

Synthesis of a Quinoidal Dithieno[2,3-d;2',3'-d]benzo [2,1-b;3,4-b']-dithiophene based Open-Shell Singlet Biradicaloid

Debin Xia,^{a, b†} Ashok Keerthi,^{b, c†} Cunbin An^b, and Martin Baumgarten^{*b}

^aMIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 150001 Harbin, China.

^bMax Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

^cSchool of Physics and Astronomy, Condensed Matter Physics Group, the University of Manchester, M13 9PL Manchester, UK

† These authors contributed equally to this work.

*E-mail: martin.[baumgarten@mpip-mainz.mpg.de](mailto:martin.baumgarten@mpip-mainz.mpg.de)

Table of Contents

Experimental section	2
DHB-QDTB chemical structure	4
TGA spectrum	4
EPR measurement	5
DFT calculations	6
DSC spectra	7
Proposed polymer structure	8
IR spectra.....	9
Crystal data.....	10
References	11

Experimental section

General Methods: ^1H NMR spectra were recorded in deuterated solvents on Bruker DPX 500 instrument. Electrochemistry was carried out on a computer-controlled GSTAT12 in a three-electrode cell in dichloromethane solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature. A platinum wire, a silver wire, and a glassy carbon electrode were used as counter electrode, the reference electrode, and the working electrode, respectively. The energy levels were estimated from the half potential of the first reduction peak and the first oxidation peak through the equation $E_{LUMO} = - [E_{red\ onset} - E_{1/2 (Fc+/Fc)} + 4.8]$ eV and $E_{HOMO} = - [E_{oxd\ onset} - E_{1/2 (Fc+/Fc)} + 4.8]$ eV, using ferrocene as an internal standard.¹ Infrared spectroscopy was measured on a Nicolet 730 FT-IR spectrometer equipped with an attenuated total reflection (ATR) setup. The samples were deposited as pristine material on the diamond crystal and pressed on it with a stamp. Measurements with a scan number of 128 were recorded for each sample and the background was subtracted. MALDI-TOF mass spectra were recorded on a Bruker Reflex II matrix-assisted laser desorption time-of-flight mass spectrometer (MALDI-TOF), calibrated against a mixture of C60/C70. Thermogravimetry analysis (TGA) was carried out on a Mettler 500 Thermogravimetry Analyzer with heating rates of 10 K/min. Differential scanning calorimetry (DSC) were measured on a Mettler DSC 30 with heating and cooling rates of 10 K/min. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G (d) and UB3LYP/6-31G(d) level using Gaussian 09² and molecular structures were generated using GaussView 5.0.9.³

Synthetic Details: All reagents and starting materials were obtained from commercial suppliers and used without further purification. Column chromatography was performed on silica gel 60 (Macherey-Nagel, Si60) with dichloromethane, hexane, ethyl acetate or tetrahydrofuran (Sigma-Aldrich) as eluent. All reported yields are isolated yields.

In a solution of malononitrile (100 mg, 1.52 mmol) in dry THF (10 mL) was slowly added 60% sodium hydride (91 mg, 2.28 mmol) within 1 h in argon atmosphere at 0 °C. Dibromo aromatic compound, **Br₂-DTmBDT** (140 mg, 0.18 mmol), tetrakis(triphenylphosphine)palladium(0) (21 mg, 0.018 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (20 mg, 0.36 mmol) were added, followed by the adding of 10 mL THF and the mixture was reflux for 15 h. After cooling to room temperature, the reaction mixture was treated with water (5 mL) and 2 M hydrochloric acid (6 mL); the resulting mixture was stirring around 1 h and the THF was evaporated. The left small amount of water was taken away by pipette. Methanol (20 mL) was added. The 145 mg intermediate was collected by filtration. This intermediate was thoroughly dissolved in acetonitrile (20 mL). DDQ (227 mg, 1.0 mmol) was added. The mixture was turned to dark blue after the adding of DDQ. The reaction was stopped 10 h later; resulting residue was purified by column chromatography on silica gel with DCM/Hex (2:1) as eluent to afford **4CN-DTmBDT** as gray green color solid in a yield of 68% (93 mg).

¹H NMR (500 MHz, 298 K, C₂D₂Cl₄): δ 7.32 (s, 2H), 2.77 – 2.79 (m, 4H), 1.49 – 1.56 (m, 12H), 1.22 – 1.36 (m, 28H), 0.84 (t, 6H).

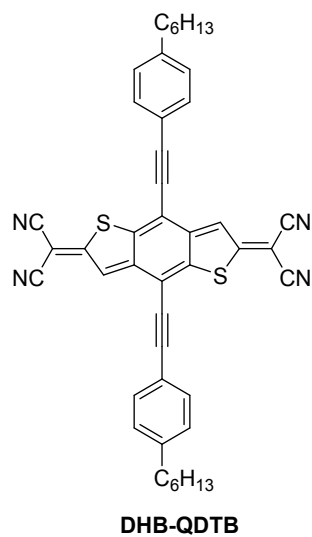
¹³C NMR: No satisfied spectrum was obtained due to its bad solubility and aggregation in common solvents. High-temperature (100 °C) ¹³C NMR spectrum was also measured but a satisfied spectrum cannot be obtained.

HR-MS (MALDI-TOF using TCNQ as matrix) m/z calculated for C₄₄H₅₂N₄S₄ [M⁺] 764.3069. Found 764.3069.

Melting point has not been observed below 300 °C.

Crystallographic data (CCDC deposition number): CCDC. **1414138**

DHB-QDTB chemical structure



Scheme S1. Chemical structure of DHB-QDTB.

TGA spectrum

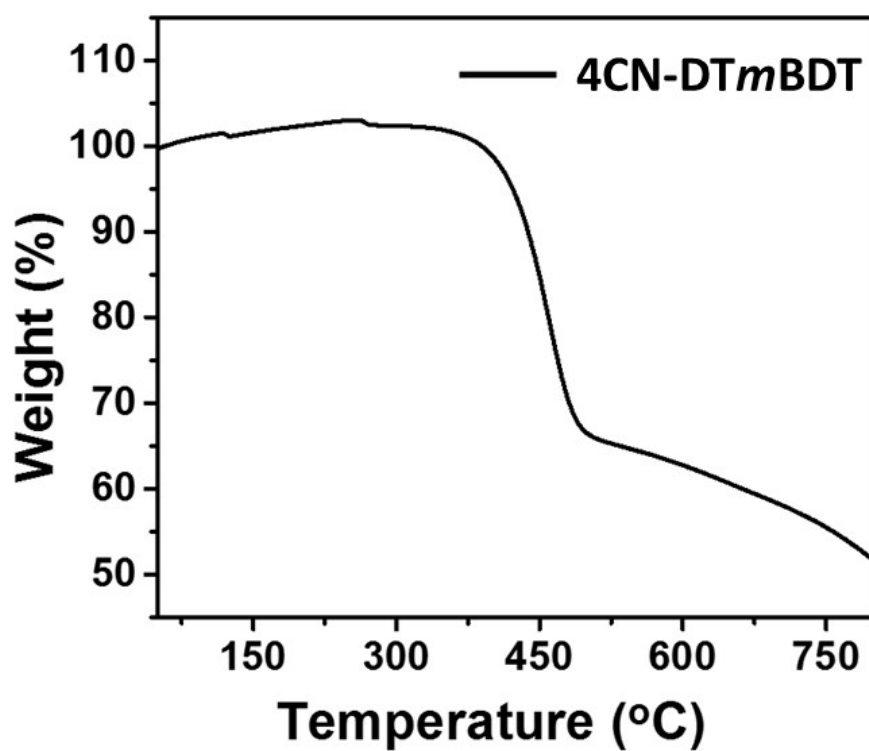


Figure S1 TGA curve of 4CN-DTmBDT.

EPR measurement

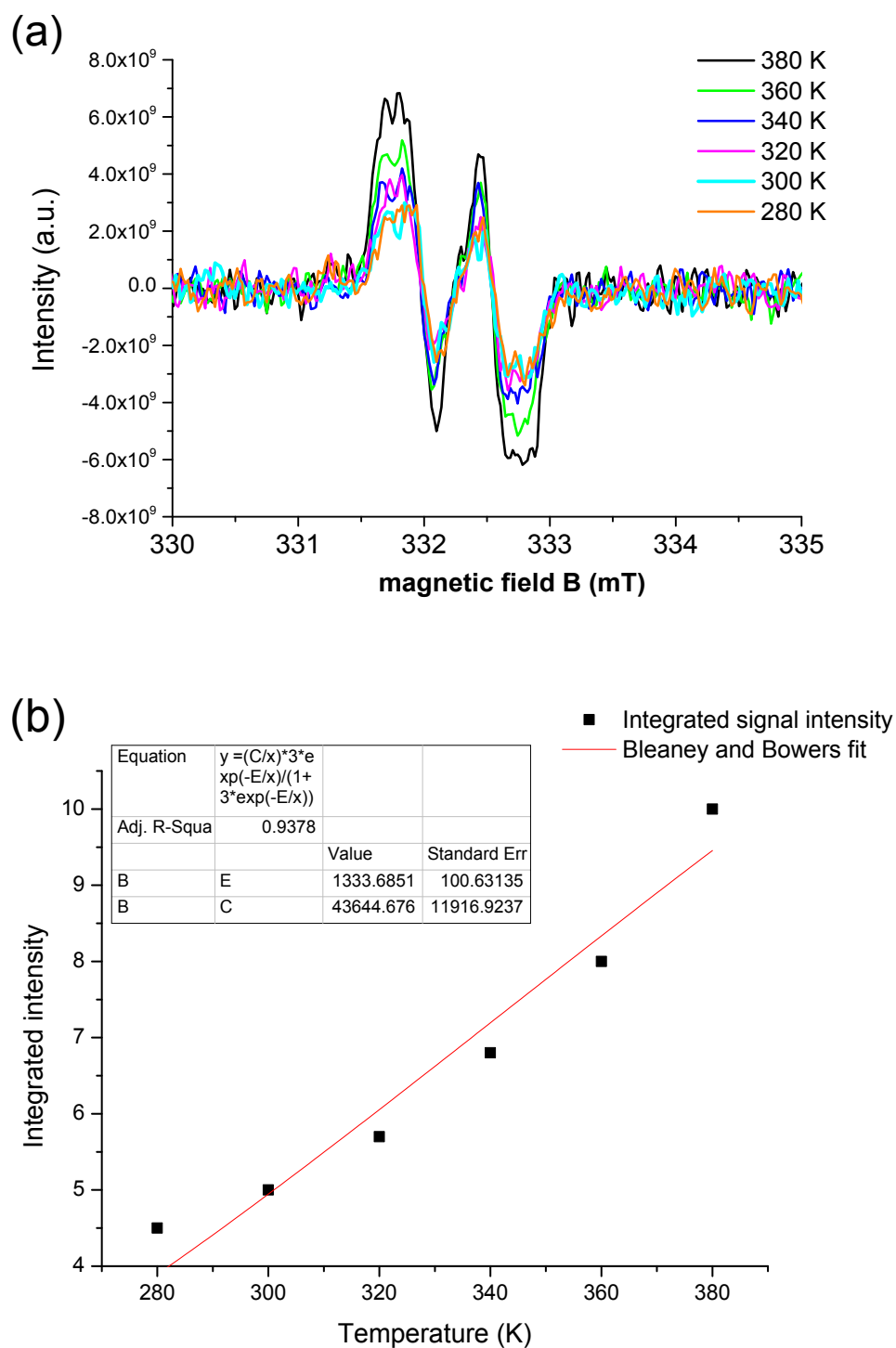


Figure S2. (a) EPR spectra of 4CN-DTmBDT in tetrachloroethane-D₂ solution at different temperature and (b) change in signal intensity with temperature (black dot) and Bleaney and Bowers fit (red line).

DFT calculations

Table S1. Energy difference between closed-shell singlet and the open-shell singlet.

E closed-shell (kcal/mol)	E T (kcal/mol)	E BS (kcal/mol)	E(BS)-E(T) (kcal/mol)	S ² (T)	S ² (BS)	S ² (T)-S ² (BS)	E _{ST} (kcal/mol)
-1665906.99	-1665904.17	-1665908.74	-4.57	2.04	0.72	1.32	-6.88

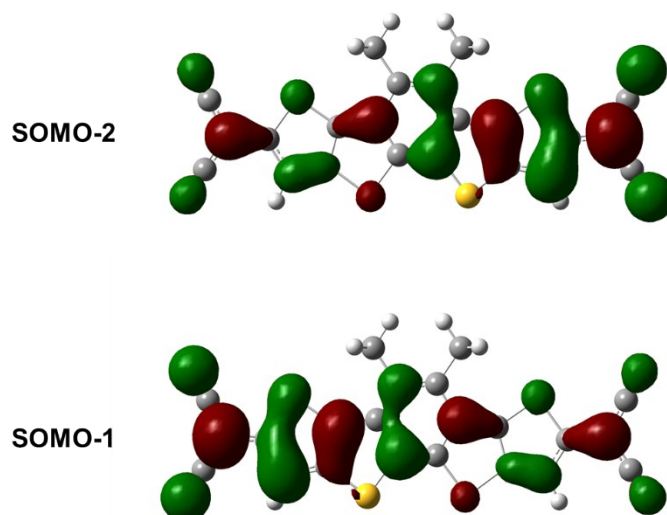


Figure S3. Calculated SOMOs of BS singlet **4CN-DTmBDT** using DFT Gaussian UB3LYP /6-31G (d) level.

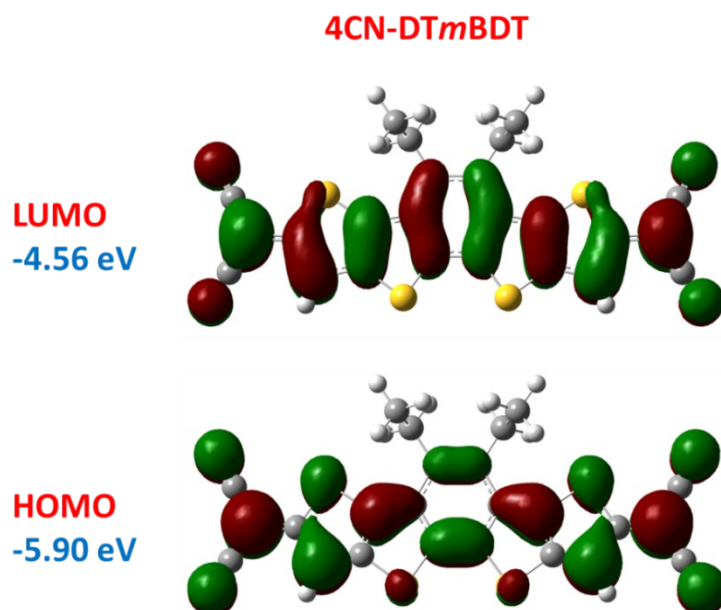


Figure S4. Calculated energy levels of closed-shell quinoidal **4CN-DTmBDT** using DFT Gaussian B3LYP /6-31G (d) level.

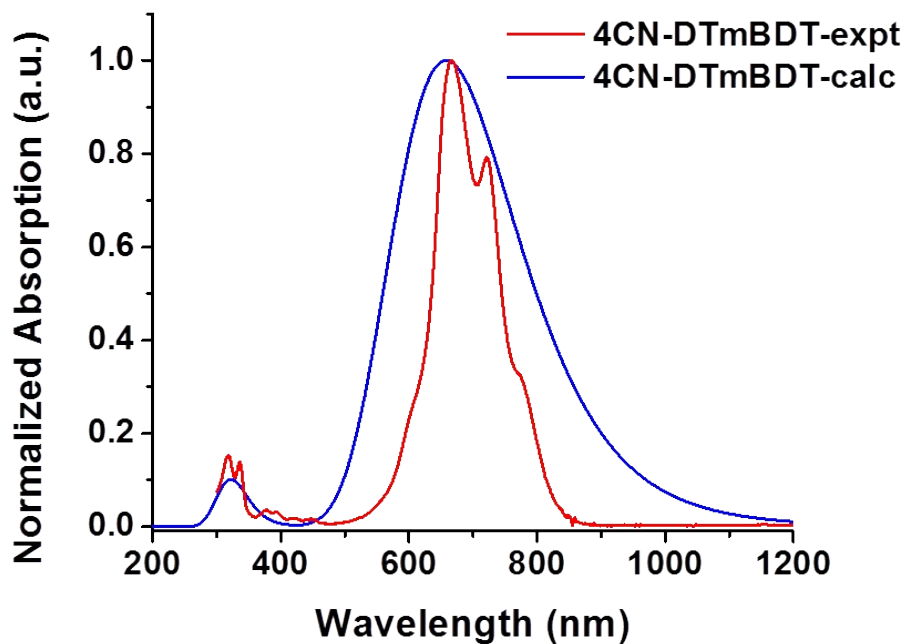


Figure S5. Calculated UV-vis absorption spectra [using TD-SCF, B3LYP/6-31G(d)] and experimental UV-vis absorption spectra of 4CN-DT*m*BDT.

DSC spectra

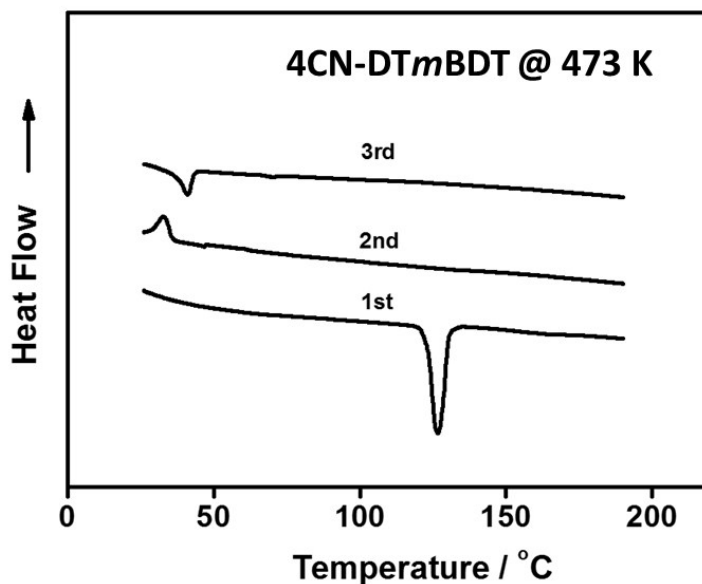


Figure S6. DSC thermograms of 4CN-DT*m*BDT heated up to 473 K with 10 K/min heating rate under N₂ atmosphere.

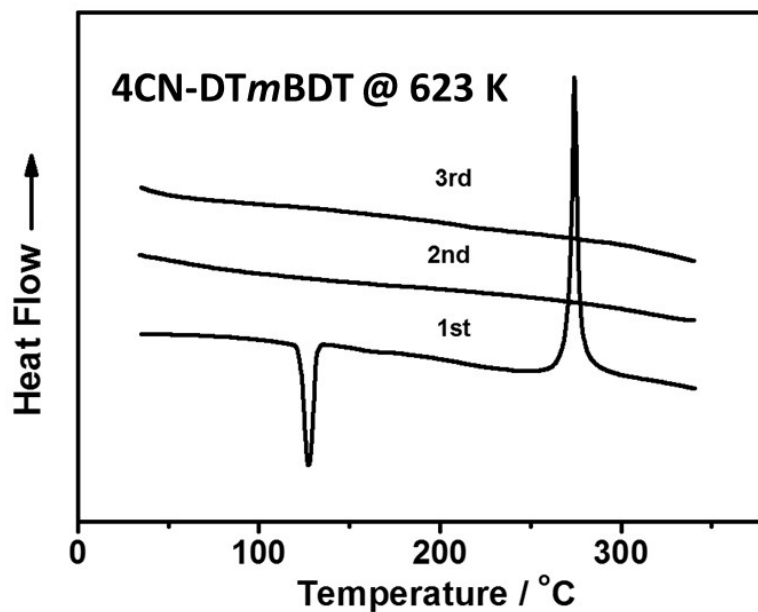


Figure S7. DSC thermograms of **4CN-DTmBDT** heated up to 623 K with 10 K/min heating rate under N₂ atmosphere (polymerized).

Proposed polymer structure

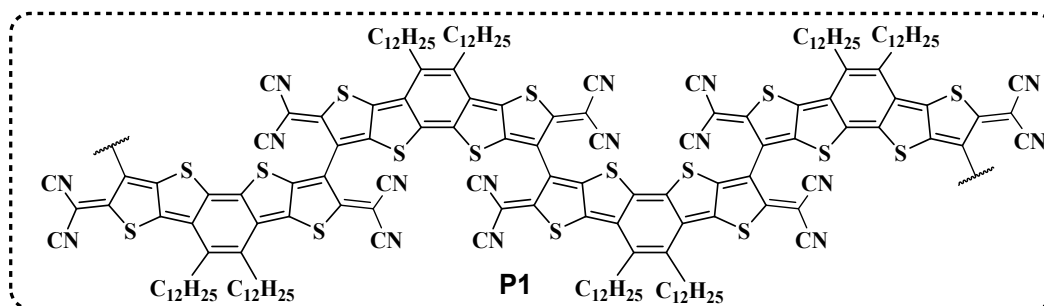


Figure S8. Proposed polymer structure.

IR spectra

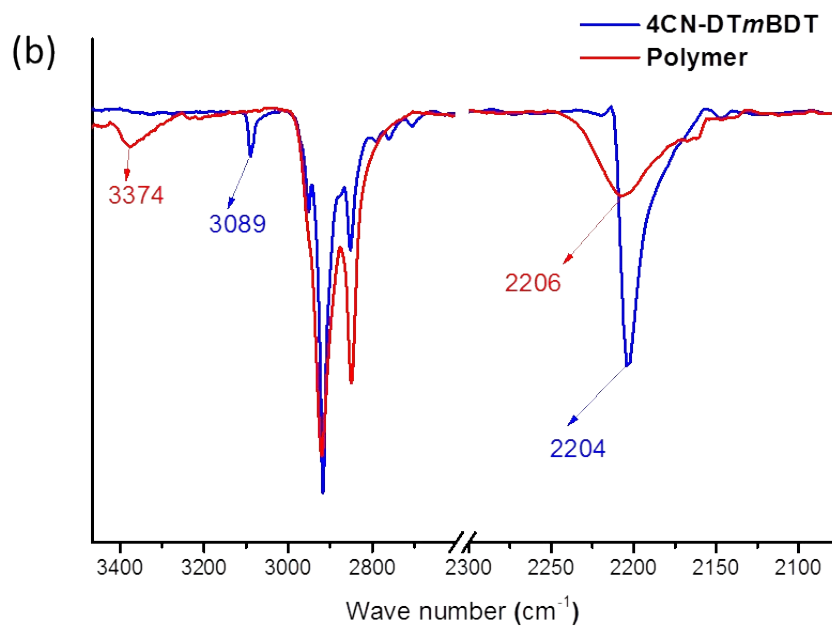
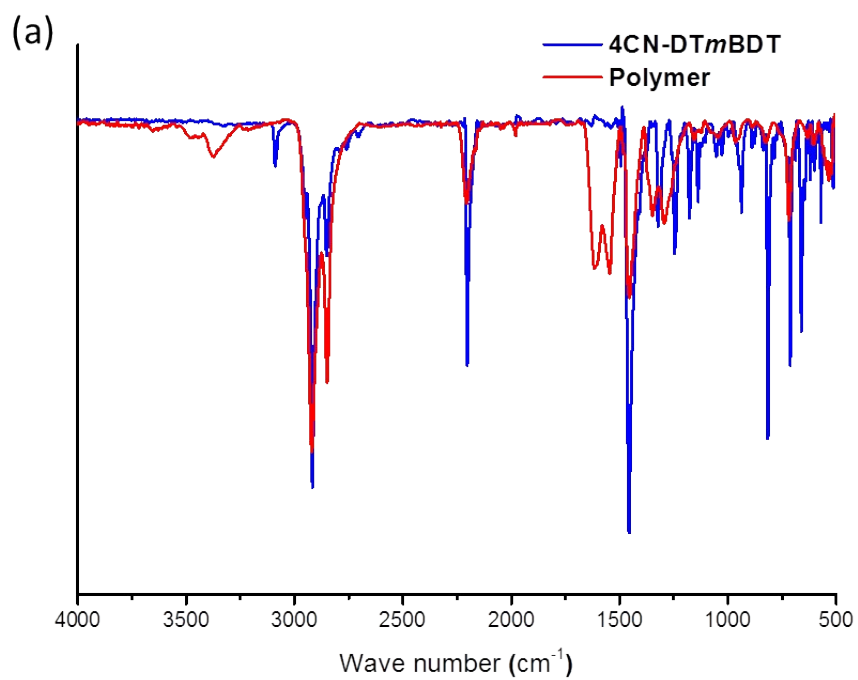


Figure S9. IR spectra of **4CN-DTmBDT** and **Polymer** (formed at 623 K).

Crystal data

Cambridge Crystallographic Data Centre deposition number: CCDC 1414138

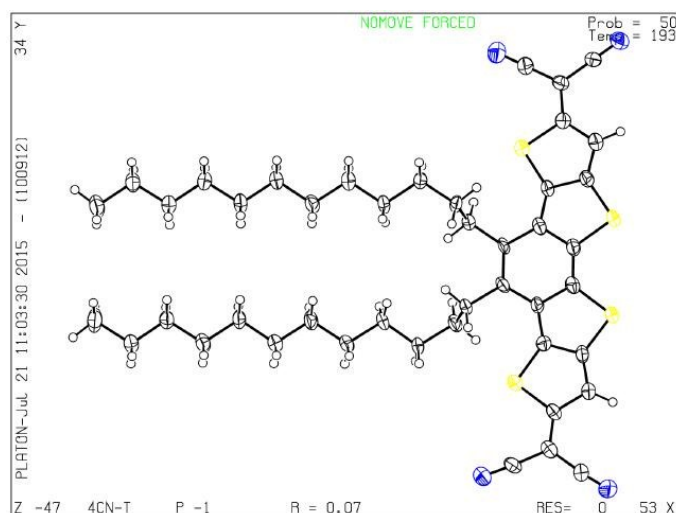


Table S2. Crystallographic table.

Compound	4CN-DT<i>m</i>BDT
Molecular formula	$C_{44}H_{52}N_4S_4$
Formula weight	765.13 g mol^{-1}
Absorption coefficient	$\mu = 2.427 \text{ mm}^{-1}$
Crystal size	0.02 x 0.02 x 0.16 mm^3 ; blue needle
Space group	P-1 (triclinic)
Lattice parameters	$a = 9.3265 (10) \text{ \AA}$ $\alpha = 78.225 (8)^\circ$ $b = 9.7095 (9) \text{ \AA}$ $\beta = 84.988 (8)^\circ$ $c = 23.593 (2) \text{ \AA}$ $\gamma = 75.520 (8)^\circ$
Volume	2023.6(4) \AA^3
Z value	2
F (000)	816
Calculated density	$d_{\text{xray}} = 1.256 \text{ g cm}^{-3}$
Temperature	-80 $^\circ\text{C}$
Scan type	ω -scans
Theta range for data collection	$1.9^\circ < \theta < 67.6^\circ$
Limiting indices	$-10 \leq h \leq 9, -11 \leq k \leq 11, -28 \leq l \leq 24$
Total number of reflections	21364
Unique number of reflections	6932 ($R_{\text{int}} = 0.1181$)
Observed number of reflections	2517 ($ F /\sigma(F) > 4.0$)
Structure solution	Program: SIR-2004 (Direct methods)
R-values	$wR2 = 0.2042$ ($R1 = 0.0676$ for observed reflections, 0.1924 for all reflections)
Goodness of fit	$S = 0.802$
Max Shift / Error	0.001 * e.s.d
Largest diff. peak and hole	0.37 and -0.52 e \AA^{-3}

References

- (1) Keerthi, A.; An, C.; Li, M.; Marszalek, T.; Ricciardulli, A. G.; Radha, B.; Alsewailam, F. D.; Mullen, K.; Baumgarten, M. *Polym. Chem.* **2016**, *7*, 1545.
- (2) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox; CT, W., Ed.; Gaussian, Inc.: 2009; Vol. Revision A.02.
- (3) Dennington, R.; Keith, T.; Millam, J. *Semichem Inc.*, *Shawnee Mission KS, GaussView, Version 5*, 2009.