ELECTRONIC SUPPLEMENTARY INFORMATION

Convenient synthesis of EDOT based dyes by CH-activation and their testing in dye-sensitized solar cells

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1. Synthesis:

Table S1. One-pot C-H activation method development for the synthesis of compound **4a**.

EDOT	Bz	DMA	Ligand	Solvent	Time	Yield
1 eq	1.2 eq	1.2 eq	$PH(Cy)_3.BF_4$	DMF	24 hrs	27%[1]
2 eq	1 eq	1.5 eq	$PH(Cy)_3.BF_4$	DMF	42 hrs	4%[2]
2 eq	1 eq	1.5 eq	$PH(Cy)_3.BF_4$	THF	42 hrs	---[2]
2 eq	1.5 eq	1 eq	$PH(Cy)_3.BF_4$	DMF	42 hrs	43%[3]
2 eq	1.5 eq	1 eq	$PH(Cy)_3.BF_4$	THF	42 hrs	14%[3]
2 eq	2 eq	1 eq	$PH(iPr)_3.BF_4$	DMF	42 hrs	51%[3]
2 eq	2 eq	1 eq	$PH(tBu)_3.BF_4$	DMF	42 hrs	58%[3]

Bz: 4-Bromobenzaldehyde; DMA: 4-bromo-*N,N*-dimethylaniline; PivOH: pivalic acid; DMF: Dimethylformamide; THF: Tetrahydrofuran

All reactions were undertaken in an oven-dried flask flushed with Argon.

[1]EDOT, Bz, DMA, Cs_2CO_3 (1.5 eq), PivOH (0.3 eq), $Pd(OAc)_2$ (10%), ligand (30%) were dissolved in the solvent and left to stir for 24 hrs at 100°C.

[2]Bz, EDOT, Cs_2CO_3 (2.5 eq), PivOH (40%), $Pd(OAc)_2$ (5%), ligand (15%) were dissolved in the solvent and initially left to react for 18 hrs. DMA was then added with $Pd(OAc)_2$ (5%) and ligand (15%) and the reaction was left to stir for 24 hrs at 100°C.

[3]DMA, EDOT, Cs_2CO_3 (2.5 eq), PivOH (40%), $Pd(OAc)_2$ (5%), ligand (15%) were dissolved in the solvent and initially left to react for 18 hrs. Bz was then added with $Pd(OAc)_2$ (5%) and ligand (15%) and the reaction was left to stir for 24 hrs at 100°C.

2. Electrochemistry:

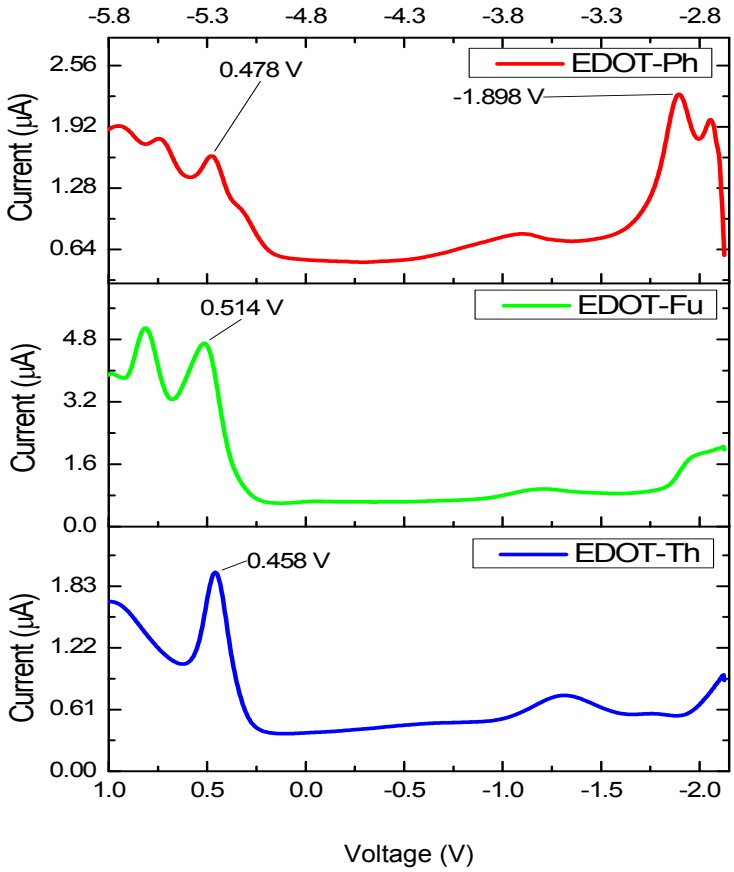


Fig. S1 Square-wave voltammograms of the dyes (1×10^{-5} M) recorded in DMF (V vs. Fc/Fc^{+}).

3. Device manufacture and testing:

TiO_2 photo-anodes (0.5 x 2 cm) were prepared on TEC7™ FTO glass (NSG) by doctor blading 2 layers of DSL18NR-T colloid (Dyesol) and then 1 layer of WER4-O scattering colloid (Dyesol). Each TiO_2 layer was sintered 500°C for 30 min prior to immersion in 50 mM solution of $TiCl_4$:THF_2 in DI water at 70°C for 30 min, rinsing and re-sintering at 500°C for 30min. Photo-anodes were dyed by immersion in 0.5mM THF solutions for 18h before rinsing with THF. Counter electrodes were platinized by depositing Pt colloid (Dyesol) on TEC8™ glass pre-drilled with 2 fill holes 2cm apart and sintering at 400°C for 30min. The 2 electrodes were sealed together using Surlyn™ (DuPont) at 120°C and the cavity filled with electrolyte (1-methyl-3-propyl-immidazolium iodide, LiI, I_2, benzimidazole and guanidine thiocyanate in acetonitrile. Fill holes were sealed with a glass cover slip and further Surlyn™ at 120°C.

I-V data were measured with a Xe arc lamp solar simulator (ABET) and a Keithley 2400 at 1 Sun calibrated using a certified crystalline Si reference cell (Oriel 91150V). Spectral response was measured at 1 Sun on a QEX10 Quantum Efficiency Measurement System in

DC mode at 10 nm resolution.

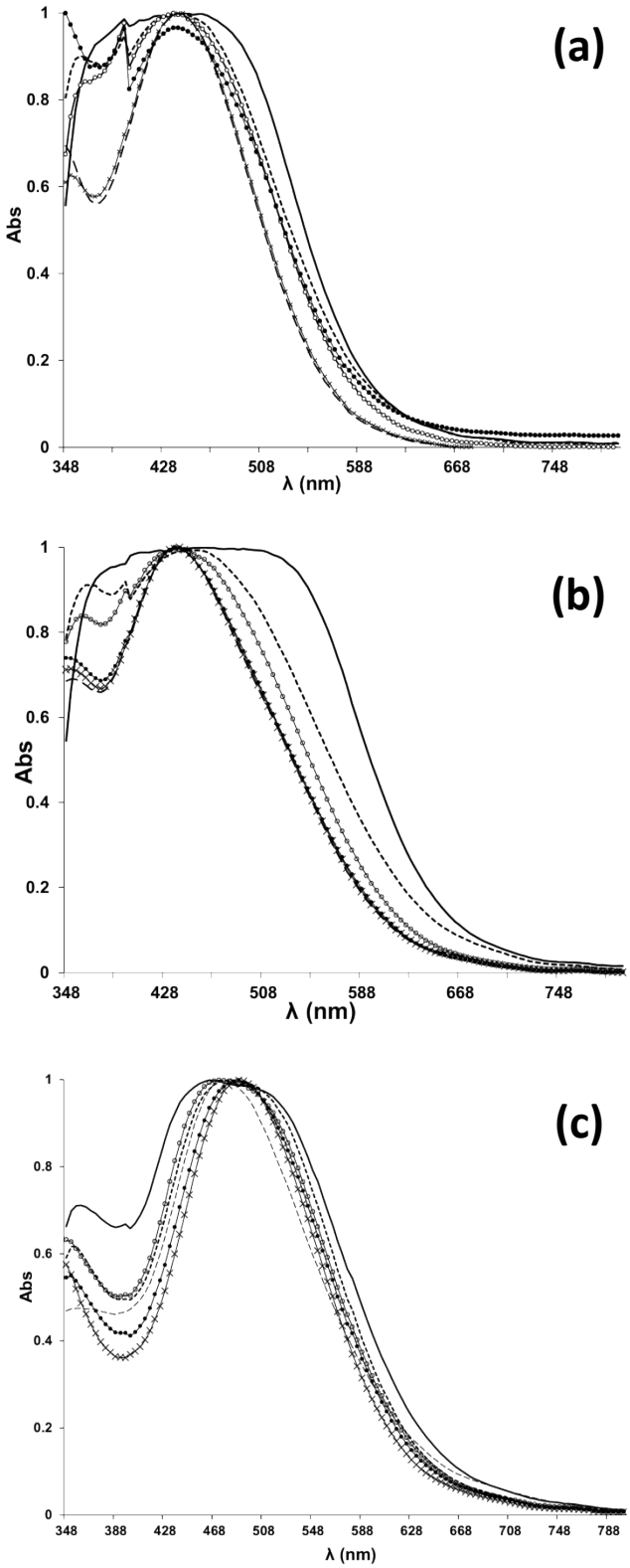


Fig. S2 Normalised UV-vis spectra of (a) **EDOT-Ph**, (b) **EDOT-Fu** and (c) **EDOT-Th** adsorbed on transparent, mesoporous TiO_2 films with varying concentrations of CDCA; 0mM (solid line), 1mM (short dashes), 5mM (open circles), 10mM (closed circles), 15mM (black crosses) and 20mM (long dashes).

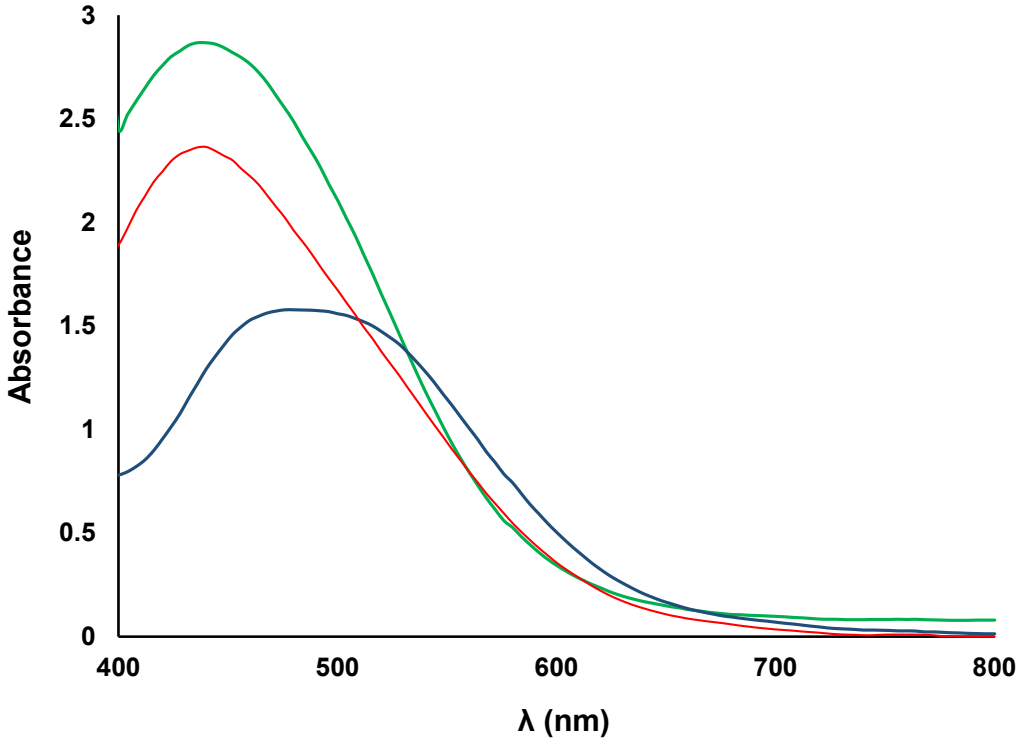


Fig. S2 cont. (d) Raw UV-vis spectral data of **EDOT-Ph** (green), **EDOT-Fu** (red) and **EDOT-Th** (blue) adsorbed on transparent, mesoporous TiO_2 films.

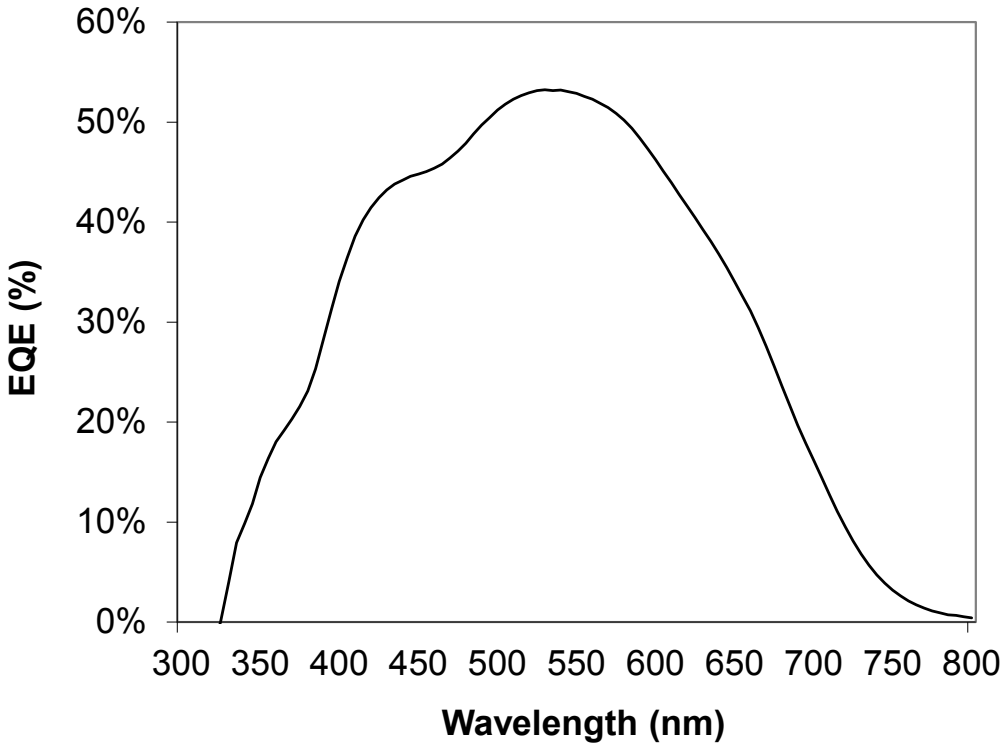


Fig. S3 EQE of N719 dyed DSSC device.

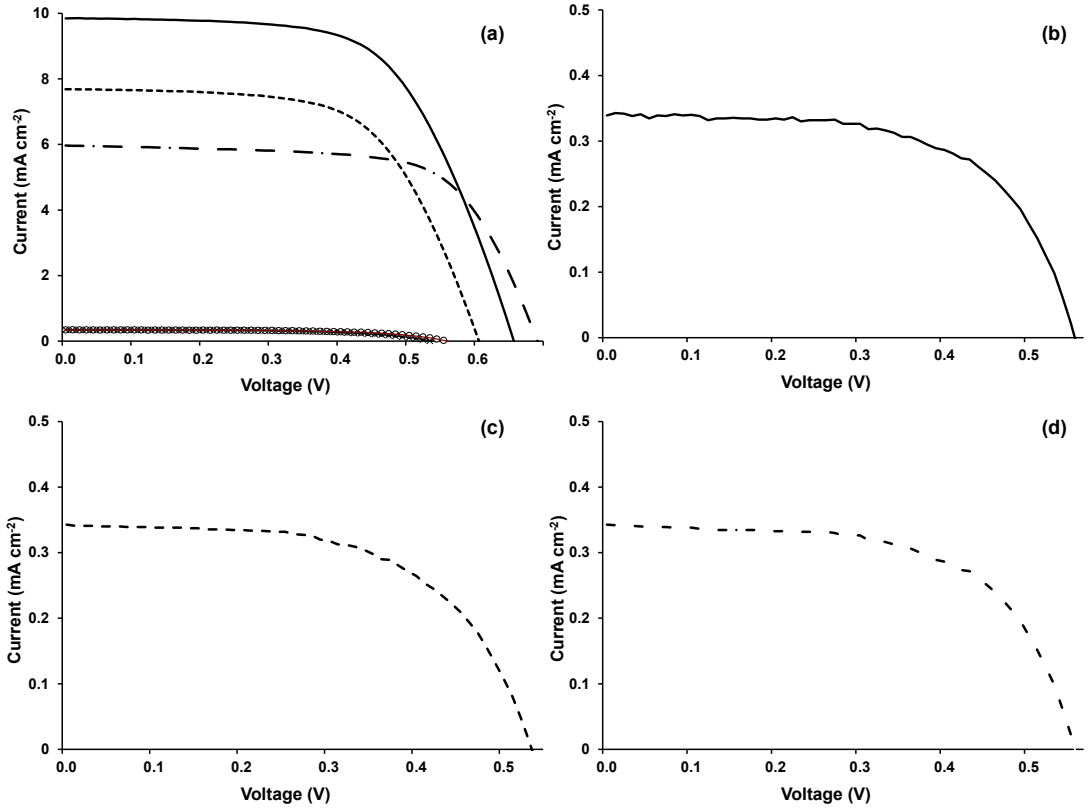
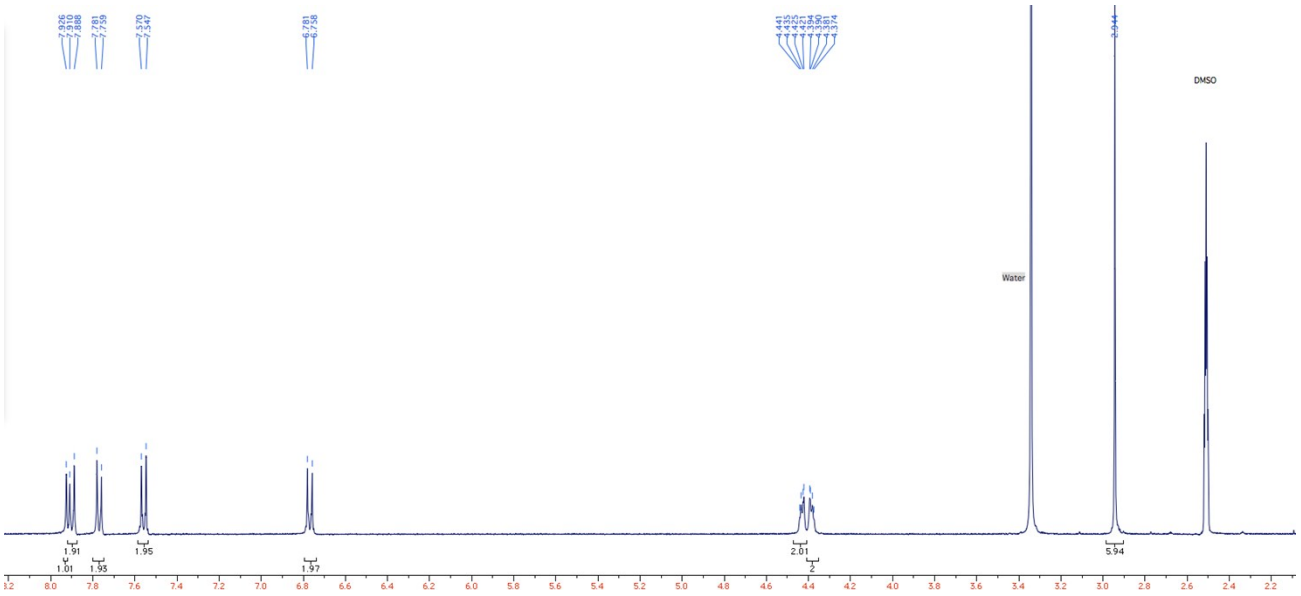


Fig. S4 (a) I-V data for EDOT dyes under illumination in the dark and replotted IV data for dark currents for (b) **EDOT-Ph**, (c) **EDOT-Fu** and (d) **EDOT-Th**. Key for all data = **EDOT-Ph** (solid line), (c) **EDOT-Fu** (dashed line) and (d) **EDOT-Th** (dot-dashed lines).

4. ^{1}H NMR spectra.

EDOT-Ph:



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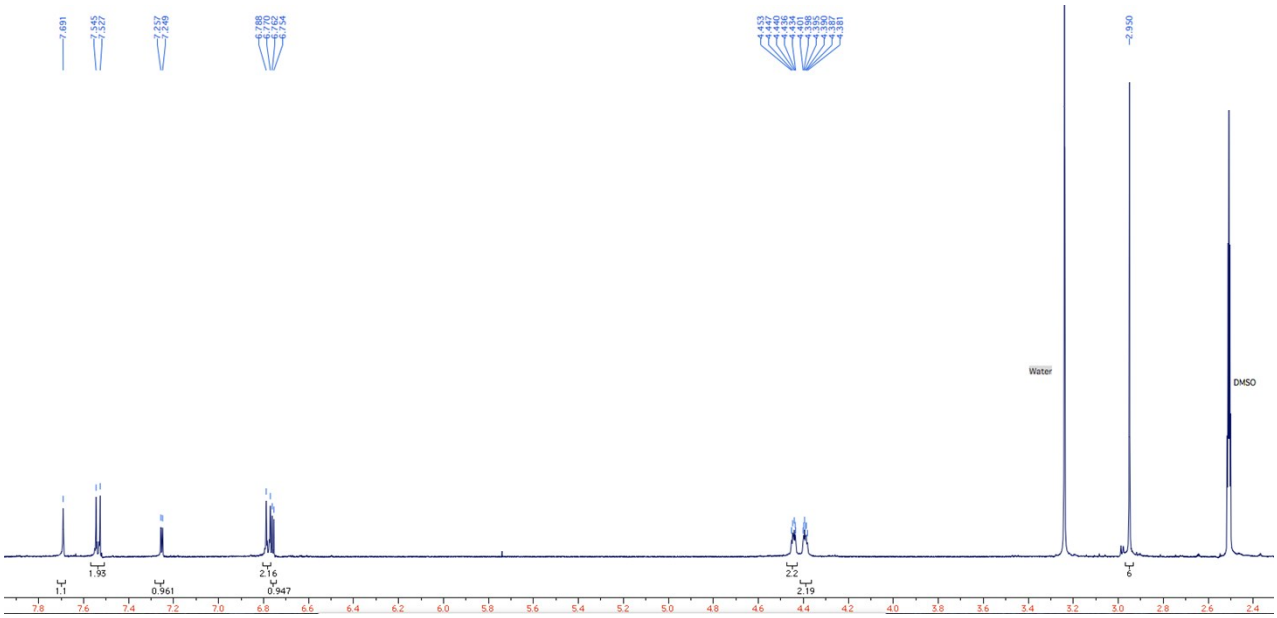
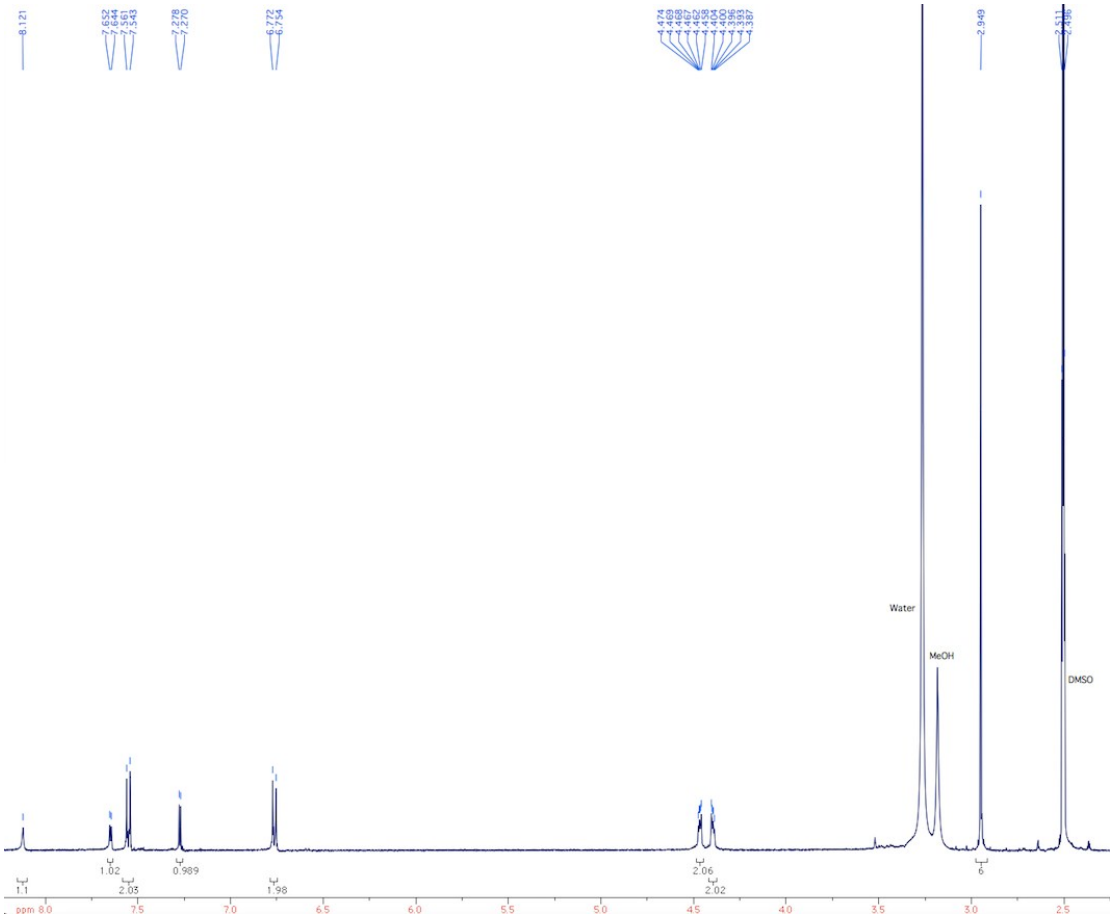


EDOT-Th: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4.400
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2.511
2.496
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DMSO
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2.05
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1.98
2.06
2.02
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5.0
4.5
4.0
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2.5