

Supporting Information

Orthogonally Functionalized Donor/Acceptor Homo- and Heterodimeric Dyes for Dye-Sensitized Solar Cells: An Approach to Introduce Panchromaticity and Control the Charge Recombination

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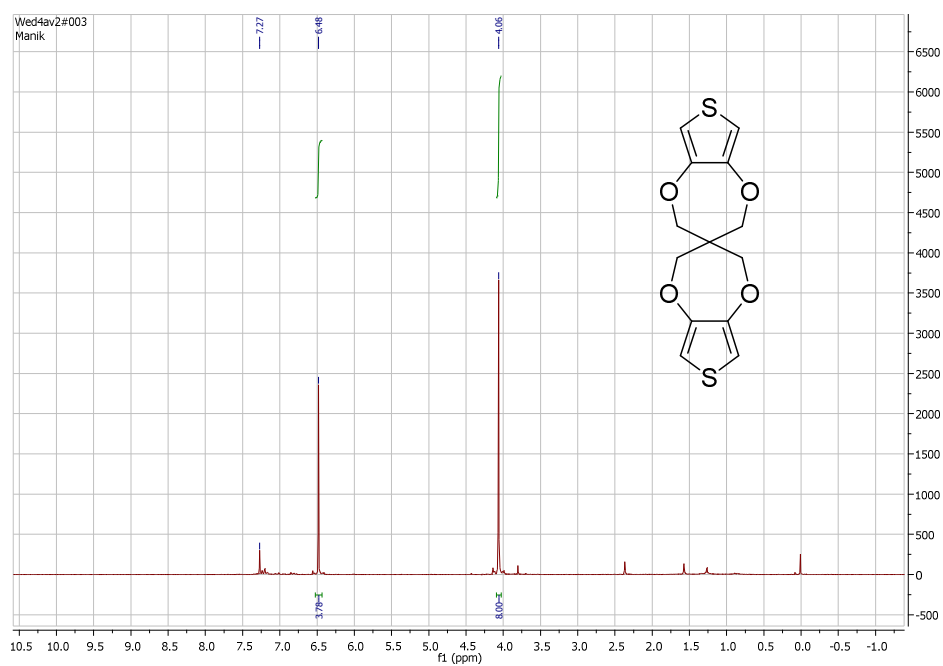
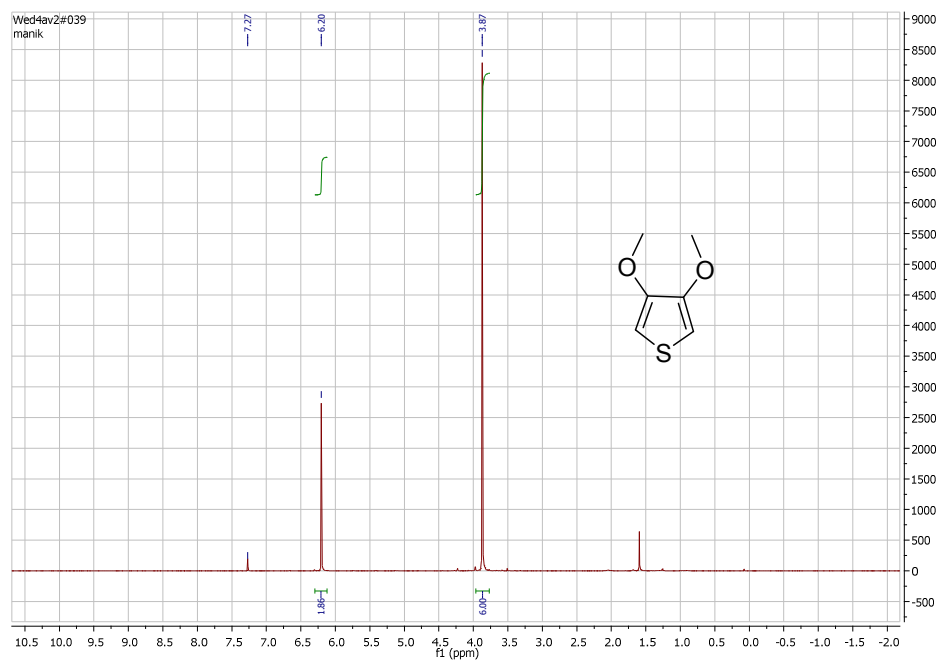


Figure S1. ^1H NMR (CDCl_3) of 3,4-dimethoxythiophene and 2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine] .

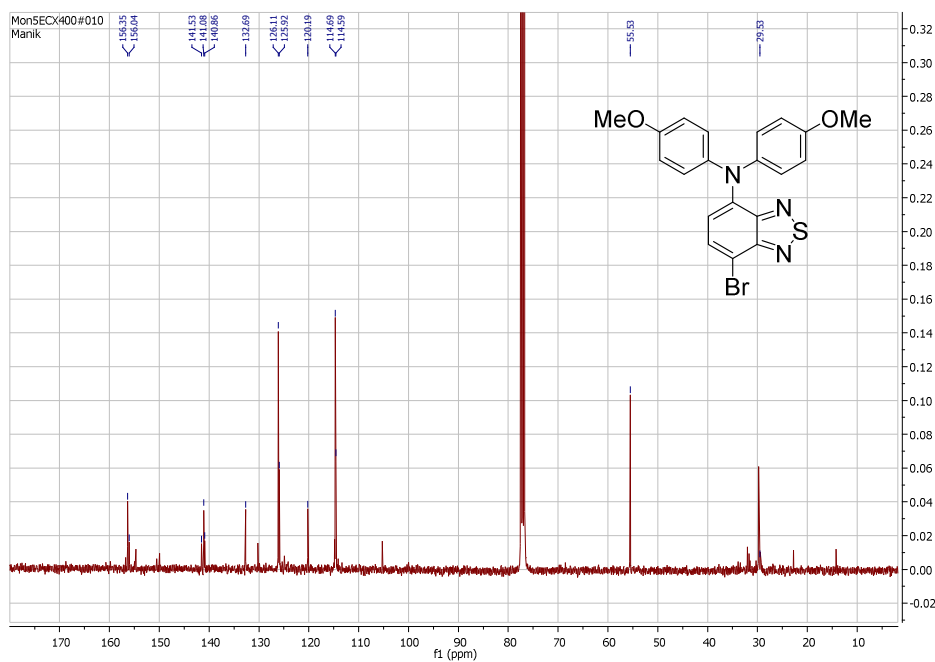
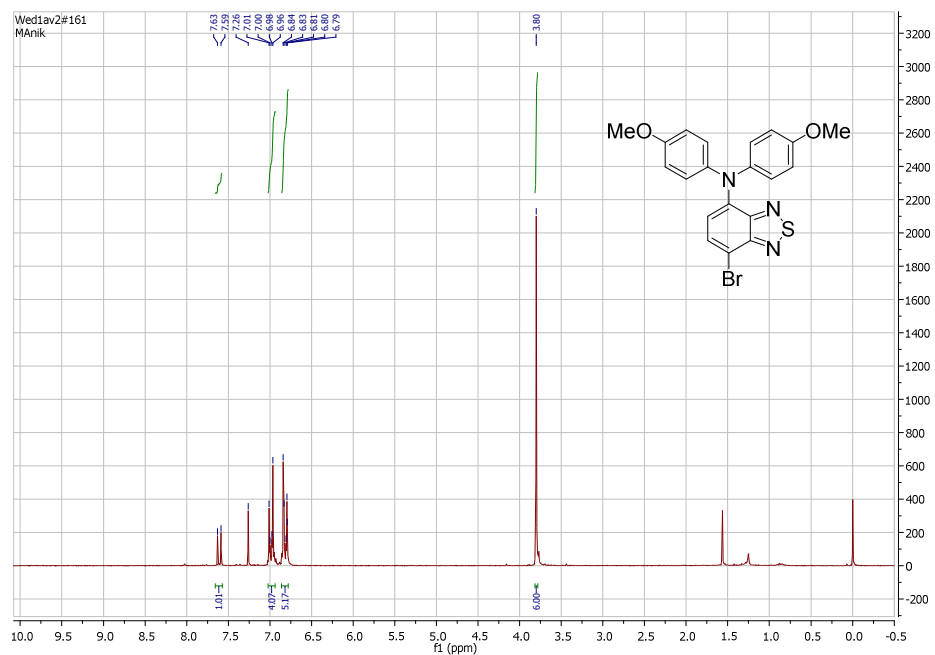


Figure S2. ¹H and ¹³C NMR (CDCl₃) spectra of Synthesis of 7-bromo-N, N-bis(4-methoxyphenyl)benzo[c][1,2,5]thiadiazol-4-amine (5).

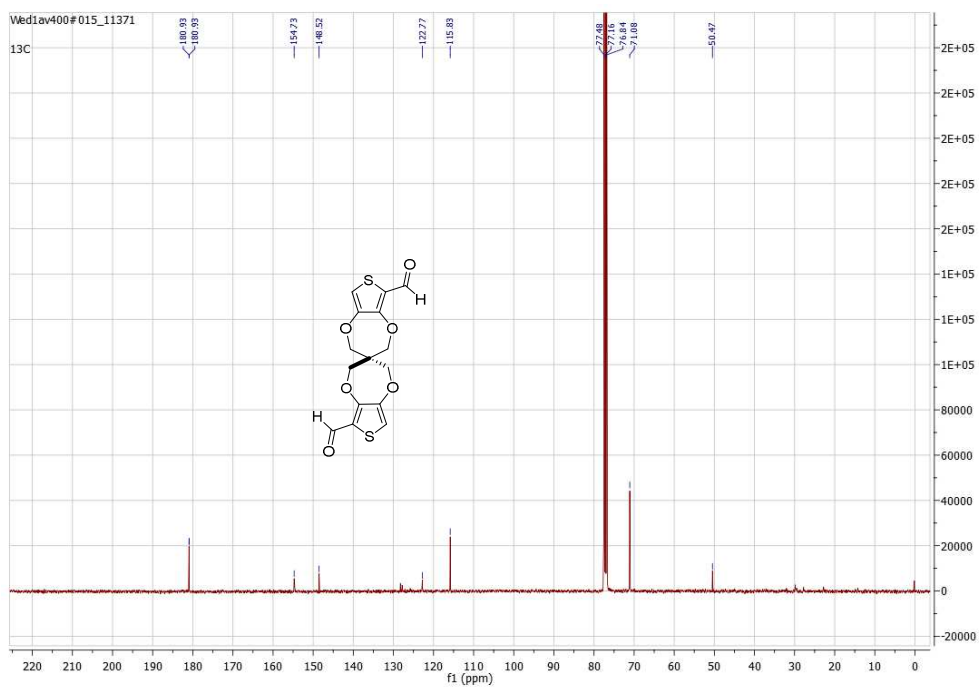
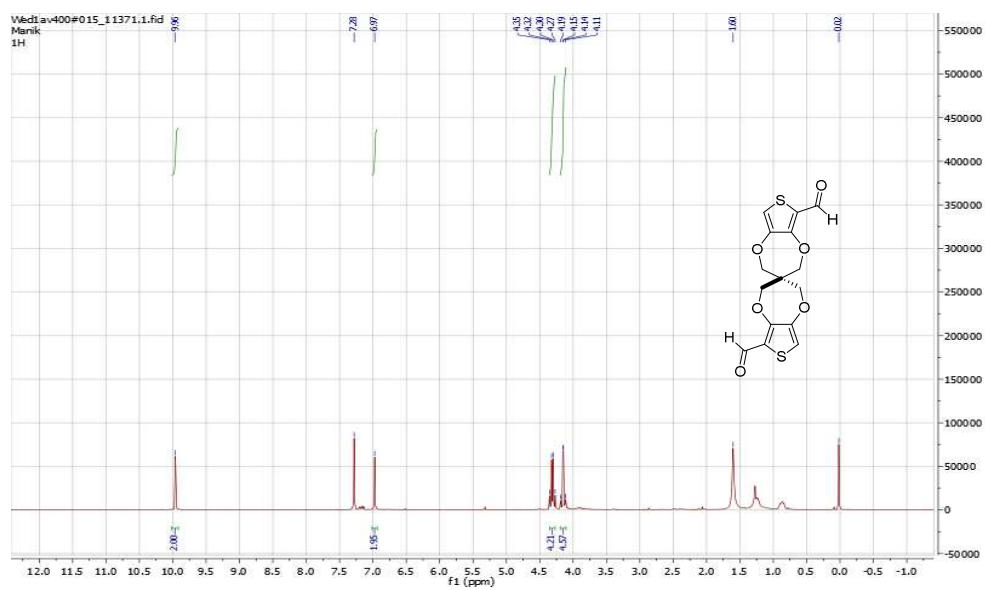


Figure S3. ^1H and ^{13}C NMR (CDCl_3) spectra of 2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-6,6'-dicarbaldehyde (1).

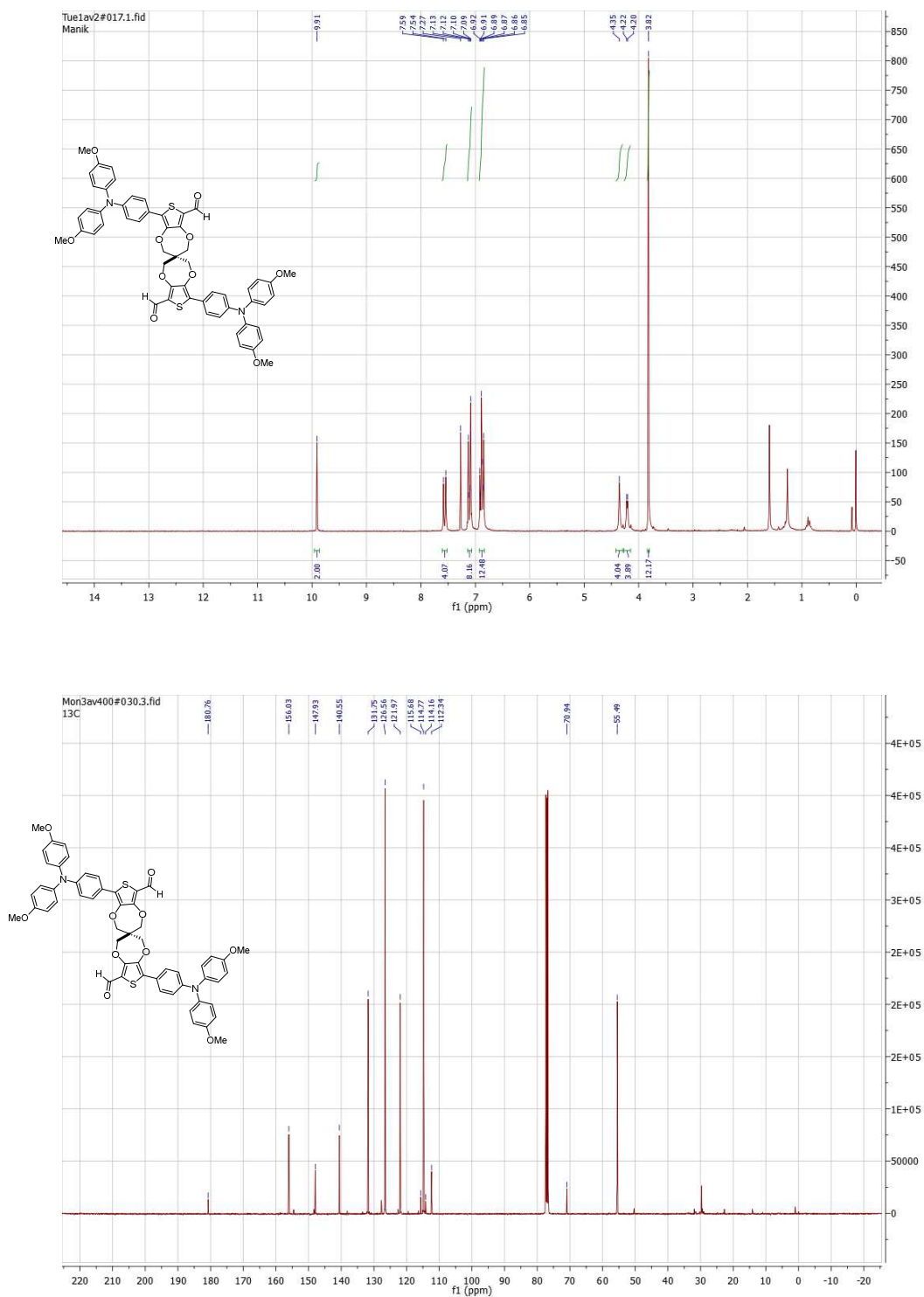


Figure S4. ¹H and ¹³C NMR (CDCl₃) spectra of 6,6'-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-8,8'-dicarbaldehyde (3).

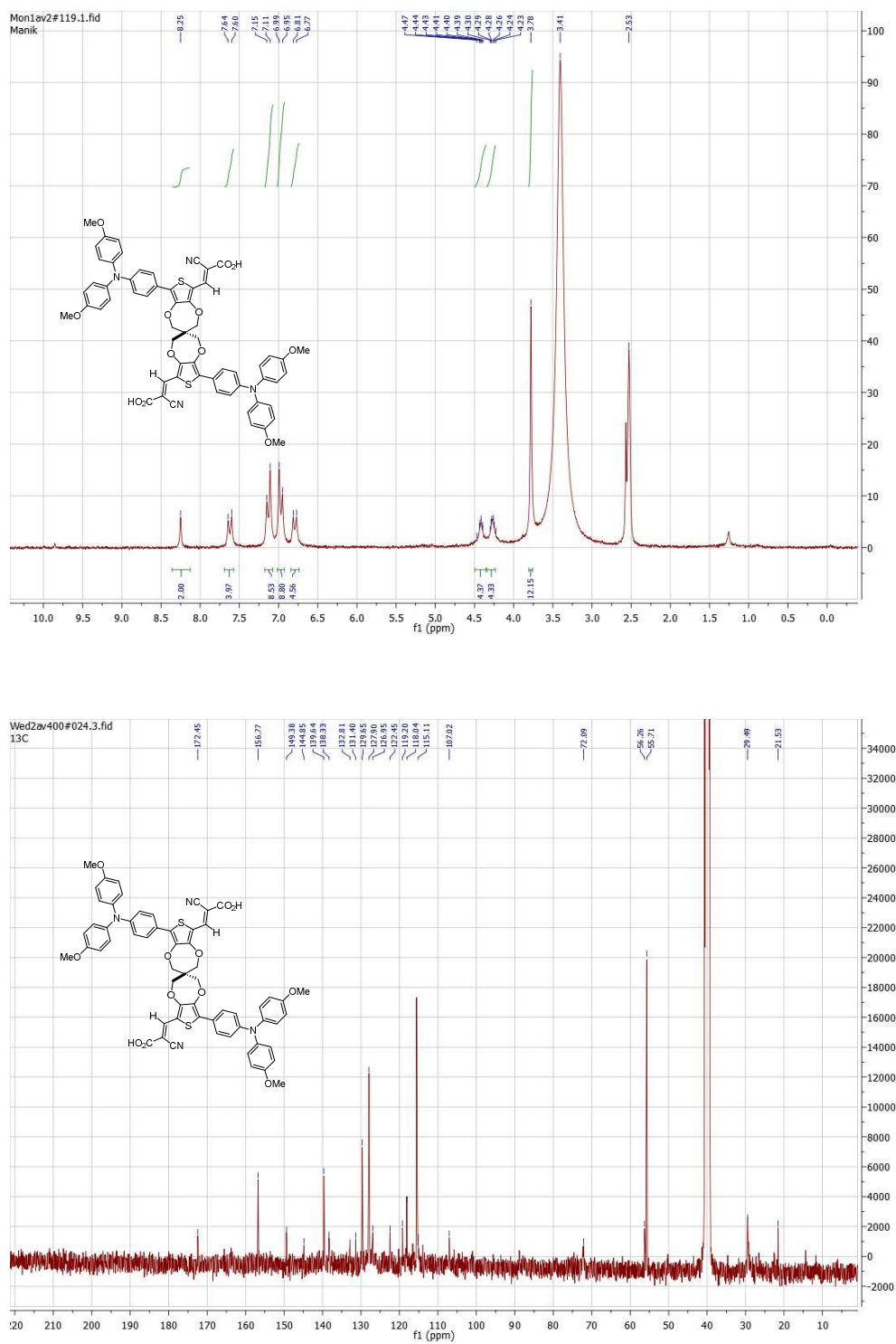


Figure S5. ¹H and ¹³C NMR (DMSO-d₆) spectra D₁-D₁ (4).

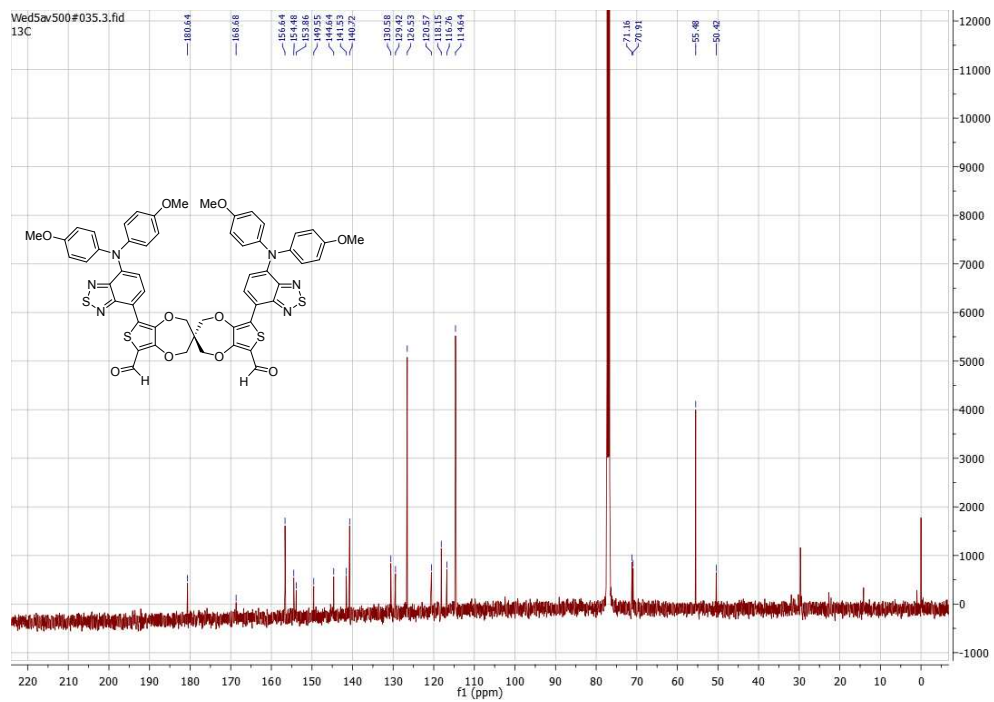
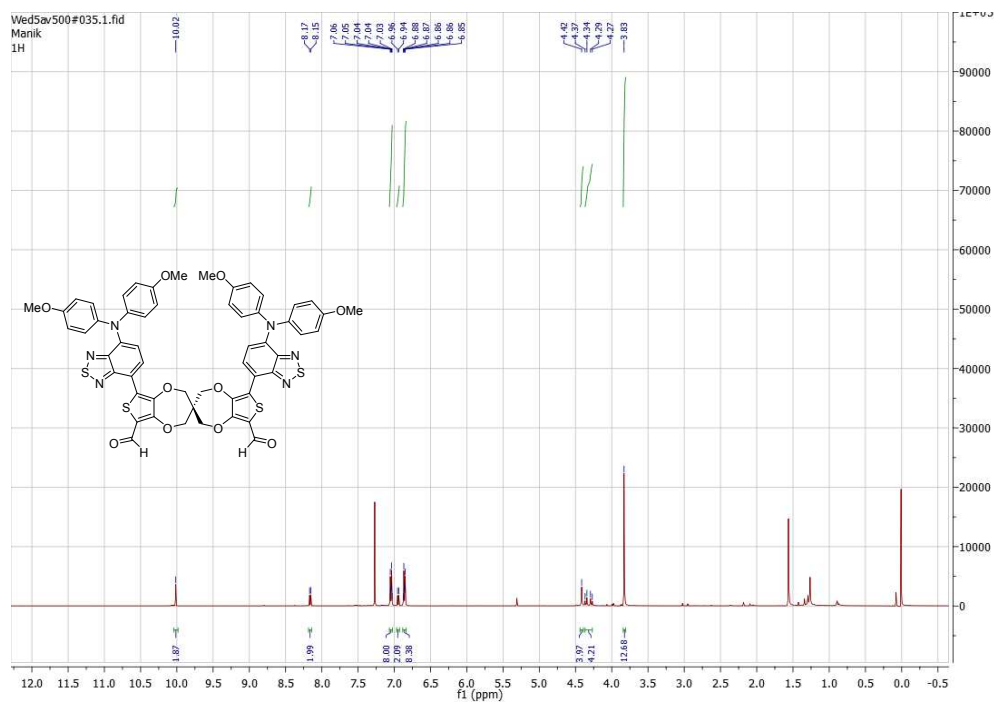


Figure S6. ^1H and ^{13}C NMR (CDCl_3) spectra of 6,6'-bis(7-(bis(4-methoxyphenyl)amino)benzo[*c*][1,2,5]thiadiazol-4-yl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-*b*][1,4]dioxepine]-8,8'-dicarbaldehyde (6).

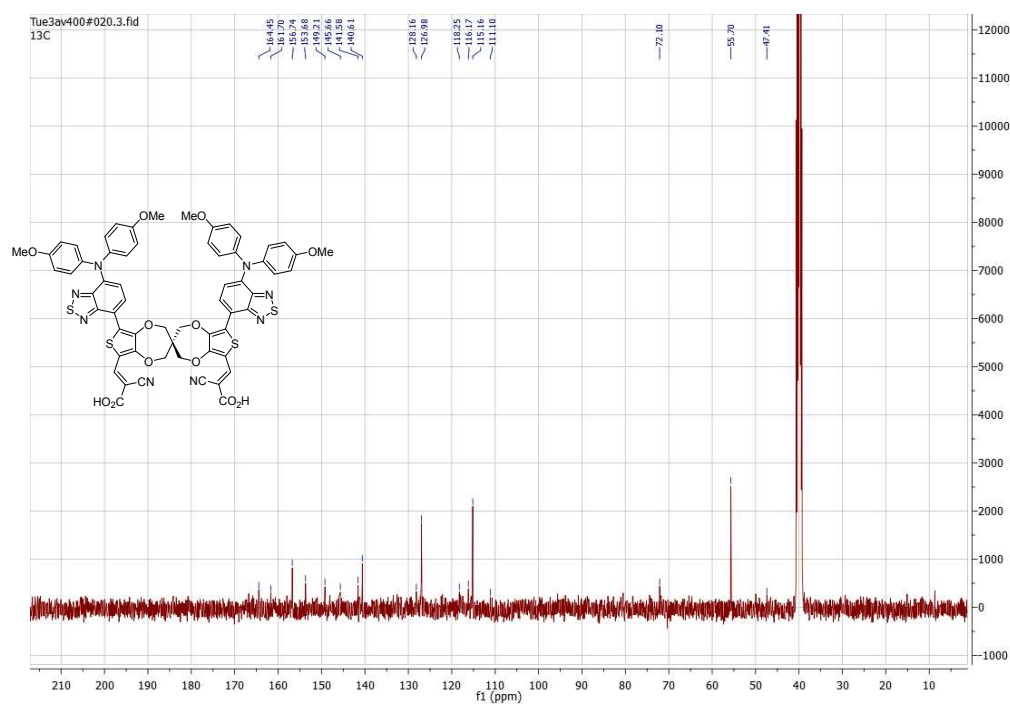
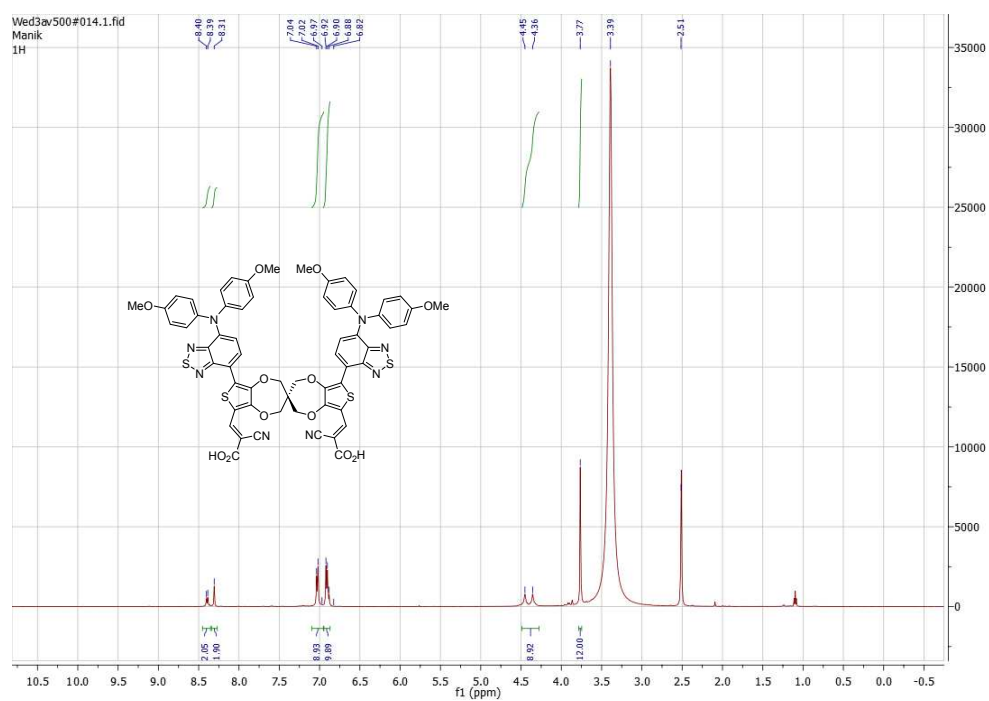


Figure S7. ^1H and ^{13}C NMR (DMSO- d_6) spectra of D₂-D₂ (7).

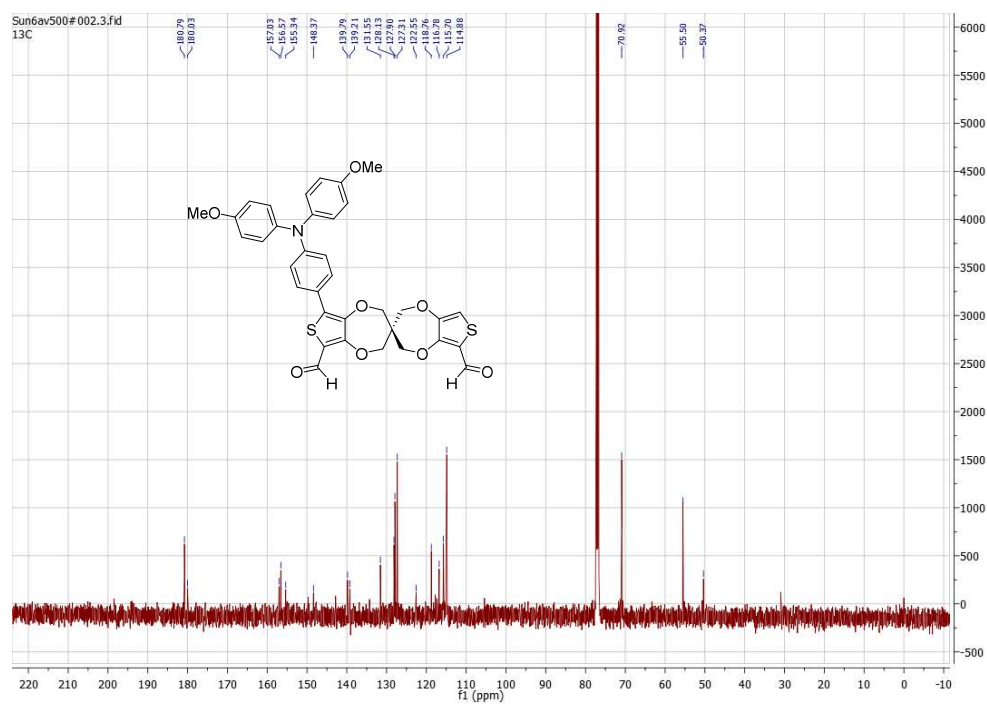
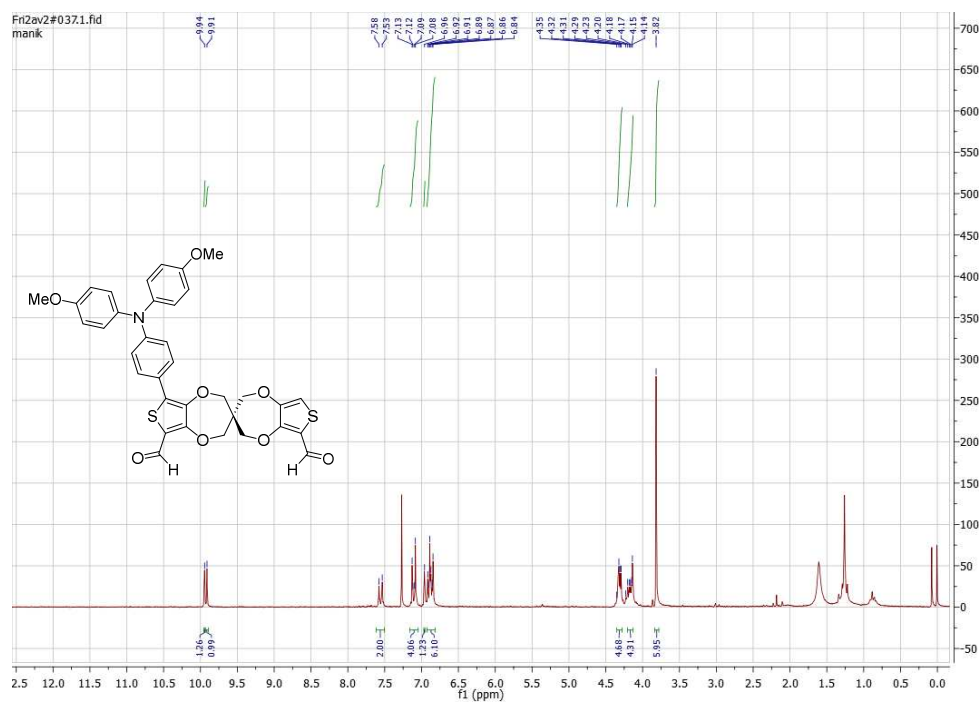


Figure S8. ^1H and ^{13}C NMR (CDCl_3) spectra of 6'-(4-(bis(4-methoxyphenyl)amino)phenyl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-6,8'-dicarbaldehyde (8).

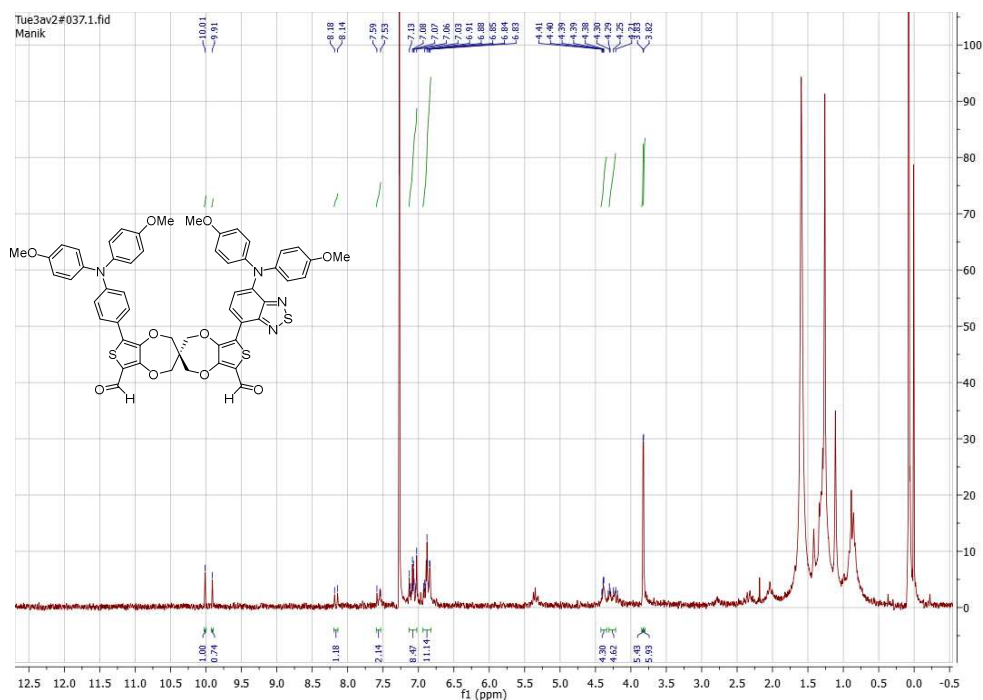
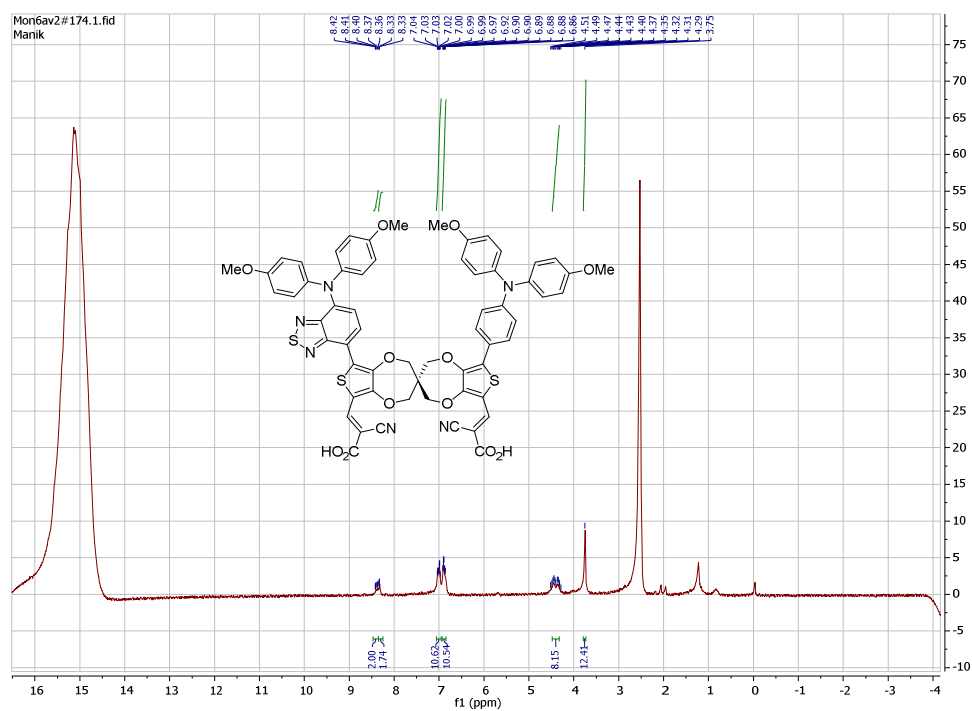
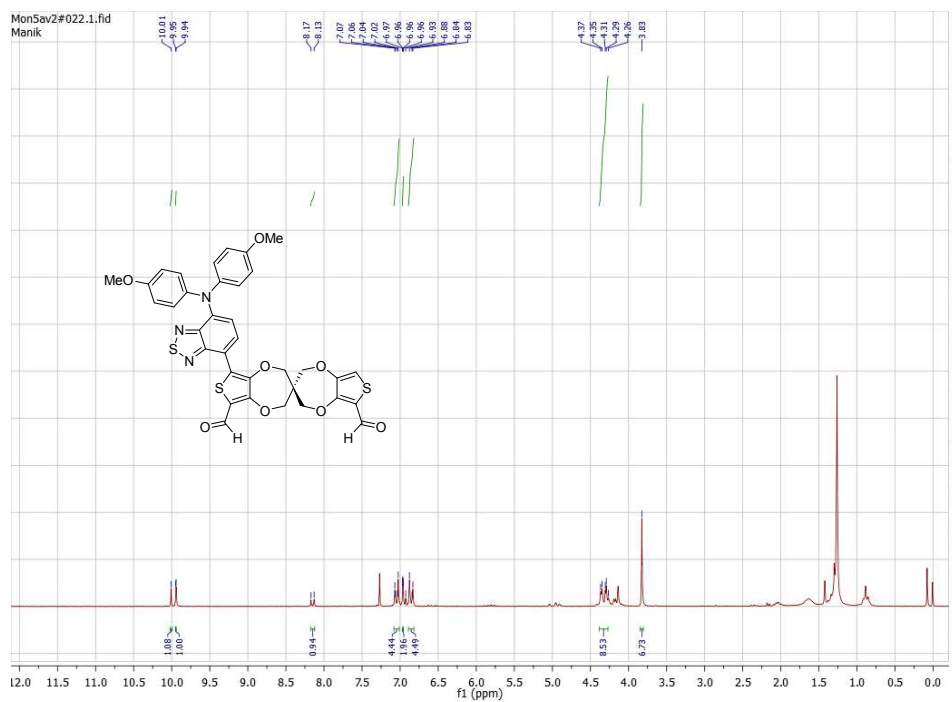
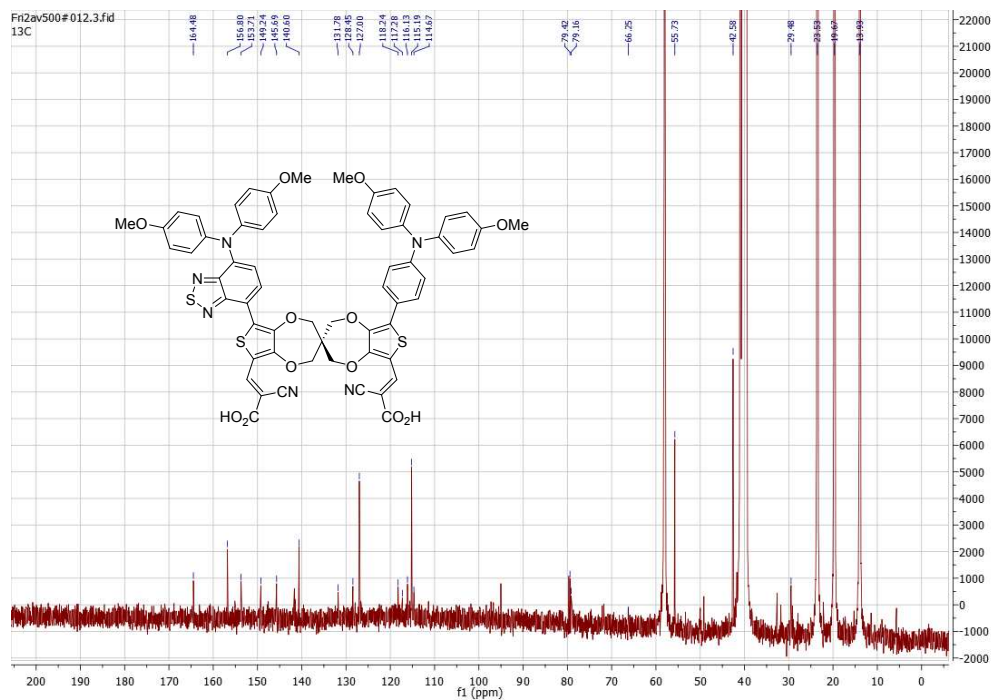


Figure S9. ¹H-NMR spectrum of 6-(7-(bis(4-methoxyphenyl)amino)benzo[c][1,2,5]thiadiazol-4-yl)-6'-(4-(bis(4-methoxyphenyl)amino)phenyl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-8,8'-dicarbaldehyde (9).





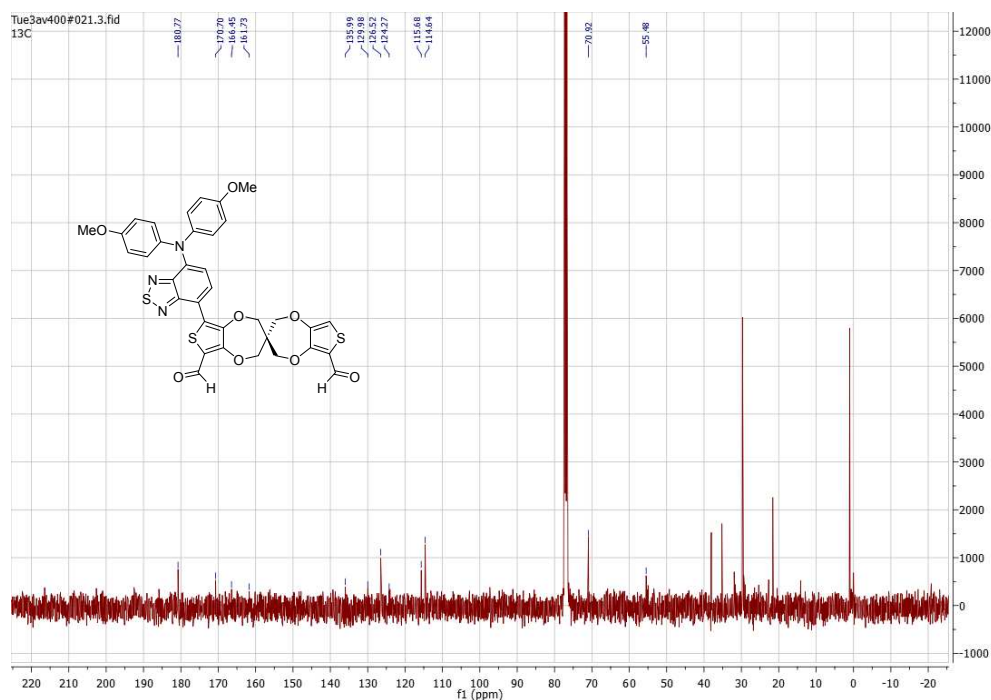
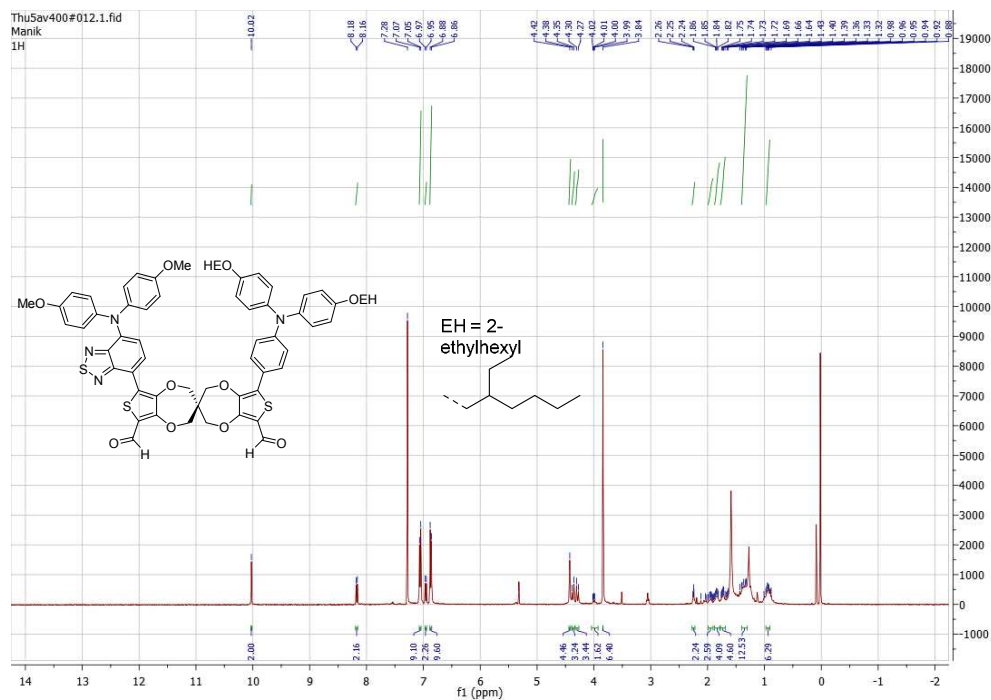


Figure S11. ^1H and ^{13}C NMR (CDCl_3) spectra of 6'-(7-(bis(4-methoxyphenyl)amino)benzo[c][1,2,5]thiadiazol-4-yl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-6,8'-dicarbaldehyde (11).



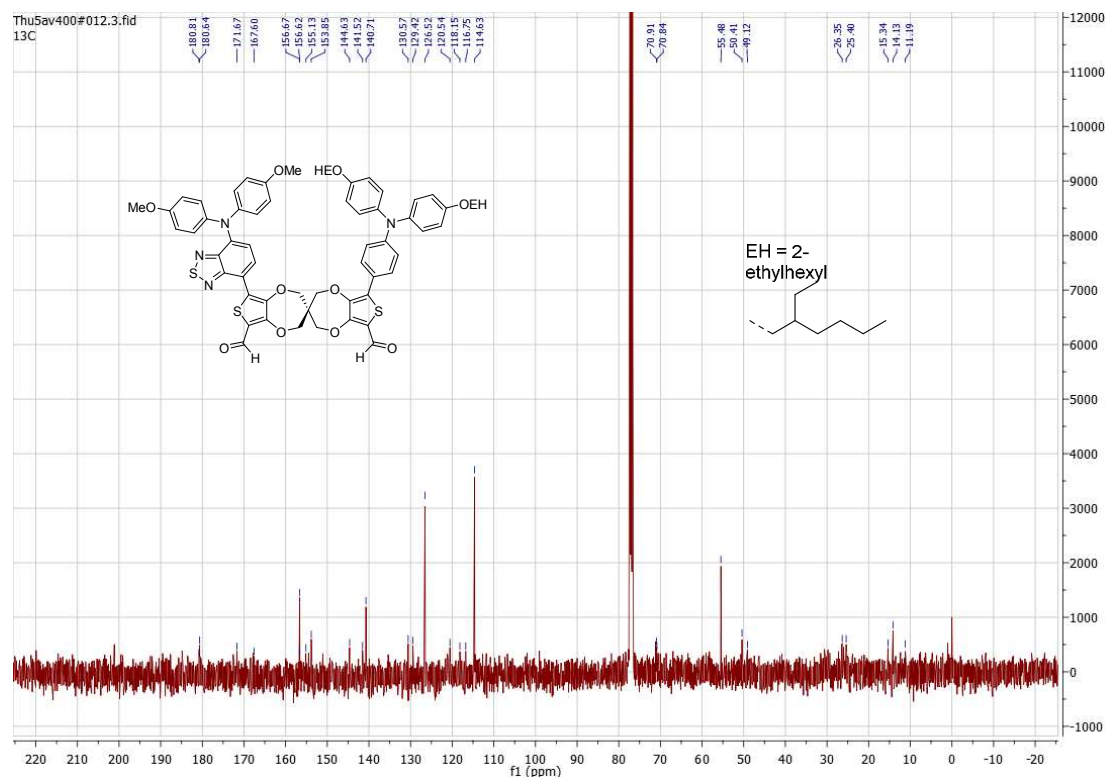
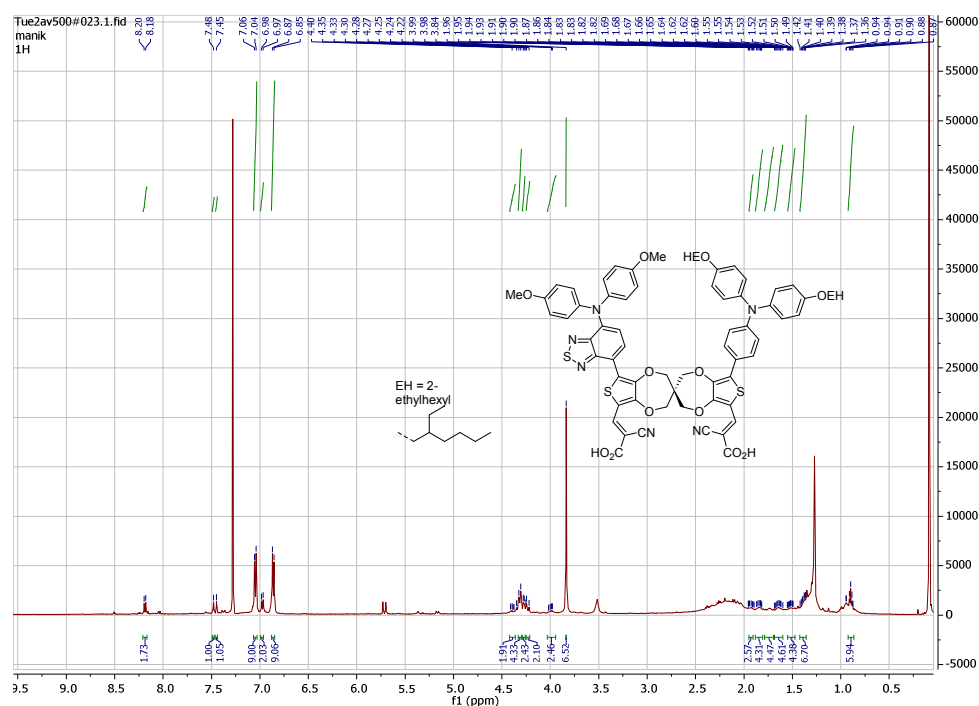


Figure S12. ^1H and ^{13}C NMR (CDCl_3) spectra of 6-(4-(bis(4-(2-ethylhexyl)oxy)phenyl)amino)phenyl)-6'-(7-(bis(4-methoxyphenyl)amino)benzo[*c*][1,2,5]thiadiazol-4-yl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-*b*][1,4]dioxepine]-8,8'-dicarbaldehyde (13).



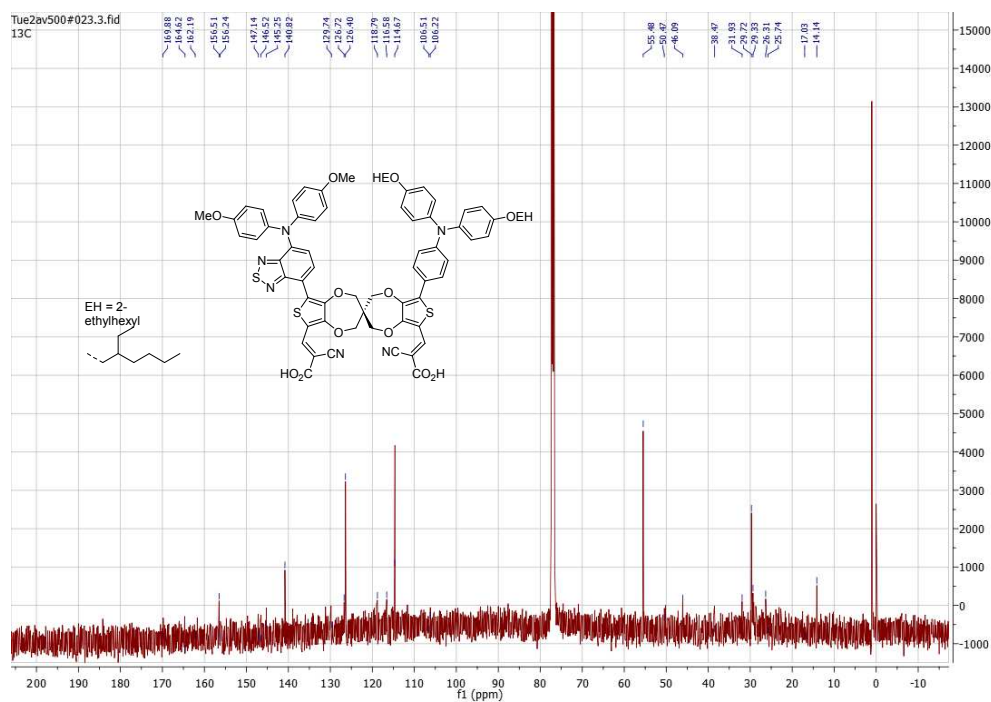
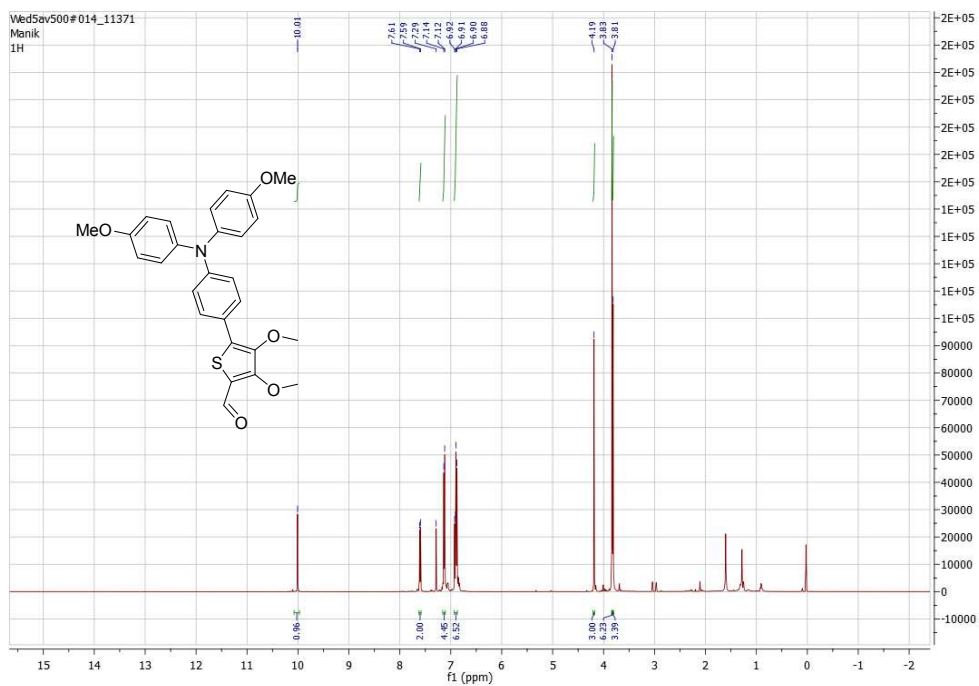


Figure S13. ^1H and ^{13}C NMR (CDCl_3) spectra of $\text{D}_2\text{-D}_4$ (14).



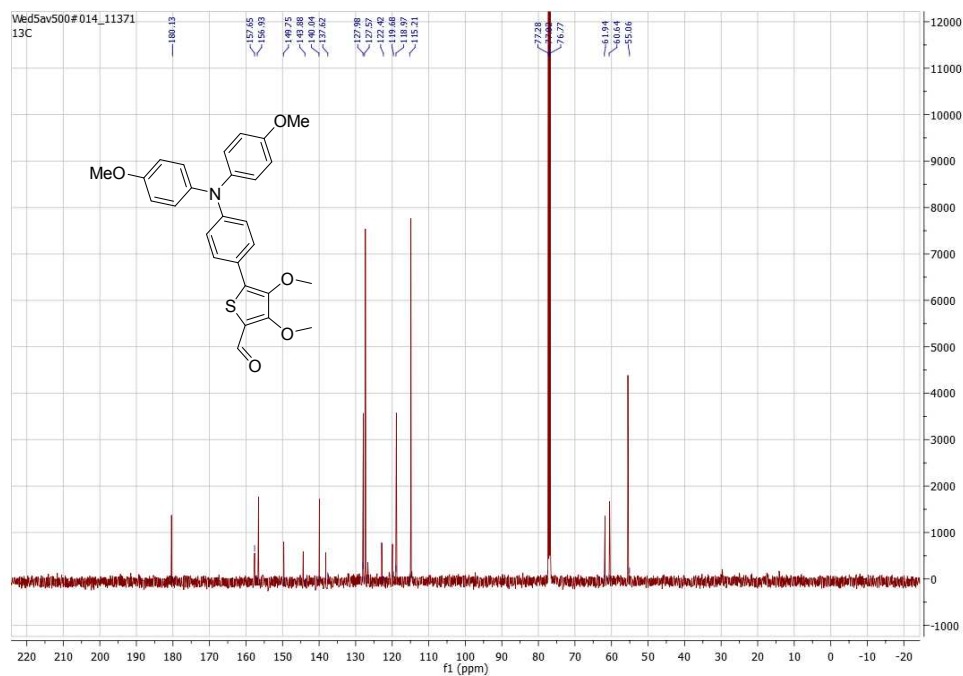
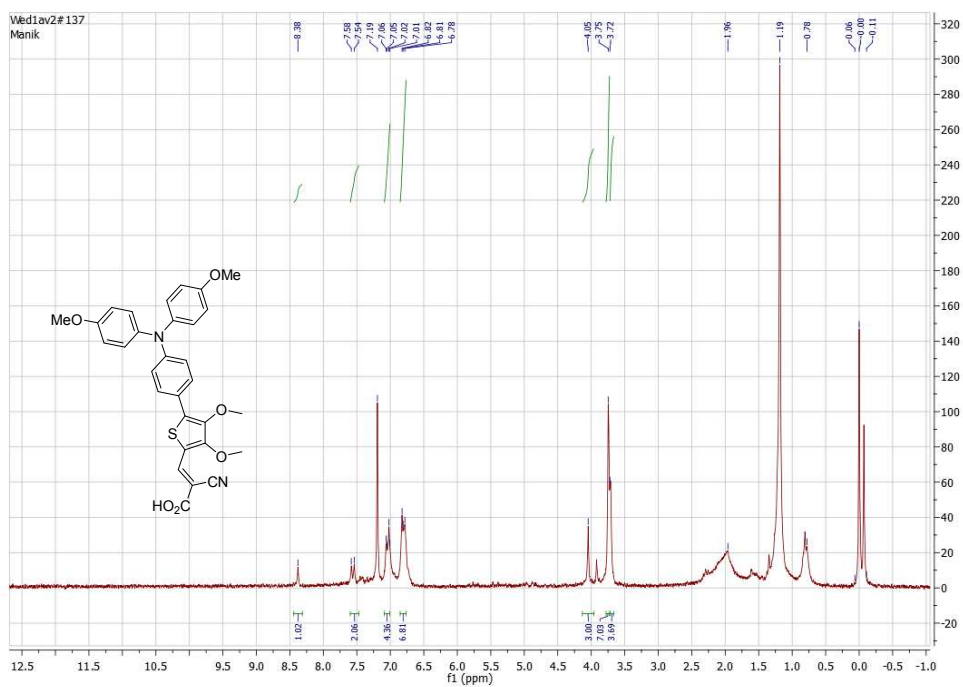


Figure S14. ^1H and ^{13}C NMR (CDCl_3) spectrum of 5-(4-(bis(4-methoxyphenyl)amino)phenyl)-3,4-dimethoxythiophene-2-carbaldehyde (16).



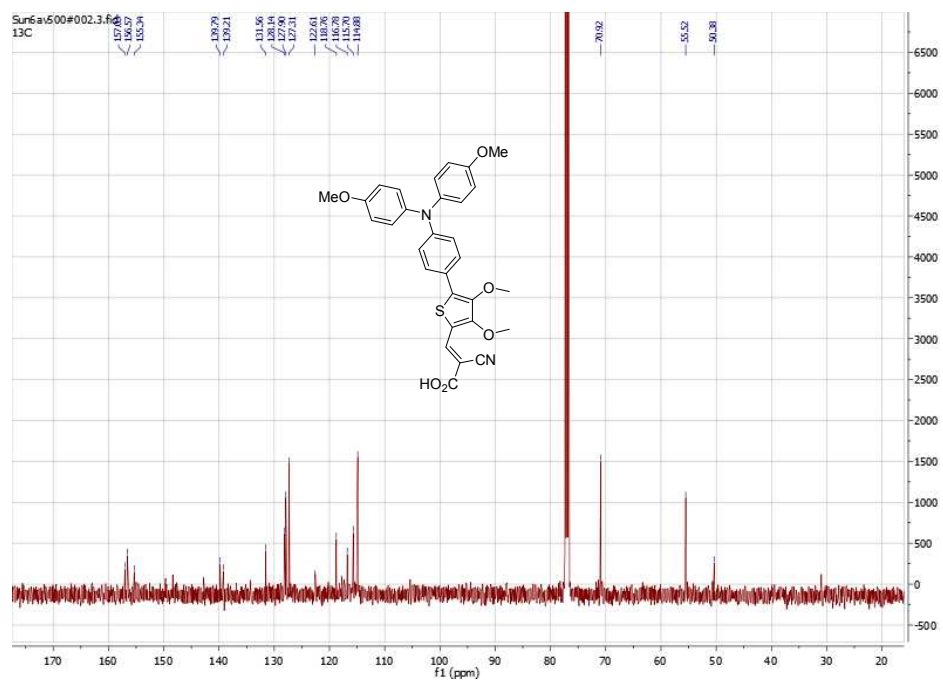


Figure S15. ^1H and ^{13}C NMR (CDCl_3) spectra D_1 (17).

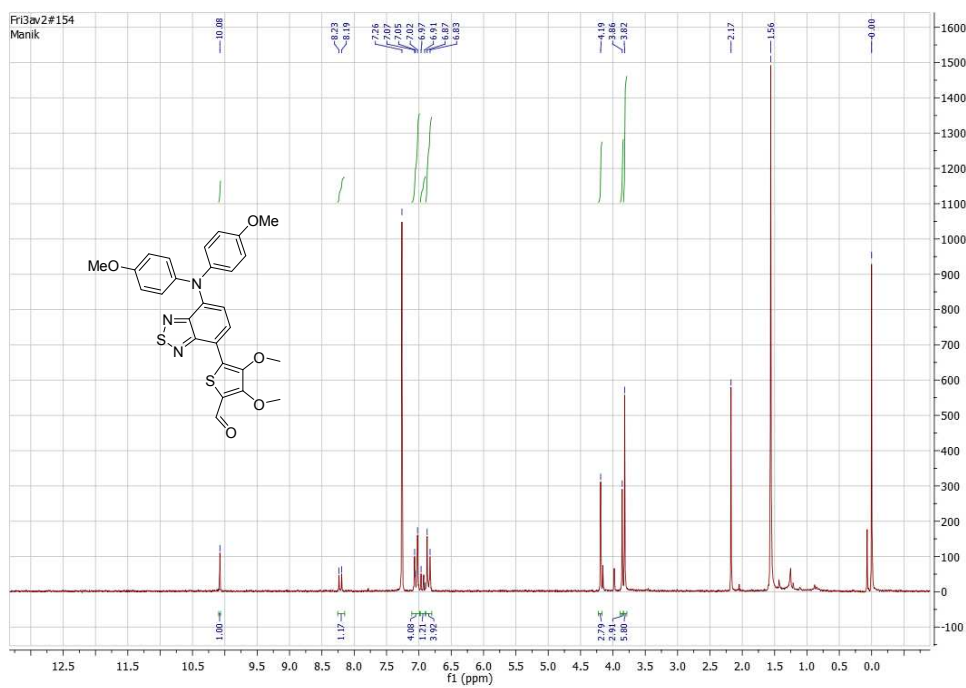


Figure S16. ^1H spectrum (CDCl_3) of 5-(7-(bis(4-methoxyphenyl)amino)benzo[c][1,2,5]thiadiazol-4-yl)-3,4-dimethoxythiophene-2-carbaldehyde (18).

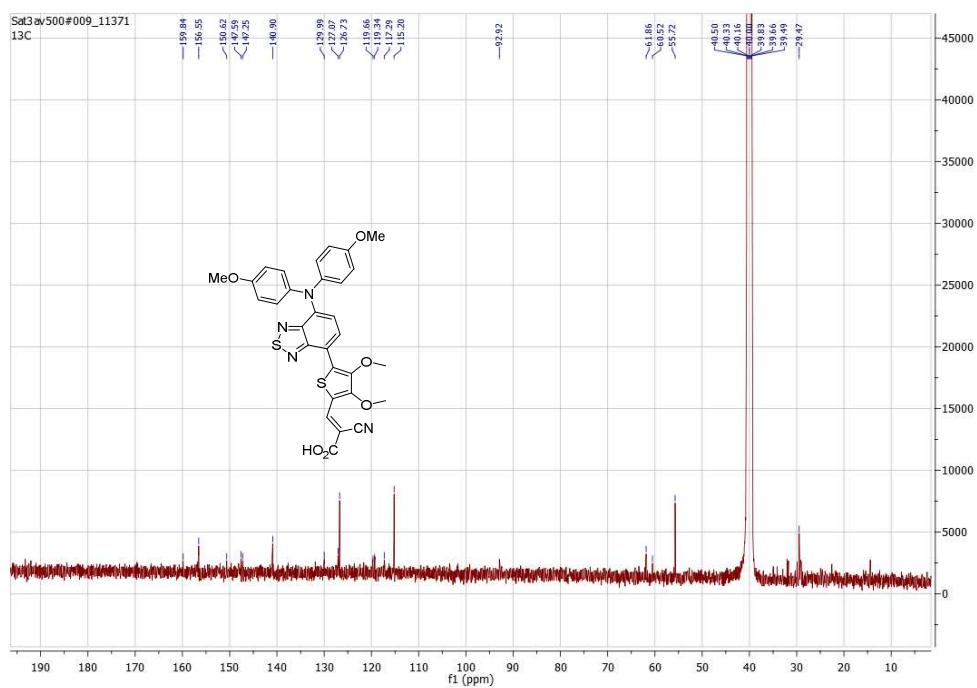
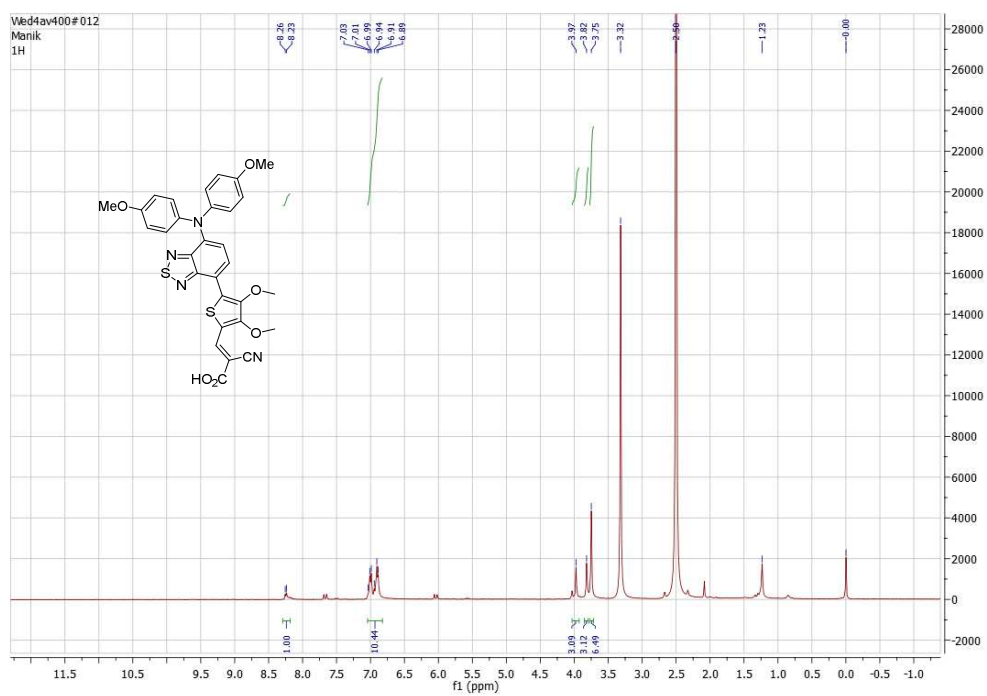


Figure S17. ¹H and ¹³C NMR (DMSO-d₆) spectra of D₂ (19).

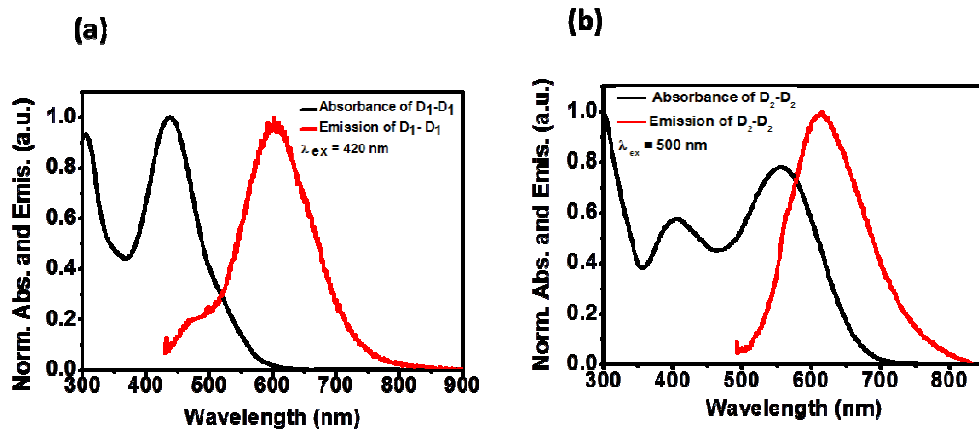


Figure S18. Normalised Absorption and emission spectra of D₁-D₁ (a) and D₂-D₂ (b).

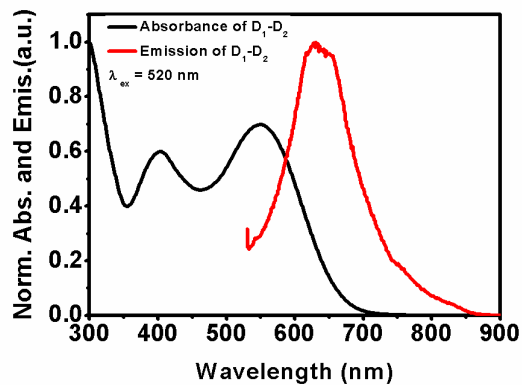


Figure S19. Normalised Absorption and emission spectra of D₁-D₂.

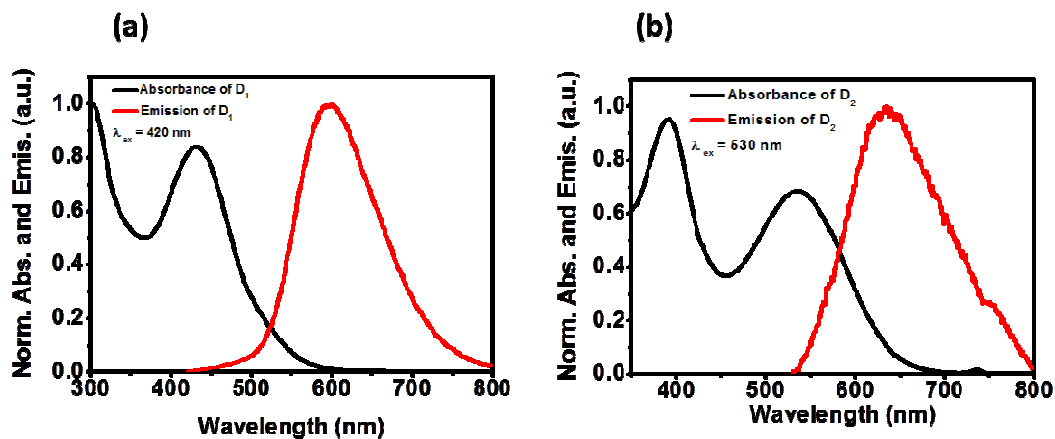


Figure S20. Normalised absorption and emission spectra of D₁ (a) and D₂ (b).

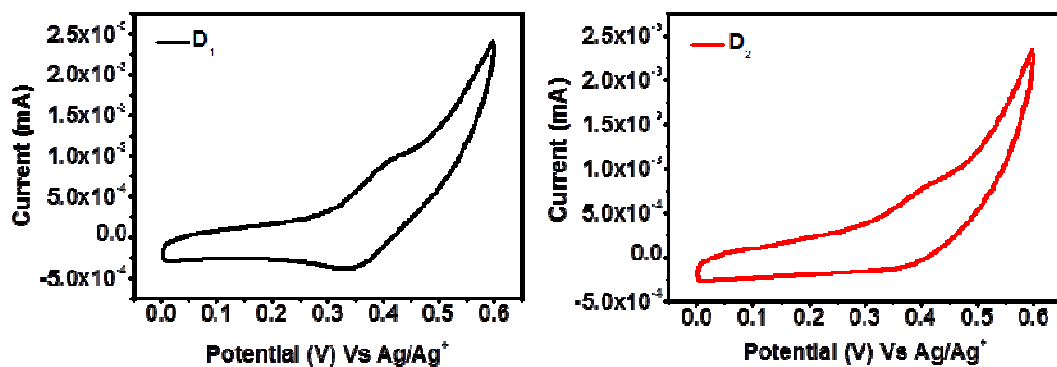


Figure S21. Cyclic voltammograms of (a) D_1 and (b) D_2 .

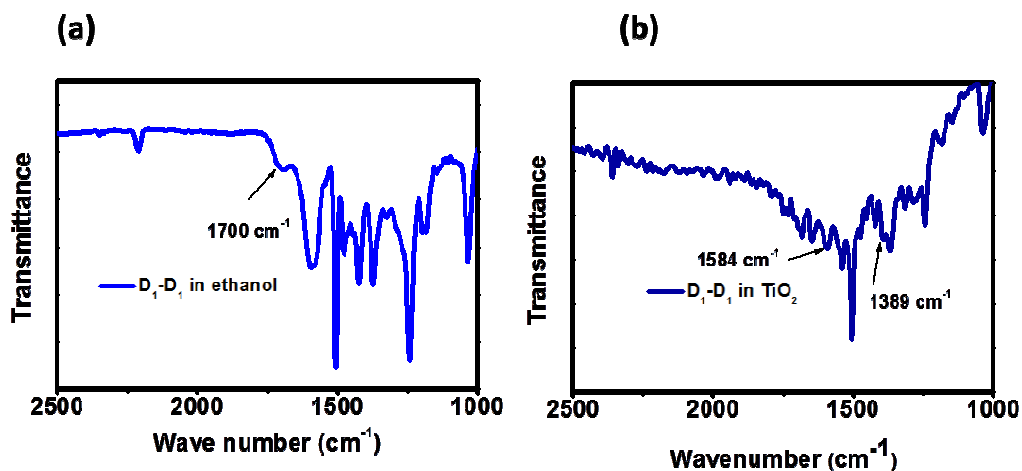
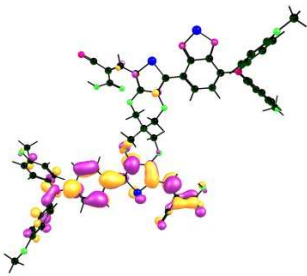
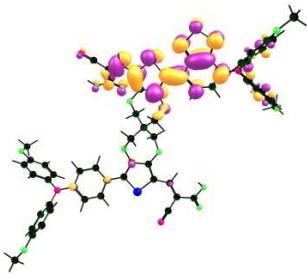
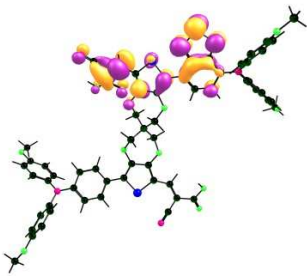
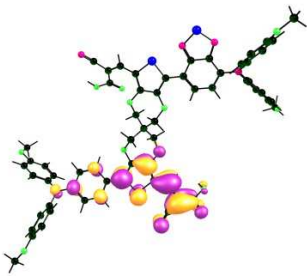
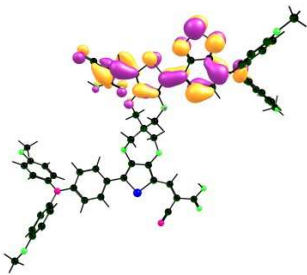


Figure S22. IR spectra of D_1 - D_1 in ethanol (a) and D_1 - D_1 in TiO_2 (b).

Description	Molecular orbital	Energy (eV)
LUMO + 1 of D ₁ in D ₁ -D ₂		-0.70
LUMO + 2 of D ₂ in D ₁ -D ₂		-0.75
LUMO + 1 of D ₂ in D ₁ -D ₂		-2.25
LUMO of D ₁ in D ₁ -D ₂		-2.58
LUMO of D ₂ in D ₁ -D ₂		-2.87

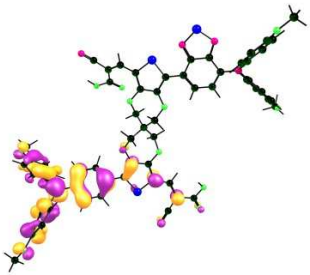
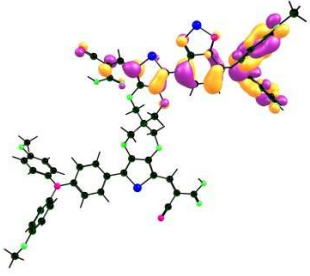
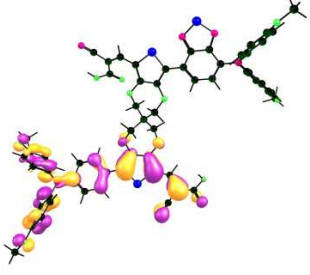
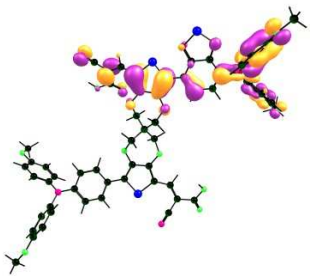
HOMO of D ₁ in D ₁ -D ₂		-4.91
HOMO of D ₂ in D ₁ -D ₂		-5.11
HOMO - 1 of D ₁ in D ₁ -D ₂		-5.92
HOMO - 1 of D ₂ in D ₁ -D ₂		-6.04

Figure S23. DFT study of D₁-D₂.

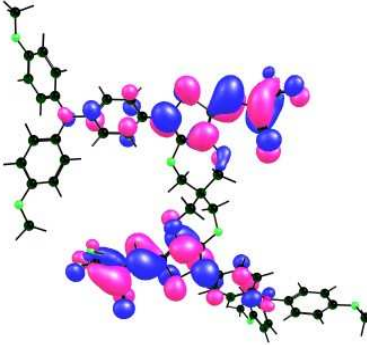
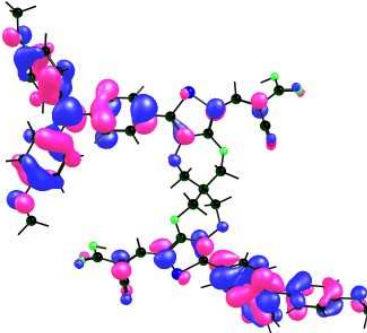
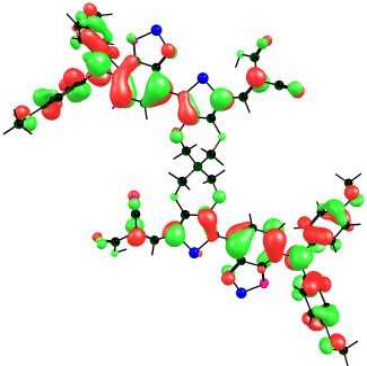
Description	Molecular orbital	Energy (eV)
LUMO of D ₁ -D ₁		-2.63
HOMO of D ₁ -D ₁		-4.93

Figure S24. DFT study of of D₁-D₁.

Description	Molecular orbital	Energy (eV)
LUMO of D ₂ -D ₂		-2.91

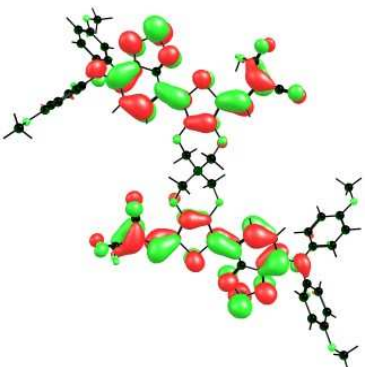
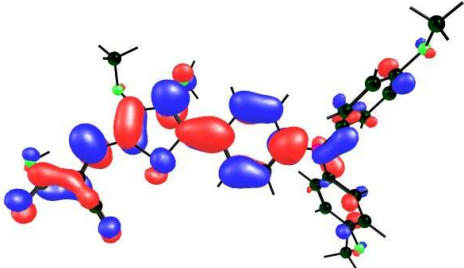
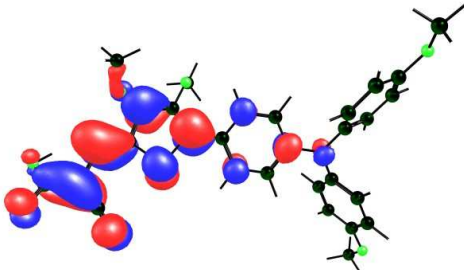
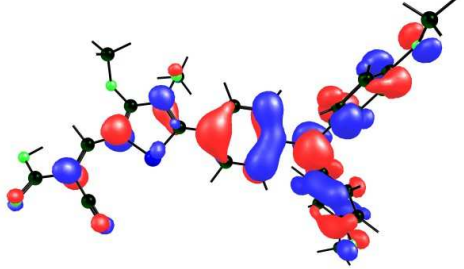
HOMO of D ₂ -D ₂		-5.03
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Figure S25. DFT study of D₂-D₂.

Description	Molecular orbital	Energy (eV)
LUMO + 1 of D ₁		-0.75
LUMO of D ₁		-2.46
HOMO of D ₁		-4.96

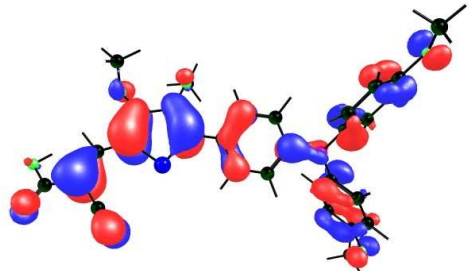
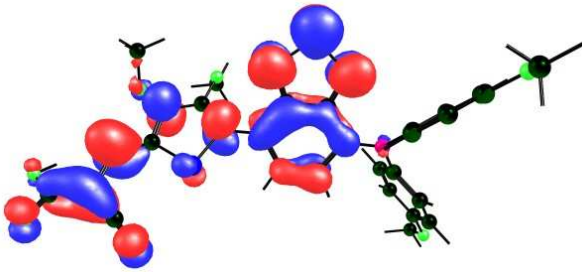
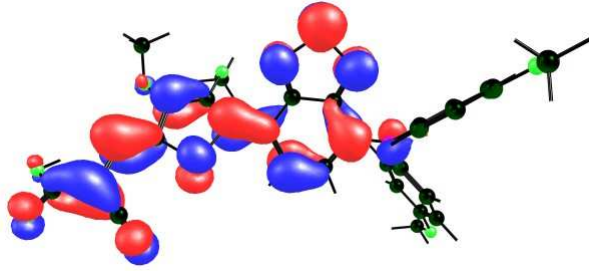
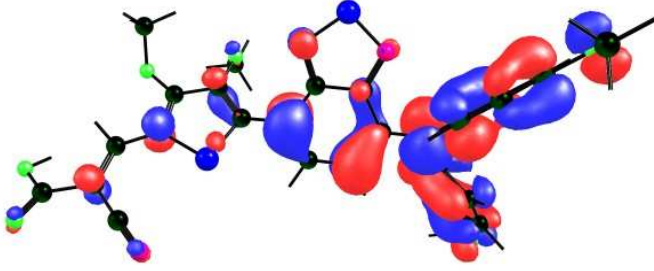
HOMO - 1 of D ₁		-5.97
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Figure S26. DFT study of D₁.

Description	Molecular orbital	Energy (eV)
LUMO + 1 of D ₂		-2.21
LUMO of D ₂		-2.66
HOMO of D ₂		-5.08

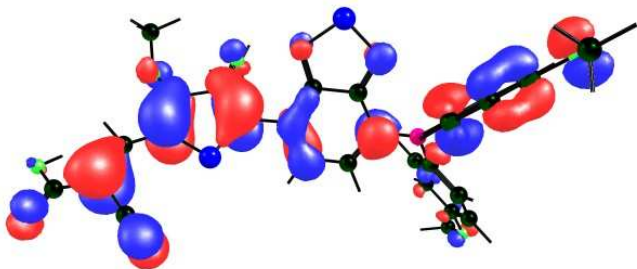
HOMO - 1 of D ₂		-6.05
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Figure S27. DFT study of D₂.

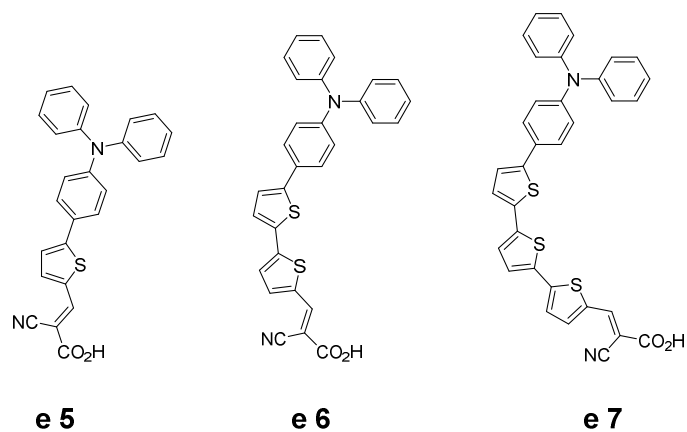


Figure S28. Molecular structures of TPA-based dyes e5 – e7.¹

Table S1. Optical and DSSC data of e5 -e7

dye	λ_{max} (nm) (absorption) ^a	redox	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF	PCE (%)
e5	415	I ⁻ /I ₃ ⁻	0.685	8.58	0.70	4.11
e6	473	I ⁻ /I ₃ ⁻	0.63	16.0	0.61	6.15
e7	480	I ⁻ /I ₃ ⁻	0.61	15.2	0.58	5.41

^aAbsorption was measured in solution of dyes.

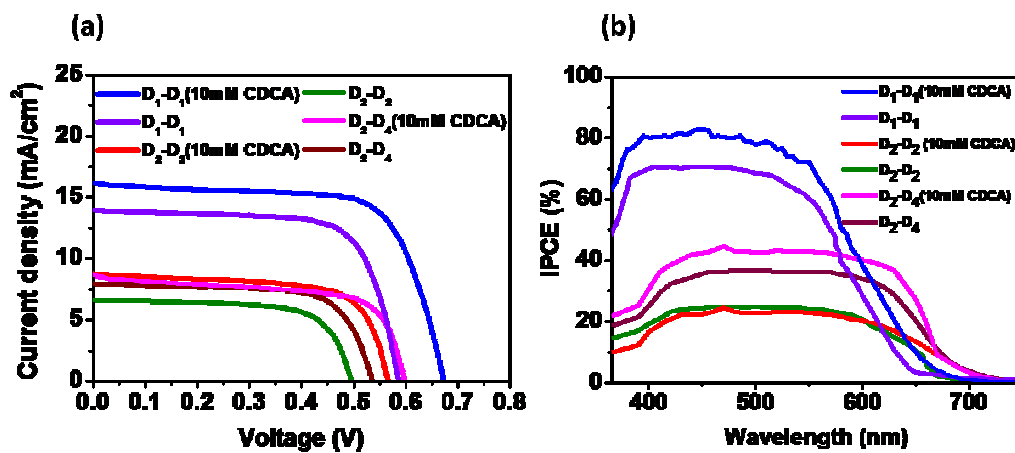


Figure S29. IV and IPCE profile of D_1-D_1 , D_2-D_2 and D_2-D_4 with and without CDCA.

Reference:

- (1) Wang, J.; Liu, K.; Ma, L.; Zhan, X. Triarylamine: Versatile Platform for Organic, Dye-Sensitized, and Perovskite Solar Cells. *Chem. Rev.* **2016**, *116*, 14675–14725.