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Supplementary Materials

Side-Group Effect on Electron Transport of Single Molecular Junctions

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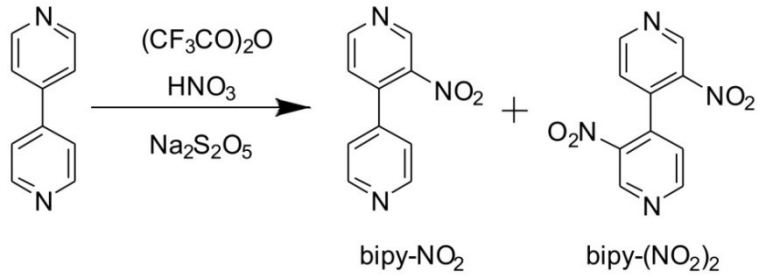
1. Detail of Synthesis



Synthesis of 3-nitro-4,4′-bipyridine and 3,3′-dinitro-4,4′-bipyridine:

The bipy-NO_2 and bipy-$(NO_2)_2$ was synthesized according to a reported procedure with slight modification [1]. Trifluoroacetic anhydride (12 mL) was chilled in an ice bath and 4,4'-bipyridine (3.0 g, 19 mmol) was added in portions and stirred 2 h at chilled conditions. To the chilled suspension, concentrated nitric acid (2.1 mL, 41 mmol) was added dropwise, and the suspension turned into clear solution. After stirring for 12 h at room temperature, thesolution was dripped slowly into a chilled aqueous solution of sodium metabisulfite (3.2 g, 17 mmol in 25 mL of water). After 24 h, the solution was brought to pH 6–7 by addition of 25% NaOH solution. The solution was extracted with DCM (4 x 50 mL), the combined organic phase was dried overanhydrous sodium sulfate; the solvent was evaporated to give the crude product which was furtherpurified by column chromatography using DCM: ethyl acetate (20: 1). First, the 3,3′-dinitro-4,4′-bipyridine was eluted. Elution of 3-nitro-4,4′-bipyridine followed. Evaporation of the solvent resulted in 3,3′-dinitro-4,4′-bipyridine (0.4 g) and 3-nitro-4,4′-bipyridine (1.2 g).

3-nitro-4,4′-bipyridine: 1H NMR: (400 MHz, DMSO-d_6): (δ, ppm) 9.30 (s, 1H). 8.99 (d, 1H), 8.73 (d, 2H), 7.70 (d, 1H), 7.50 (d, 2H). FT-IR (cm^{-1}): 1589 (s), 1533(s), 1519(s), 1408(w), 1384(w), 1358(s), 1190(w), 855(m), 822(m), 765(m), 613(m), 529(m).

3,3′-dinitro-4,4′-bipyridine: 1H NMR: (400MHz, DMSO-d_6): (δ, ppm) 9.5 (s, 2H). 9.0 (d, 2H), 7.7 (d, 2H). FT-IR (cm^{-1}): 1595(s), 1524(s), 1408(w), 1349(s), 1194(s), 855(m), 763(m), 620(m), 589(m).

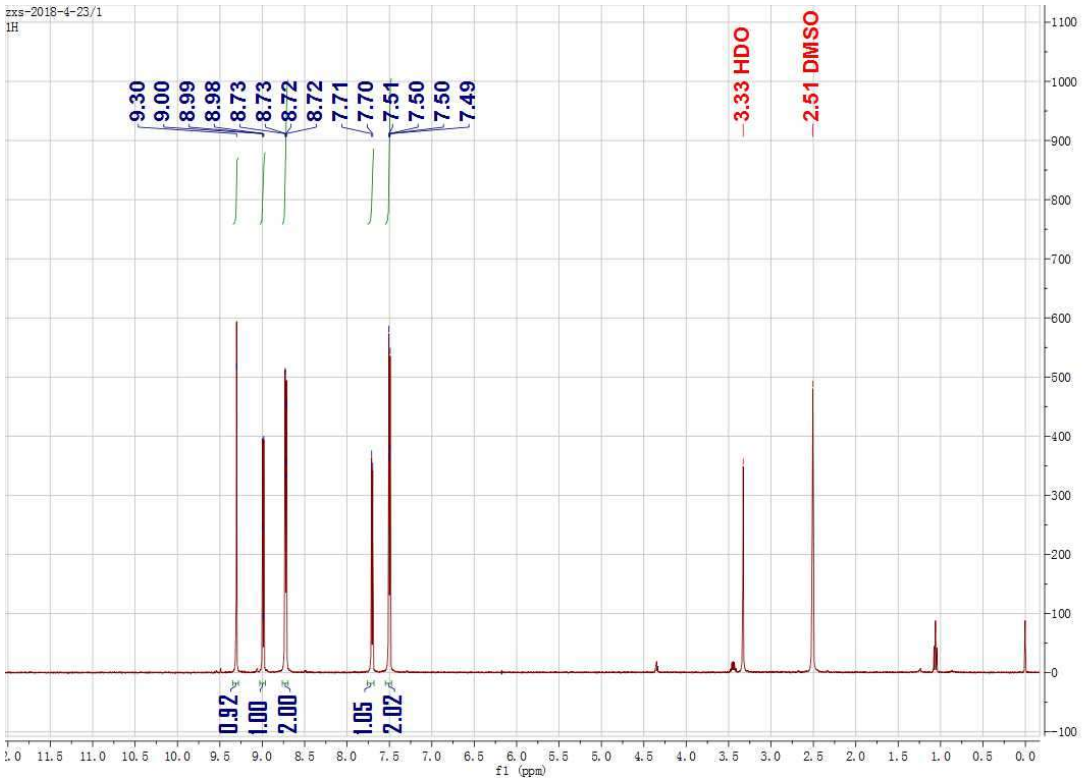


Figure S1. [1]HNMR spectra of 3-nitro-4,4′-bipyridine.

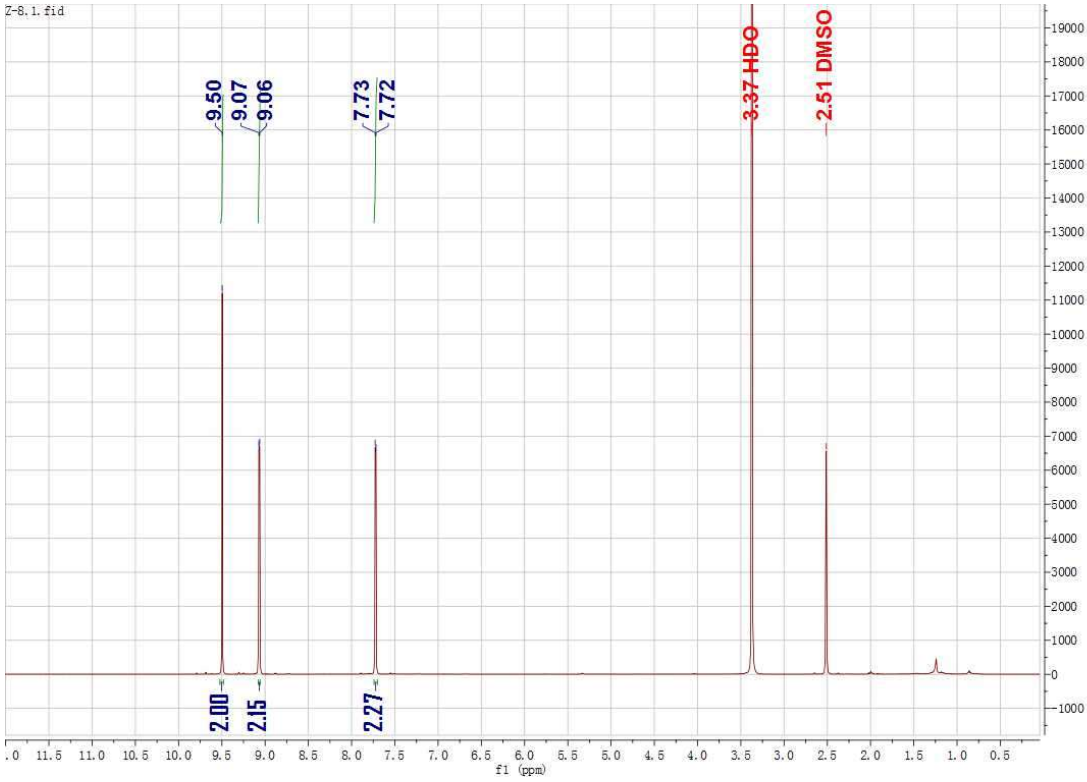


Figure S2. [1]HNMR spectra of 3,3′-dinitro-4,4′-bipyridine.

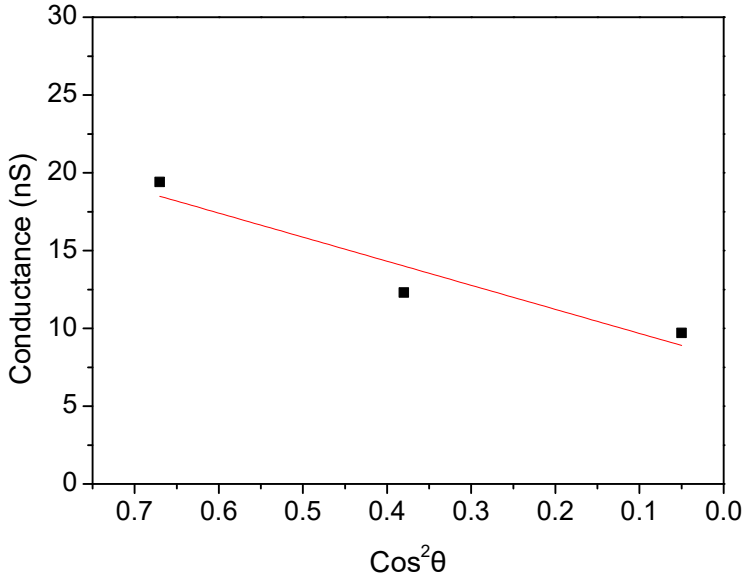


Figure S3. Conductance pyridine-based molecules of BPY, BPY-N and BPY-2N vs. $\cos^2\theta$, here θ is the twist angle between two rings.

Reference

[1] L. Zhang, Y. Jian, J. Wang, C. He, X. Li, T. Liu, C. Duan, *Dalton Trans* **2012**, *41*, 10153–10155.