Supplementary Information

Molecular Diodes Enabled by Quantum Interference

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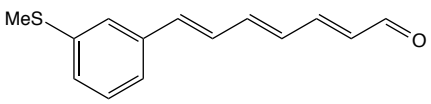
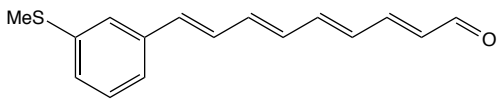
Synthesis Details:

General: Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker DRX500 (500 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to NMR solvent ($C_2D_2Cl_4$: δ 5.91). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and referenced to the carbon resonances of the solvent ($C_2D_2Cl_4$: δ 74.2). Spectra were analyzed with MestraNova software (Version 7.1). Data are represented as follows: chemical shift, multiplicity (s = singlet, bs=broad singlet, d = doublet, m = multiplet), coupling constants in Hertz (Hz), and integration. High resolution mass spectroscopic data (HRMS) were obtained at the Columbia University mass spectrometry facility using a JEOL JMSHX110A/110A tandem mass spectrometer.

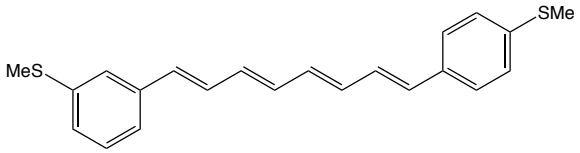
Synthesis: Preparation of molecules 1-3 has been described previously[1, 2]. Here we describe procedures for preparing molecules 4-5.



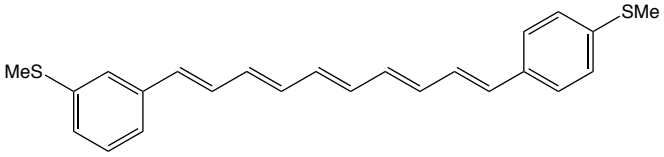
7-(3-(methylthio)phenyl)hepta-2,4,6-trienal: General Wittig homologation procedure described previously.[3] HRMS: m/z calcd for ($C_{14}H_{14}OS$): 230.0765, found: 230.0754.



9-(3-(methylthio)phenyl)nona-2,4,6,8-tetraenal: General Wittig homologation procedure. HR-MS: m/z calcd for ($C_{16}H_{16}OS$): 256.0922, found: 256.0922.



1-(3-(methylthio)phenyl)-8-(4-(methylthio)phenyl)-octa-1,3,5,7-tetraene: A General Horner Wadsworth Emmons (HWE) procedure reported previously[1] was followed. The product was prepared from the corresponding trienal and dimethyl 4-(methylthio)benzyl phosphonate and was isolated by recrystallization from CH_2Cl_2/MeOH as a yellow solid in 49% yield. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.28 (bs, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.21 (m, 3H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.94-6.78 (m, 2H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.55 (d, *J* = 15.5 Hz, 1H), 6.47 (m, 4H), 2.52 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ 138.21, 137.43, 137.29, 133.66, 133.54, 133.33, 132.74, 132.69, 131.67, 131.35, 129.38, 128.64, 128.08, 126.30, 125.95, 124.93, 123.66, 122.68, 15.24, 15.17; HRMS: m/z calcd for ($C_{22}H_{22}S_2$): 350.1163, found: 350.1169.



1-(3-(methylthio)phenyl)-10-(4-(methylthio)phenyl)-deca-1,3,5,9-pentaene : General HWE procedure was followed. The product was prepared from the corresponding trienal and dimethyl 4-(methylthio)benzyl phosphonate and was isolated by recrystallization from CH_2Cl_2/MeOH as a light orange solid in 40% yield. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 (bs,1H), 7.25(d,J=87.7 Hz,1H), 7.20 (m, 3H), 7.12 (d, J=7.7 Hz,1H), 6.91-6.79 (m, 2H), 6.54 (d,J=15.5 Hz, 1H), 6.53 (d,J=15.5 Hz, 1H), 6.49-6.37 (m,6H), 2.51 (s,3H), 2.50 (s,3H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ 138.21, 137.44, 137.26, 133.69, 133.63, 133.31, 133.23, 132.90, 132.79, 131.73, 131.59, 131.35, 129.41, 128.64, 128.14, 126.29, 125.95, 124.94, 123.66, 122.68, 15.24, 15.18; HRMS could not be obtained due to insolubility in methanol.

References:

1. J. S. Meisner, S. Ahn, S. V. Aradhya, M. Krikorian, R. Parameswaran, M. Steigerwald, L. Venkataraman and C. Nuckolls, *J Am Chem Soc*, 2012, **134**, 20440-20445.
2. S. V. Aradhya, J. S. Meisner, M. Krikorian, S. Ahn, R. Parameswaran, M. L. Steigerwald, C. Nuckolls and L. Venkataraman, *Nano Lett.*, 2012, **12**, 1643-1647.
3. J. S. Meisner, D. F. Sedbrook, M. Krikorian, J. Chen, A. Sattler, M. E. Carnes, C. B. Murray, M. Steigerwald and C. Nuckolls, *Chemical Science*, 2012, **3**, 1007-1014.