Synthesis, Nonlinear Optical Analysis and DFT Studies of D-π-D and A-π-A Configured Schiff bases derived from Bis-phenylenediamine

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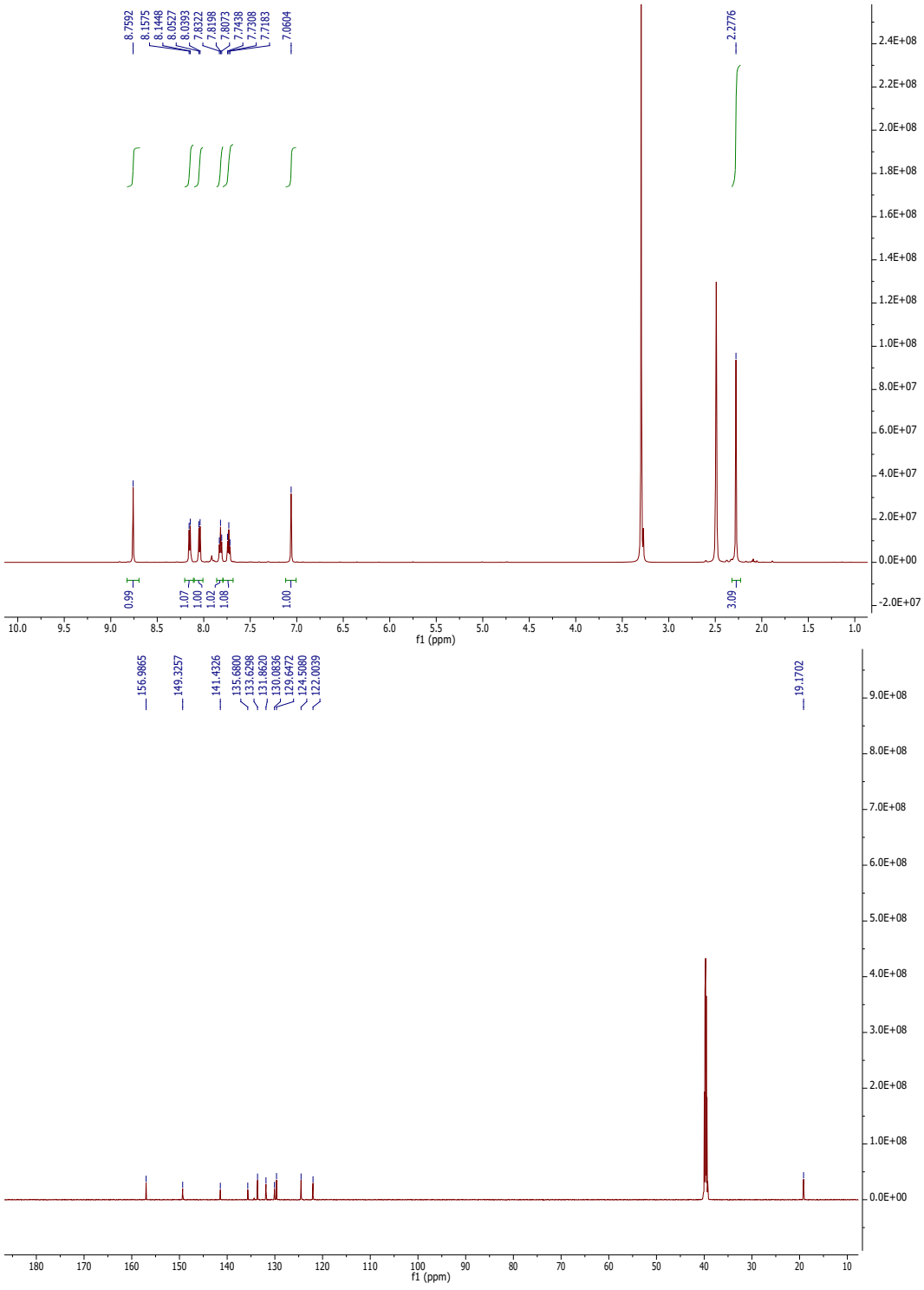


Figure S1: ^{1}H & ^{13}C NMR spectrum of **DMA**

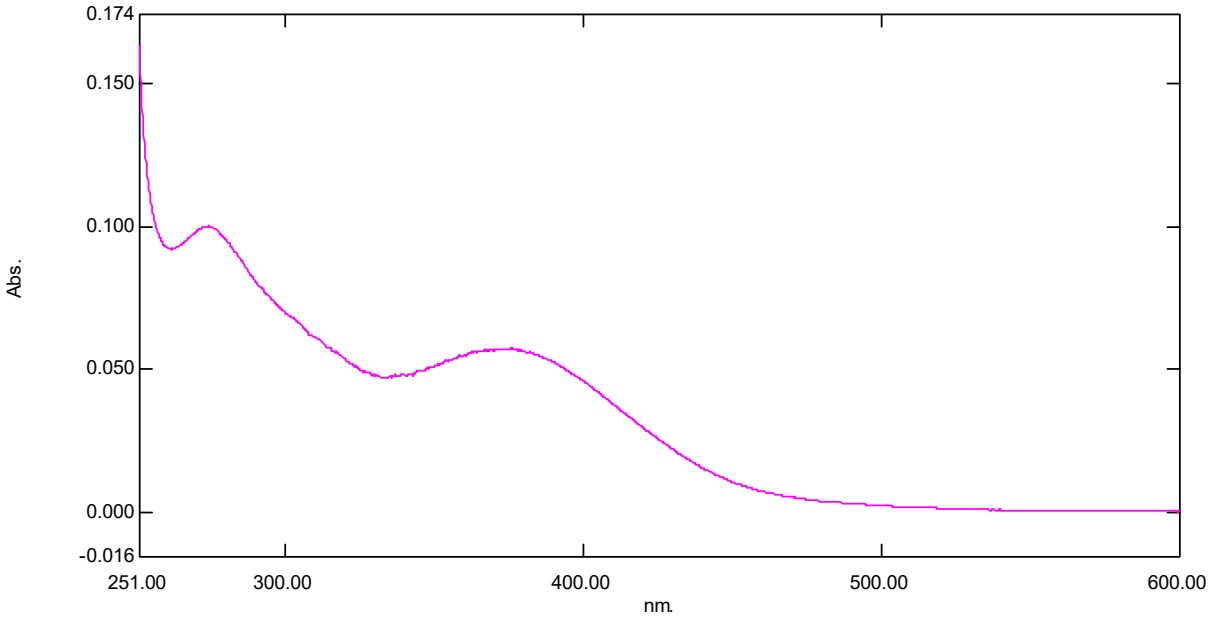


Figure S2: UV spectrum of **DMA** in acetonitrile

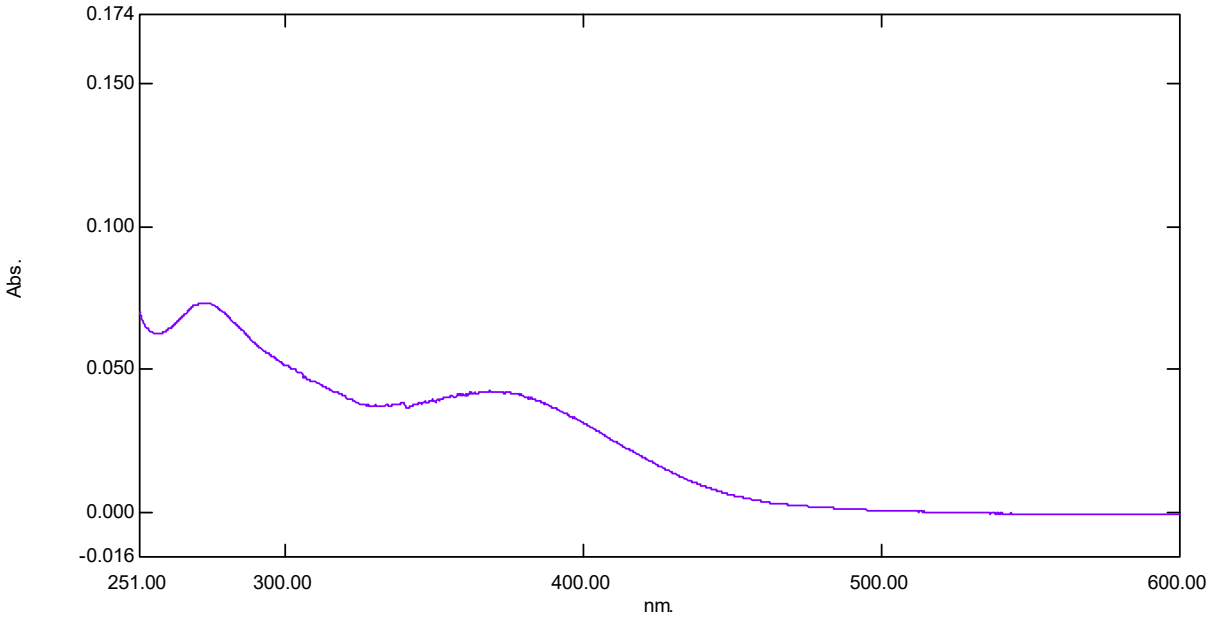


Figure S3: UV spectrum of **DMA** in MeOH

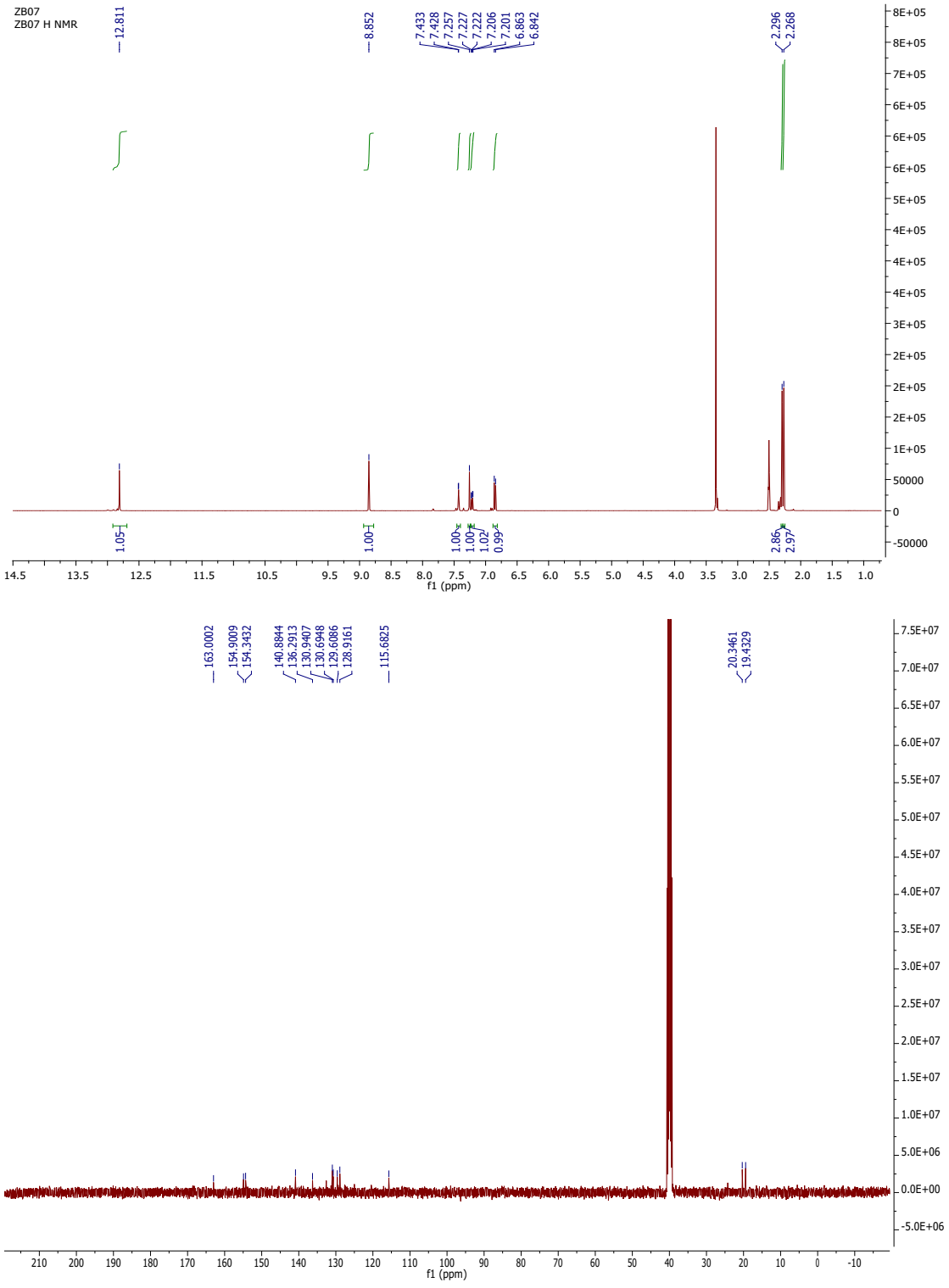


Figure S4: ^{1}H & ^{13}C NMR spectrum of **DMM**

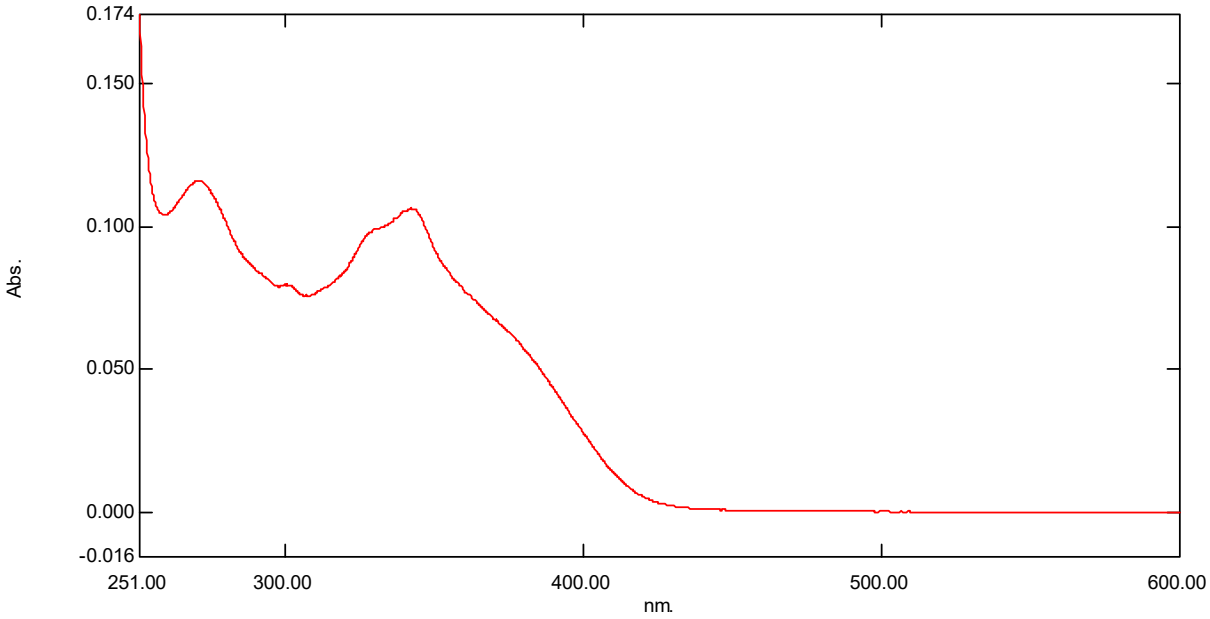


Figure S5: UV spectrum of **DMM** in acetonitrile

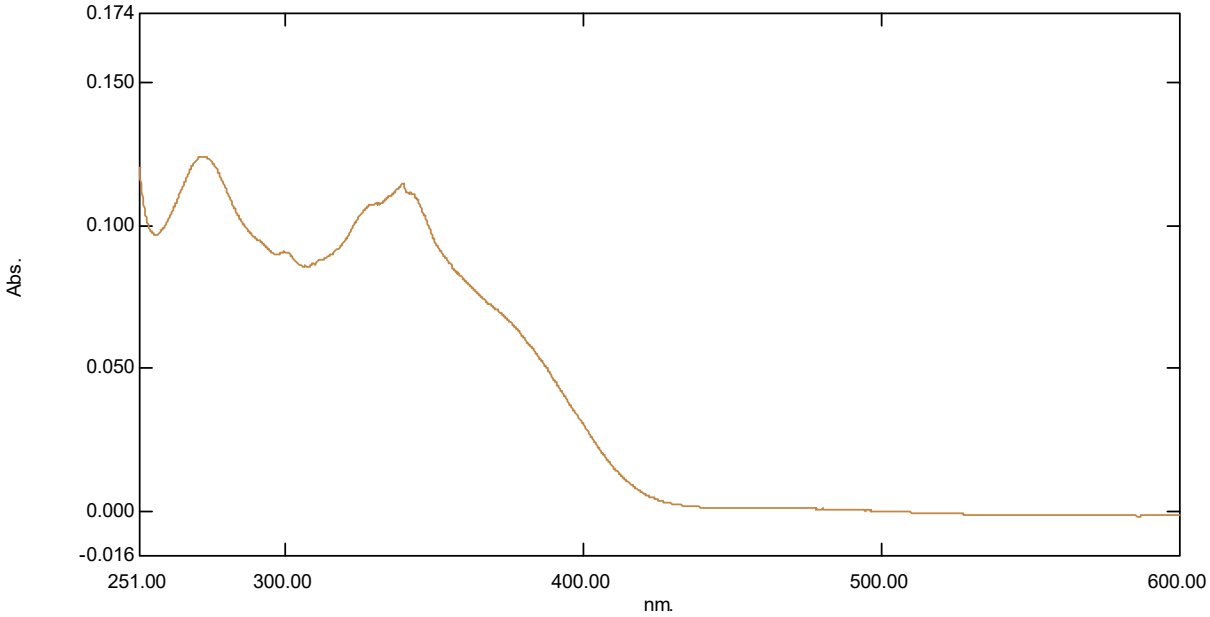


Figure S6: UV spectrum of **DMM** in MeOH

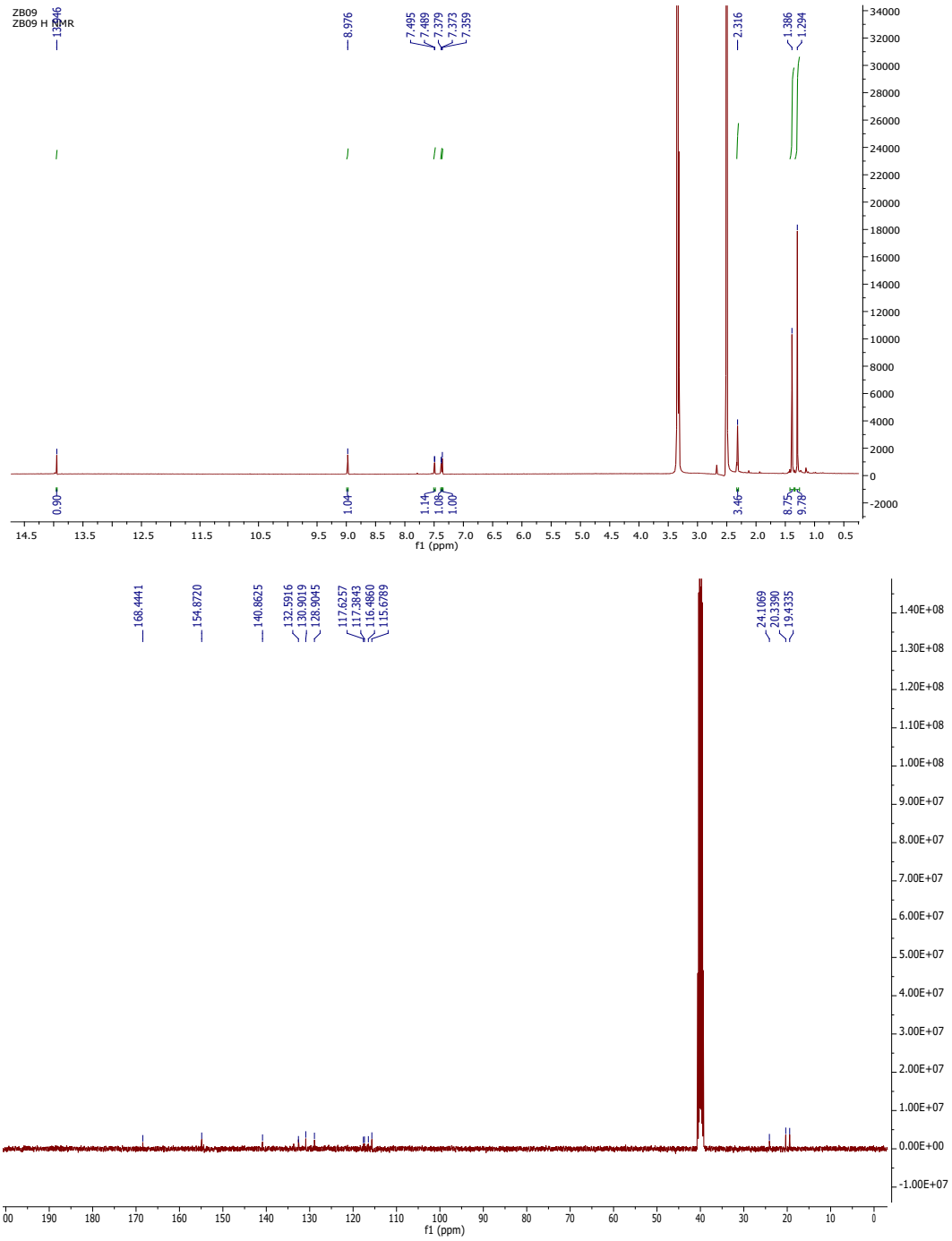


Figure S7: ^{1}H & ^{13}C NMR spectrum of **DAM**

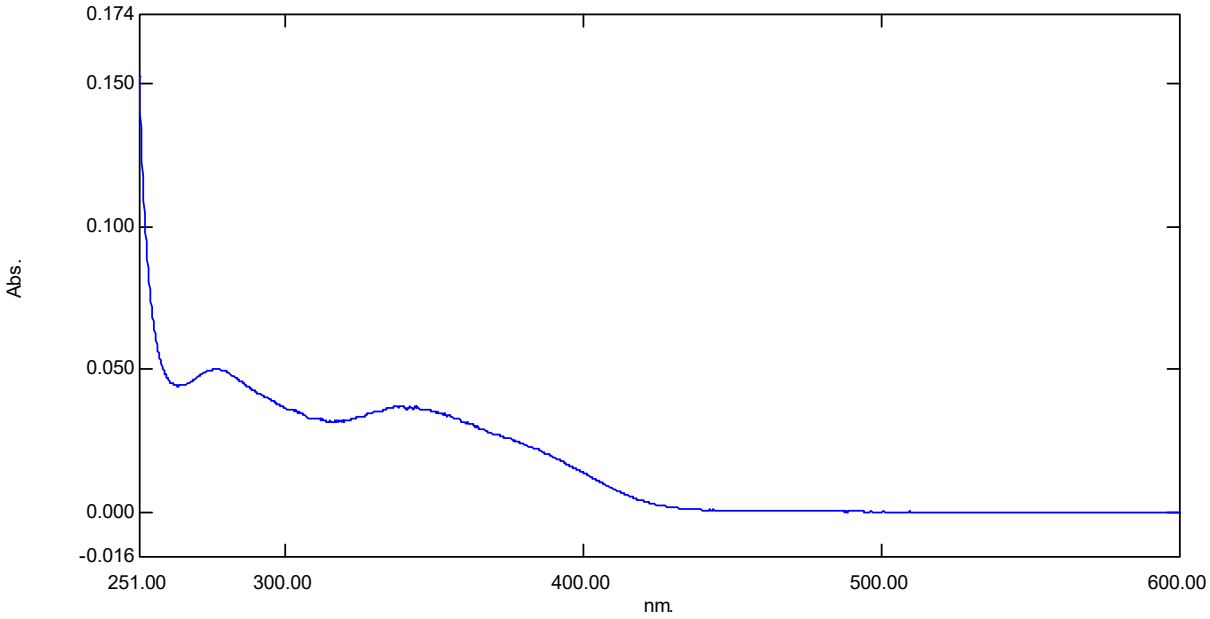


Figure S8: UV spectrum of **DMB** in acetonitrile

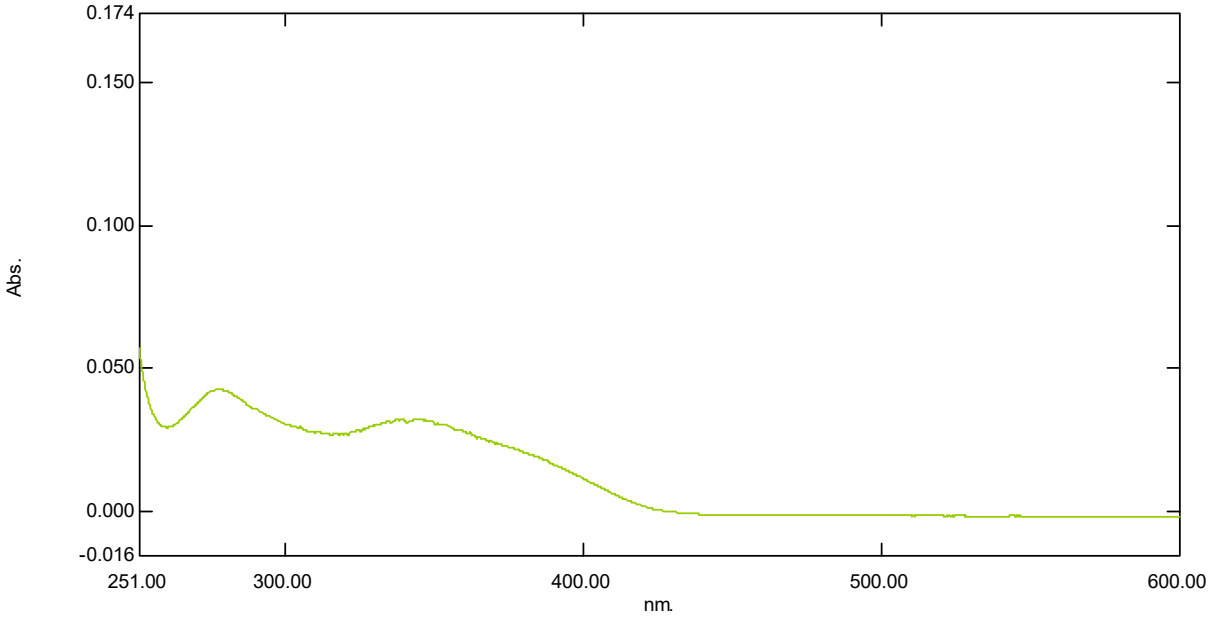


Figure S9: UV spectrum of **DMB** in MeOH

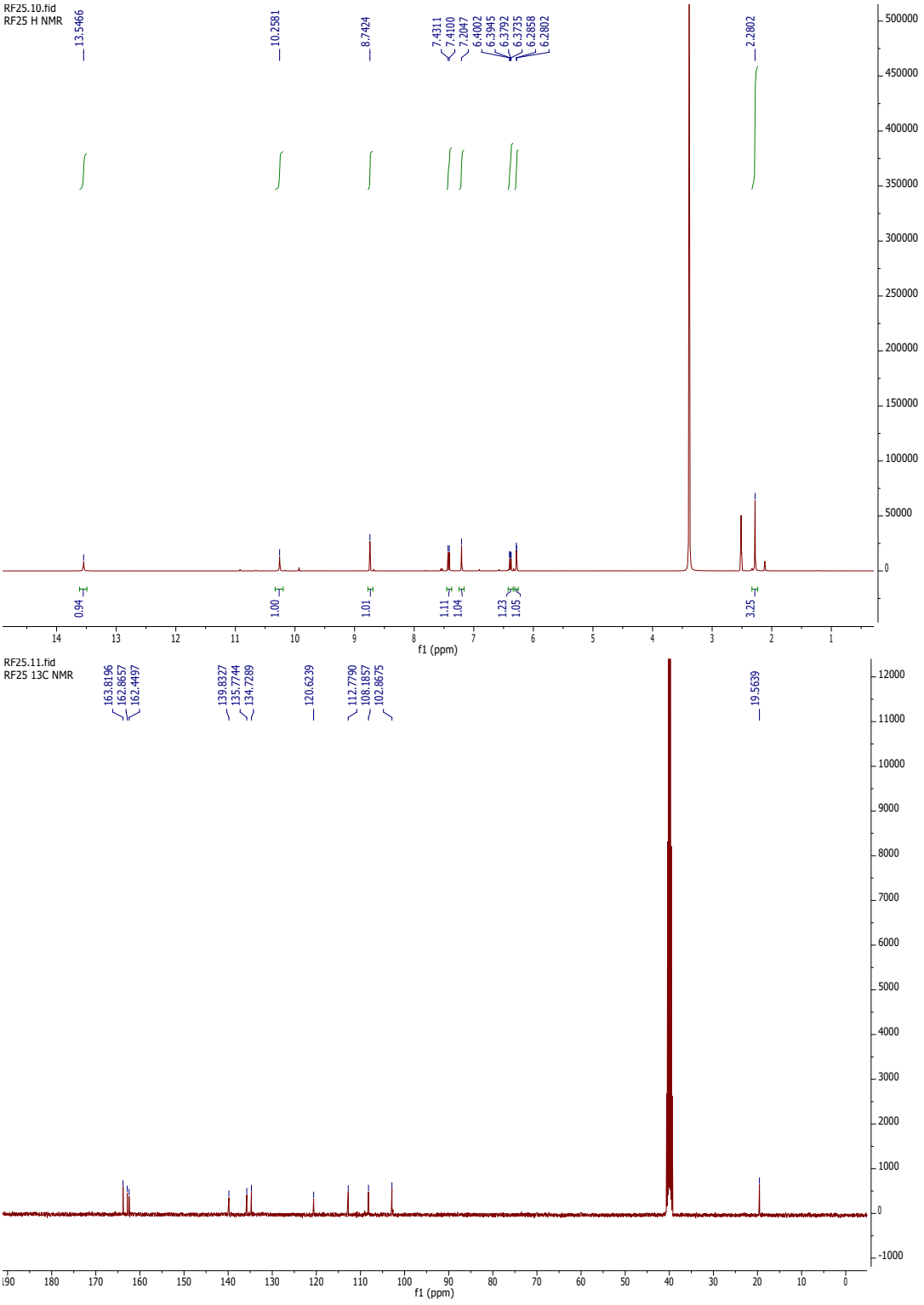


Figure S10: ^{1}H & ^{13}C NMR spectrum of **DMD**

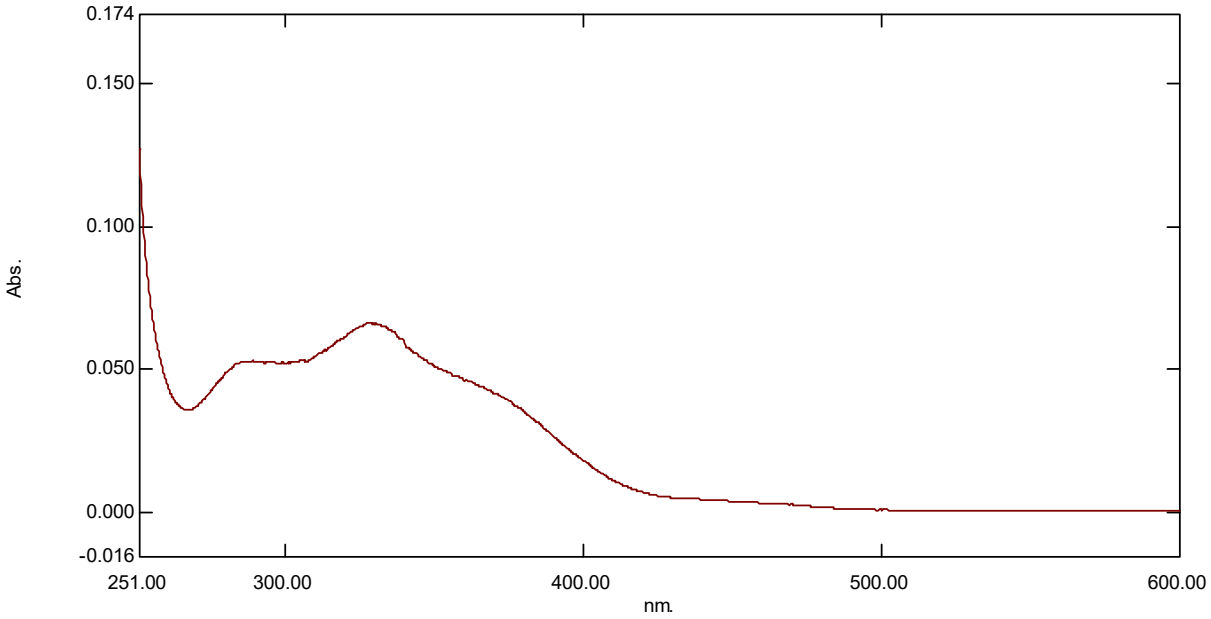


Figure S11: UV spectrum of **DMD** in acetonitrile

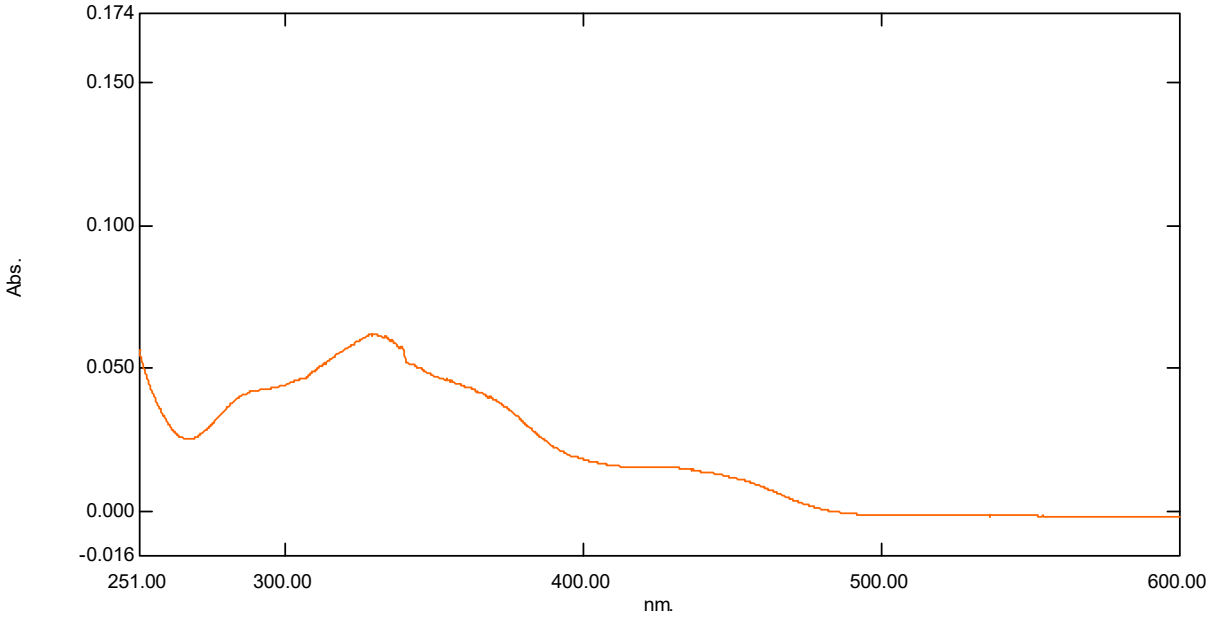
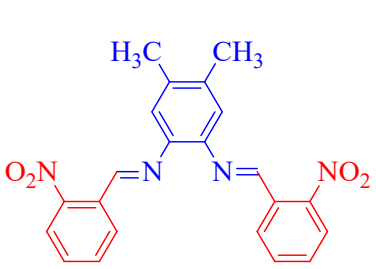
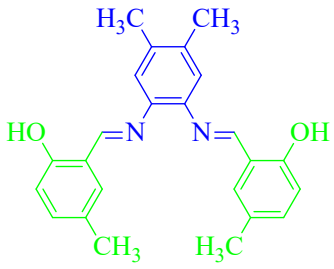


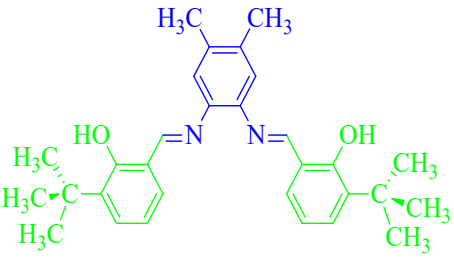
Figure S12: UV spectrum of **DMD** in MeOH



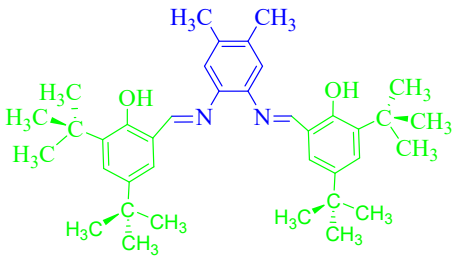
DMA



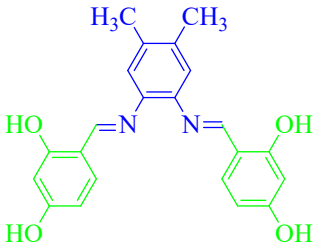
DMM



DMB-D



DAM



DMD

Figure S13: Chemical structures of the investigated compounds

Table S1: Natural bond orbital (NBO) analysis of **DMA** by using M06-2x/6-311G(d,p)

Donor(*i*)	**Type**	**Acceptor(*j*)**	**Type**	***E*$^{(2)}$ [*kcal/mol*]**	***E*(*j*)-*E*(*i*) (*a.u.*)**	**F(*i,j*) (*a.u.*)**
C19-C20	σ	C24-N43	σ*	5.89	1.11	0.073
C23-C24	σ	C19-C24	σ*	5.83	1.42	0.081
C32-H36	σ	C28-C33	σ*	5.03	1.21	0.070
C19-C24	σ	C23-C24	σ*	4.99	1.43	0.075
C29-C30	σ	C28-N46	σ*	4.85	1.12	0.067
C21-H41	σ	C19-C20	σ*	4.59	1.21	0.067
C1-C2	σ	C1-C6	σ*	4.29	1.41	0.070
C22-H26	σ	C20-C21	σ*	3.99	1.24	0.063
C2-C3	σ	C1-C2	σ*	3.78	1.43	0.066
C23-C24	σ	C19-C37	σ*	3.53	1.32	0.061
C31-C32	σ	C32-C33	σ*	3.11	1.41	0.059
C19-C37	σ	C19-C20	σ*	2.88	1.36	0.056
C29-C30	σ	C31-H42	σ*	2.45	1.35	0.052
C4-N17	σ	C2-C3	σ*	2.21	1.48	0.051
C1-C2	σ	C1-C13	σ*	1.97	1.26	0.045
C33-C38	σ	N18-C38	σ*	1.55	1.44	0.042
C28-C33	σ	C28-N46	σ*	0.53	1.14	0.022
C21-C22	π	C23-C24	π*	34.52	0.34	0.097
C1-C2	π	C5-C6	π*	27.73	0.36	0.090
C19-C20	π	N17-C37	π*	12.37	0.38	0.066
C3-C4	π	N18-C38	π*	8.33	0.36	0.053
N46-O48	π	C28-C29	π*	2.90	0.59	0.041
O44	LP(3)	N43-O45	π*	214.63	0.22	0.197
O45	LP(2)	N43-O44	σ*	23.14	0.88	0.128
O48	LP(2)	C28-N46	σ*	15.50	0.71	0.094
O44	LP(3)	N43-O44	σ*	6.18	0.82	0.073
O47	LP(2)	C28-C29	σ*	0.65	1.00	0.023

Table S2: Natural bond orbital (NBO) analysis of **DMM** by using M06-2x/6-311G(d,p)

Donor(*i*)	**Type**	**Acceptor(*j*)**	**Type**	$E^{(2)}$ **[*kcal/mol*]**	***E*(*j*)-*E*(*i*) (*a.u.*)**	**F(*i*,*j*) (*a.u.*)**
O47-H48	σ	C28-C33	σ*	5.72	1.46	0.082
C32-H36	σ	C28-C33	σ*	5.08	1.21	0.07
C5-H8	σ	C3-C4	σ*	4.95	1.21	0.069
C5-H8	σ	C1-C6	σ*	4.61	1.23	0.067
C13-H16	σ	C1-C6	σ*	4.49	1.22	0.066
C30-H35	σ	C28-C29	σ*	4.35	1.22	0.065
C5-C6	σ	C4-N17	σ*	4.19	1.28	0.066
C19-C24	σ	C19-C20	σ*	4.06	1.43	0.068
C30-C31	σ	C31-C32	σ*	3.84	1.43	0.066
C28-C33	σ	C28-C29	σ*	3.54	1.41	0.063
C21-C37	σ	C22-C23	σ*	2.68	1.34	0.053
C28-C29	σ	C29-C30	σ*	3.21	1.44	0.061
C32-C33	σ	C33-C50	σ*	2.88	1.31	0.055
C19-C24	σ	O45-H46	σ*	2.17	1.33	0.048
C4-N17	σ	C4-C5	σ*	1.86	1.49	0.047
C5-H8	σ	C4-C5	σ*	1.23	1.23	0.035
N17-C49	σ	C49-H51	σ*	0.84	1.5	0.032
C5-H8	σ	C4-N17	σ*	0.53	1.1	0.022
C20-C21	π	C22-C23	π*	32.9	0.35	0.096
C1-C6	π	C2-C3	π*	29.84	0.35	0.091
C20-C21	π	C19-C24	π*	25.41	0.34	0.085
C19-C24	π	N17-C49	π*	19.33	0.38	0.082
N17-C49	π	C19-C24	π*	8.23	0.45	0.06
O45	LP(2)	C19-C24	π*	33.66	0.46	0.12
N17	LP(1)	C49-H51	σ*	14.33	0.93	0.105
N18	LP(1)	C2-C3	π*	8.29	0.48	0.061
N18	LP(1)	C2-C3	σ*	5.89	1.05	0.072
O45	LP(1)	C19-C24	σ*	0.55	1.31	0.024

Table S3: Natural bond orbital (NBO) analysis of **DMB-D** by using M06-2x/6-311G(d,p)

Donor(*i*)	**Type**	**Acceptor(*j*)**	**Type**	$E^{(2)}$ **[*kcal/mol*]**	***E*(*j*)-*E*(*i*) (*a.u.*)**	**F(*i*,*j*) (*a.u.*)**
C20-H25	σ	C19-C24	σ*	5.06	1.21	0.07
C3-N18	σ	C32-C38	σ*	4.80	1.38	0.073
C5-H8	σ	C1-C6	σ*	4.58	1.23	0.067
C23-C24	σ	C19-C24	σ*	4.17	1.4	0.068
C52-H55	σ	C23-C43	σ*	3.99	1.02	0.057
C3-C4	σ	C4-C5	σ*	3.76	1.41	0.065
C44-H46	σ	C23-C43	σ*	3.59	1.02	0.054
C28-C29	σ	C28-C56	σ*	3.21	1.24	0.056
C20-C21	σ	C21-C22	σ*	2.96	1.42	0.058
C27-C28	σ	C28-C56	σ*	2.63	1.24	0.051
C3-C4	σ	C2-H7	σ*	2.31	1.32	0.049
C9-H11	σ	C5-C6	σ*	2.02	1.22	0.044
N17-C37	σ	C19-C24	σ*	1.87	1.59	0.049
C21-C22	σ	C22-H26	σ*	1.48	1.33	0.04
C43-C44	σ	C43-C52	σ*	1.02	1.09	0.03

C22-C23	σ	C43-C48	σ*	0.51	1.21	0.022
C28-C29	π	C27-C32	π*	30.73	0.35	0.094
C2-C3	π	C4-C5	π*	26.39	0.36	0.088
C27-C32	π	N18-C38	π*	20.44	0.38	0.083
N18-C38	π	C2-C3	π*	9.53	0.46	0.065
N17-C37	π	C19-C24	π*	7.8	0.45	0.058
C19-C24	π	C19-C24	π*	1.29	0.36	0.019
O35	LP(2)	C19-C24	π*	29.12	0.46	0.112
N17	LP(1)	C37-H39	σ*	14.52	0.91	0.104
N18	LP(1)	C2-C3	π*	8.05	0.48	0.06
N18	LP(1)	C2-C3	σ*	5.86	1.05	0.072
O36	LP(2)	C27-C32	σ*	0.55	1.02	0.022
O36	LP(1)	C27-C28	σ*	0.5	1.29	0.023

Table S4: Natural bond orbital (NBO) analysis of **DMD** by using M06-2x/6-311G(d,p)

Donor(*i*)	**Type**	**Acceptor(*j*)**	**Type**	$E^{(2)}$ **[*kcal/mol*]**	***E*(*j*)-*E*(*i*) (*a.u.*)**	**F(*i*,*j*) (*a.u.*)**
O37-H38	σ	C27-C32	σ*	5.62	1.46	0.081
O47-H48	σ	C29-C30	σ*	5.55	1.45	0.08
C31-H34	σ	C27-C32	σ*	5.06	1.21	0.07
C21-H44	σ	C22-C23	σ*	4.82	1.21	0.068
C23-H26	σ	C21-C22	σ*	4.51	1.22	0.066
C23-C24	σ	C22-O45	σ*	4.47	1.23	0.066
C21-H44	σ	C19-C20	σ*	4.30	1.22	0.065
C20-C21	σ	C22-O45	σ*	4.18	1.21	0.064
C2-C3	σ	C1-C2	σ*	3.87	1.43	0.066
C5-C6	σ	C1-C13	σ*	3.68	1.25	0.061
C20-C21	σ	C19-C39	σ*	3.48	1.33	0.061
C23-C24	σ	C22-C23	σ*	3.27	1.42	0.061
C19-C39	σ	C23-C24	σ*	2.98	1.36	0.057
C1-C13	σ	C1-C6	σ*	2.69	1.34	0.054
C19-C24	σ	C23-H26	σ*	2.31	1.32	0.049
C13-H15	σ	C1-C2	σ*	1.98	1.22	0.044
C19-C20	σ	C39-H41	σ*	1.47	1.29	0.039
C2-H7	σ	C3-N18	σ*	0.52	1.1	0.021
C22-C23	π	C19-C24	π*	36.31	0.36	0.105
C19-C24	π	C20-C21	π*	33.6	0.37	0.101
C2-C3	π	C1-C6	π*	28.13	0.37	0.092
C27-C32	π	N18-C40	π*	21.48	0.38	0.086
C28-C29	π	C30-C31	π*	18.13	0.38	0.074
N17-C39	π	C19-C24	π*	7.97	0.44	0.058
C30-C31	π	C30-C31	π*	0.52	0.37	0.012
O45	LP(2)	C22-C23	π*	38.03	0.45	0.125
O35	LP(2)	C19-C24	π*	35.46	0.45	0.123
N17	LP(1)	C39-H41	σ*	14.22	0.93	0.104
N18	LP(1)	C2-C3	π*	7.66	0.48	0.058
O45	LP(1)	C21-C22	σ*	0.55	1.3	0.024

Table S5: Wave length, excitation energy and oscillator strength of investigated compound **DMA**

NO.	DFT λ (*nm*)	*E*(*eV*)	f_{os}	MO contributions
1	364.068	3.405	0.254	H→L (67%), H→L+2 (15%), H-6→L (3%), H-1→L+1 (2%)
2	328.137	3.778	0.218	H→L+1 (58%), H→L+3 (13%), H-7→L (5%), H-6→L+1 (2%), H-1→L (6%)
3	312.057	3.973	0.034	H-13→L+1 (14%), H-12→L (18%), H-9→L+1 (14%), H-12→L+2 (7%), H-8→L (6%), H-8→L+2 (2%), H-5→L+1 (7%), H-4→L (5%), H-2→L (2%)
4	311.273	3.983	0.002	H-13→L (12%), H-12→L+1 (23%), H-9→L (11%), H-13→L+2 (4%), H-12→L+3 (2%), H-12→L+6 (3%), H-9→L+2 (4%), H-8→L+1 (7%), H-5→L (6%), H-4→L+1 (5%)
5	284.875	4.352	0.118	H-2→L (20%), H→L (18%), H→L+2 (30%), H-7→L+3 (3%), H-6→L+2 (5%), H-3→L+1 (7%), H-1→L+1 (5%)
6	280.632	4.418	0.104	H-1→L (53%), H-1→L+2 (11%) H-14→L+1 (3%), H-13→L (3%), H →L+1 (6%), H→L+4 (3%)

Table S6: Wave length, excitation energy and oscillator strength of investigated compound **DMM**

NO.	DFT λ (*nm*)	*E*(*eV*)	f_{os}	MO contributions
1	346.196	3.581	0.286	H→L (77%), H-7→L+1 (3%), H-6→L (5%), H-4→L (2%), H-2→L (3%), H-1→L+1 (3%)
2	307.887	4.027	0.364	H→L+1 (60%) H-7→L (9%), H-6→L+1 (6%), H-4→L+1 (3%), H-3→L (3%), H-1→L (8%)
3	287.098	4.318	0.386	H-2→L (51%), H-1→L+1 (18%) H-7→L+1 (3%), H-6→L (4%), H-4→L (6%), H-3→L+1 (4%), H→L (6%)
4	281.339	4.407	0.149	H-2→L+1 (30%), H-1→L (54%) H-7→L (2%), H-3→L (3%)
5	266.139	4.659	0.001	H-3→L (40%), H→L+1 (15%) H-7→L (2%), H-6→L+1 (3%), H-5→L (5%), H-1→L (9%), H→L+2 (9%), H→L+4 (5%)
6	257.939	4.807	0.112	H-4→L (42%) H-7→L+1 (5%), H-6→L (9%), H-5→L+1 (9%), H-3→L+1 (4%), H-2→L (6%), H-1→L+1 (7%), H→L (7%), H→L+3 (2%)

Table S7: Wave length, excitation energy and oscillator strength of investigated compound **DMB-D**

NO.	DFT λ (*nm*)	*E*(*eV*)	f_{os}	MO contributions
1	347.811	3.564	0.352	H→L (79%), H-7→L+1 (3%), H-6→L (5%), H→L (3%), H-1→L+1 (3%)
2	308.810	4.014	0.337	H→L+1 (61%), H-7→L (9%), H-6→L+1 (6%), H-4→L+1 (4%), H-3→L (2%), H-1→L (7%)
3	283.976	4.366	0.495	H-4→L (13%), H-2→L (43%), H-1→L+1 (16%) H-7→L+1 (3%), H-6→L (6%), H-5→L+1 (3%), H-3→L+1 (3%), H→L (5%)
4	278.609	4.450	0.124	H-2→L+1 (28%), H-1→L (55%) , H-3→L (3%)
5	267.929	4.627	0.005	H-5→L (11%), H-3→L (38%), H→L+1 (14%), H-6→L+1 (3%), H-1→L (9%), H→L+2 (5%), H→L+4 (8%)
6	262.784	4.718	0.162	H-4→L (36%), H-2→L (15%), H-7→L+1 (4%), H-6→L (9%), H-5→L+1 (6%), H-3→L+1 (9%), H-1→L+1 (5%), H→L (5%)

Table S8: Wave length, excitation energy and oscillator strength of investigated compound **DAM**

NO.	DFT λ (*nm*)	*E*(*eV*)	f_{os}	MO contributions
1	348.956	3.553	0.353	H→L (77%), H-7→L+1 (2%), H-6→L (5%), H-4→L (3%), H-2→L (3%), H-1→L+1 (3%)
2	309.542	4.005	0.389	H→L+1 (59%), H-7→L (7%), H-6→L+1 (5%), H-4→L+1 (4%), H-3→L (2%), H-1→L (9%)
3	290.994	4.260	0.390	H-2→L (48%), H-1→L+1 (19%), H-7→L+1 (2%), H-6→L (5%), H-4→L (8%), H→L (6%)
4	285.829	4.337	0.069	H-2→L+1 (30%), H-1→L (54%), H-7→L (2%), H-3→L (2%)
5	268.364	4.620	0.017	H-5→L (11%), H-3→L (42%), H→L+1 (14%), H-6→L+1 (2%), H-1→L (7%), H→L+2 (8%), H→L+4 (3%)
6	266.083	4.659	0.182	H-4→L (42%), H-2→L (11%), H-7→L+1 (4%), H-6→L (9%), H-5→L+1 (7%), H-3→L+1 (7%), H-1→L+1 (5%), H→L (5%)

Table S9: Wave length, excitation energy and oscillator strength of investigated compound **DMD**

NO.	DFT λ (*nm*)	*E*(*eV*)	f_{os}	MO contributions
1	341.477	3.631	0.408	H→L (79%), H-7→L+1 (2%), H-6→L (4%), H-2→L (4%), H-1→L+1 (4%)
2	303.256	4.088	0.524	H→L+1 (62%) H-7→L (8%), H-6→L+1 (5%), H-2→L+1 (5%), H-1→L (9%)
3	282.544	4.388	0.403	H-6→L (11%), H-2→L (52%), H-1→L+1 (10%) H-7→L+1 (5%), H-3→L+1 (5%), H→L (7%)
4	274.221	4.521	0.418	H-2→L+1 (21%), H-1→L (64%) H-7→L (3%), H→L+3 (3%)
5	264.227	4.692	0.059	H-3→L (31%), H→L+1 (16%), H→L+4 (10%) H-7→L (7%), H-6→L+1 (7%), H-5→L (5%), H-2→L+1 (6%), H-1→L (4%), H-1→L+2 (2%)
6	249.759	4.964	0.051	H-5→L+1 (11%), H-4→L (32%), H→L+2 (11%) H-7→L+1 (3%), H-6→L (6%), H-3→L+1 (5%), H-→L+2 (4%), H-1→L+1 (7%), H-1→L+3 (8%), H→L (4%)

Table S10: Dipole moment along and major contributing tensors of investigated compounds

Dipole Moment	μ_x	μ_y	μ_z	μ_{tot}
DMA	0.000	-2.385	-4×10^{-5}	2.385
DMM	0.000	-0.705	-8×10^{-5}	0.705
DMB-D	-0.000	0.882	-3×10^{-4}	0.882
DAM	0.000	0.659	-0.000	0.659
DMD	0.000	-0.202	1×10^{-3}	0.202

Units in *D*

Table S11: Dipole polarizabilities and major contributing tensors (*e.s.u.*)

Linear Polarizability	$\alpha_{xx}\times10^{-25}$	$\alpha_{yy}\times10^{-25}$	$\alpha_{zz}\times10^{-25}$	$\langle\alpha\rangle\times10^{-25}$
DMA	724.537	747.510	213.058	561.702
DMM	666.537	727.566	304.093	566.066
DMB-D	845.437	784.062	473.231	700.910

DAM	981.133	983.541	667.640	877.438
DMD	675.571	716.639	257.379	549.863

Table S12: The computed first hyperpolarizability (β_{tot}) and major contributing tensors (*e.s.u.*)

1st Hyperpolar-izability	$\beta_{xxx}\times10^{-33}$	$\beta_{xxy}\times10^{-33}$	$\beta_{xyy}\times10^{-33}$	$\beta_{yyy}\times10^{-33}$	$\beta_{xxz}\times10^{-33}$	$\beta_{yyz}\times10^{-33}$	$\beta_{xzz}\times10^{-33}$	$\beta_{yzz}\times10^{-33}$	$\beta_{zzz}\times10^{-33}$	$\beta_{tot}\times10^{-33}$
DMA	-0.388	12747.514	-0.120	9565.689	-0.086	-0.095	0.008	-1183.745	0.008	21129.545
DMM	1.529	-46.971	1.468	-274.701	0.207	0.034	-0.155	160.102	-0.013	161.594
DMB-D	3.066	-23.913	1.641	-924.465	0.812	0.120	-0.025	6.038	-0.215	942.348
DAM	-0.440	-1120.178	0.224	-3391.291	-0.233	0.008	0.224	1176.196	0.449	3335.274
DMD	-1.304	-9867.717	0.129	-15952.49	0.112	0.958	0.388	380.946	0.103	25438.874

Table S13: 2nd Hyper-polarizability and major contributing tensors (*e.s.u.*)

2nd Hyperpolarizability	γ_X	$\gamma_Y\times10^{-35}$	$\gamma_Z\times10^{-35}$	$\gamma_{tot}\times10^{-35}$
DMA	10.496	1.019	0.0651	20.761
DMM	7.756	9.181	0.228	17.170
DMB-D	9.715	8.859	0.774	19.320
DAM	9.982	10.199	10.546	21.239
DMD	9.645	10.577	14.984	20.373

Table S14: Percentages of donor, π-spacer and acceptor for HOMO and LUMO of entitled compounds

Comp.	**LUMO**			**HOMO**		
	Donor	**π-spacer**	**Acceptor**	**Donor**	**π-spacer**	**Acceptor**
DMA	---	14.4	85.6	---	81.8	18.2
DMM	66.6	33.4	---	30.3	69.7	---
DMB-D	64.9	35.1	---	28.5	71.5	---
DAM	65.2	34.8	---	34.4	65.6	---
DMD	64.9	35.1	---	37.6	62.4	---