

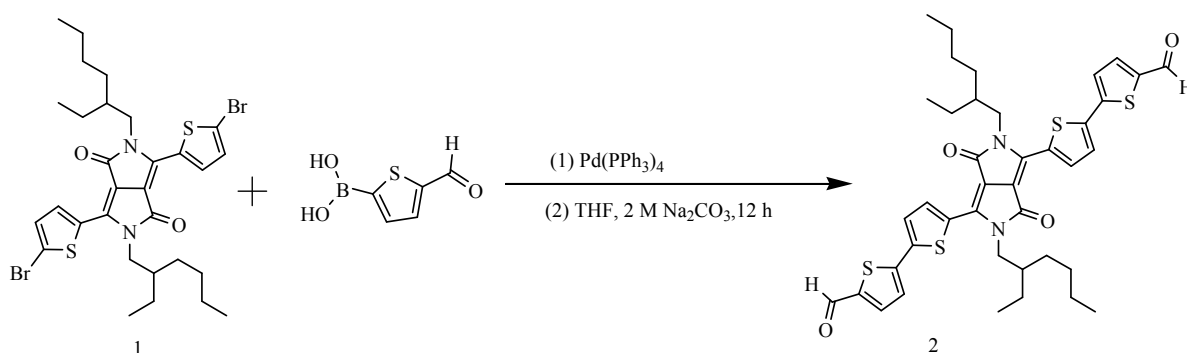
Supporting information

Dithiafulvalene Functionalized Diketopyrrolopyrrole Based Sensitizers for Efficient Hydrogen Production

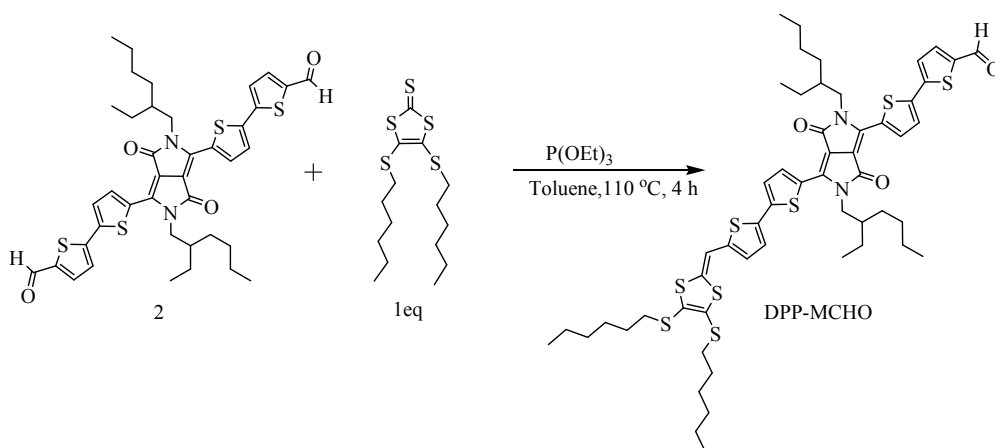
K. Narayanaswamy, Amritanjali Tiwari, Indranil Mondal, Ujjwal Pal, S. Niveditha, K. Bhanuprakash, Surya Prakash Singh

Experimental section

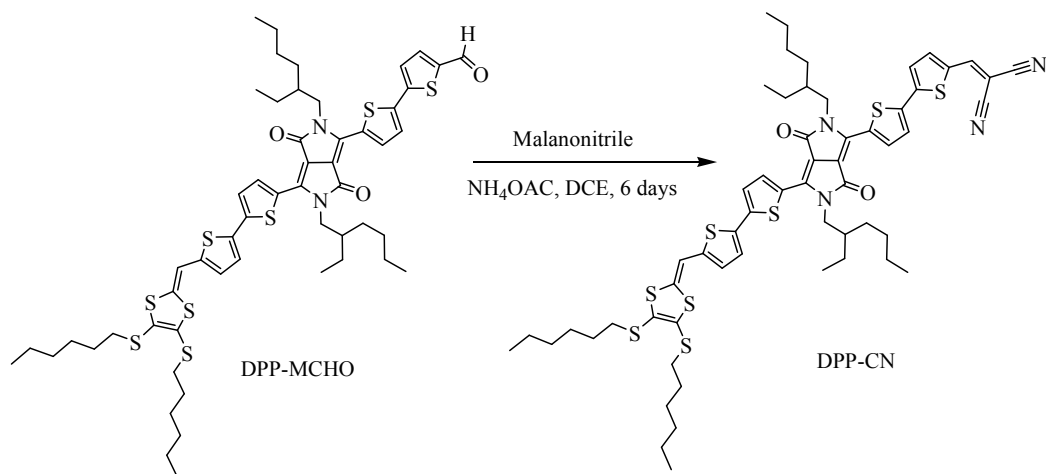
Synthesis of 5',5''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis[(2,2'-bithiophene)-5-carbaldehyde] (2).



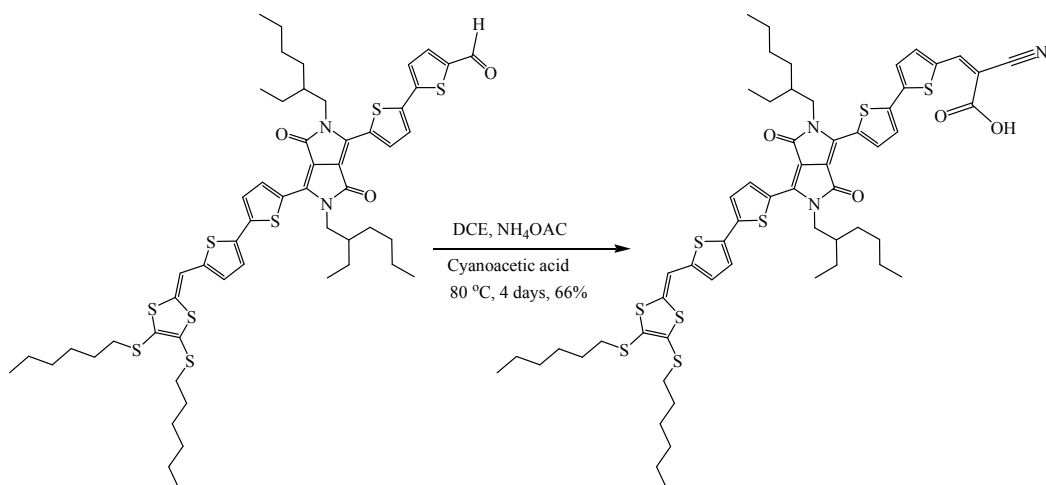
Synthesis of 5'-(4-(5'((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)-[2,2'-bithiophen]-5-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2'-bithiophen]-5-carbaldehyde:



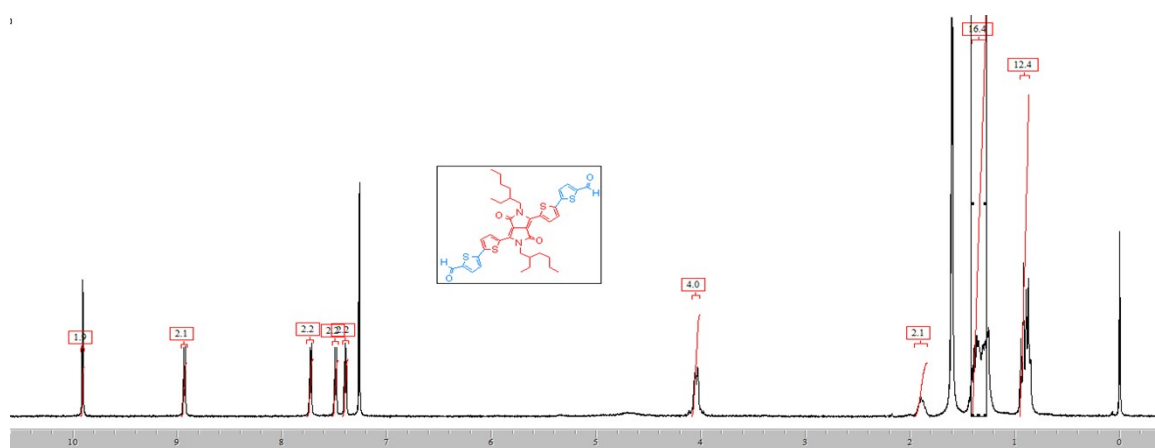
Synthesis of 2-((5'-(4-(5'-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)-[2,2'-bithiophen]-5-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2'-bithiophen]-5-yl)methylene)malononitrile. (DPP-CN)



Synthesis of (Z)-3-(5'-(4-(5'-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)-[2,2'-bithiophen]-5-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (DPP-CA)



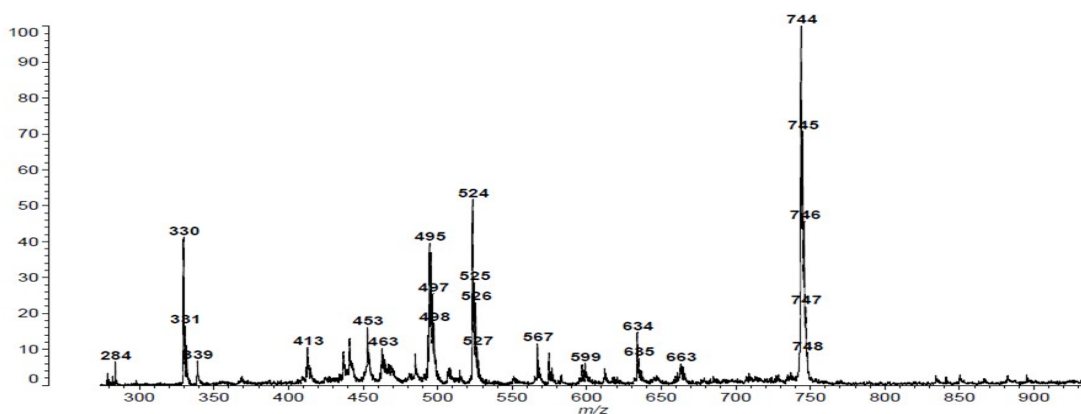
NMR spectra of 2:



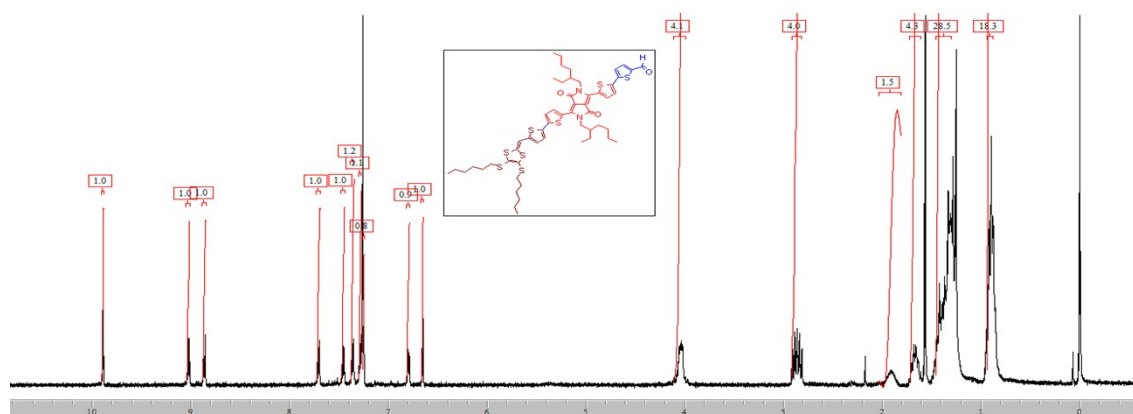
Mass spectra of 2

K N SWAMY , MLK-1

Data: KNS0005.412[c] 23 Jan 2014 16:06 Cal: NPR28DEC 28 Dec 2012 14:44
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 67, Blanked, P.Ext. @ 1200 (bin 51)
%Int. 1389 mV[sum= 9720 mV] Profiles 1-7 Smooth Gauss 5



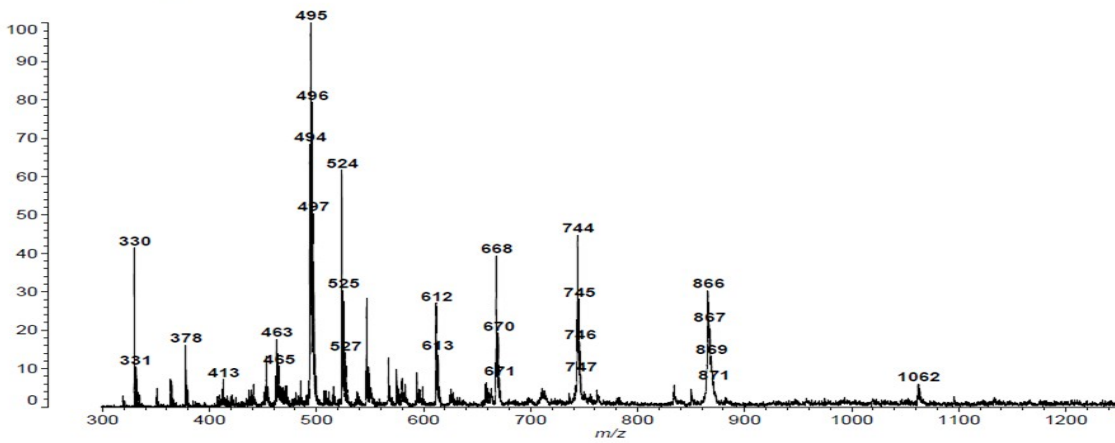
NMR spectra of DPP-MCHO;



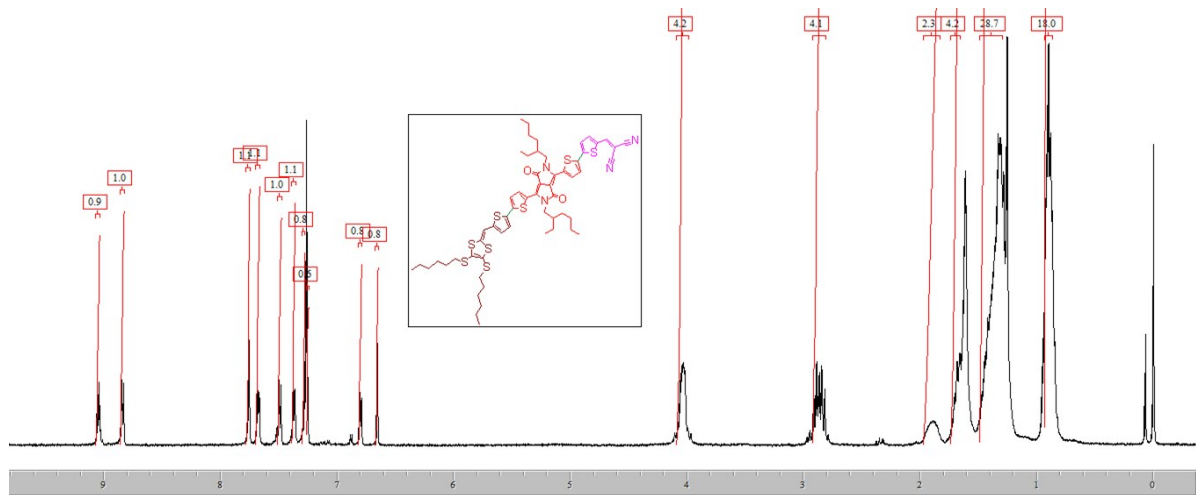
Mass spectra of DPP-MCHO

: N SWAMY , MLK-2

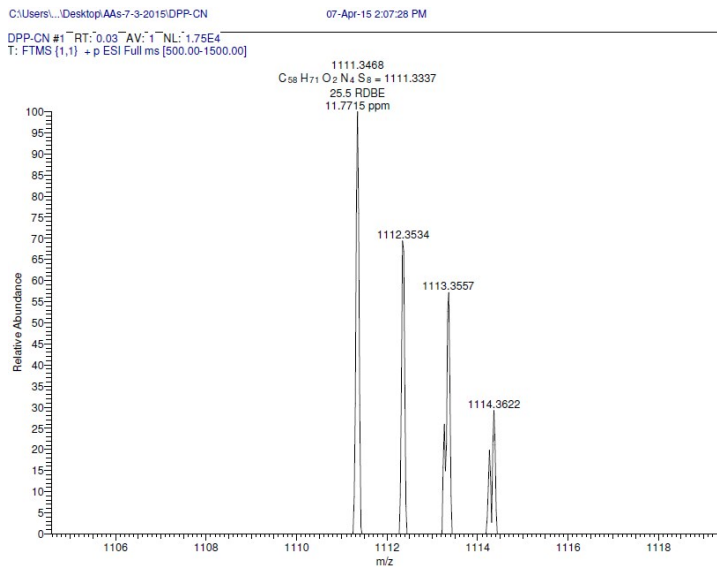
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%Int. 913 mV[sum= 8214 mV] Profiles 1-9 Smooth Gauss 5



NMR spectra of DPP-CN:



HRMS spectra of DPP-CN



HRMS spectra of DPP-CA;

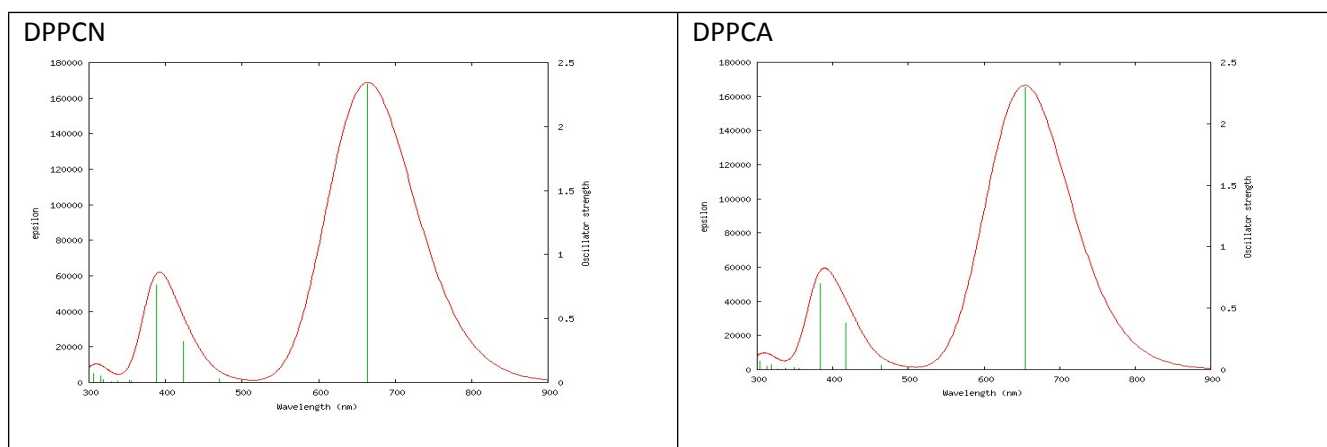
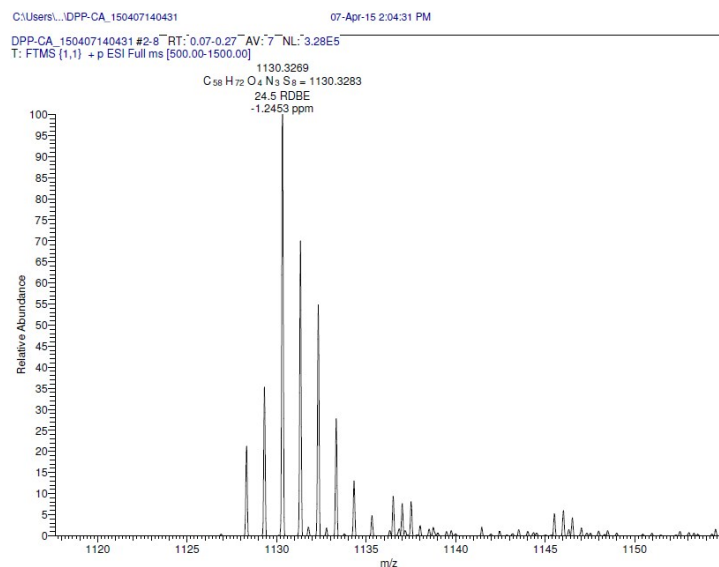


Figure S1. Simulated absorption spectra of DPPCA and DPPCN in DMF solvent.

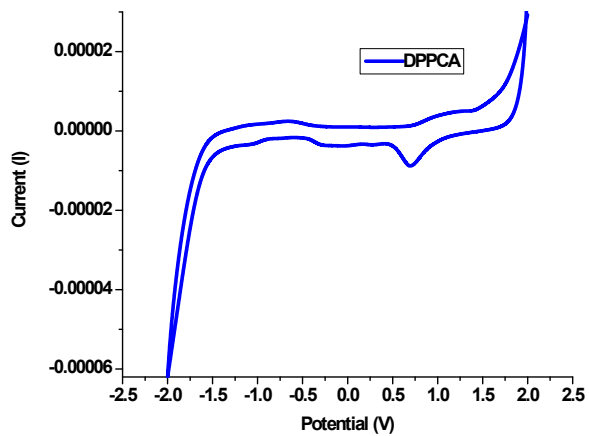


Figure S2. Cyclic voltammetry of DPP-CA recorded in dichloromethane.

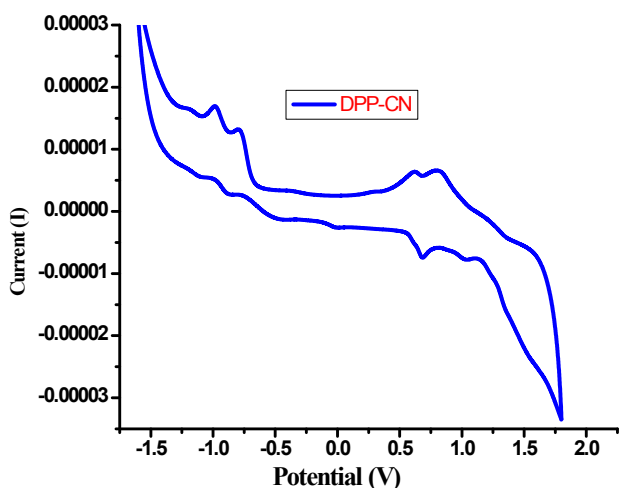


Figure S3. Cyclic voltammetry of DPP-CN recorded in dichloromethane

Table. S1 Absorption spectra simulated at CAM-B3YP/6-311+G (d, p) level of theory in DMF solvent.

Dye	Excited state	λ_{max} (nm)	Osc. Strength (<i>f</i>)	Major contribution
DPPCA	S1	654	2.297	H-1->LUMO (11%), HOMO->LUMO (74%), HOMO->L+1 (10%)
	S3	417	0.379	H-1->LUMO (19%), H-1->L+1 (33%), HOMO->L+1 (24%)
	S4	383	0.700	H-2->LUMO (48%), HOMO->L+2 (17%)
	S9	318	0.042	H-1->L+3 (24%), HOMO->L+3 (31%), HOMO->L+4 (10%)
	S11	304	0.070	H-10->LUMO (10%), H-3->LUMO (24%), H-3->L+1 (16%), H-2->L+1 (10%)
DPPCN	S1	664	2.328	H-1->LUMO (11%), HOMO->LUMO (72%), HOMO->L+1 (11%)
	S3	422	0.322	H-1->LUMO (21%), H-1->L+1 (34%), HOMO->LUMO (11%), HOMO->L+1 (22%)
	S4	388	0.761	H-2->LUMO (51%), HOMO->L+2 (16%)
	S10	315	0.051	HOMO->L+4 (20%)
	S11	305	0.071	H-10->LUMO (11%), H-3->LUMO (22%), H-3->L+1 (16%), H-2->L+1 (10%)