Supporting information available for

End-functionalization of dithiarubicene: Modulation of optoelectronic properties by metal-catalyzed coupling reactions and device application

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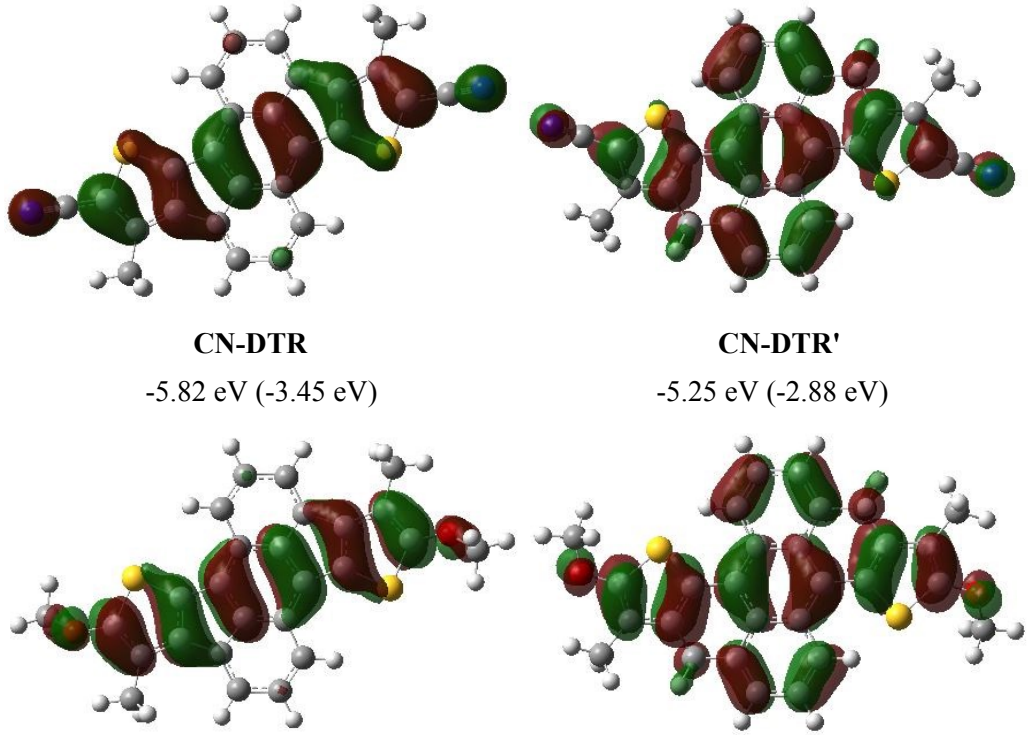
S1. Theoretical calculation[1]



CN-DTR
-5.82 eV (-3.45 eV)

CN-DTR'
-5.25 eV (-2.88 eV)

MeO-DTR
-4.74 eV (-2.57 eV)

MeO-DTR'
-4.16 eV (-1.81 eV)

Figure S1. HOMO surfaces of dithiarubicene derivatives having the fused five-membered ring (**CN-DTR** and **MeO-DTR**, left) and virtual reference compounds having the six-membered ring (**CN-DTR'** and **MeO-DTR'**, right). The numbers indicate energy levels of HOMO and LUMO (in parenthesis) based on the DFT calculation using a B3LYP density functional and a 6-31G(d,p) basis set.

Table S1. HOMO and LUMO energy levels of five DTR derivatives.[a]

	Ethynyl-DTR	**Th-DTR**	**Py-DTR**	**CN-DTR**	**MeO-DTR**
LUMO (eV)	−2.89	−2.77	−2.98	−3.45	−2.57
HOMO (eV)	−5.01	−4.87	−5.24	−5.82	−4.74

[a] Based on the DFT calculation using a B3LYP density functional and a 6-31G(d,p) basis set.

S2. Optoelectronic properties

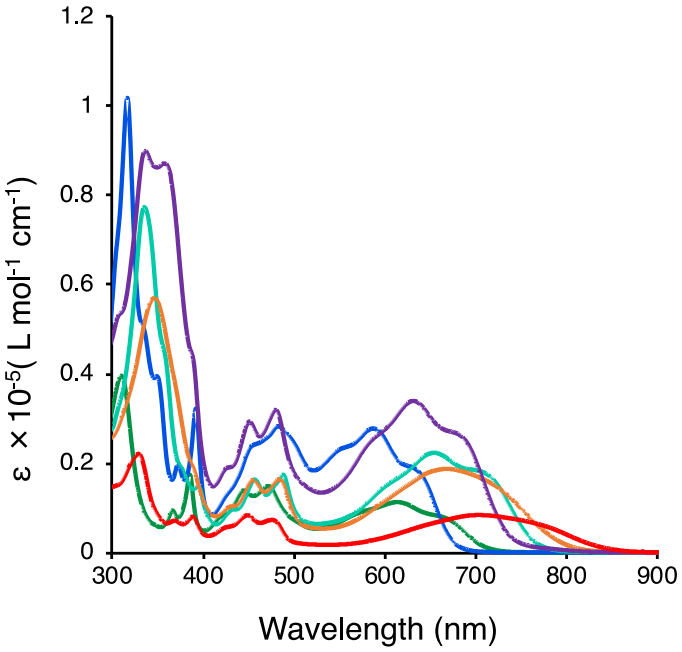


Figure S2. UV-Vis-NIR absorption spectra of **DTR** (green line), **CN-DTR** (blue line), **Py-DTR** (purple line), **Ethynyl-DTR** (light green line), **Th-DTR** (orange line), and **MeO-DTR** (red line) in $CHCl_3$ solution (10^{-5} M).

Table S2. Comparison of absorption bands between the observed value and theoretical value estimated by TD-DFT calculation (B3LYP/6-31G(d,p)).[1]

Compound	λ_{obsd} [nm]	λ_{calcd} [nm]	Oscillator strength
DTR	615	648	0.12
CN-DTR	587	635	0.21
Py-DTR	631	682	0.28
Ethynyl-DTR	654	720	0.35
Th-DTR	668	733	0.31
MeO-DTR	703	724	0.15

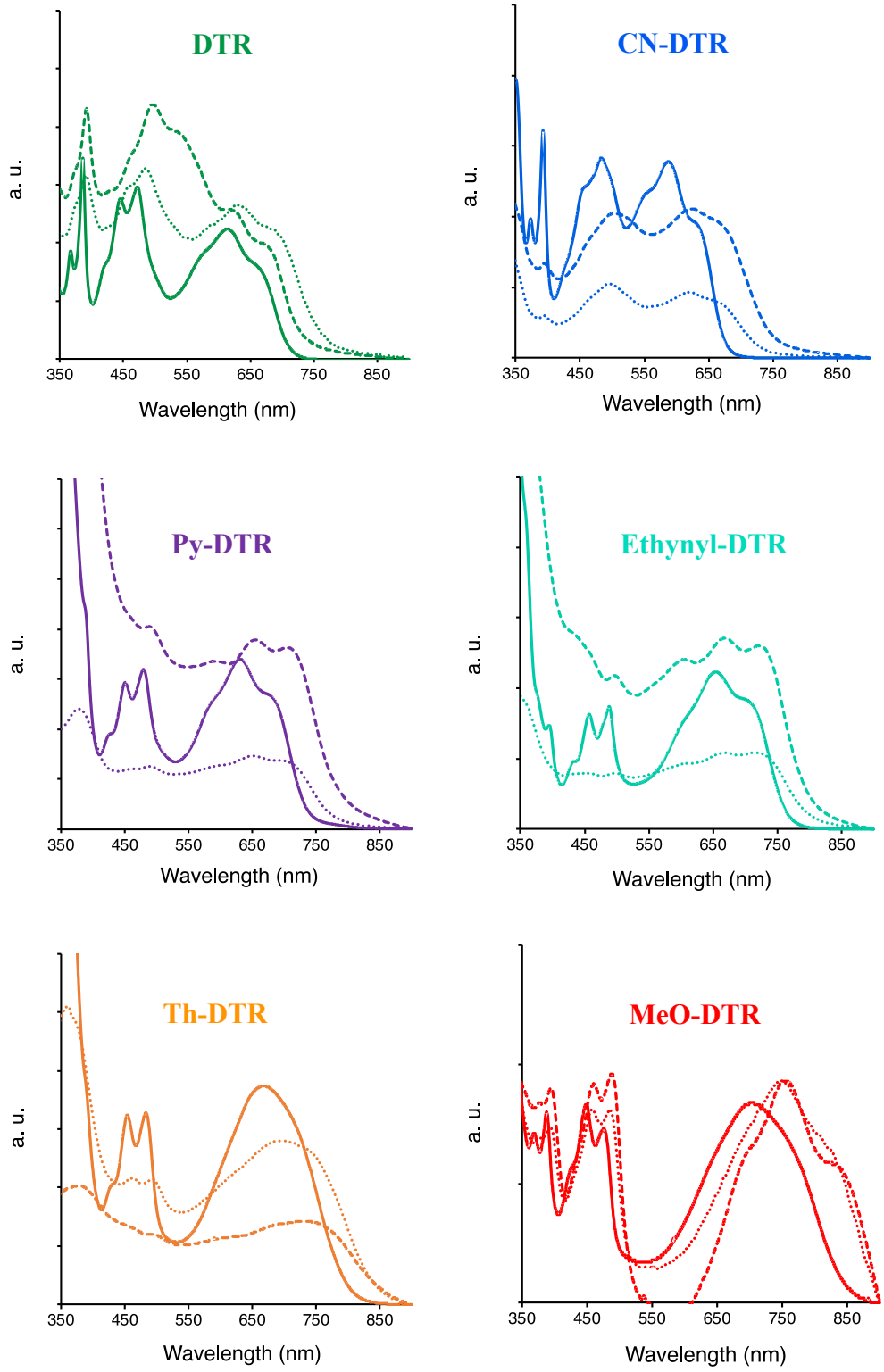


Figure S3. UV-Vis-NIR absorption spectra in thin film deposited by spin-coating (dotted lines) and drop-casting (dashed lines). Absorption spectra in solution are depicted in solid lines.

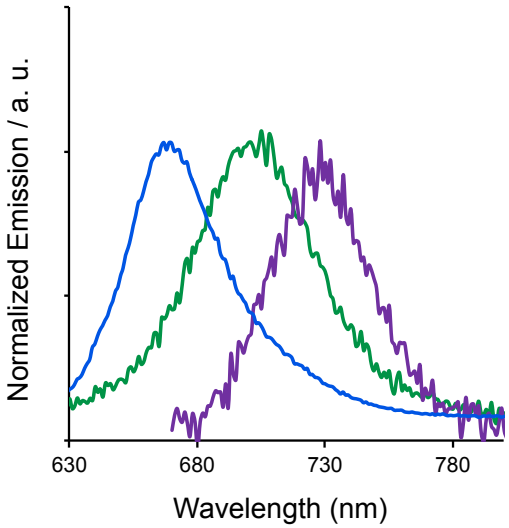


Figure S4. Normalized emission spectra of **DTR** (green line), **CN-DTR** (blue line), and **Py-DTR** (purple line) in $CHCl_3$ solution (10^{-4} M).

Table S3. Absorption maximum wavelengths and the fluorescence maximum wavelengths.

Compound	λ_{abs} [nm]	λ_{em} [nm]
DTR	615	702
CN-DTR	587	671
Py-DTR	631	728

Table S4. Reduction potentials.

Compound	$E_{red(1st)}^{1/2}$ [V]	$E_{red(2nd)}^{1/2}$ [V]	ΔE [V]
DTR	-1.56	-2.04	0.48
CN-DTR	-1.24	-1.60	0.36
Py-DTR	-1.42	-1.76	0.34
Ethynyl-DTR	-1.41	-1.81	0.40
Th-DTR	-1.45	-1.88	0.43
MeO-DTR	-1.59	-2.09	0.50

Table S5. Comparison of electrochemical properties between the observed value and theoretical value estimated by DFT calculation (B3LYP/6-31G(d,p)).[1]

Compound	E_{HOMO}^{obsd} [eV]	E_{HOMO}^{calcd} [eV]	E_{LUMO}^{obsd} [eV]	E_{LUMO}^{calcd} [eV]	E_g^{obsd} [eV]	E_g^{calcd} [eV]
DTR	(-5.07)	-5.04	-3.24	-2.66	(1.83)	2.38
CN-DTR	-5.82	-5.82	-3.56	-3.45	2.26	2.37
Py-DTR	-5.37	-5.24	-3.38	-2.98	1.99	2.26
Ethynyl-DTR	(-5.05)	-5.01	-3.39	-2.89	(1.66)	2.12
Th-DTR	-5.06	-4.87	-3.35	-2.77	1.71	2.1
MeO-DTR	-4.77	-4.74	-3.21	-2.57	1.56	2.17

S3. OFET characteristics

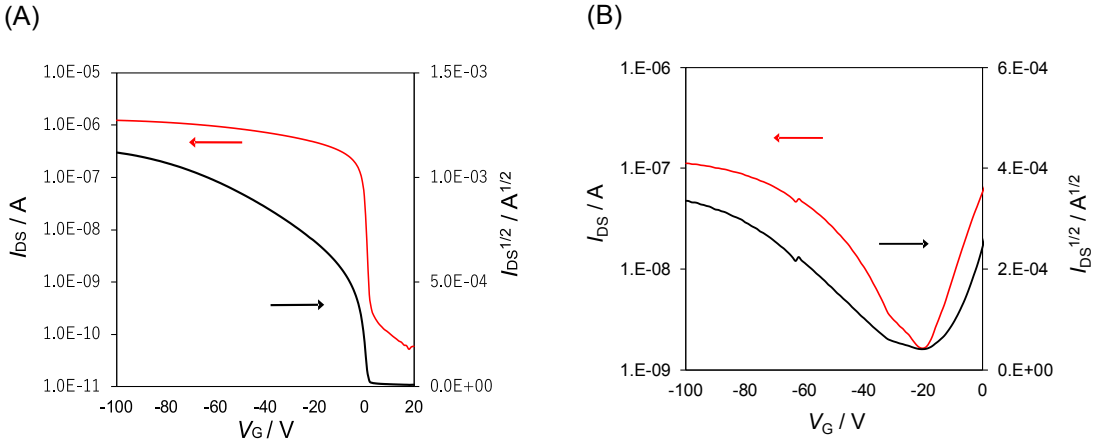


Figure S5. Transfer plots of (A) **OD-MeO-DTR** and (B) **OD-CN-DTR**-based OFET device fabricated on HMDS-treated SiO_2 insulation surface in an as-cast film.

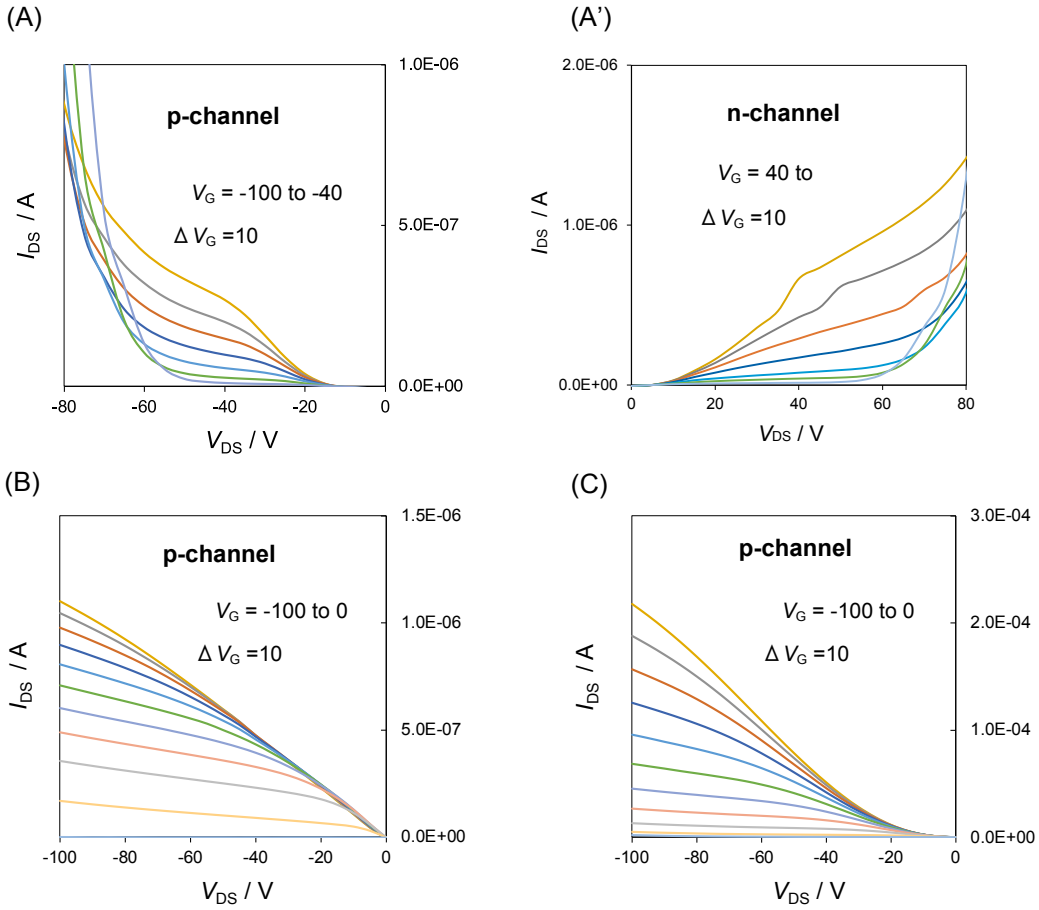


Figure S6. Output plots of (A) and (A') **OD-CN-DTR** [annealed at 100 °C], (B) **OD-MeO-DTR** [as-cast], and (C) **EH-MeO-DTR** [annealed at 100 °C]-based OFET device fabricated on HMDS-treated SiO_2 insulation surface.

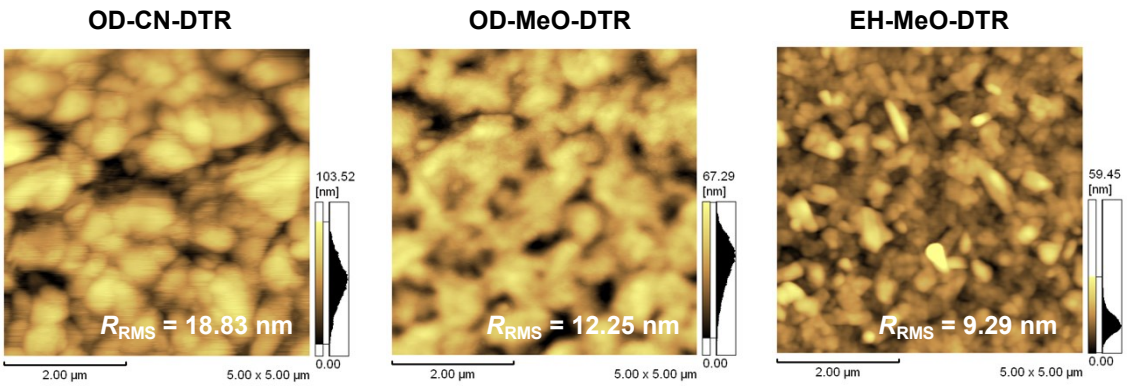


Figure S7. AMF image (5 µm × 5 µm) of the films fabricated on HMDS-treated SiO_2 insulation surface. The inset values indicate the root-mean-square roughness (R_{RMS}).

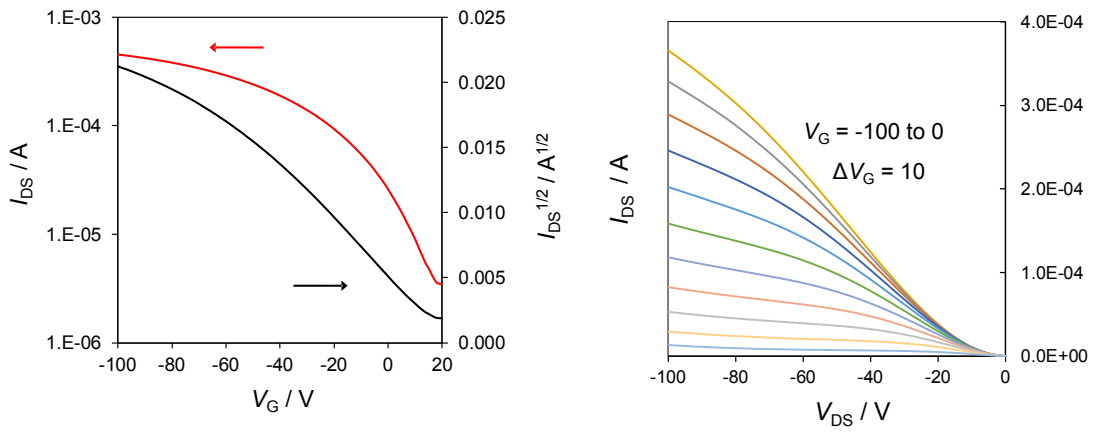


Figure S8. Transfer (left) and output (right) curves of **EH-MeO-DTR**-based OFET device fabricated on HMDS-treated SiO_2 insulation surface using Au electrodes modified with 1-hexadecanethiol.

S4. OPV characteristics

Table S6. OPV characteristic with the device architecture ITO/ZnO/P3HT:**OD-CN-DTR**/MoO_3/Ag.

solv.	conc. [mg/mL]	PCE [%]	J_{sc} [mA/cm^2]	V_{oc} [V]	FF [%]
chlorobenzene	20	0.21	0.84	0.56	44
chloroform	10	0.10	0.59	0.40	43

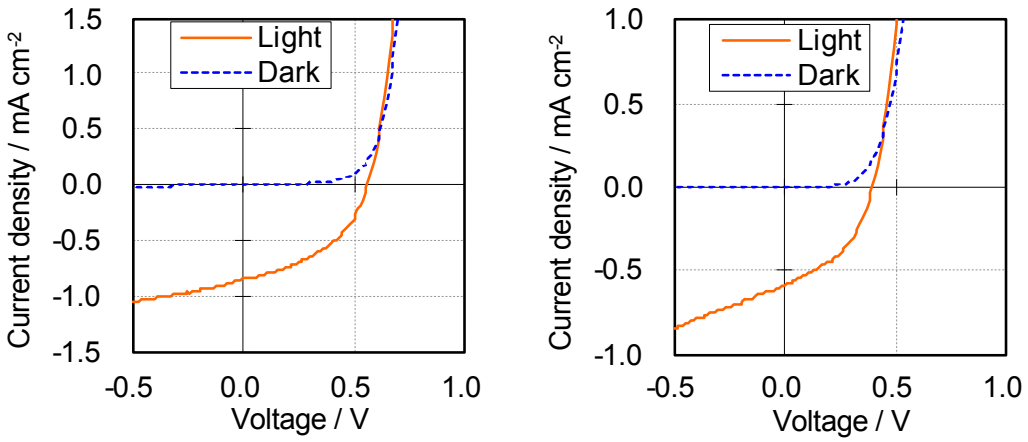


Figure S9. *J-V* curve for ITO/ZnO/P3HT:**OD-CN-DTR**/MoO_3/Ag device. The active layer was fabricated from chlorobenzene (left) and chloroform (right) solutions.

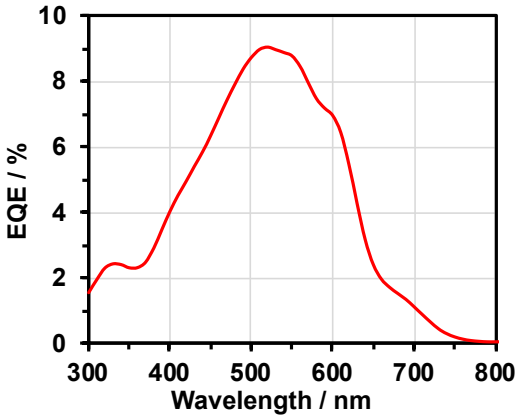


Figure S10. EQE spectrum for ITO/ZnO/P3HT:**OD-CN-DTR**/MoO_3/Ag device, in which the active layer was fabricated from chlorobenzene solution.

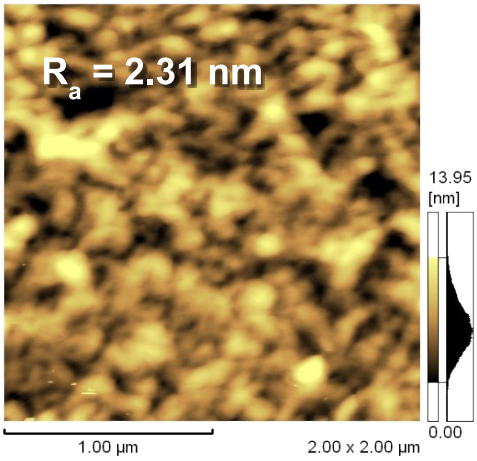
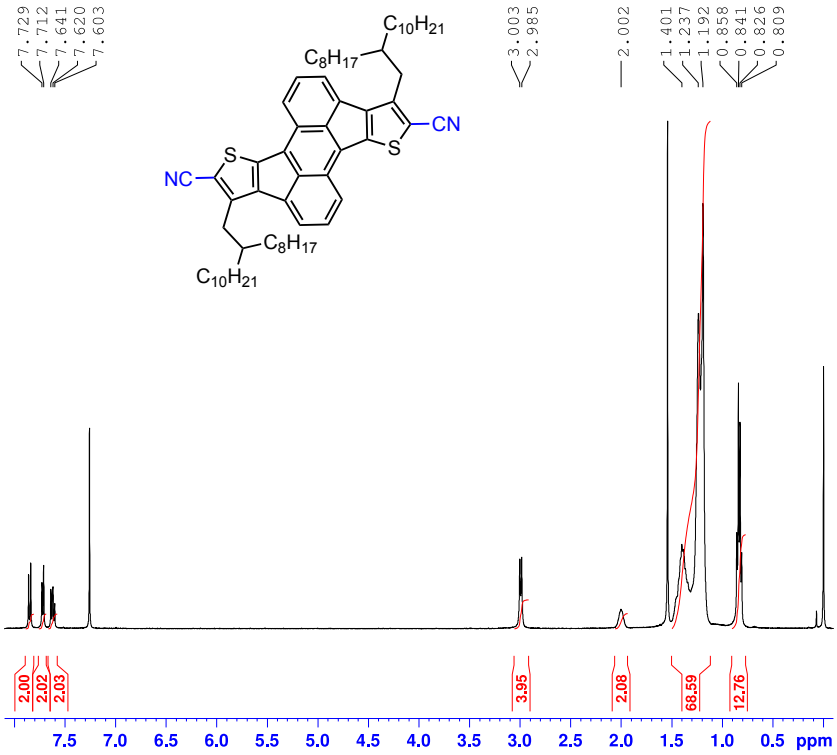


Figure S11. AFM image of the active layer.

S5. NMR spectra

OD-CN-DTR

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DE                  6.50 usec
TE                 300.7 K
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TD0                    1

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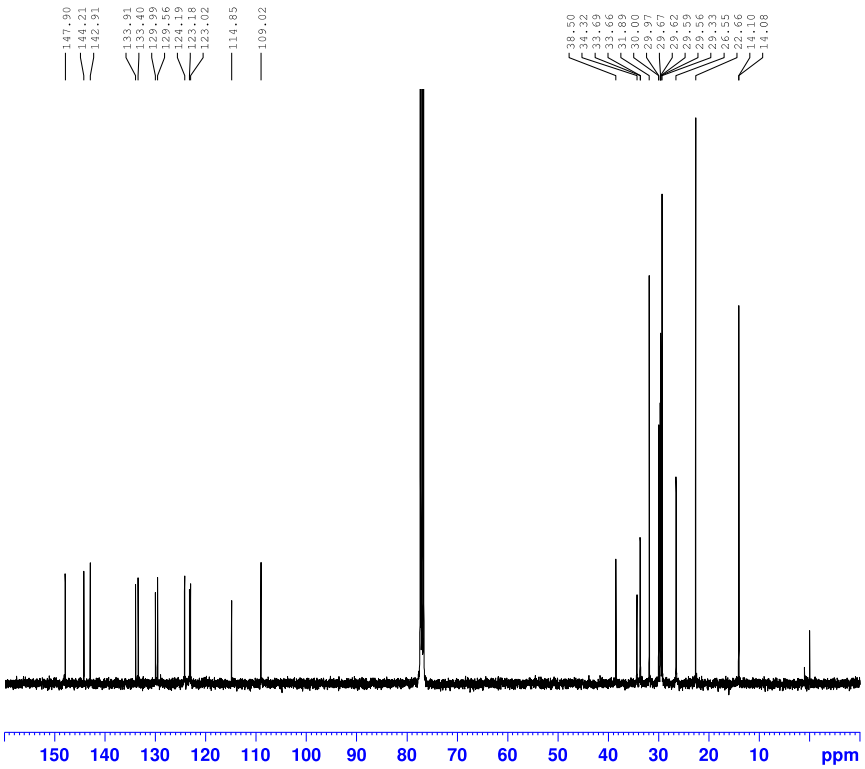


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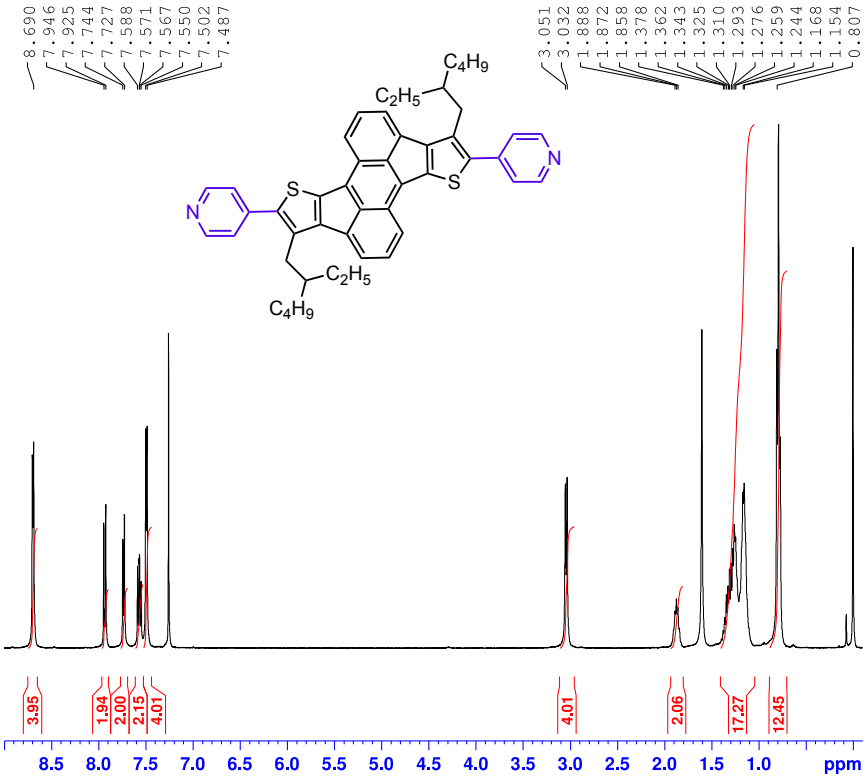
EH-Py-DTR

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SOLVENT            CDCl3
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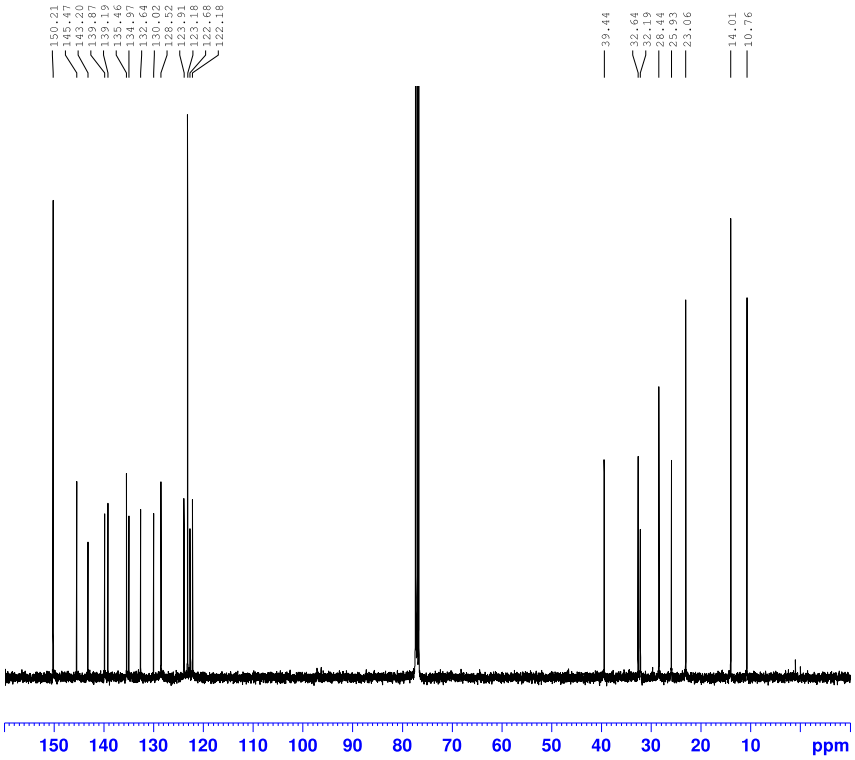


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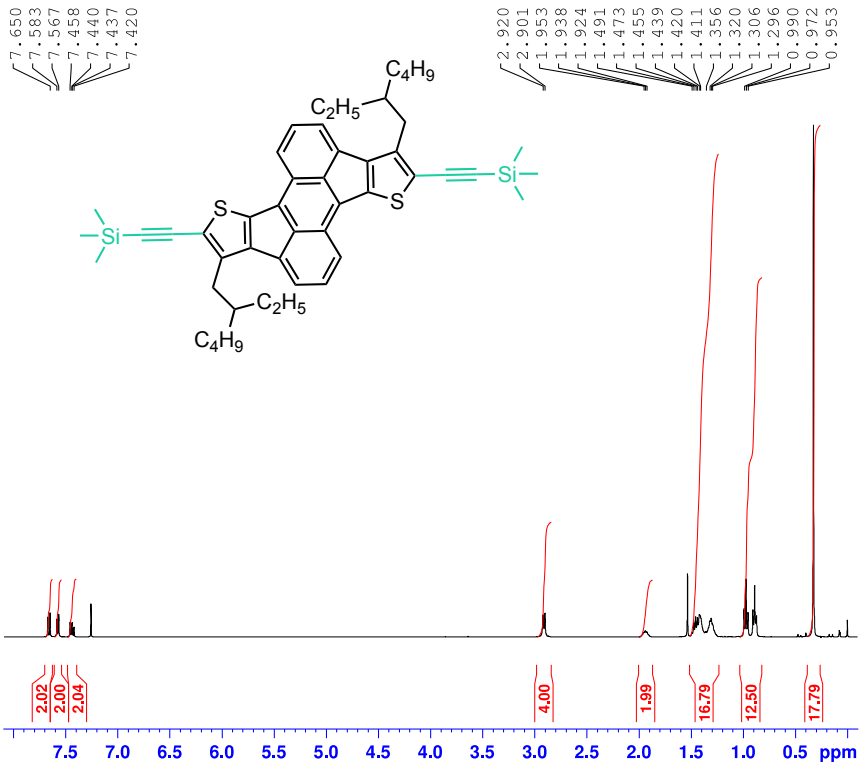
EH-Ethynyl-DTR

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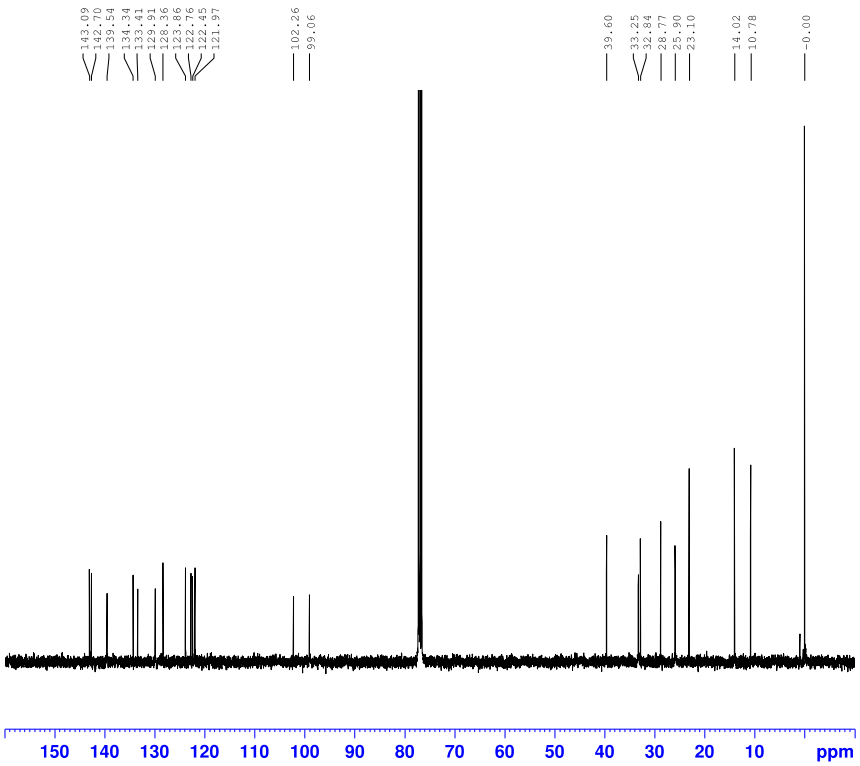


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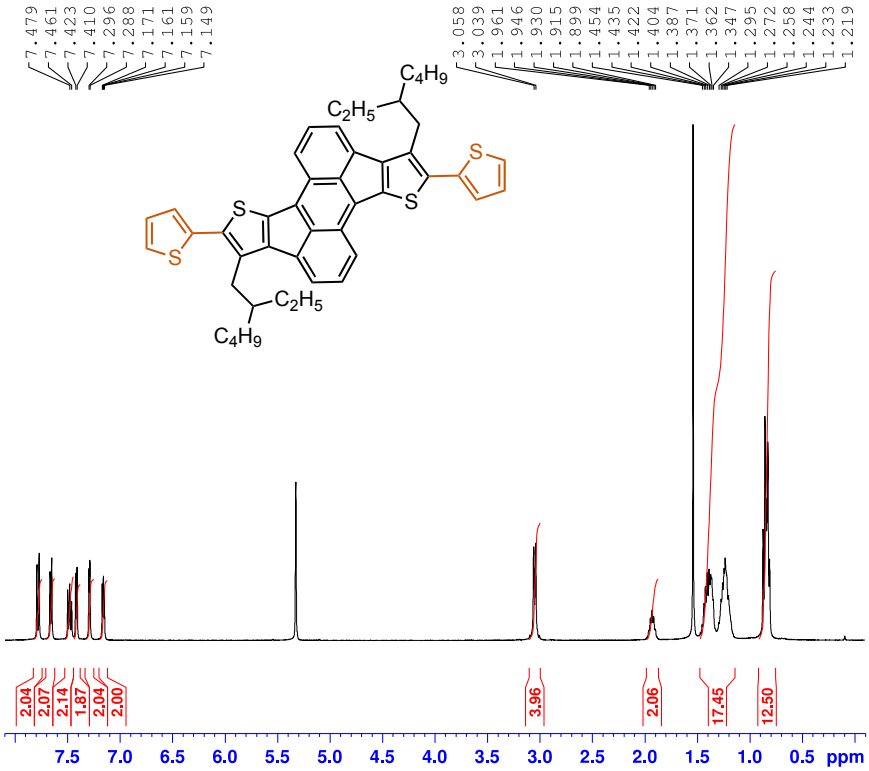
EH-Th-DTR

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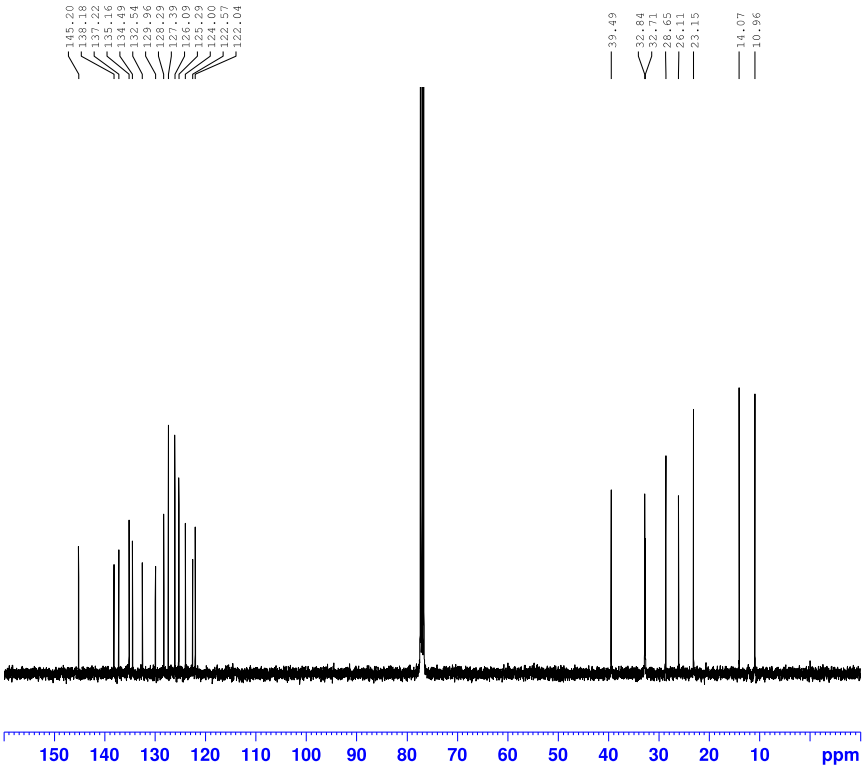


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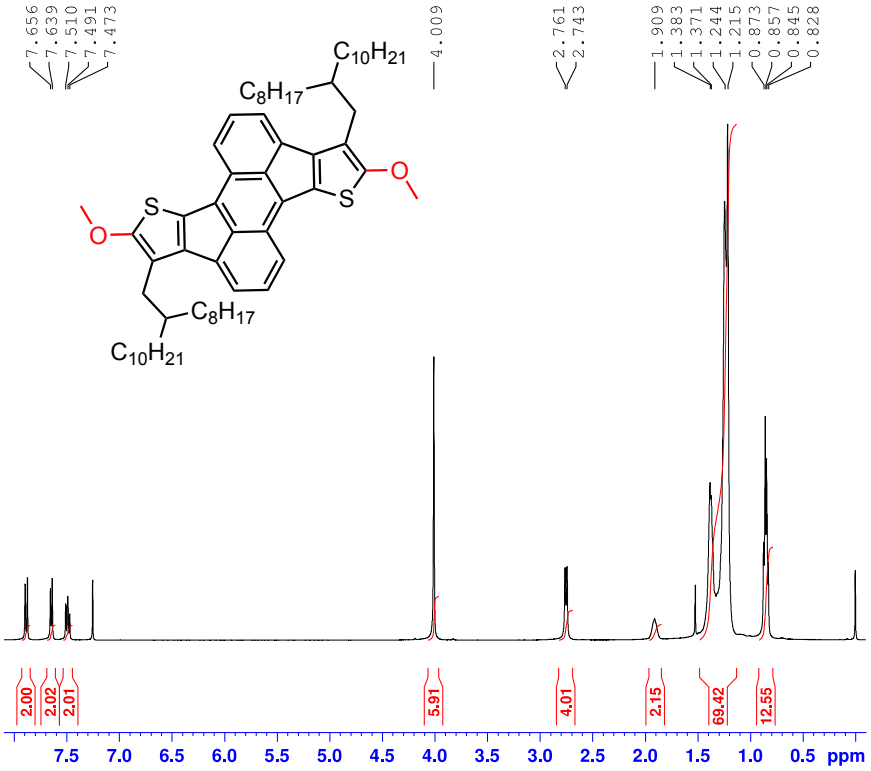
OD-MeO-DTR

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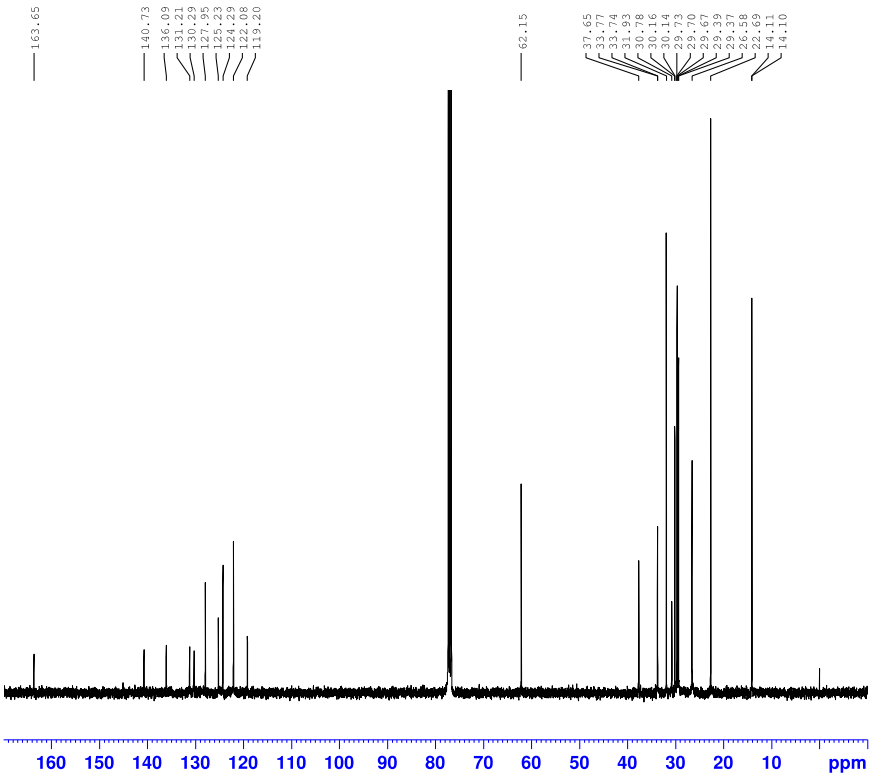


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NUC2                      1H
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PCPD2                  90.00 usec
PLW2             17.00000000 W
PLW12             0.20987999 W
PLW13             0.17000000 W

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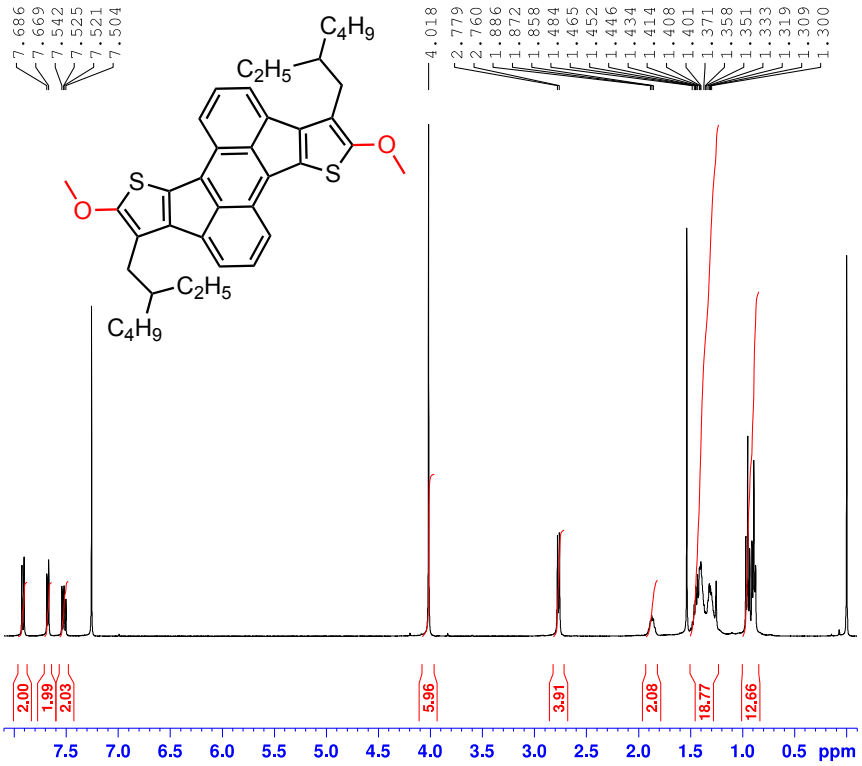
EH-MeO-DTR

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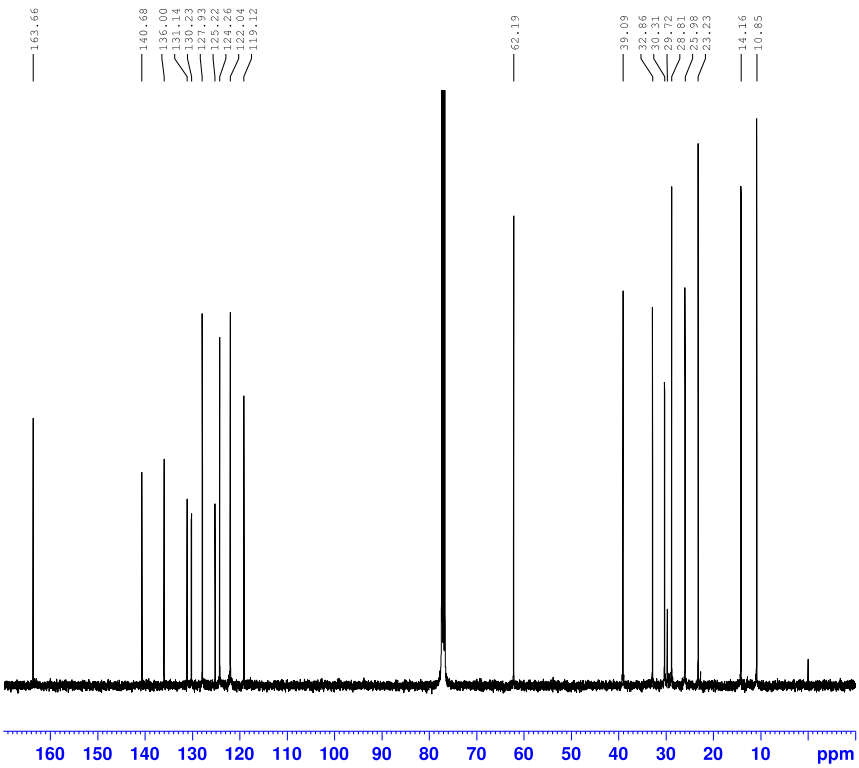
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ           4.0894465 sec
RG              116.18
DW              62.400 usec
DE               6.50 usec
TE              299.4 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                10.00 usec
PLW1        17.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1300110 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
Current Data Parameters
NAME            NMR_data
EXPNO                656
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200923
Time               0.17
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3072
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ           1.3631488 sec
RG              204.99
DW              20.800 usec
DE               6.50 usec
TE              299.9 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        71.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        17.00000000 W
PLW12        0.20987999 W
PLW13        0.17000000 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

S6. Reference

1) Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, 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, T. Keith, 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, Gaussian, Inc., Wallingford CT, 2013.