Supporting Information

D-π-A1-π-A2 push pull small molecule donor for solution processed bulk heterojunction organic solar cells

Prabhat Gautam,[1] Rajneesh Misra,*[1] , S. Biswas[2], Ganesh D. Sharma*[2]

[1]Department of Chemistry, Indian Institute of Technology, Indore (MP) 452017

[2]Molecular Electronic and Optoelectronic Device Research Laboratory

Department of Physics

The LNM Institute of Information technology

Jamdoli, Jaipur 302031 (Raj), India

Table of Contents

I. Experimental Section: Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on on the Bruker Avance (III) 400 MHz instrument by using $CDCl_3$. Chemical shifts for ^{1}H NMR spectra are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard {$CDCl_3$, 7.26 ppm}. Chemical shifts for ^{13}C NMR spectra are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as internal standard {$CDCl_3$, 77.0 ppm}. The ^{1}H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". Thermogravimetric analyses were performed on the Metler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from HoribaYovin (model: FM-100). The excitation and emission slits were 2/2 nm for the emission measurements. All of the measurements were done at 25°C. The density functional theory (DFT) calculation were carried out at the B3LYP/6-31G** level for C, N, S, H in the Gaussian 09 program. HRMS was recorded on Brucker-Daltonics, micrOTOF-Q II mass spectrometer.

Preparation of TPA-BTD-NPI.

To a stirred solution of the TPA-BTD-Br (1 mmol), 2-butyl-6-ethynyl-1H-benzo[*de*]isoquinoline-1,3(2H)-dione (1 mmol) in THF, and TEA (1:1, v/v) were added [$PdCl_2(PPh_3)_2$] (20 mg, 0.028 mmol) and CuI (4 mg, 0.02 mmol) under an argon flow at room temperature. The reaction mixture was stirred for 12 h at 70 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure, and the mixture was purified by SiO_2 chromatography with DCM/hexane (2:1, v/v), to obtain **TPA-BTD-NPI**. Red

solid (460 mg, Yield: 68%); ^{1}H NMR (400 MHz, ($CDCl_3$, δ in ppm): 9.05 (d, J = 8.5 Hz, 1H), 8.68 (d, J = 6.5 Hz, 1H), 8.62 (d, J = 6.8 Hz, 1H), 8.08 (d, J = 6.2 Hz, 1H), 7.95-7.91 (m, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.3 Hz, 2H), 7.33–7.29 (m, 4H), 7.16–7.03 (m, 8H), 4.20 (t, J = 7.8 Hz, 2H), 1.77-1.69 (m, 2H), 1.50-1.41 (m, 2H), 0.98 (t, J = 7.52 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 163.9, 163.7, 154.5, 154.4, 148.9, 146.9, 133.1, 133.0, 132.6, 131.8, 131.7, 131.66, 131.0, 129.5, 128.0, 127.8, 126.8, 125.3, 124.0, 123.0, 122.7,121.6, 119.0, 115.33, 114.6, 99.5, 94.7, 93.8, 84.9, 40.4, 30.2, 20.4, 13.8 HRMS (ESI-TOF) *m/z* calcd for $C_{44}H_{30}O_2N_4S$ + H: 679.2162 $[M + H]^+$, found 679.2175 $[M + H]^+$.

Melting point of TPA-BTD-NPI is 232–233 °C.

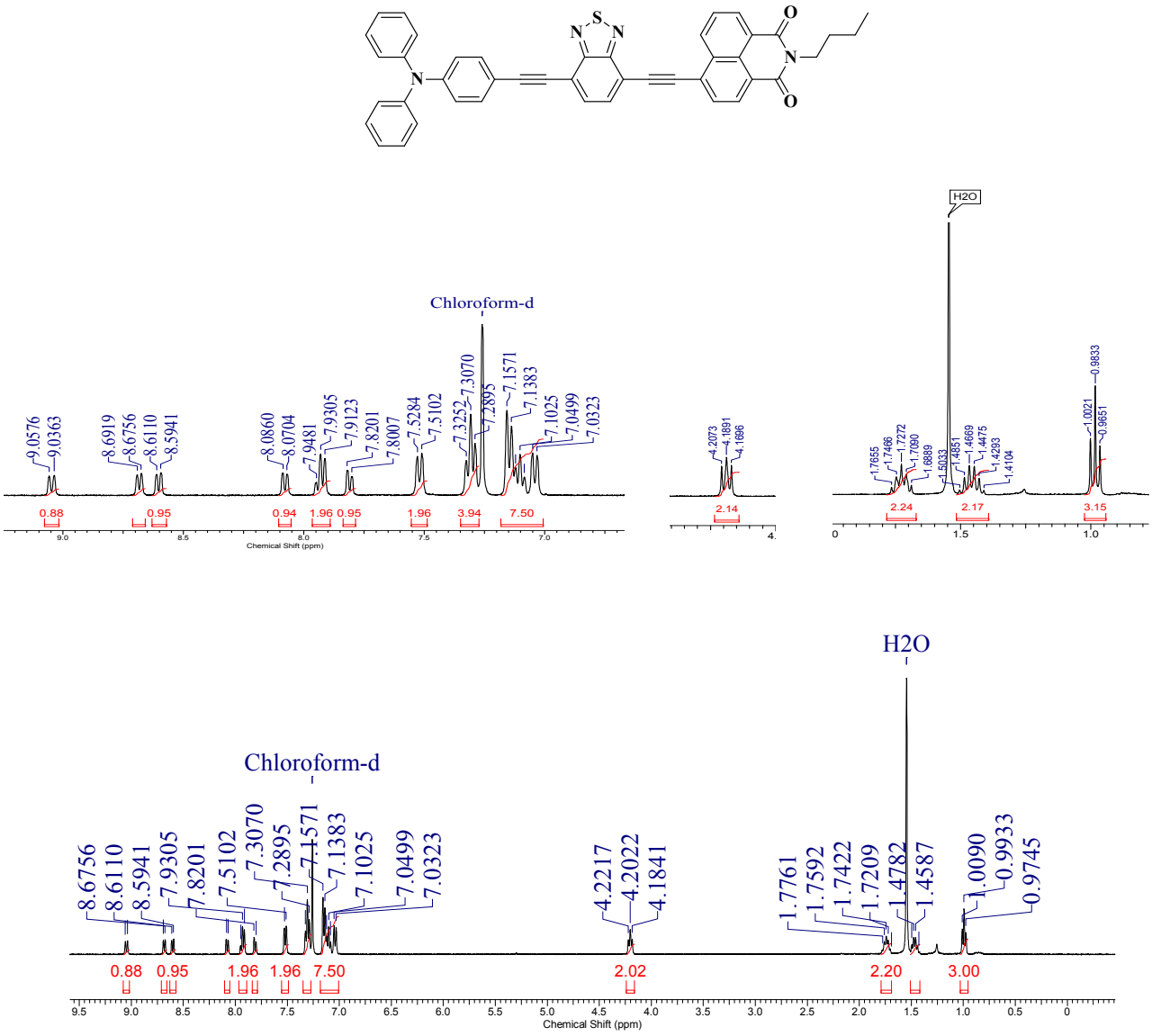

Figure S1 ^{1}H NMR of TPA-BTD-NPI

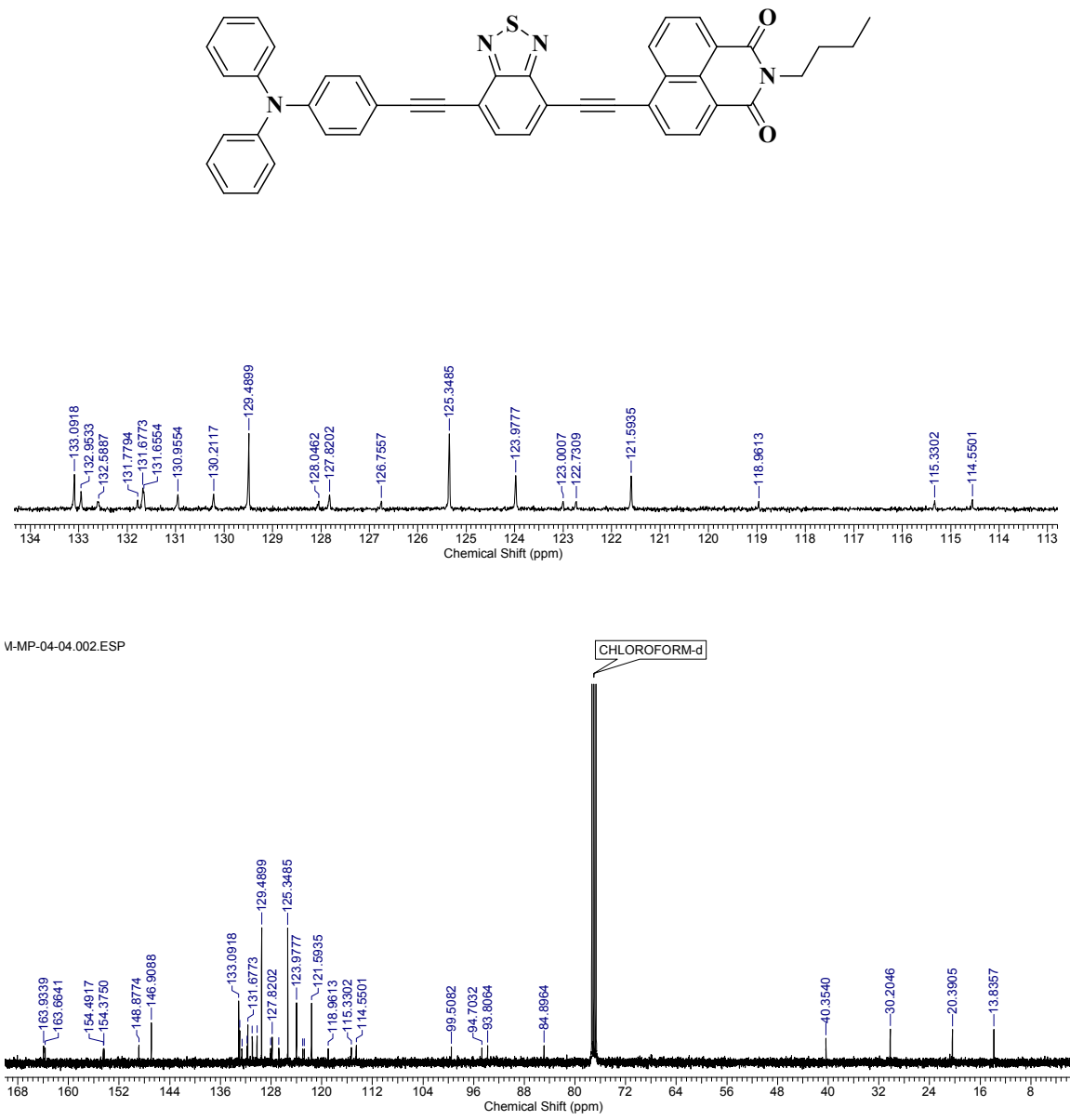

Figure S2 ^{13}C NMR of TPA-BTD-NPI

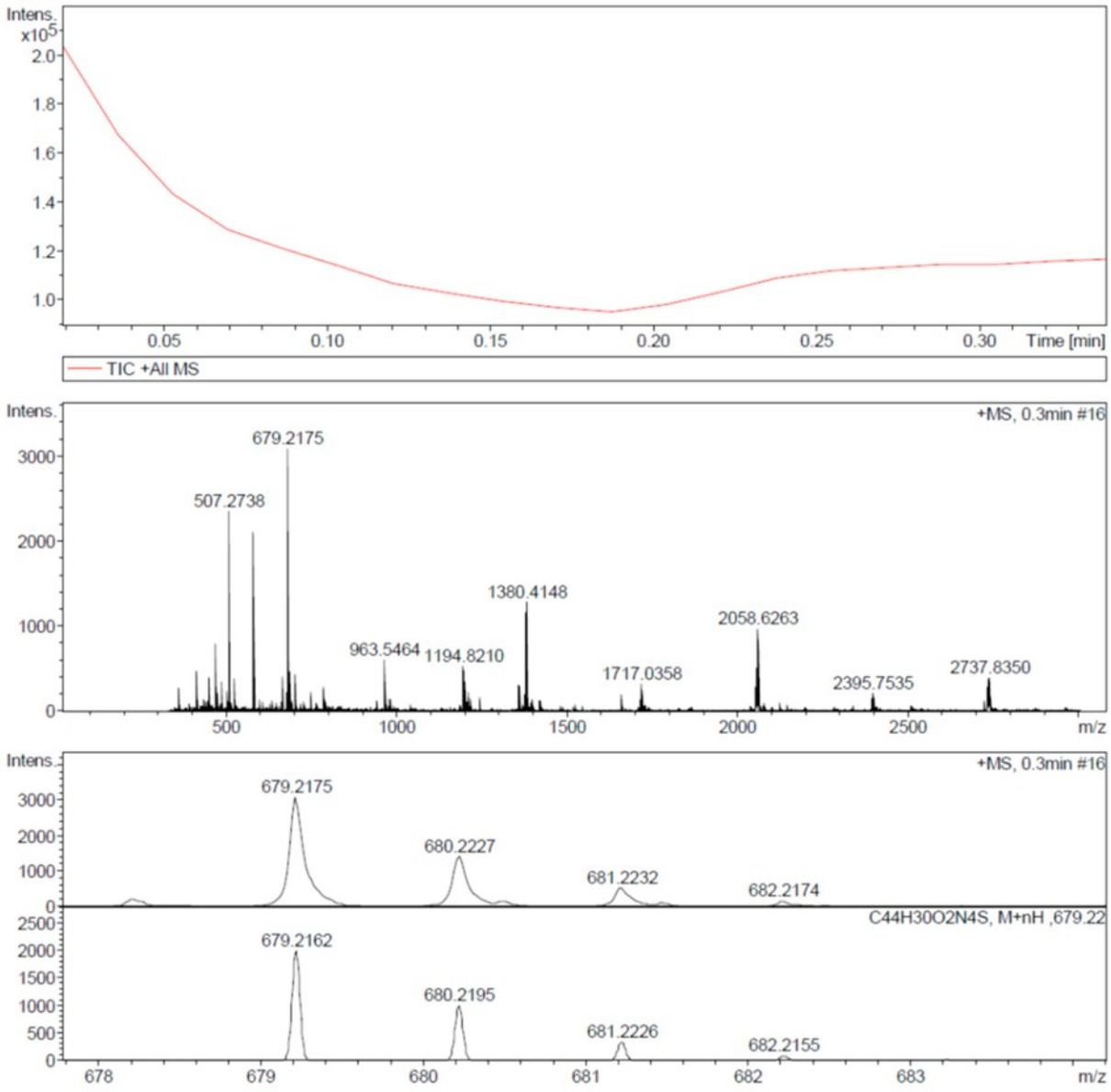

Figure S3 Full HRMS of TPA-BTD-NPI

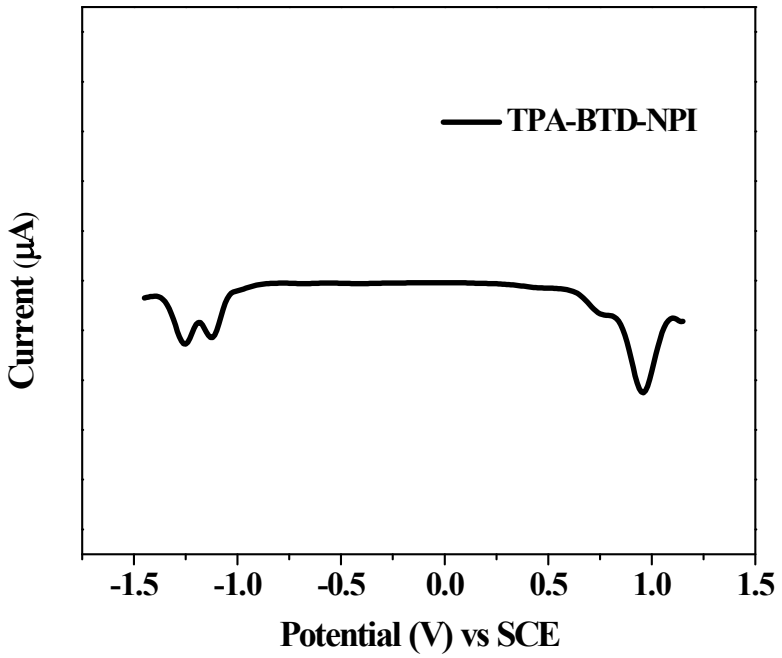

Figure S4b. Differential pulse voltammogram of ferrocenyl BTDs **5a**, and **5b** at 0.01 M concentration in 0.1 M Bu_4NPF_6 in dichloromethane recorded at 50 mVs^{-1} scan speed.