Supplementary Information

Molecular Diodes Enabled by Quantum Interference

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Synthesis Details:

General: Proton nuclear magnetic resonance (\textsuperscript{1}H NMR) spectra and carbon nuclear magnetic resonance (\textsuperscript{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\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}: $\delta$ 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\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}: $\delta$ 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\textsuperscript{1, 2}. Here we describe procedures for preparing molecules 4-5.

\[ \text{MeS} \]

7-(3-(methylthio)phenyl)hepta-2,4,6-trienal: General Wittig homologation procedure described previously.\textsuperscript{3} HRMS: m/z calcd for (C\textsubscript{14}H\textsubscript{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\(_2\)Cl\(_2\)/MeOH as a yellow solid in 49% yield.\(^1\)\(^1\)H NMR (500 MHz, C\(_2\)D\(_2\)Cl\(_4\)): \(\delta\) 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); \(^1\)\(^3\)C NMR (125 MHz, C\(_2\)D\(_2\)Cl\(_4\)): \(\delta\) 138.21, 137.43, 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, 15.17; 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\(_2\)Cl\(_2\)/MeOH as a light orange solid in 40% yield.\(^1\)\(^1\)H NMR (500 MHz, C\(_2\)D\(_2\)Cl\(_4\)): \(\delta\) 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,J=6H), 2.51 (s, 3H), 2.50 (s, 3H); \(^1\)\(^3\)C NMR (125 MHz, C\(_2\)D\(_2\)Cl\(_4\)): \(\delta\) 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:

