Supporting Information

Bulk Photovoltaic Effect in Organic Polar Crystal

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Table of Contents

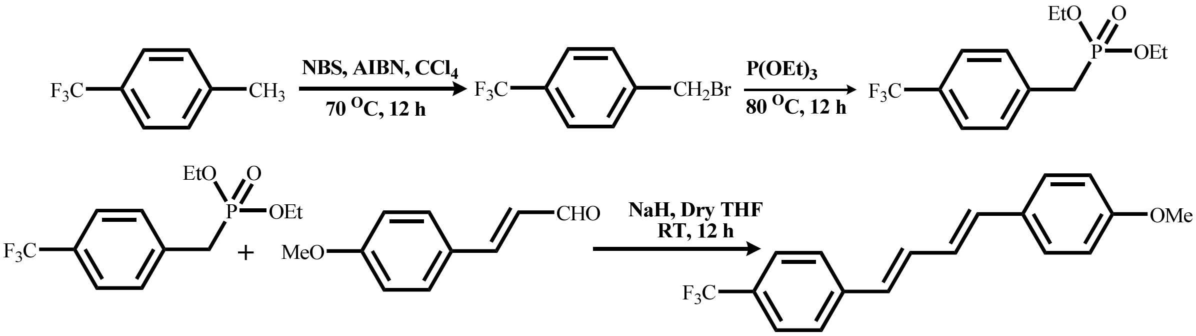
S1. Experimental Techniques

IR spectra were recorded on a Nicolet Impact, Bomem MB Series 400 D Fourier transform infrared (FT-IR) spectrometer. NMR spectra were measured on Bruker DPX 300/500 MHz spectrometers. Tetramethylsilane (TMS) was used as the internal standard, and chloroform-d ($CDCl_3$) was used as the solvent. High-resolution mass spectral (HRMS) analysis was obtained from JEOL JMS600 instrument. Absorption spectra were recorded on a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer. The excitation and emission spectra were recorded on a SPEX Fluorolog F112X spectrofluorimeter. Fluorescence quantum yields, with an estimated reproducibility of around 10%, were determined by comparison with 9, 10 diphenyl anthracene in ethanol (0.95), which was used as the fluorescence standard. Single crystal analyses were carried out in a Bruker SMARTCCD diffractometer, structure determination and refinement was carried out with SAINT (SAINTPLUS Version 6.22, Bruker AXS, Madison, WI) and SHELXTL1 software packages, and the empirical absorption correction was carried out with the SADABS program. For crystal structure visualization, Mercury (CSD software) and Chem Craft were used. To obtain the electronic structure of **1**, HOMO and LUMO orbitals were calculated using the B3LYP/6-31G(p,d) functional by adopting a molecular geometry obtained from single crystal X-ray diffraction experiments.

Photocurrent and voltages were measured using the UV output of a continuous wave argon ion laser (Spectra-Physics model 2020). Currents and voltages were measure using a lockin-in amplifier (Stanford Research SR830 operated in either current of voltage mode) using mechanical modulation of the incoming beam (Stanford Research SR540).

S2. Synthesis and Characterization

1 was synthesised by the Wittig Horner reaction between the 4-methoxycinnamaldehydes and the corresponding phosphonate esters using NaH as base in dry tetrahydrofuran (THF) as indicated in Scheme S1. The compounds were purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and hexane/ethyl acetate mixture as the eluent. The structures of these derivatives were confirmed using IR, NMR and high resolution mass spectrometry (HRMS).



Scheme S1. Detailed synthetic procedure of **1**.

S2.I Synthesis of 1-(bromomethyl)-4-(trifluoromethyl) benzene

p-triflouromethyltoluene (2 gm) and N- bromosuccinimide (1.1 eq.) were taken in a round bottom flask, added 25 mL of dry CCl_4 and stirred for 5 minutes. Catalytic amount of AIBN was added and the mixture was refluxed at 70 ^{o}C for 12 hrs. The reaction mixture then cooled and filtered off the white byproduct generated. The filtrate was concentrated and dried.

Yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 4.481(s, 2H, CH_2Br), 7.508(d, 2H, aromatic), 7.650(d, 2H, aromatic), ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 33.48, 112.21, 124.37, 129.73, 132.60, 142.83. MS (FAB^{+}) M/Z 239.2 (M^{+})

S2.II. Synthesis of diethyl 4-(trifluoromethyl)benzylphosphonate

4-trifluoromethylbenzylbromide (14.98 g, 76.82 mmol) and Triethyl phosphite (15.3 mL, 92.18 mmol) were added to a 250 mL RB and heated to 100 °C for 12 hrs. After 12 hrs temperature was raised to 130 °C and excess Triethylphosphite was removed by purging argon. Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.27(t, 6H, CH_3), 3.23(d, 2H, CH_2PO), 4.04(q, 4H, OCH_2), 7.428(d, 2H, aromatic), 7.624(d, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 16.36, 34.65, 62.44, 110.88, 124.69, 130.57, 132.26, 137.59. MS (FAB^+) M/Z 295.2 (M^+).

S2.III. Synthesis of 1-methoxy-4-((1E, 3E)-4-(4- (trifluoromethyl) phenyl) buta-1,3-dienyl)benzene (1)

Diethyl 4-(trifluoromethyl)benzylphosphonate and 4-methoxycinnamaldehyde (1:1 ratio) were taken in a two necked RB flask and were dissolved in dry THF under argon atmosphere. The solution was then cooled to 0 ^{o}C. NaH (1.6 eq) in paraffin oil was added to the above mixture and the reaction was allowed to stir for 12 hrs. THF was evaporated and the reaction mixture was poured to ice cold water. The product precipitated was filtered and dissolved in $CHCl_3$. Concentrated and purified by column chromatography using silica (100-200 mesh) as the stationary phase and 5% Ethylacetate: Hexane as the eluent.

1: ^{1}H NMR (500 MHz, $CDCl_3$): d 0.86-0.89 (m, 6H, CH3), 1.29-1.88 (m, 24H, CH_2), 3.98-4.05 (m, 4H,OCH_2), 6.57-6.62 (d, 1H, olefinic), 6.65-6.77 (dd, 1H, olefinic), 6.70-6.82 (dd, 1H, olefinic), 6.85 (s, 1H, aromatic), 6.96-6.98 (d, 1H, aromatic), 6.98-7.02 (d, 1H, aromatic), 7.02-7.07 (d, 1H, olefinic), 7.46-7.49 (d, 2H, aromatic), 7.57-7.60 (d, 2H, aromatic) ppm; 13C NMR (75 MHz, CDCl3): d 14.08, 19.994, 22.65, 26, 29.22, 29.26, 31.80, 69.2, 69.36, 111. 54,113. 52, 120.51, 126.31, 126.46, 129.33, 132.4, 133.12, 135.54, 136.11 ppm

S3. Single Crystal Structure

Single crystals of **1** could be grown at room temperature using Tolune-Chloroform (20:80 vol %) solvent mixtures. The single crystal data of **1** are summarized in **Table S1**.

Table S1. Summary of crystallographic data for **1**.

Empirical Formula	$C_{18}H_{15}F_3O$
Molecular Weight	304.30
Crystal System	Orthorhombic
Space Group	*Pca2(1)*
Z	4
a, Å	a = 6.2444(6)
b, Å	b = 7.3727(7)
c, Å	c = 31.712(3)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1460.0(2)
d_{calc}, g/cm^3	1.384
Total Reflections	8224
Unique Reflections	1726
R_{int}	0.0243
Final R indices $R1$, $wR2$	0.0753, 0.2137

1 has four molecules per unit cell (Figure S1) in which the molecules arranged in two non-equivalent stacks A and B with the molecules arranged in a herringbone fashion (Figure S1).

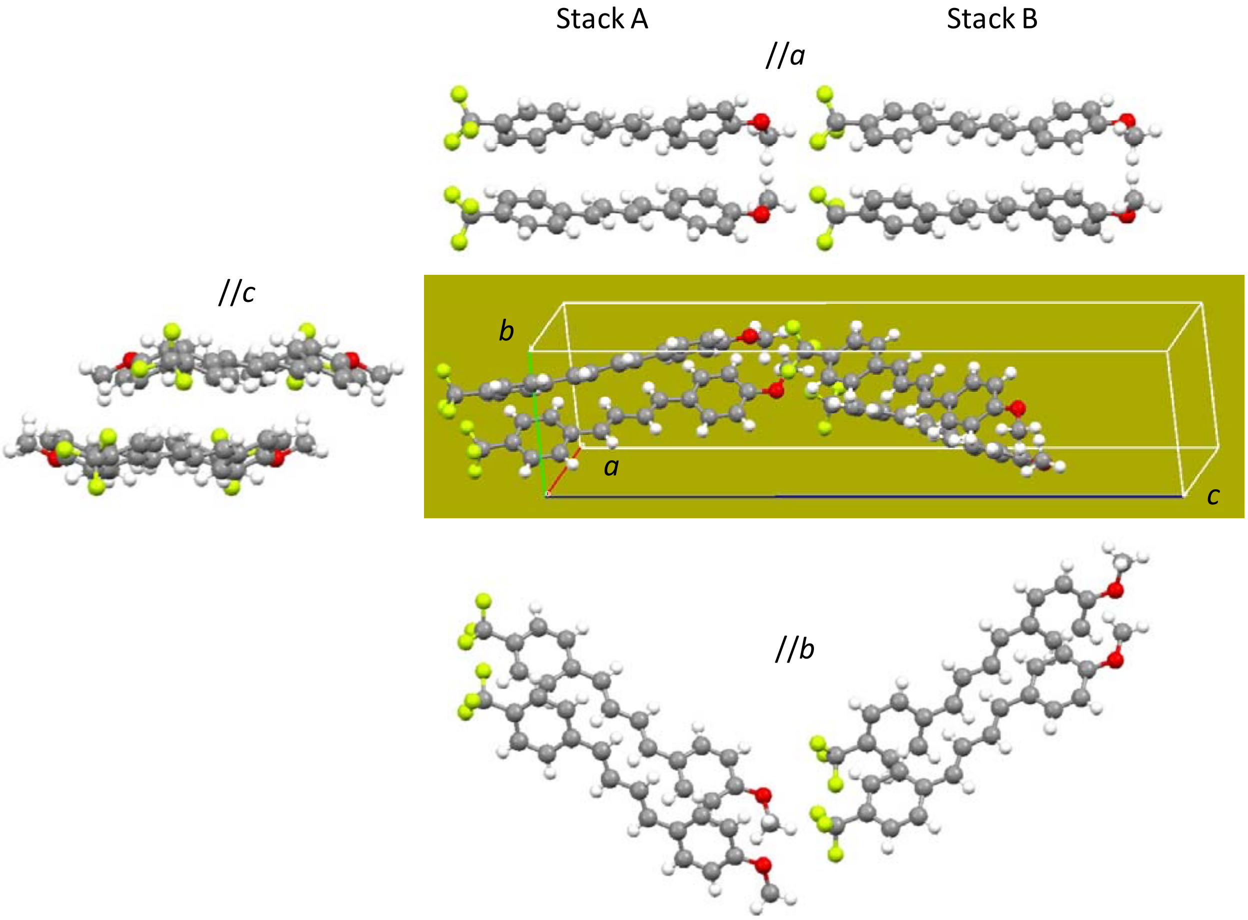


Figure S1. Projections of the unit cell packing of **1** along the three different crystallographic axes