

Supplementary information

Y-shaped Meal-Free D- π -(A)₂ Sensitizers for High-Performance Dye-Sensitized Solar Cells

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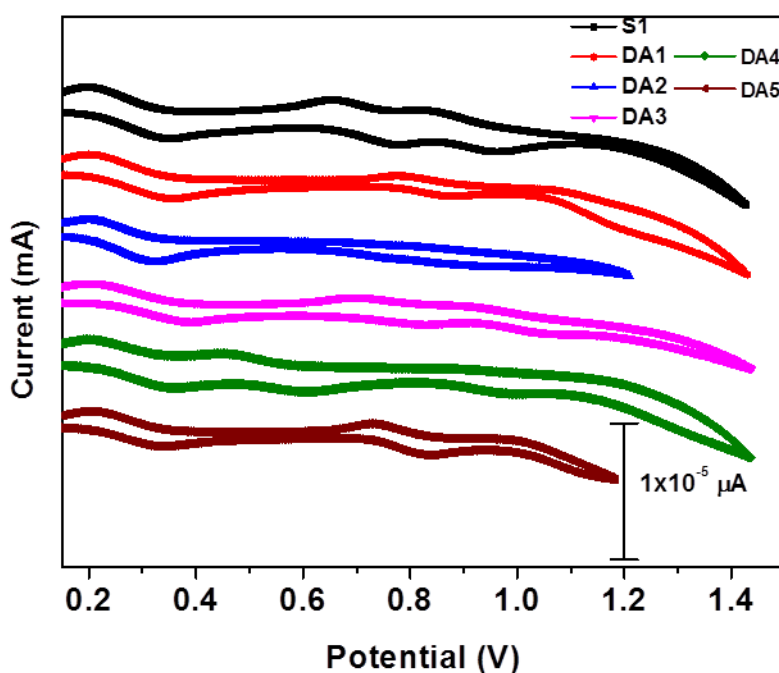


Fig. S1 Cyclic voltammograms of DA dyes recorded in THF.

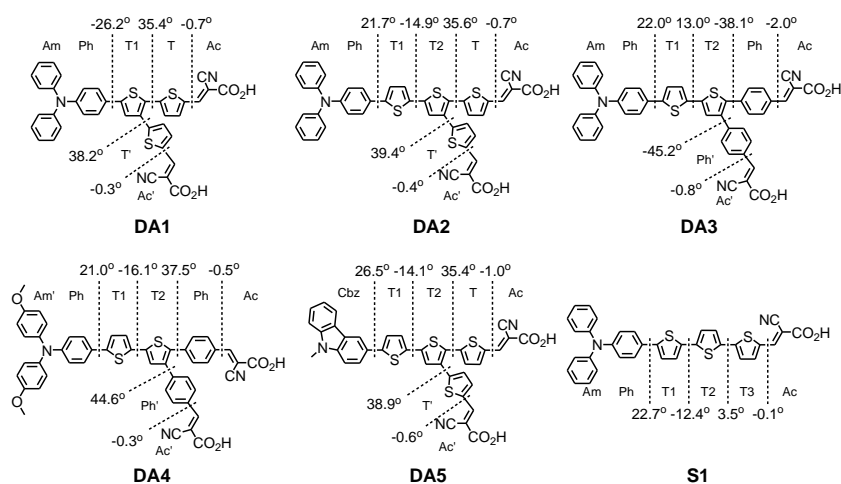
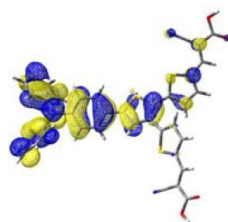
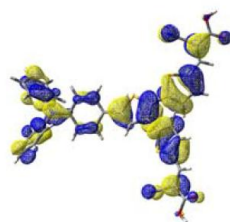


Fig. S2 Schematic division and dihedral angles of molecules.

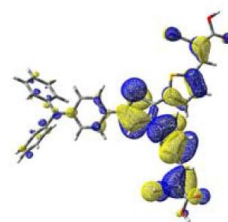
DA1



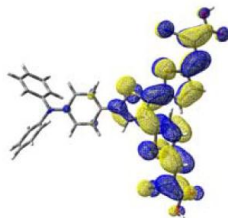
HOMO



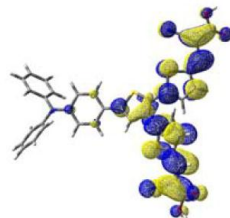
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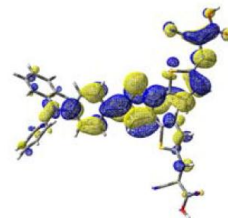
HOMO-2



LUMO

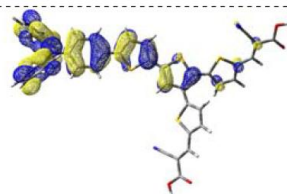


LUMO+1

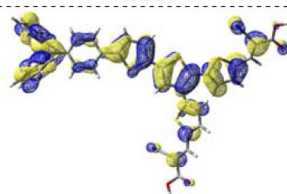


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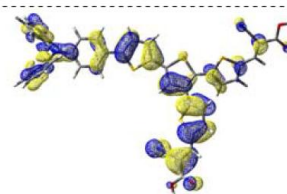
DA2



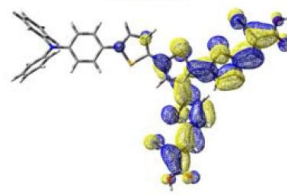
HOMO



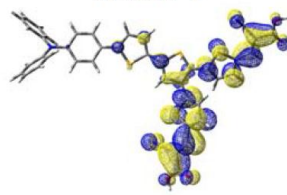
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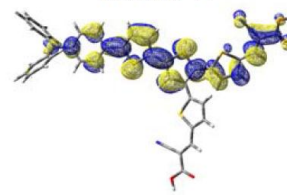
HOMO-2



LUMO

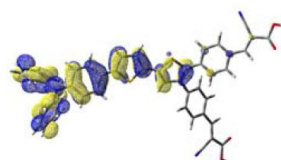


LUMO+1

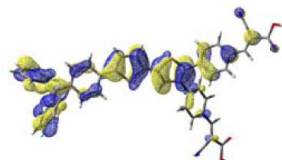


LUMO+2

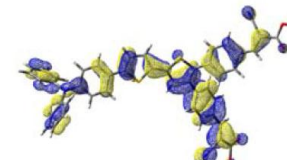
DA3



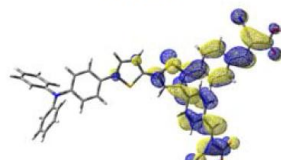
HOMO



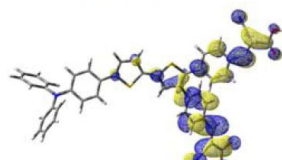
HOMO-1



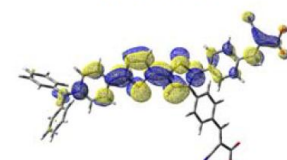
HOMO-2



LUMO



LUMO+1



LUMO+2

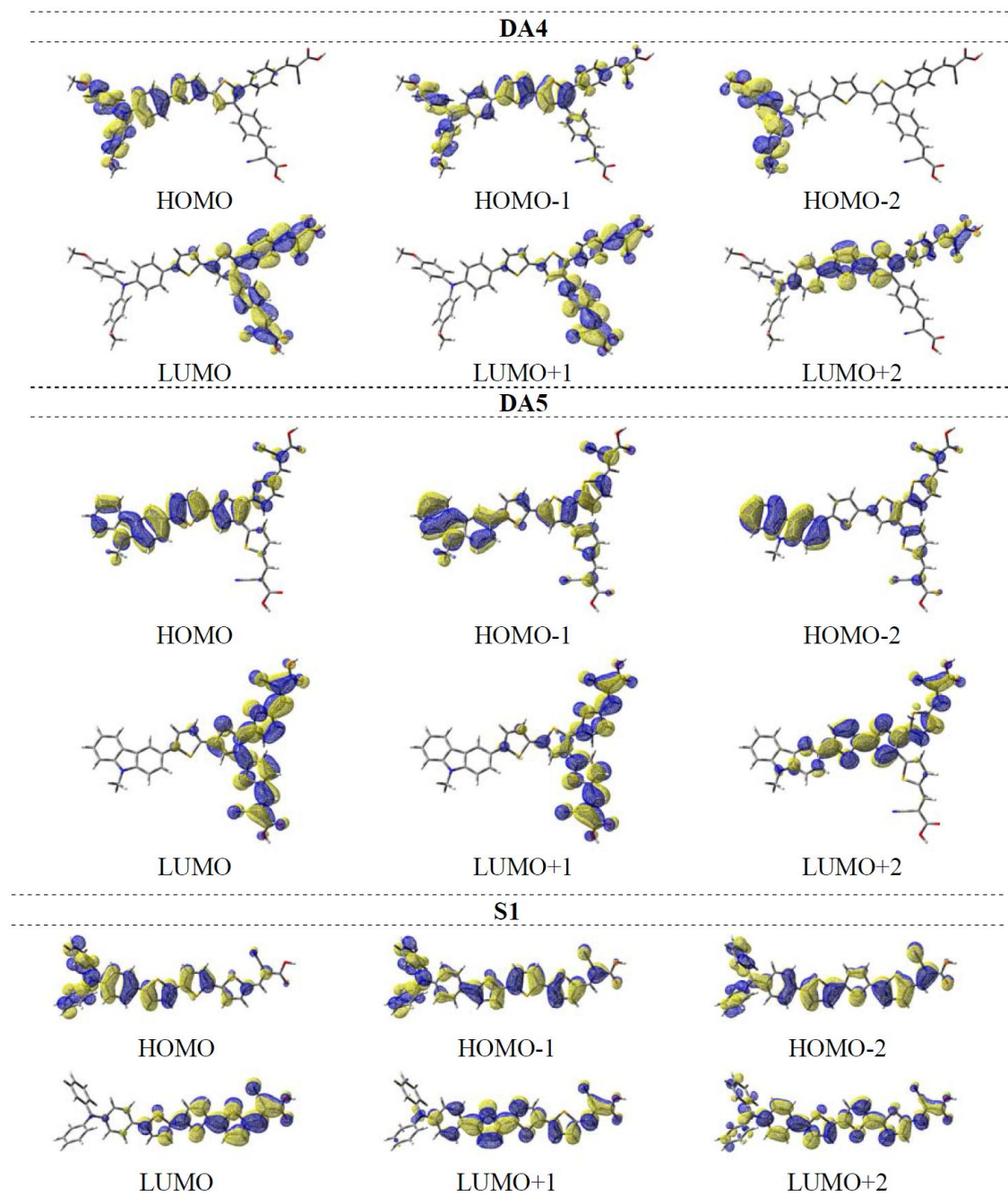


Fig. S3 Selected frontier orbitals of the dyes.

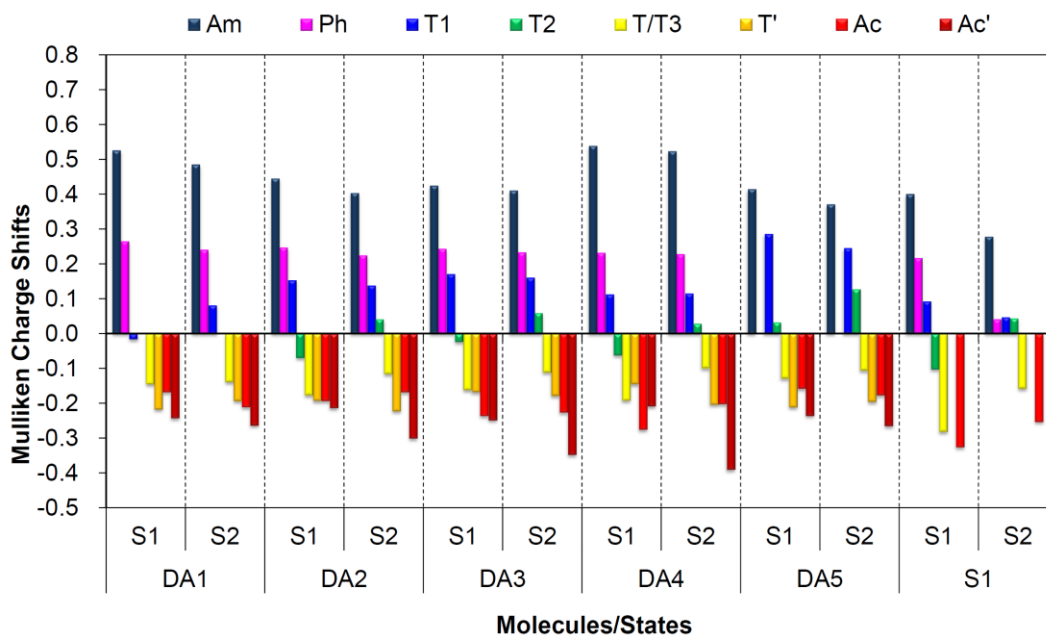


Fig. S4 Plot of the difference in the Mulliken charges between the ground and the excited states.

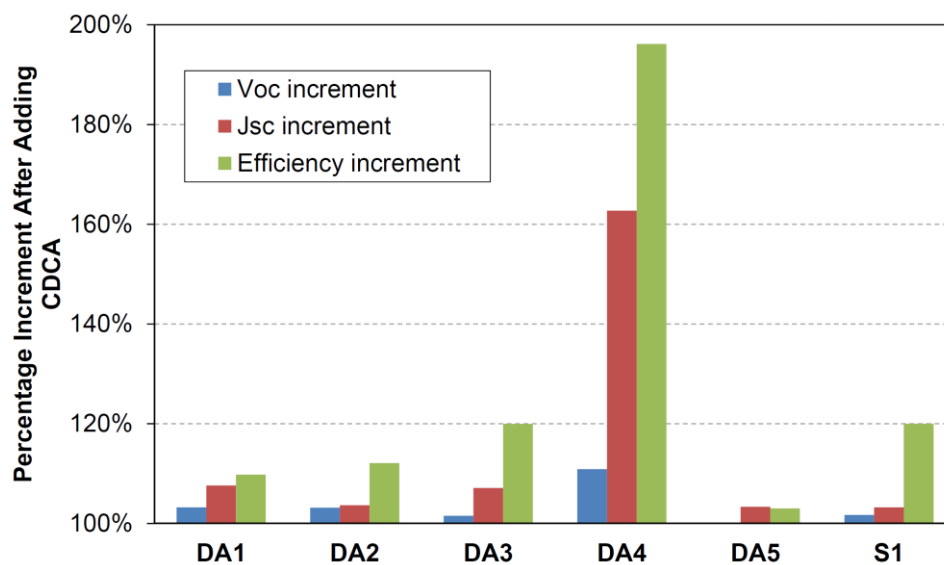


Fig. S5 Plot of the percentage increments of the device performance parameters after addition of CDCA.

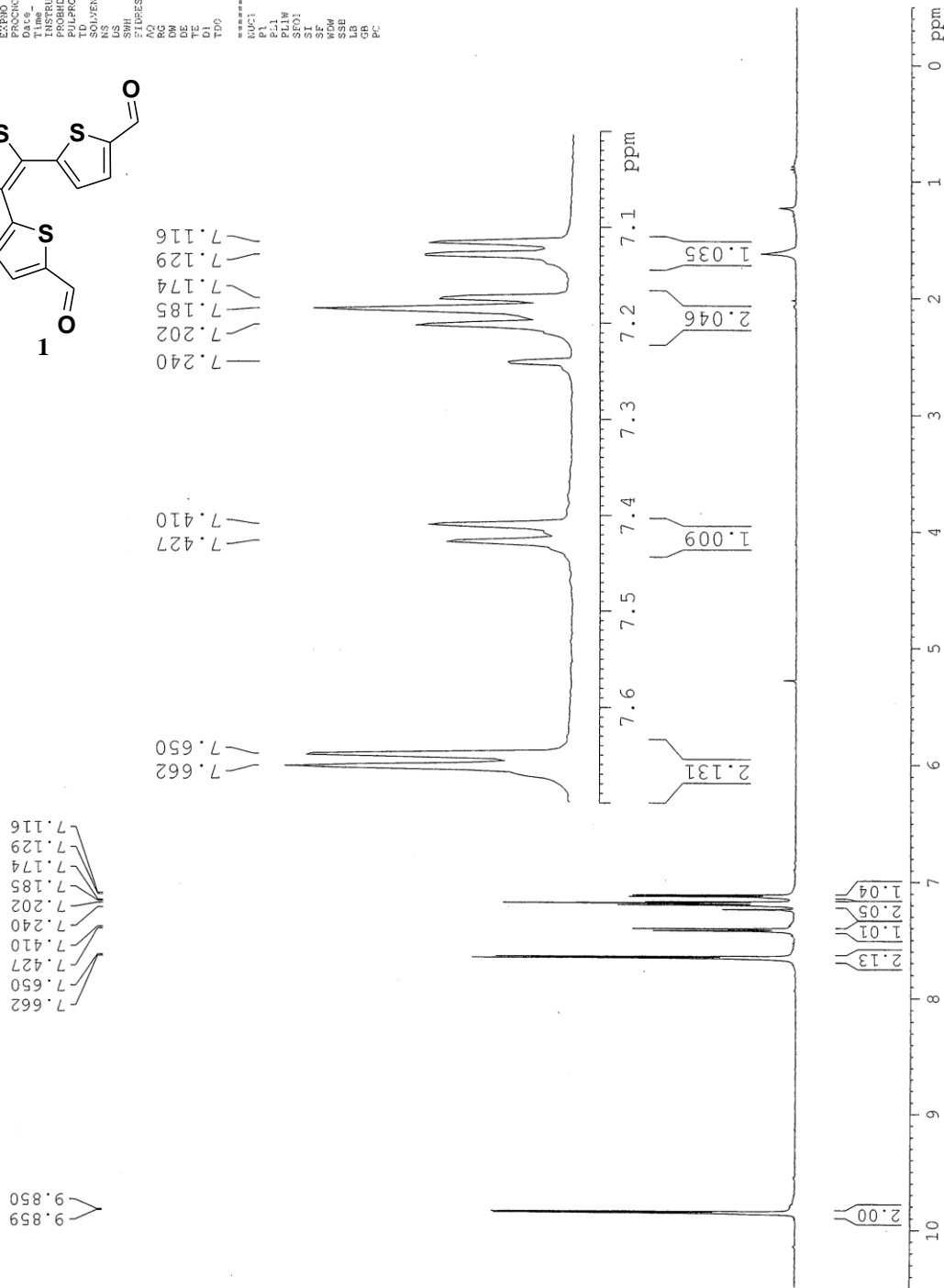
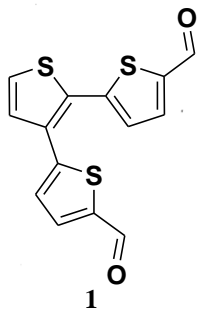
Table S1. Calculated lower-lying transitions of the dyes.^a

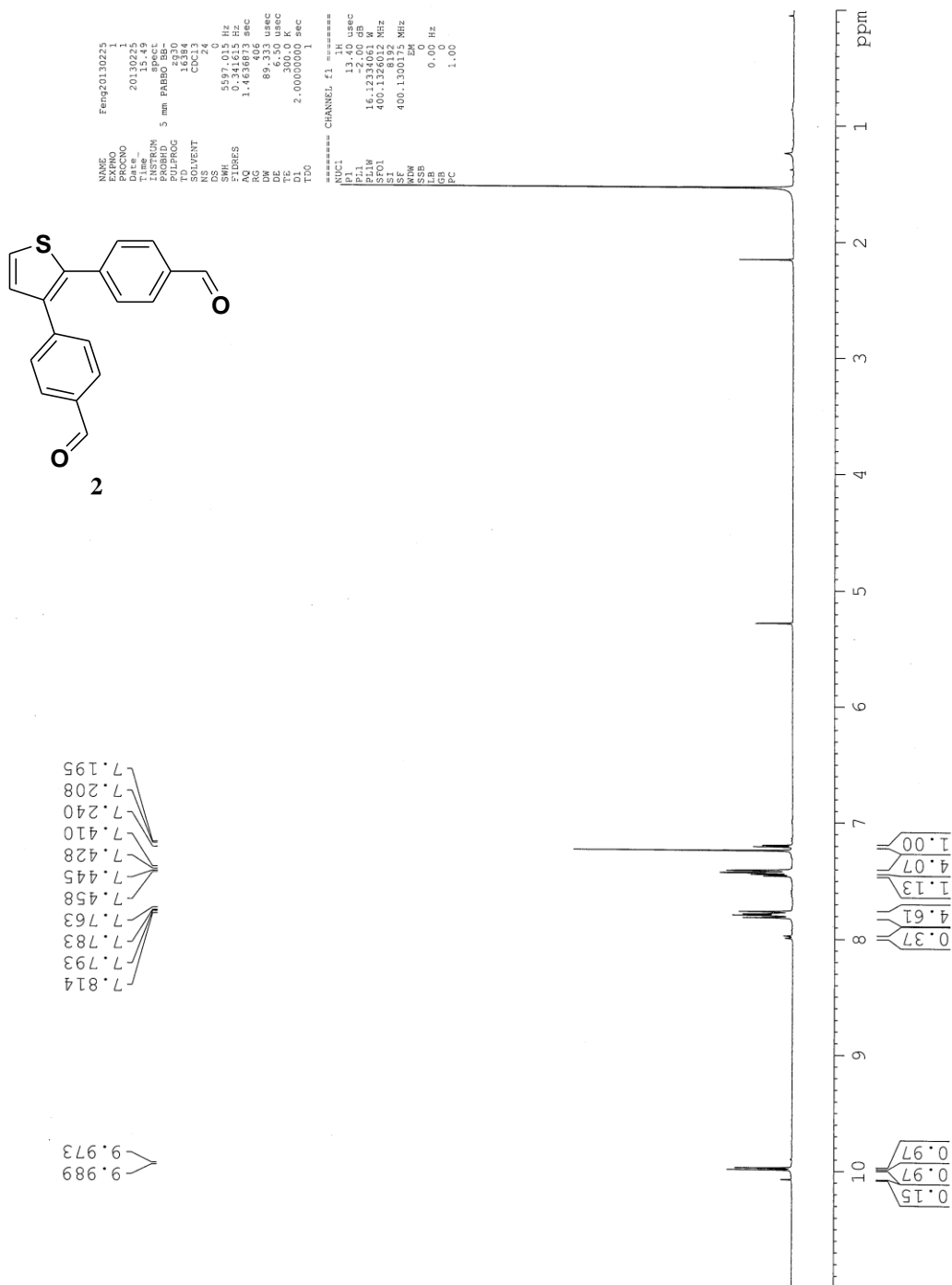
Dye	State	Excitation ^a	λ_{cal} , eV	f^b	Δ (Mulliken charge), ^c e	$f \times \Delta q$	Dye	State	Excitation ^a	λ_{cal} , eV	f^b	Δ (Mulliken charge), ^c e	$f \times \Delta q$				
DA1	S ₁	H → L (99%)	1.86	0.22	Am: 0.53	-0.04	DA2	S ₁	H → L (99%)	1.73	0.25	Am: 0.45	-0.05				
					Ph: 0.27	-0.05						Ph: 0.25	-0.05				
					T1: -0.02							T1: 0.15					
	T: -0.15		T2: -0.07														
	T': -0.22		T: -0.18														
	Ac: -0.17		T': -0.19														
	Ac': -0.24		Ac: -0.19														
			Ac': -0.21														
					S ₂	H → L1 (97%)		2.29	0.24	Am: 0.49	-0.05	S ₂	H → L1 (96%)	2.15	0.25	Am: 0.40	-0.04
		Ph: 0.24	-0.06	Ph: 0.23	-0.08												
		T1: 0.08		T1: 0.14													
		T: -0.14		T2: 0.04													
		T': -0.19		T: -0.12													
		Ac: -0.21		T': -0.22													
		Ac': -0.26		Ac: -0.17													
				Ac': -0.30													
						S ₃	H1 → L (98%)	2.60	0.66	Am: 0.17	-0.06	S ₃	H1 → L (97%)	2.37	0.53	Am: 0.24	-0.07
		Ph: 0.04	-0.10	Ph: 0.05	-0.11												
		T1: 0.10		T1: 0.14													
		T: 0.01		T2: 0.11													
		T': -0.07		T: -0.06													
		Ac: -0.09		T': -0.16													
		Ac': -0.16		Ac: -0.13													
				Ac': -0.20													
DA3	S ₁	H → L (99%)	1.90	0.24	Am: 0.42	-0.06	DA4	S ₁	H → L (99%)	1.73	0.23	Am': 0.54	-0.06				
					Ph: 0.24	-0.06						Ph: 0.23	-0.05				
					T1: 0.17							T1: 0.11					
	T2: -0.02		T2: -0.06														
	Ph: -0.16		Ph: -0.19														
	Ph': -0.17		Ph': -0.14														
	Ac: -0.24		Ac: -0.28														
	Ac': -0.25		Ac': -0.21														
					S ₂	H → L1 (98%)		2.19	0.28	Am: 0.41	-0.06	S ₂	H → L1 (99%)	2.03	0.19	Am': 0.52	-0.04
		Ph: 0.23	-0.10	Ph: 0.23	-0.07												
		T1: 0.16		T1: 0.12													
		T2: 0.06		T2: 0.03													
		Ph: -0.11		Ph: -0.10													
		Ph': -0.18		Ph': -0.20													
		Ac: -0.23		Ac: -0.20													
		Ac': -0.35		Ac': -0.39													
						S ₃	H1 → L (97%)	2.56	0.34	Am: 0.29	-0.07	S ₃	H1 → L (97%)	2.46	0.40	Am': 0.25	-0.09
		Ph: 0.06	-0.09	Ph: 0.06	-0.09												
		T1: 0.17		T1: 0.23													
		T2: 0.18		T2: 0.17													
		Ph: -0.08		Ph: -0.11													
		Ph': -0.16		Ph': -0.14													
		Ac: -0.19		Ac: -0.23													
		Ac': -0.26		Ac': -0.23													
DA5	S ₁	H → L (99%)	1.91	0.34	Cbz: 0.42	-0.05	S1	S ₁	H → L (99%)	2.03	0.88	Am: 0.40	-0.29				
					T1: 0.29	-0.08						Ph: 0.22					
					T2: 0.03							T1: 0.09					
	T: -0.13		T2: -0.10														
	T': -0.21		T3: -0.28														
Ac: -0.16		Ac: -0.33															
Ac': -0.24				S ₂	H → L1 (95%)	2.33	0.35	Cbz: 0.37	-0.06	S ₂	H1 → L (93%)	2.63	0.93	Am: 0.28	-0.24		
		T1: 0.25	-0.09	T1: 0.25	-0.09												
		T2: 0.13		T2: 0.13													
						H → L1						Ph: 0.04					
												T1: 0.05					

				T: -0.11		(6%)		T2: 0.04			
				T': -0.20				T3: -0.16			
				Ac: -0.18				Ac: -0.25			
				Ac': -0.27							
S ₃	H1 → L (97%)	2.53	0.40	Cbz: 0.50	-0.06	S ₃	H2 → L (8%)	2.98	0.28	Am: 0.34	-0.05
				T1: 0.03	-0.07		H1 → L (5%)			Ph: 0.07	
				T2: 0.01			H → L1 (85%)			T1: -0.08	
				T: -0.09						T2: -0.08	
				T': -0.12						T3: -0.09	
				Ac: -0.15						Ac: -0.17	
				Ac': -0.17							

^a Results are based on gas-phase TD-DFT calculation. ^b H = HOMO, L = LUMO, H1 = The next highest occupied molecular orbital, or HOMO - 1, H2 = HOMO - 2, L1 = LUMO + 1, L2 = LUMO + 2. In parentheses is the population of a pair of MO excitations. ^c Oscillator strength. ^d The difference of the Mulliken charge between the ground state and excited state.

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 F2 101.626 MHz
 F1 500.136098 MHz
 AQ 1.703980 sec
 RG 181
 DW 104.000 usec
 DE 19.00 usec
 TE 25.7
 D1 2.00000000 sec
 D11 1
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 P1 9.10 usec
 PL 0.00 dB
 FWH 25.37 usec
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 SI 8192
 SF 300.1300124 MHz
 WDW no
 LB 0
 GB 0
 PC 1.00







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RG: 1.4438873 sec
AQ: 0.18 sec
DE: 89.750 usec
TE: 300.0 K
D0: 2.00000000 sec
D1: 1
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P1: 13.40 usec
PL1: -2.00 dB
PL12: 16.1377 usec
SFO1: 400.1326012 MHz
SI: 8192
WDW: nc
SSB: 0
GB: 0
PC: 1.00

7.100
7.110
7.143
7.153
7.165
7.239
7.638
7.645
7.648
7.655

9.848
9.861

7.100
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7.143
7.153
7.165
7.239
7.638
7.645
7.648
7.655

