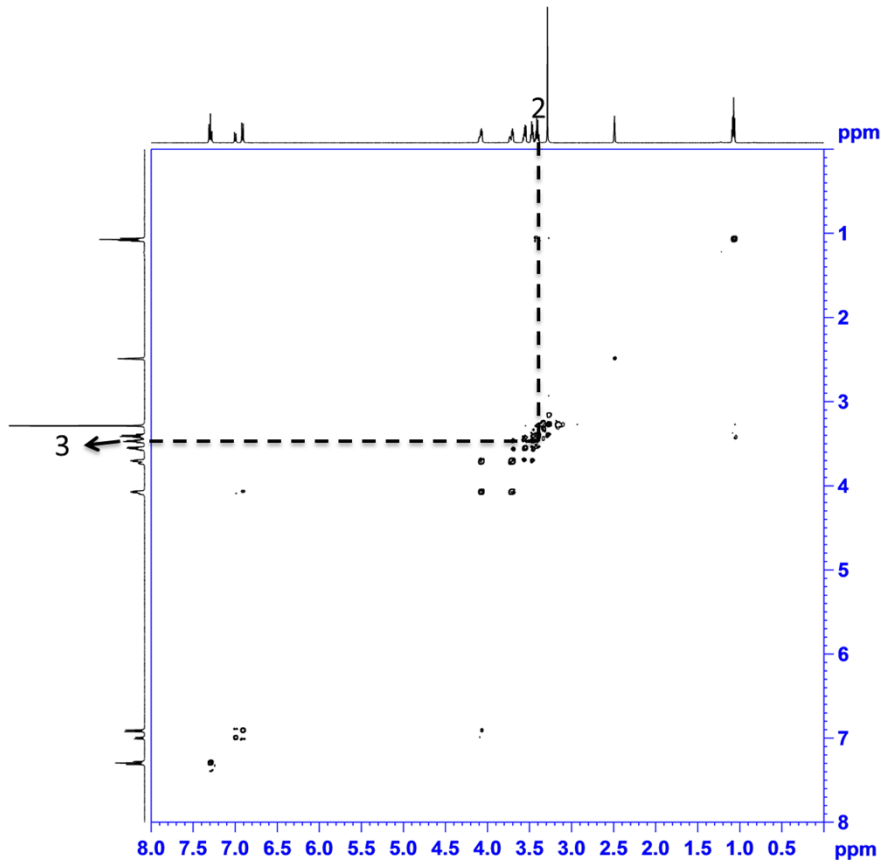


Figure S3. The NOESY spectrum of **3OTAZ**.

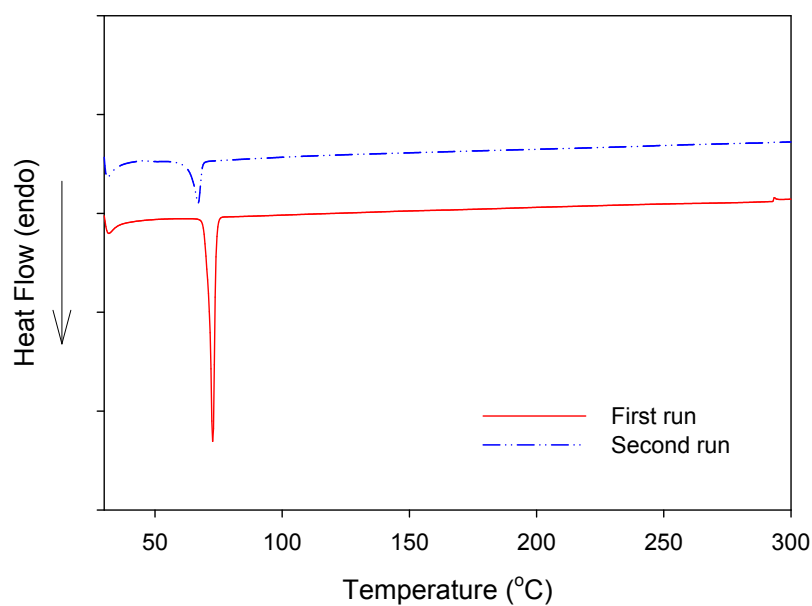


Figure S4. Differential scanning calorimetric curves of **3OTAZ** at a heating rate of 10 °C/min under nitrogen atmosphere.

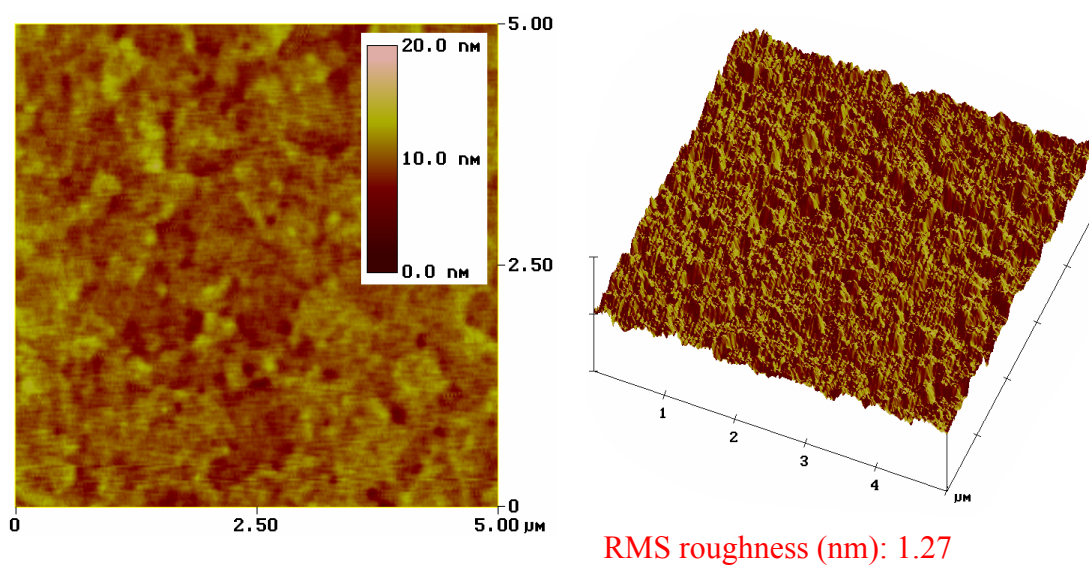
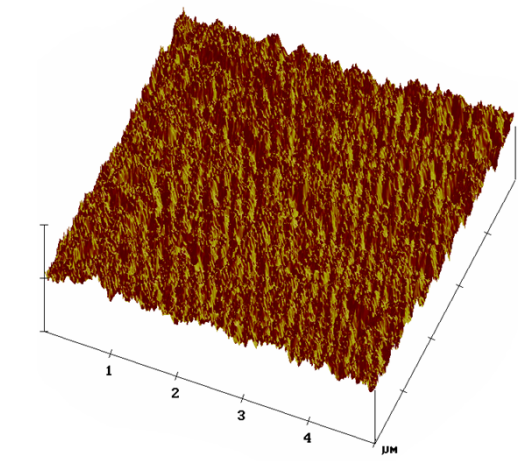
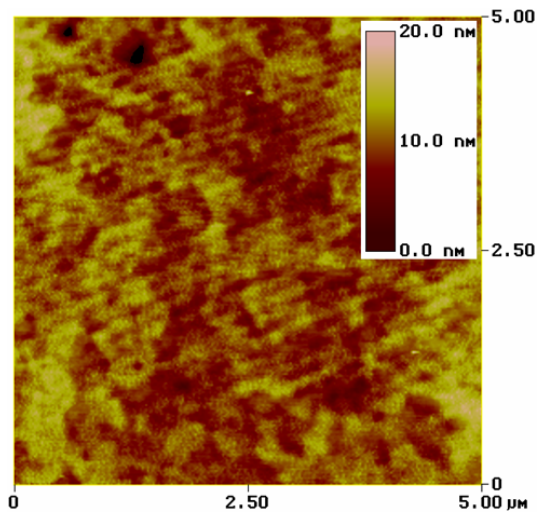
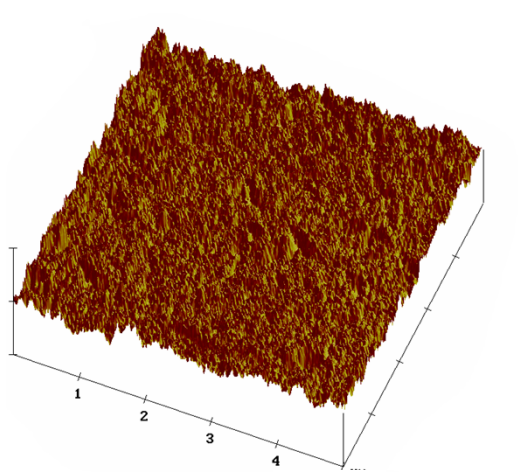
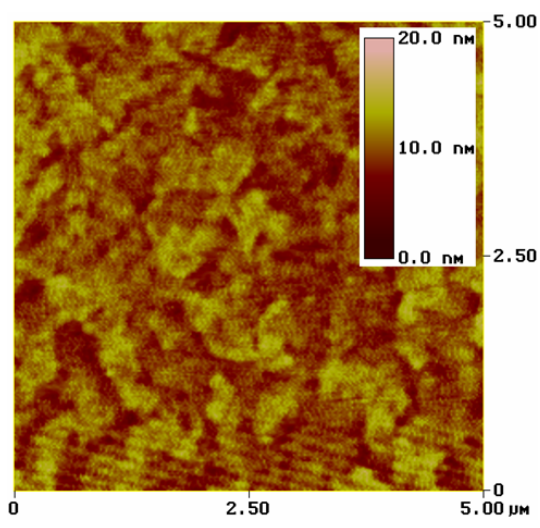


Figure S5. AFM images of HY-PPV film on top of PEDOT:PSS layer.



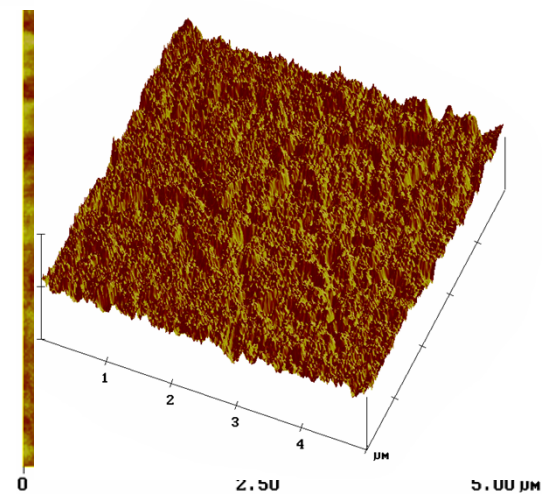
(a)

RMS roughness (nm): 2.23



(b)

(c)



RMS roug

Figure S6. AFM images of the surface of **3OTAZ** on top of HY-PPV layer by spin-coating with different spin rate. (a) 1000 rpm; (b) 2000 rpm; (c) 3000 rpm.

References

- (1) (a) C.-S. Wu and Y. Chen, *Macromolecules*, **2009**, 42, 3729. (b) C.-S. Wu and Y. Chen, *J. Mater. Chem.*, **2010**, 20, 7700. (c) C.-S. Wu and Y. Chen, *J. Polym. Sci. Part A Polym. Chem.*, **2010**, 48, 5727. (d) C.-S. Wu, S.-L. Lee and Y. Chen, *J. Polym. Sci. Part A Polym. Chem.*, **2011**, 49, 3099. (e) C.-S. Wu and Y. Chen, *J. Polym. Sci. Part A Polym. Chem.*, **2011**, 49, 3928.