Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Deep-purple-grey thiophene-benzothiadiazole-thiophene BODIPY Dye for Solution-processed Solar Cells

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Supporting information

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1) DFT calculations.

Density functional theory (DFT) calculations have been performed using SPARTAN 10 (www.wavefun.com) at the B3LYP/6-311+G* level of theory in vacuum on dye **6** and are compared below to those obtained previously on another BODIPY dye named TB2 (T. Bura, N. Leclerc, S. Fall, P. Lévêque, T. Heiser, P. Retailleau, S. Rihn, A. Mirloup, R. Ziessel *J. Am. Chem. Soc.*, **2012**, 134 (42), pp 17404–17407).

Table S1. HOMO and LUMO levels for dye **6** and TB2 as calculated by DFT.

Molecule	HOMO (eV)	LUMO (eV)	Gap (eV)
Dye **6**	-4.70	-2.85	1.85
TB2	-4.66	-2.63	2.03

2) AFM measurements.

The thin film surface morphology was investigated by dynamic amplitude modulation atomic force microscopy (tapping mode) under ambient conditions. AFM observations were conducted using phase imaging on the Nanoscope IIIa system commercialized by Veeco®.

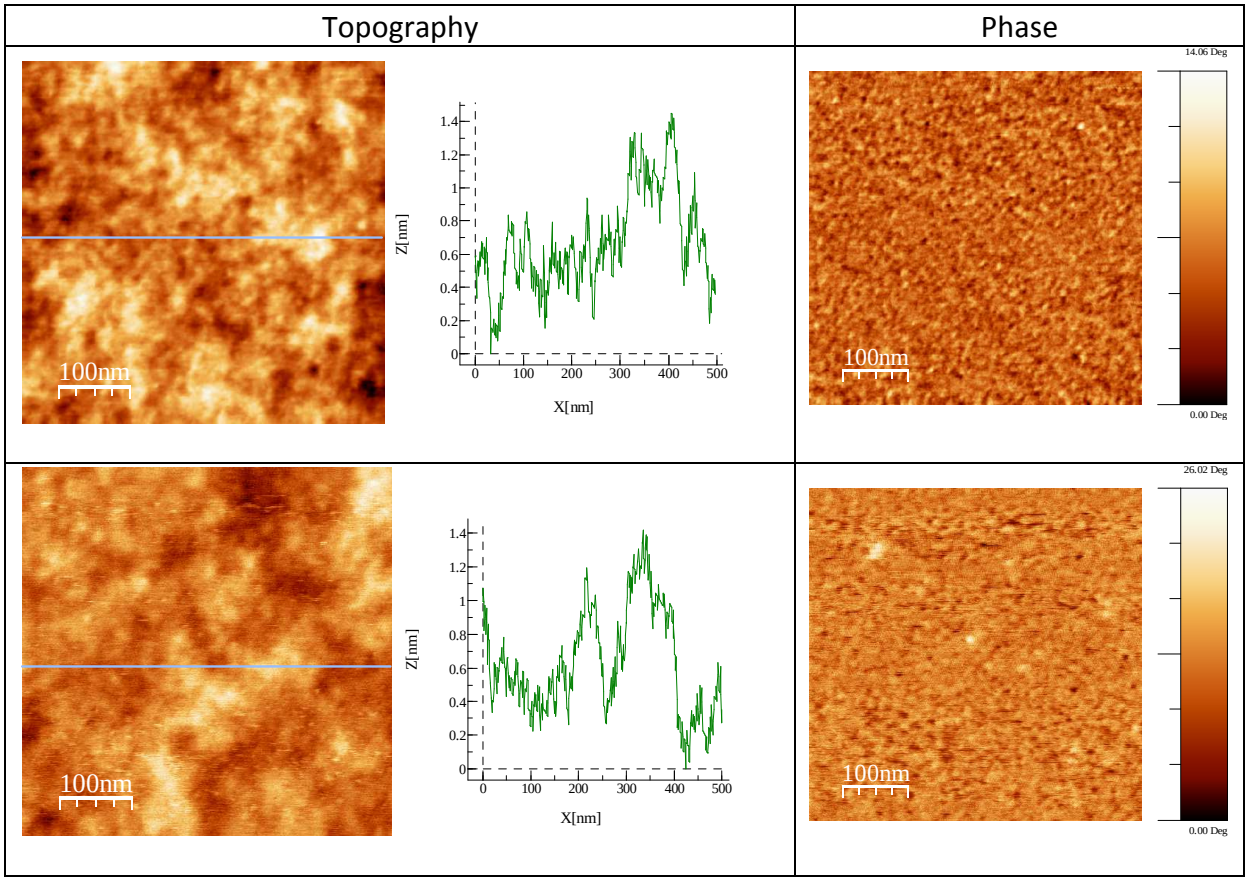


Figure S1. AFM topography image (left) with corresponding profile and phase image (right) of a film of dye **6**/PCBM processed in CB with 0.3% of 1,8-diiodoctane as co-solvent including a 1/2 ratio of AM248:$PC_{71}BM$ before (top) and after (bottom) thermal annealing (10 minutes at 80°C and 100°C for 3 minutes).

3) Mobility measurements.

Bottom contact field-effect transistors (FETs) were elaborated on commercially available pre-patterned test structures whose source and drain contacts were composed of a 30 nm thick

gold layer on top of a 10 nm thick Indium Tin Oxide (ITO) layer. A 230 nm thick silicon oxide was used as gate dielectric and n-doped ($3x10^{17}/cm^3$) silicon crystal as gate electrode. The channel length and channel width were 20 µm and 10 mm, respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently for 30 minutes in an ultra-violet ozone system. Then, hexamethyldisilazane (HMDS) was spin coated (500 rpm for 5 s and then 4000 rpm for 50 s) under nitrogen ambient and followed by an annealing step at 135°C for 10 minutes. Finally, compound **6** anhydrous chloroform solution (4 mg/ml) was spin coated (1250 rpm for 60s and 2250 rpm for 60s) to complete the FET devices. The samples were then left overnight under vacuum (<10^{-6} mbar) to remove residual solvent traces. Both, the FETs elaboration and characterization were performed in nitrogen ambient. The transistor output (**Figure S3**) and transfer characteristics (**Figure S4**) were recorded using a Keithley 4200 semiconductor characterization system. The charge carrier mobilities (holes and electron) were extracted in the saturation regime using the usual formalism (J. Zaumseil, H. Sirringhaus *Chem. Rev*. 2007, **107**, 1296–1323).

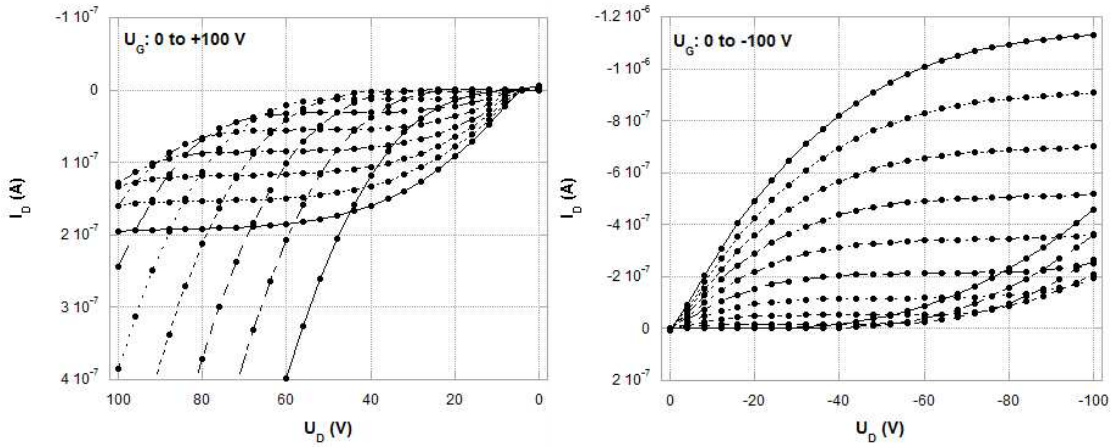


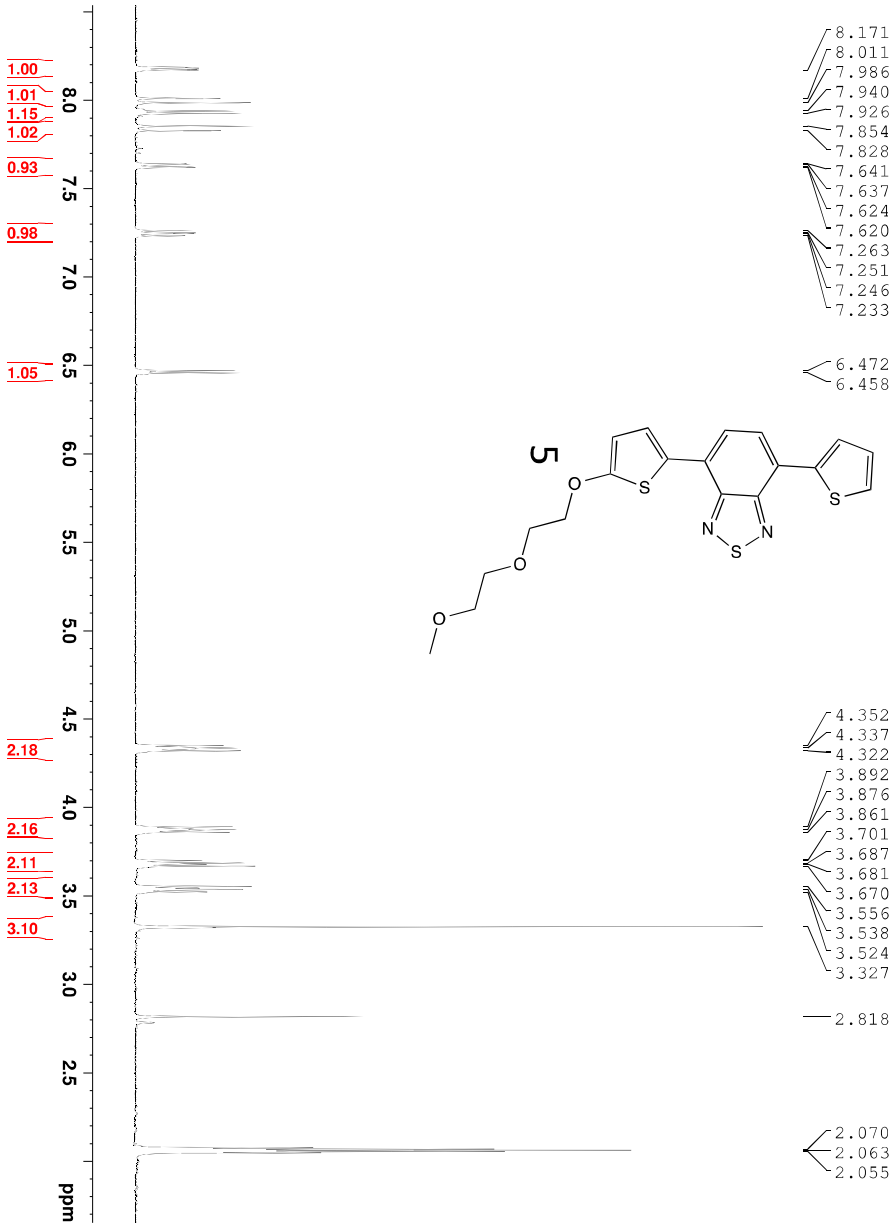
Figure S2. Output characteristics on pristine films for electrons (left) and holes (right). I_D is the drain current, U_D is the drain voltage and U_G is the gate voltage.

4) Photovoltaic devices elaboration and characterization.

Table S2. Selected thin-films compositions and deposition way with associated OPV performances.

Acceptor	Ratio (6/PCBM)	BODIPY dye concentration	Solvent	Cathode	V_{OC} (V)	J_{SC} (mA/cm²)	FF (%)	PCE (%)	Annealing (temp. °C/time min)
$PC_{61}BM$	1/2	3 mg/mL	$CHCl_3$	Al	0.54	5.8	31	0.97	80°C/10 min
$PC_{61}BM$	1/1.5	5 mg/mL	$CHCl_3$	Al	0.66	5.2	32	1.10	/
$PC_{61}BM$	1/1.5	5 mg/mL	$CHCl_3$	Al	0.69	4.5	31	0.96	80°C/10 min
$PC_{61}BM$	1/1.5	5 mg/mL	$CHCl_3$	Al	0.68	4.3	31	0.91	90°C/10 min
$PC_{61}BM$	1/1.5	3 mg/mL	$CHCl_3$	Al	0.65	5.6	32	1.16	/
$PC_{61}BM$	1/1.75	5 mg/mL	$CHCl_3$	Al	0,65	5.8	31	1.17	/
$PC_{61}BM$	1/1.75	5 mg/mL	$CHCl_3$	Al	0.67	5.4	31	1.12	60°C/10 min
$PC_{61}BM$	1/2	5 mg/mL	$CHCl_3$	Al	0.67	5.4	32	1.16	/
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Al	0.61	6.3	31	1.19	/
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Al	0.62	5.5	31	1.06	80°C/10 min
$PC_{61}BM$	1/2	3 mg/mL	$CHCl_3$	Ca/Al	0.55	5.7	37	1.16	/
$PC_{61}BM$	1/2	3 mg/mL	$CHCl_3$	Ca/Al	0.62	5.8	35	1.26	60°C/10 min before Ca/Al
$PC_{61}BM$	1/2	4 mg/mL	$CHCl_3$	Ca/Al	0.64	5.6	33	1.18	/
$PC_{71}BM$	1/2	10 mg/mL	CB+0.3 % DIO	Al	0.59	5.7	30	1.01	80°C/5min
$PC_{71}BM$	1/2	10 mg/mL	CB+0.3 % DIO	Al	0.61	7.4	28	1.26	100°C/3 min
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Ca/Al	0.55	5.7	30	0.94	/
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Ca/Al	0.60	5.4	31	1.00	100°C/1 min
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Ca/Al	0.58	5.9	30	1.02	80 °C/10 min before Ca/Al
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Ca/Al	0.65	5.9	31	1.19	80 °C/10 min before Ca/Al + 100°C/1 min
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Ca/Al	0.57	6.4	31	1.13	100°C/10 min before Ca/Al
$PC_{71}BM$	1/2	10 mg/mL	CB+0.4 % DIO	Ca/Al	0.64	6.1	31	1.21	100°C/10 min before Ca/Al + 100°C/1 min

5) NMR Traces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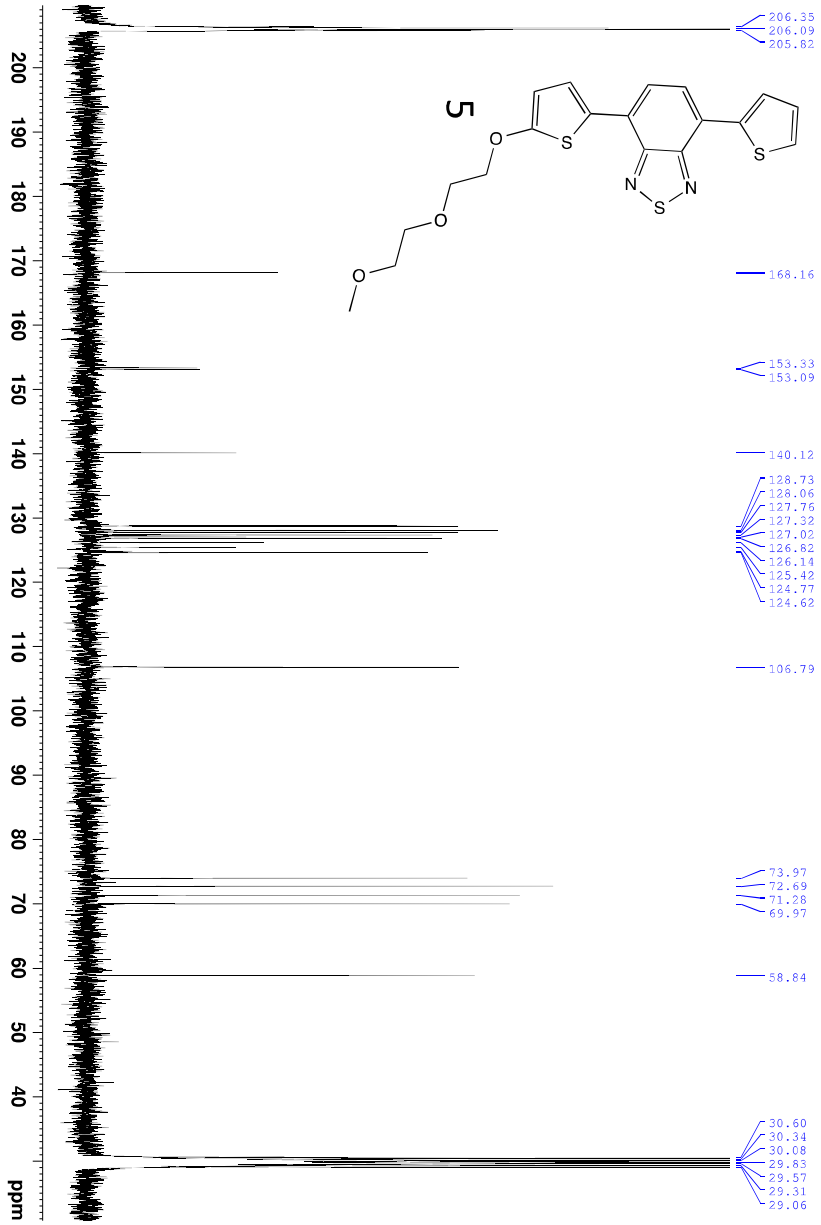
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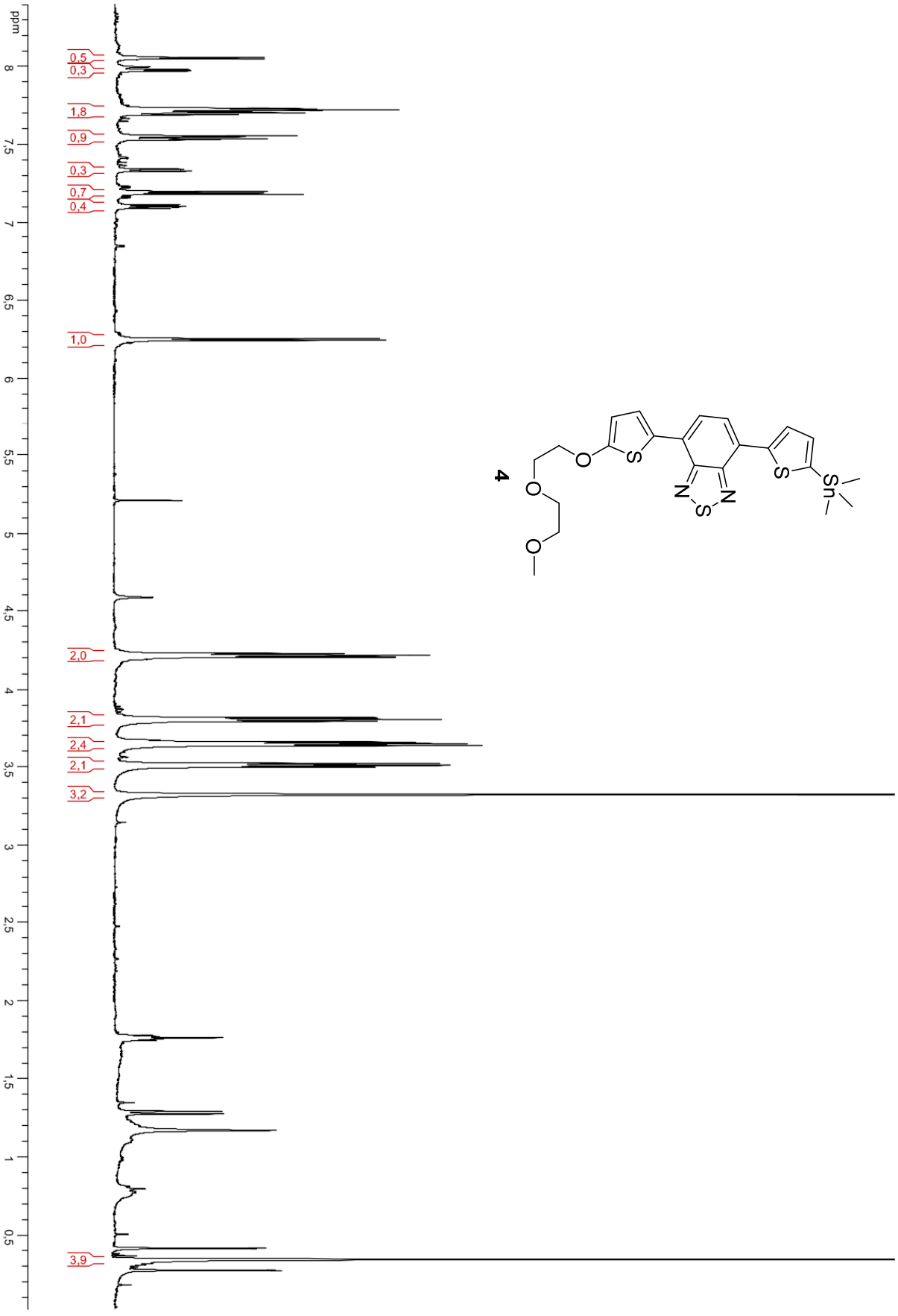
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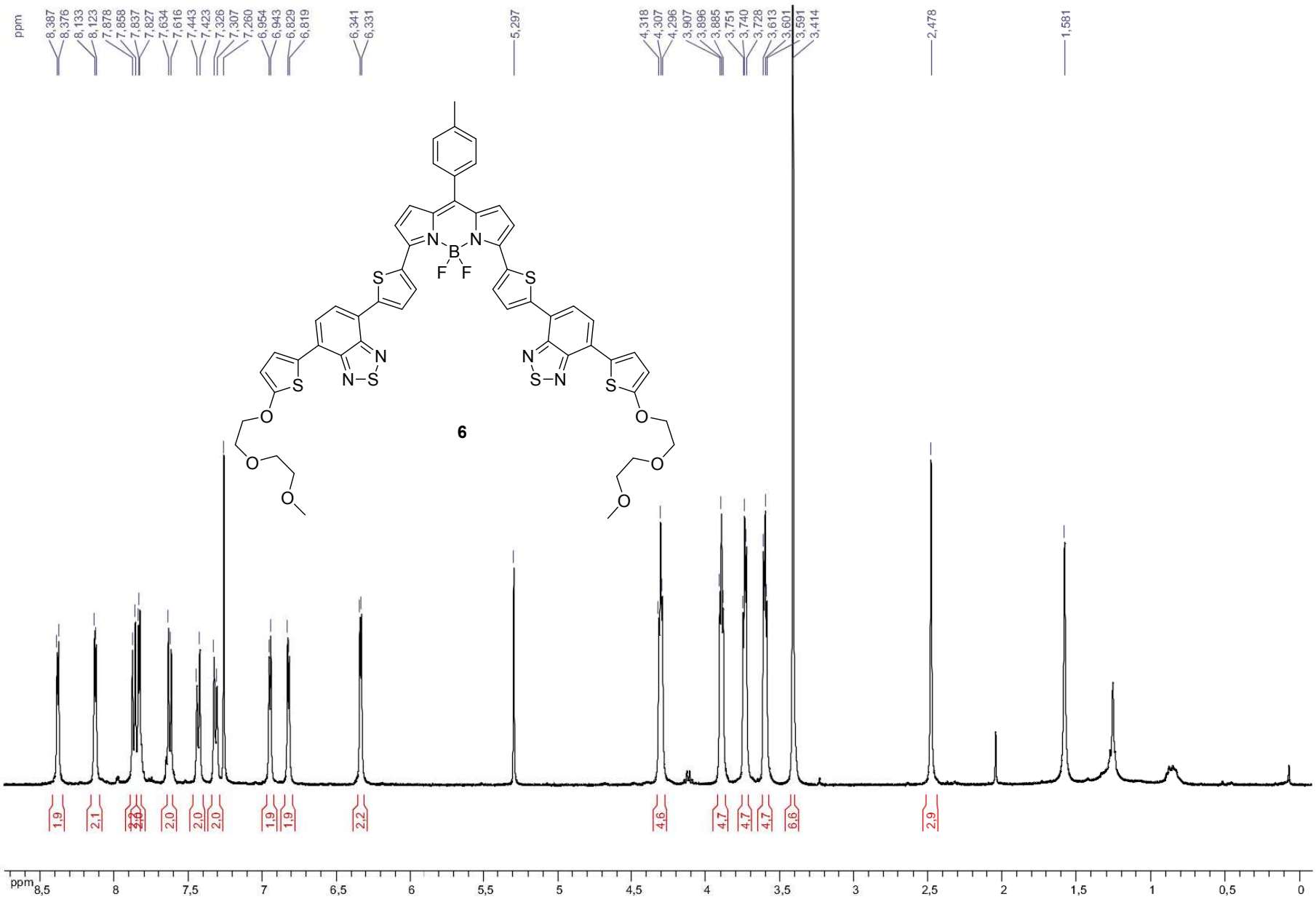
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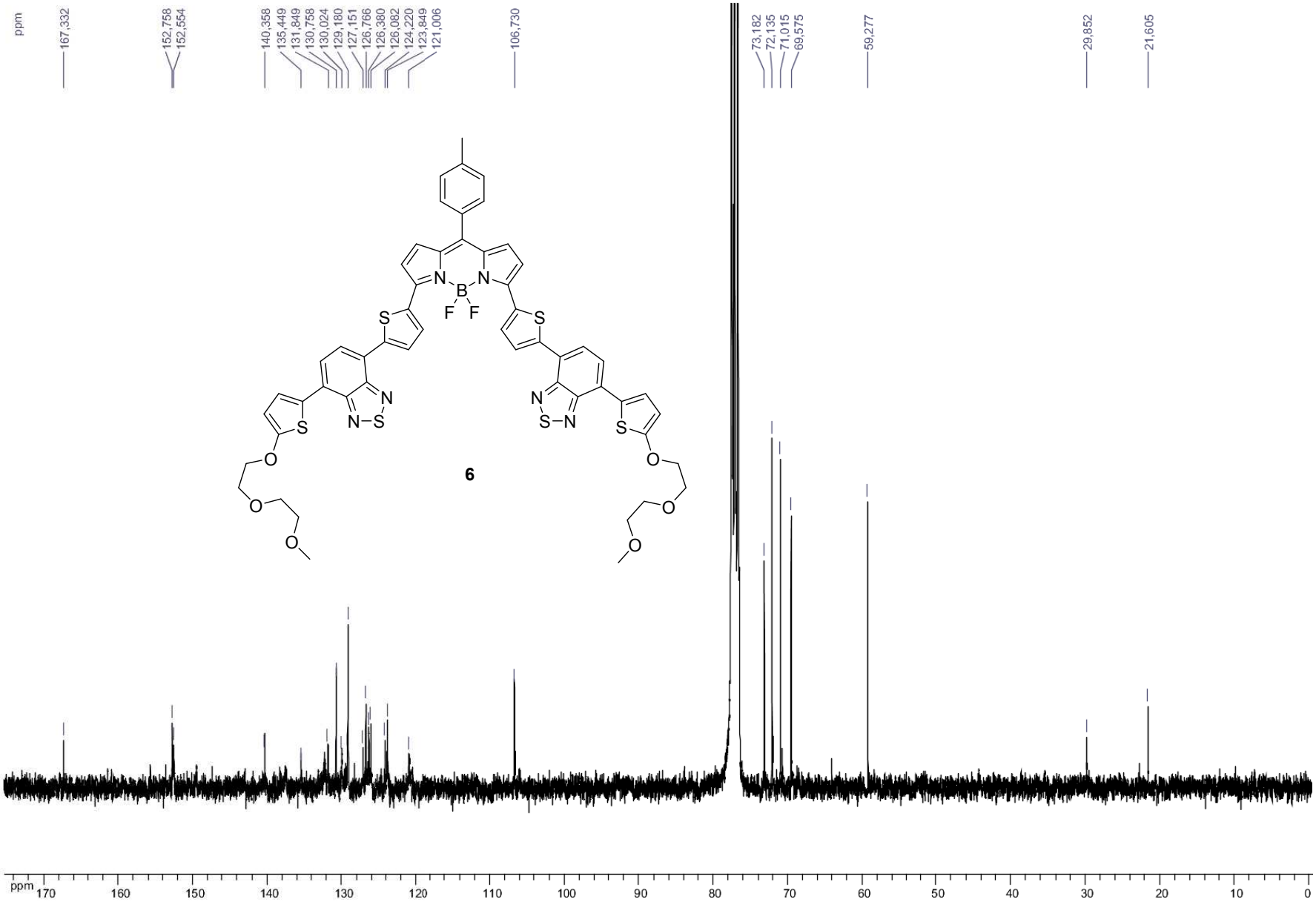
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