Supplementary Material

Synthesis and theoretical investigation of phenanthrodithiophene diimide

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1. Computational details

Quantum-chemical calculations were performed with the Gaussian09 suite[1] employing the CAM-B3LYP density functional in combination with the 6-311G(d,p) basis set. In order to reduce the computational cost, certain molecules were replaced by simplified forms on the basis of a premise that the simplified molecules should have analogous electronic properties as the original ones. Geometry optimizations were performed with tight SCF and convergence criteria and an ultrafine integration grid, applying the GEDIIS optimization algorithm. The nature of each stationary point was confirmed by a frequency analysis. Gibbs free energy is estimated by the sum of the electronic energy and thermal correction to Gibbs free energy (at 298.15 K) attained from frequency calculation. Wiberg bond order was calculated by NBO 5.9 at the same level of theory as geometry optimization. Atomic orbital composition in LUMO was obtained by Hirshfeld method implemented in MULTIWFN 3.3.8.[2] Time−dependent density functional (TDDFT) calculations were performed at the MPW1PW91/6-311G(d,p) level of theory with solvation in CH_2Cl_2 by applying the polarized continuum model (PCM) including the keyword IOP(9/40=2) in order to output information on smaller contributions to each electronic transition.[3]

1. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
2. Tian Lu, Feiwu Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, J. Comp. Chem. 33, 580-592 (2012)
3. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner. J. Comp. Chem., 2008, 29, 839-845.

2. Cartesian coordinates (Å) of the optimized structures

ADTI

C	-3.492510085240	-0.038815325444	-0.049902947334
C	-2.769972572973	-1.165911102473	0.172063076380
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H	6.322329626280	1.144768001248	1.248148494770
H	7.150999939010	-0.305805623523	0.628340845970
H	4.640396729533	-4.822839235558	1.194919966261

PDTI (one isomer)

C	-3.542595845216	-0.006030735869	-0.000213493498
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S	1.015989258643	2.696255036455	1.209948976715
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H	2.831273880563	4.193982396791	1.860719444386
H	-2.829091908593	4.201844569962	-1.844336290800
H	-4.627713720648	2.510493924938	-0.922276609039
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C	3.749121777847	-2.263488160227	-0.464684860988
C	4.989566375720	-0.348498673509	-0.116080277490
N	-5.027653842699	-1.705537503892	0.405544803242
N	5.026288491397	-1.707543580446	-0.410200013799
O	-3.517400981902	-3.425983377552	0.666665845964
O	-5.949274524810	0.366248875217	-0.012779753242
O	3.523134796634	-3.426240477204	-0.676476513050
O	5.946435603798	0.368852732759	0.015665950942
C	-6.249228015091	-2.454637444132	0.606933374091
H	-6.755820455071	-2.130967315724	1.517208764201
H	-6.920907841067	-2.311347826410	-0.239366465546

H	-5.978900857150	-3.504930484446	0.693723898752
C	6.241471099038	-2.466139878082	-0.614505751196
H	7.079213138415	-1.799733734623	-0.419504056408
H	6.274913226444	-3.315502736550	0.067766692510
H	6.297874071255	-2.835853736901	-1.639100656943

PDTI (the other isomer)

C	3.542680826589	0.049605989086	-0.008651165295
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C	1.394125778500	-1.081960630984	0.123073983973
C	0.723857253914	0.158388542339	-0.057232633520
C	1.528122283002	1.281065600734	-0.428716083932
C	2.935217229559	1.245619274726	-0.397754017658
C	0.663916377433	-2.309679191077	0.115083287852
C	-0.723868834434	0.158847771081	0.057503962419
C	-1.394679873512	-1.081109636153	-0.122608037385
C	-0.665292699008	-2.309246260596	-0.115224215242
C	-2.802394246379	-1.076814614346	-0.198463422331
C	-3.542838719097	0.050557542378	0.009728157769
C	-2.935011706913	1.246924475191	0.397927711736
C	-1.527833810407	1.281823603263	0.428703027138
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H	-1.220236455347	-3.230026294152	-0.229152921283
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S	1.013102033474	2.755440069576	-1.206973516830
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PDTI (transition state linking the two isomers)

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C	1.688184423075	1.428437087027	-0.026380422334
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C	3.102387674141	3.540157765832	-0.055226294603
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S	-1.424850569650	3.162360253126	-0.034804385208
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H	3.399440810594	4.577599568585	-0.067977815354
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C	3.655245437941	-2.339664443037	0.009058655776
C	5.039945497117	-0.493984935659	-0.016682693112
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H	-6.121917279869	-3.401702984460	-0.830536146264
H	-6.115630588781	-3.381671462708	0.942213289177

3. NMR spectra

Compounds **1**, **2**, **3**, and **4** have been reported in the literature.[4–9]

4. Guo, X.; Ortiz, R. P.; Zheng, Y.; Kim, M. G.; Zhang, S.; Hu, Y.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 13685-13697
5. Do, T. T.; Pham, H. D.; Manzhos, S.; Bell, J. M.; Sonar, P. *ACS Appl Mater Interfaces* **2017**, *9*, 16967-16976.
6. Zhao, J.; Li, Q.; Liu, S.; Cao, Z.; Jiao, X.; Cai, Y. P.; Huang, F. *ACS Energy Lett* **2020**, *5*, 367-375.
7. Jeanbourquin, X. A.; Rahmanudin, A.; Yu, X.; Johnson, M.; Guijarro, N.; Yao, L.; Sivula, K. *ACS Appl Mater Interfaces* **2017**, *9*, 27825-27831.
8. Sun, S.; Zhu, C.; Song, D.; Li, F.; Hu, A. *Polym Chem* **2014**, *5*, 1241-1247.
9. Wang, H.; Shi, Q.; Lin, Y.; Fan, H.; Cheng, P.; Zhan, X.; Li, Y.; Zhu, D. *Macromolecules* **2011**, *44*, 4213-4221.

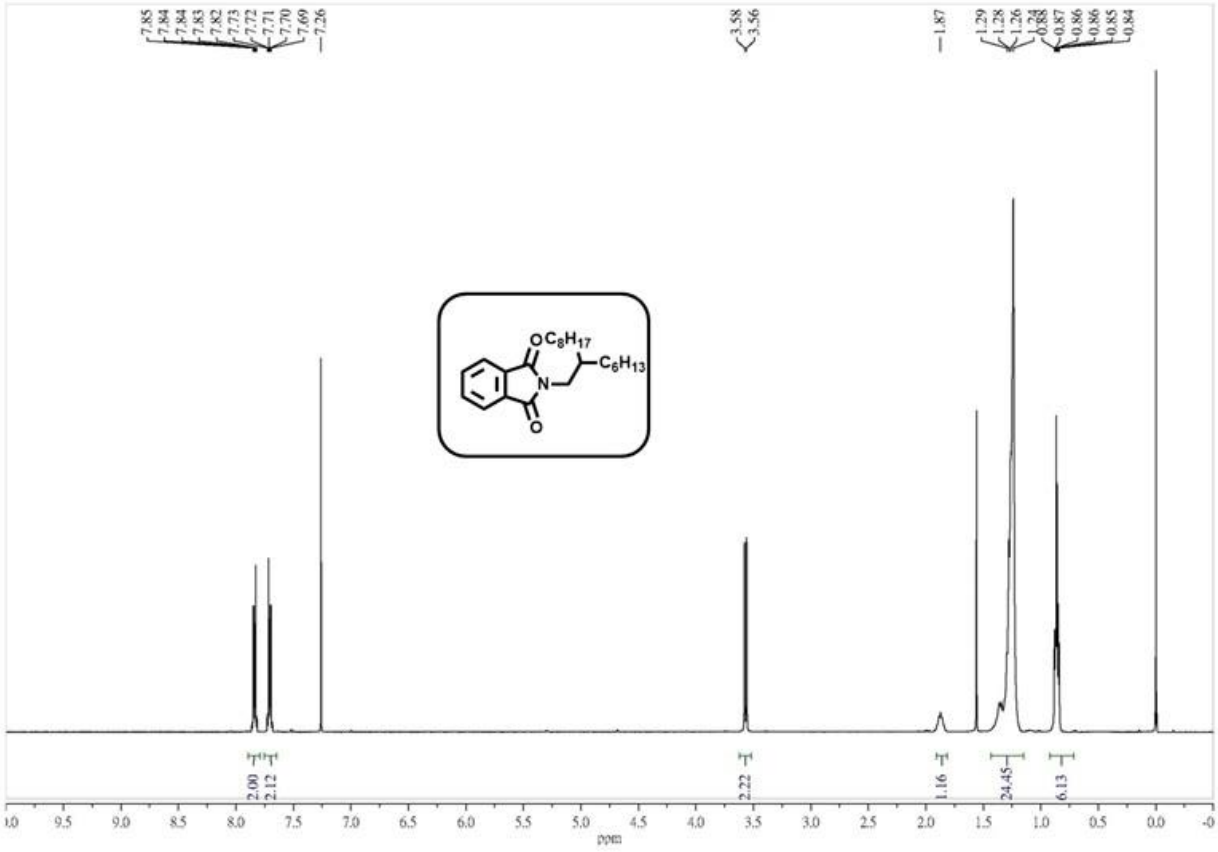

Figure S1. ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$).

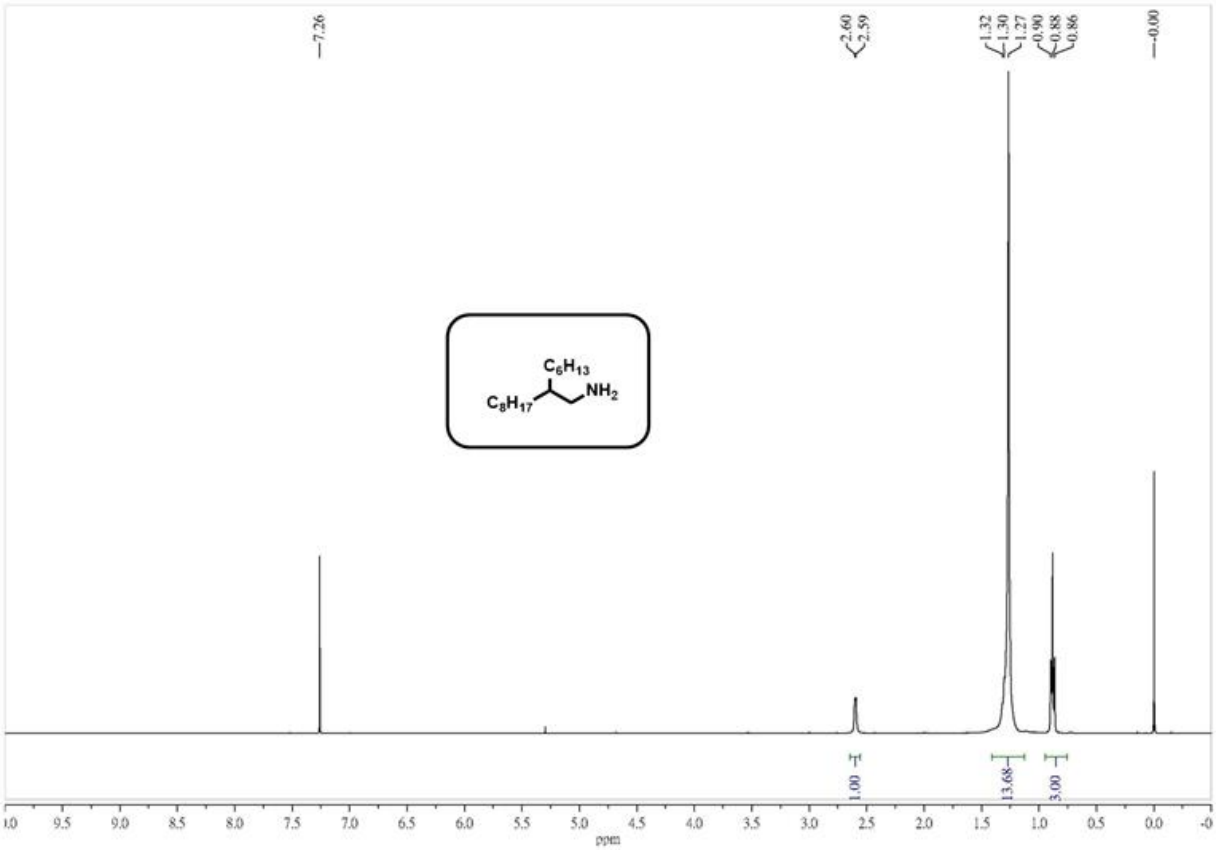

Figure S2. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

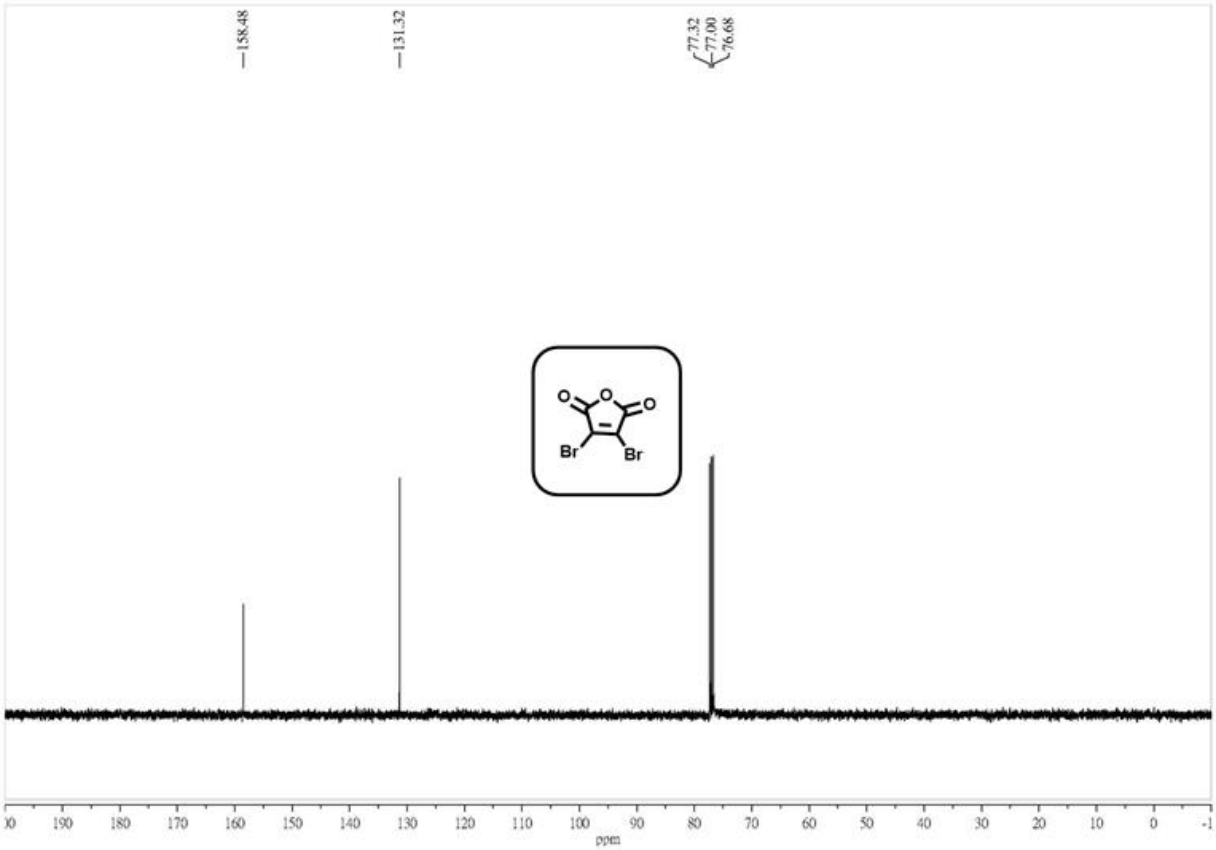

Figure S3. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

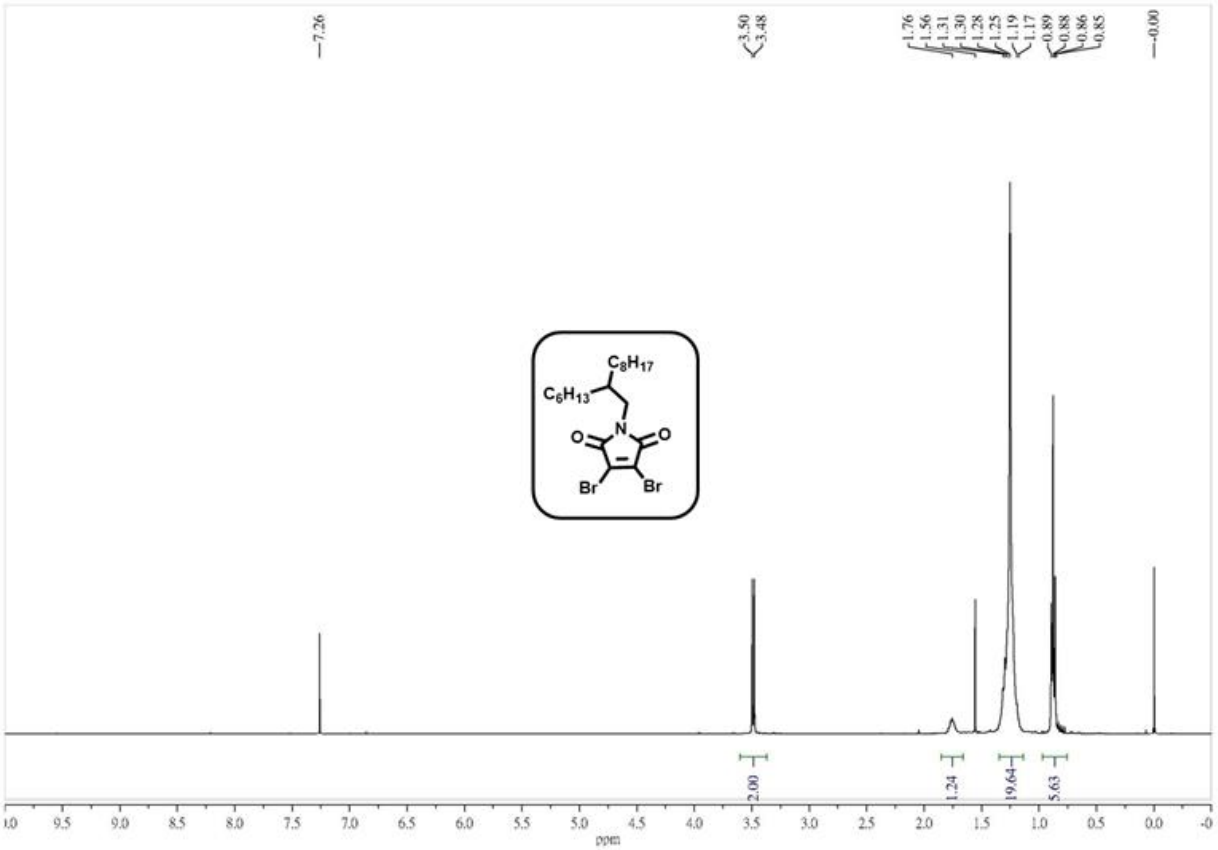

Figure S4. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

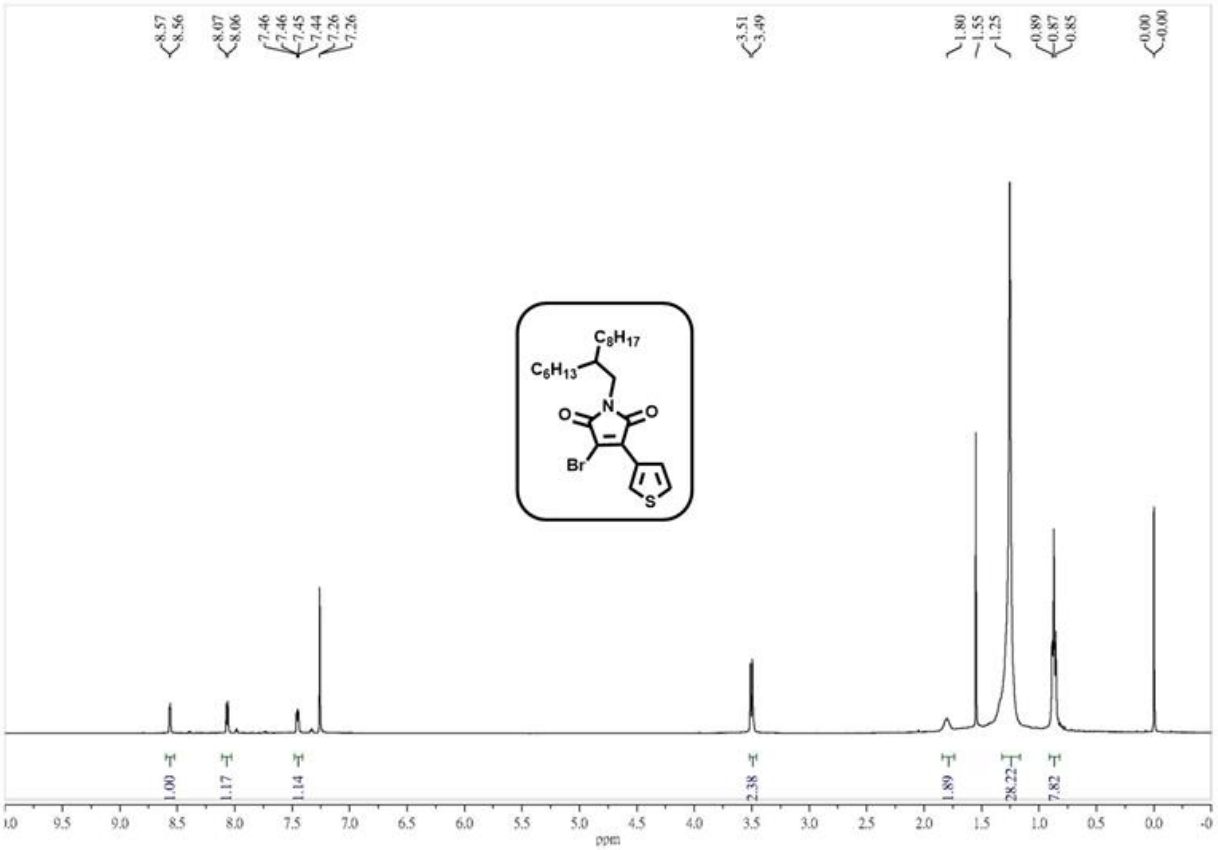

Figure S5. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

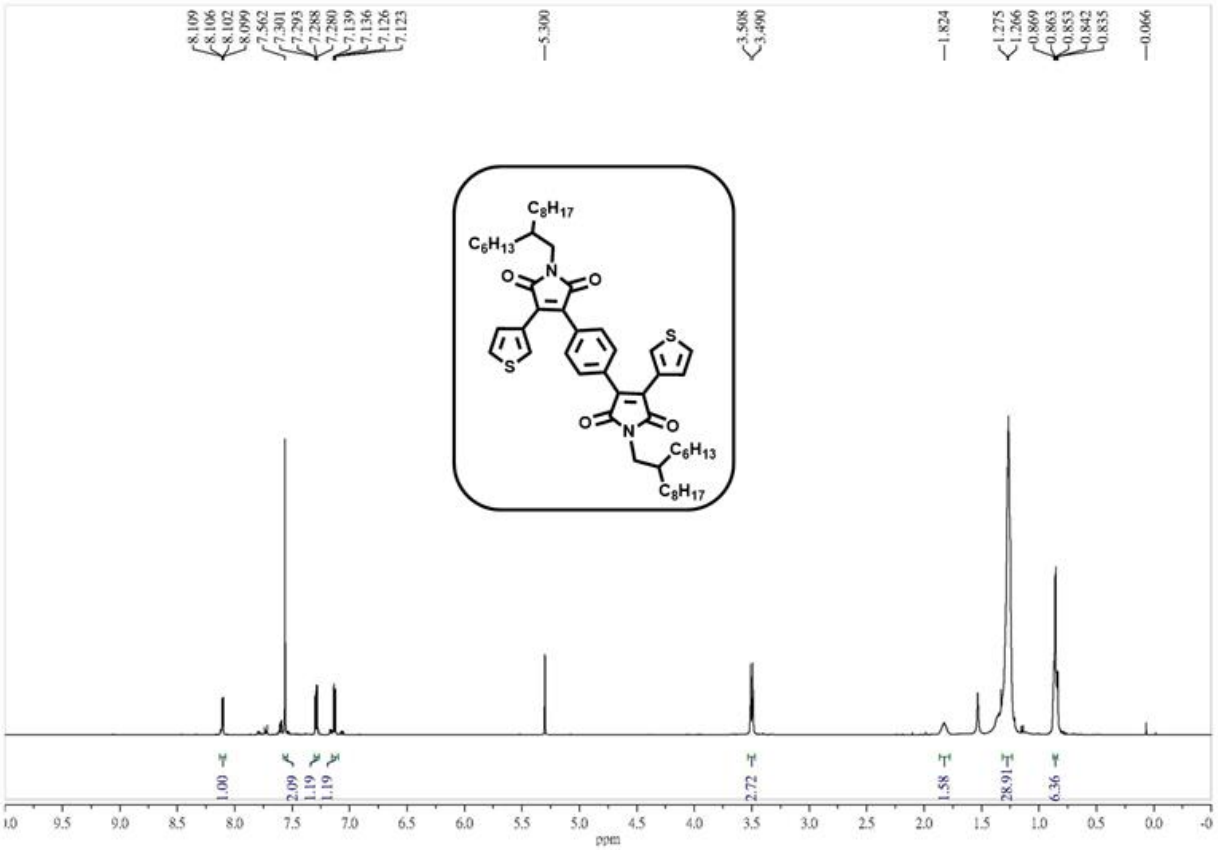

Figure S6. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

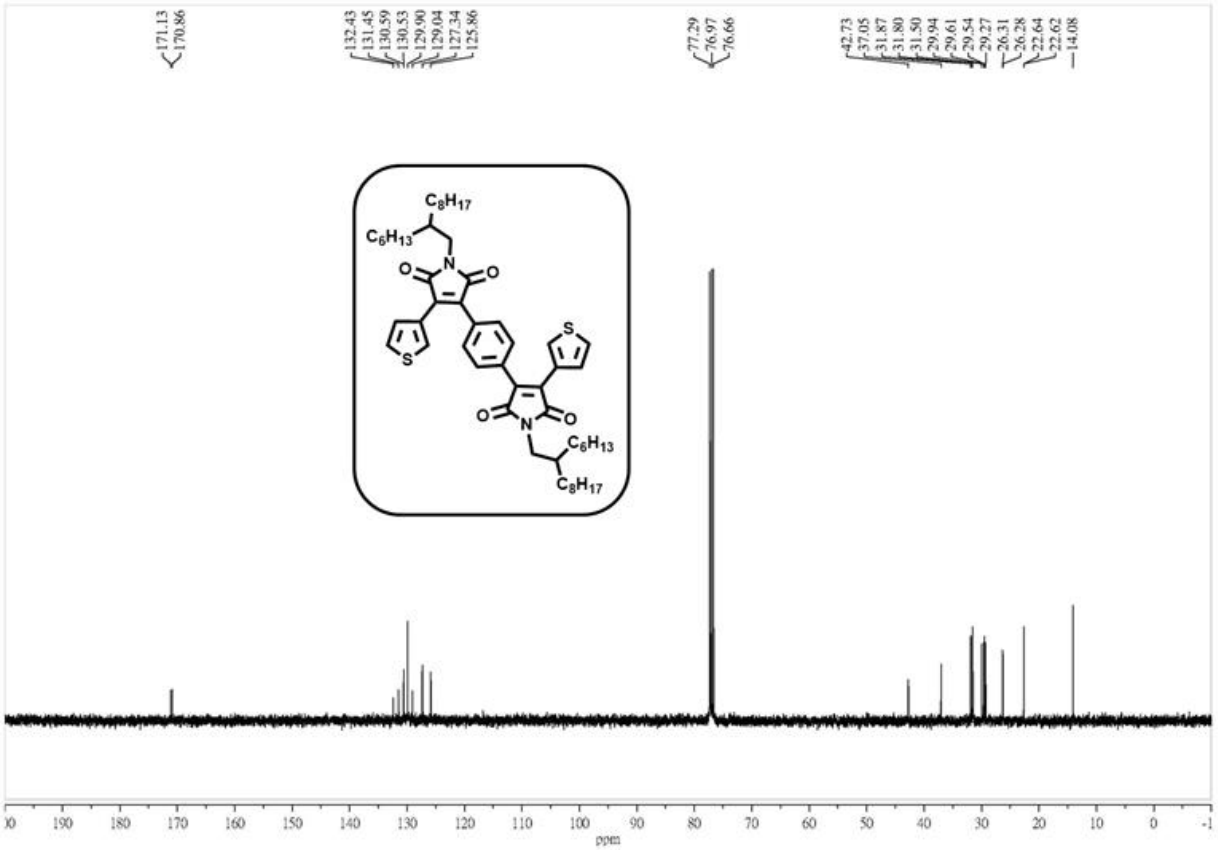

Figure S7. ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

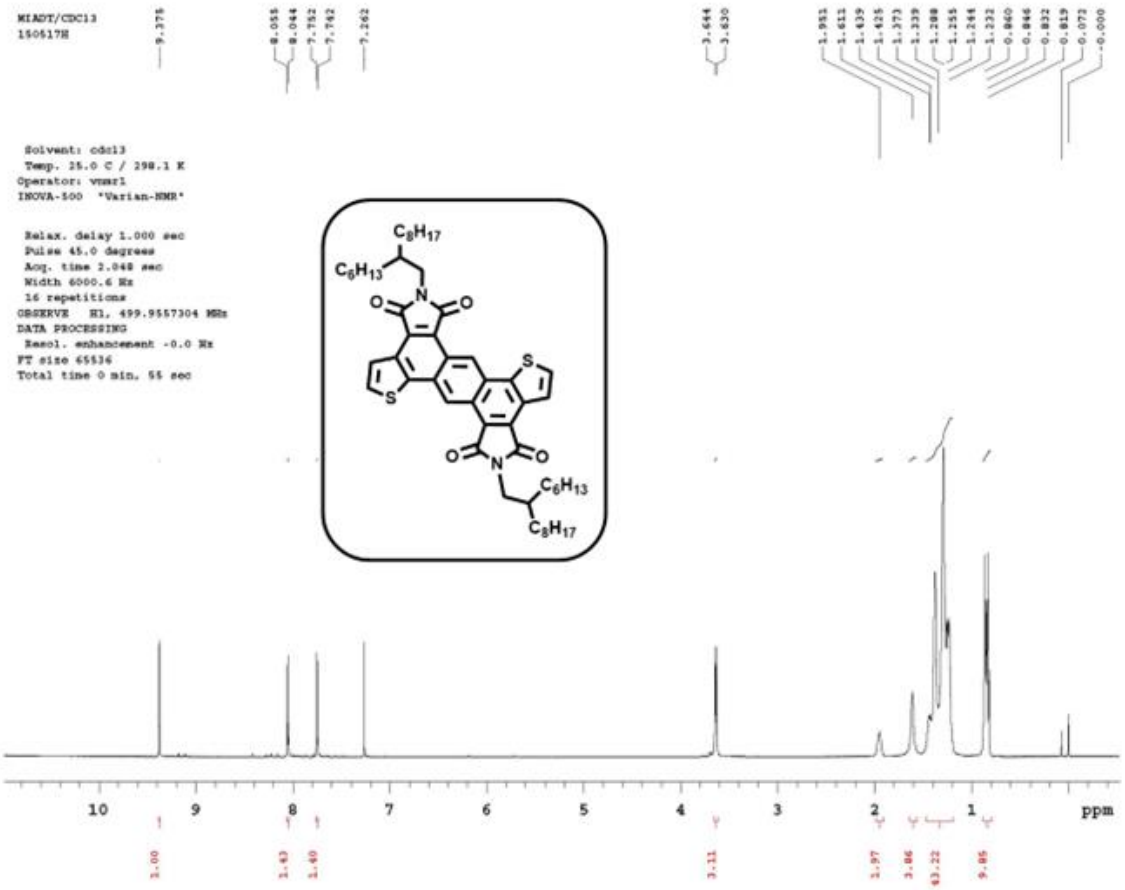

Figure S8. ^{1}H NMR spectrum of **ADTI** (500 MHz, $CDCl_3$).

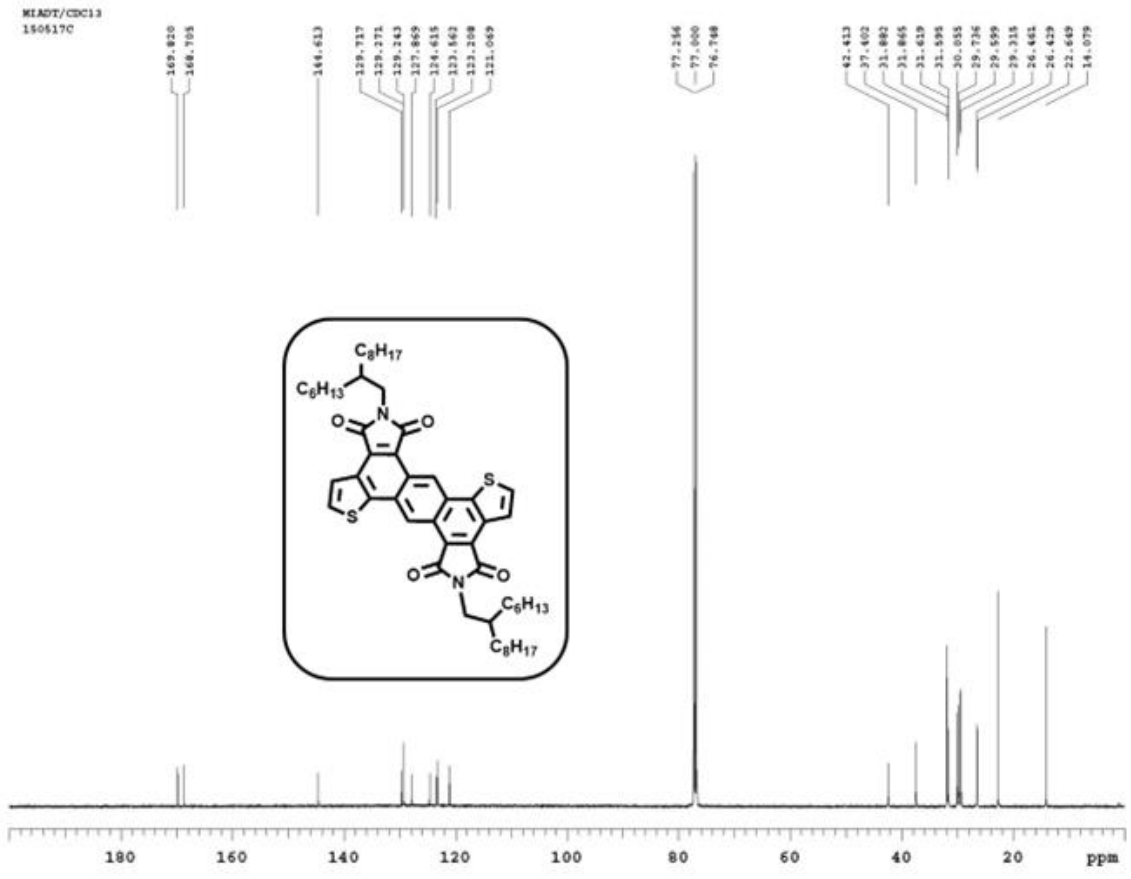

Figure S9. ^{13}C NMR spectrum of **ADTI** (125 MHz, $CDCl_3$).

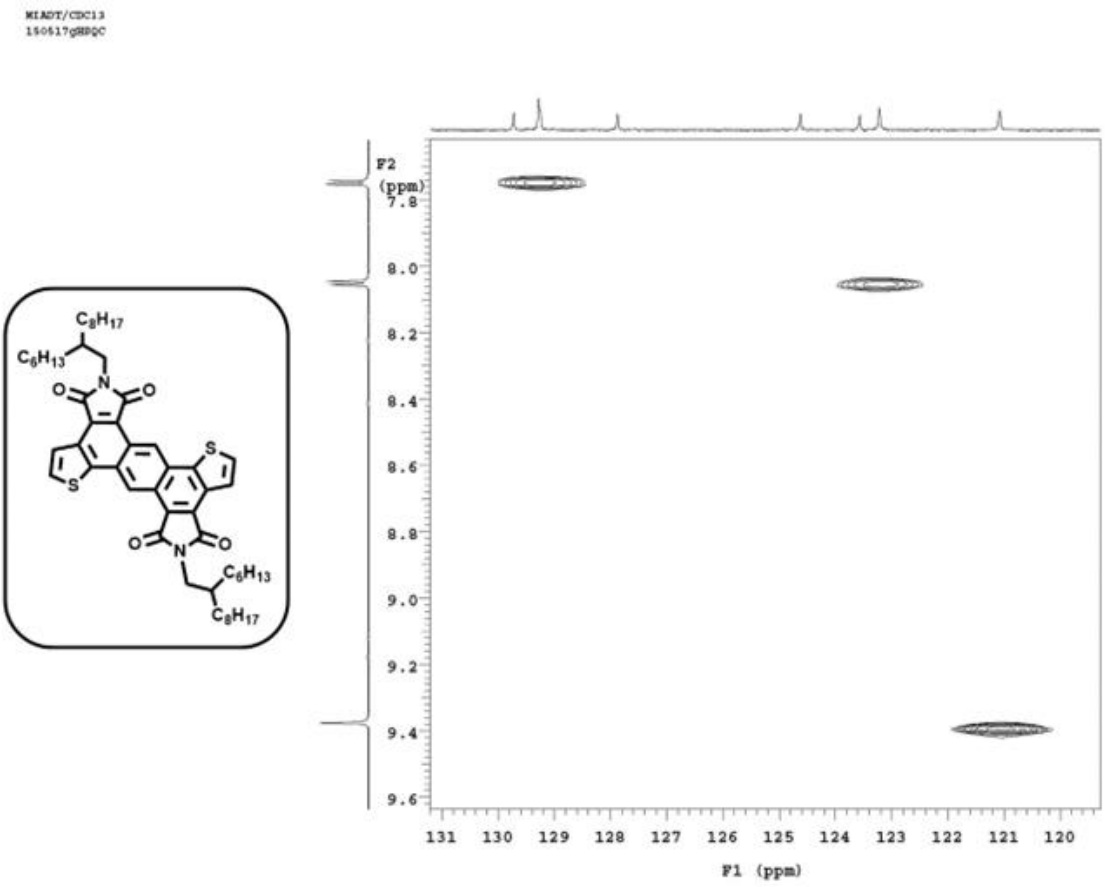

Figure S10. HSQC spectrum of **ADTI** (500 MHz, $CDCl_3$).

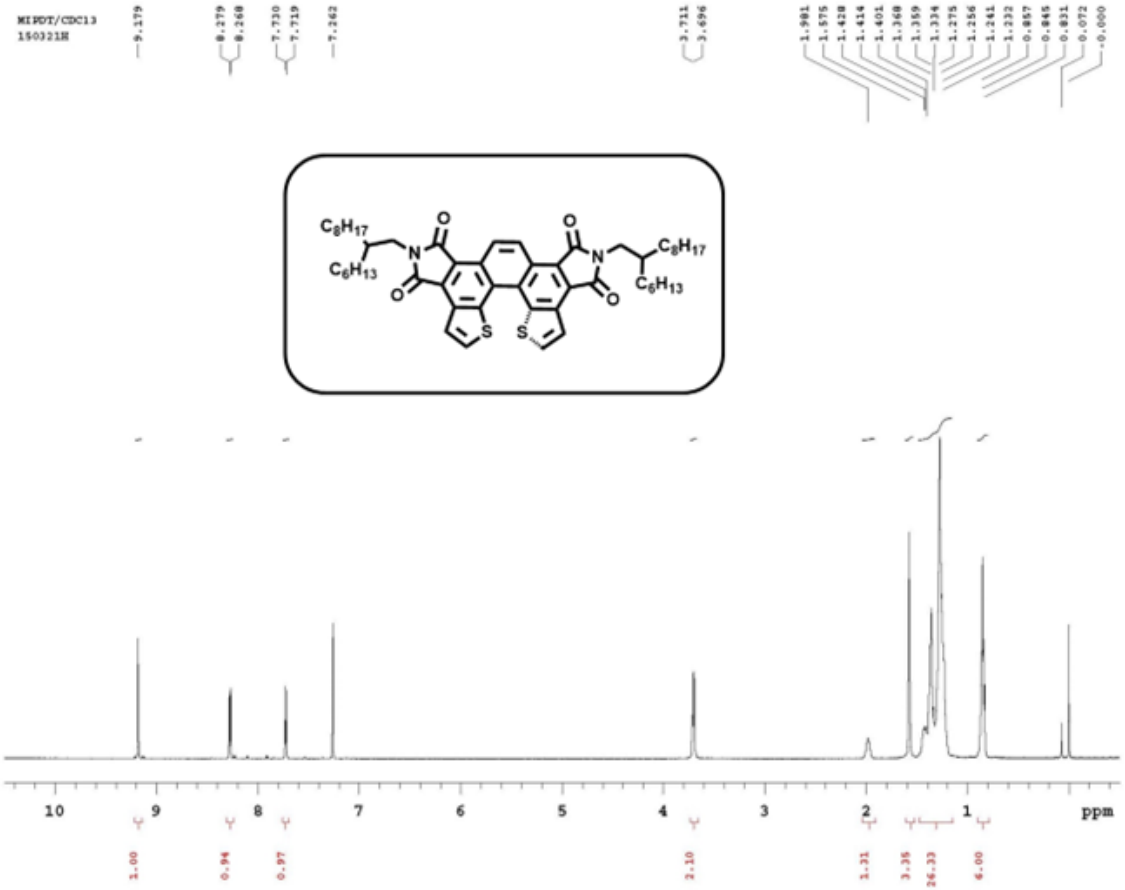

Figure S11. ^{1}H NMR spectrum of **PDTI** (500 MHz, $CDCl_3$).

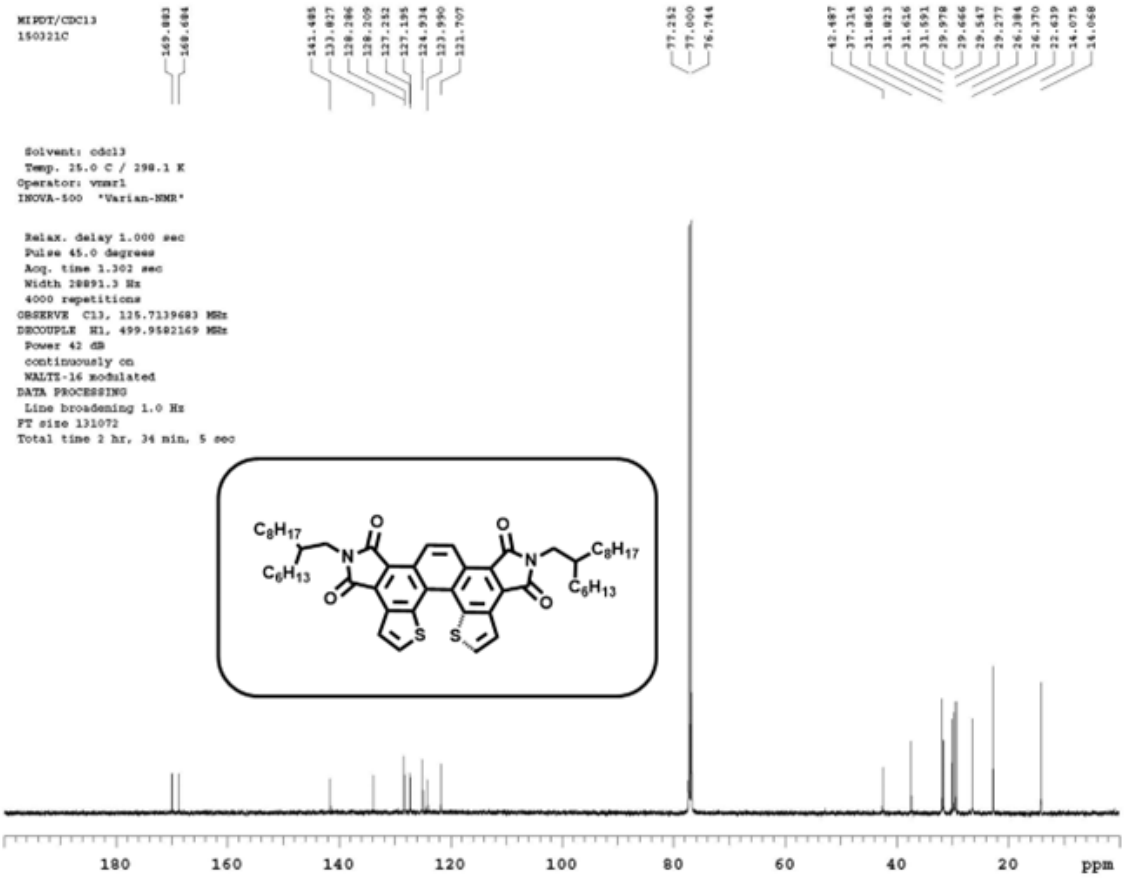

Figure S12. ^{13}C NMR spectrum of **PDTI** (125 MHz, $CDCl_3$).

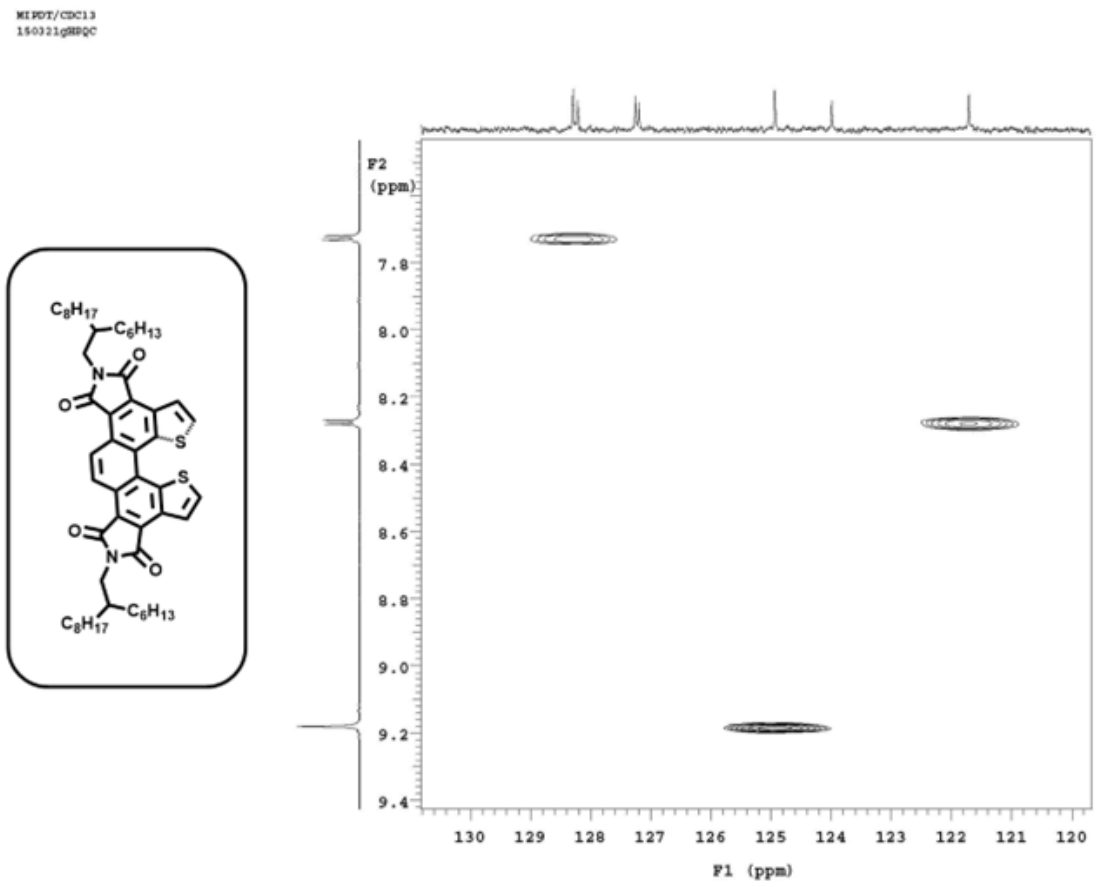

Figure S13. HSQC spectrum of **PDTI** (500 MHz, $CDCl_3$).