

Supporting information

Solution and solid state photophysical properties of positional isomeric acrylonitrile derivatives, with core pyridine and phenyl. Experimental and DFT studies.

Armando Castillo¹, Paulina Ceballos¹, Pilar Santos¹, Margarita Cerón¹, Perumal Venkatesan¹, Enrique Pérez-Gutiérrez¹, Martha Sosa-Rivadeneira², S. Thamotharan³, Maxime A. Siegler⁴ and M. Judith Percino¹

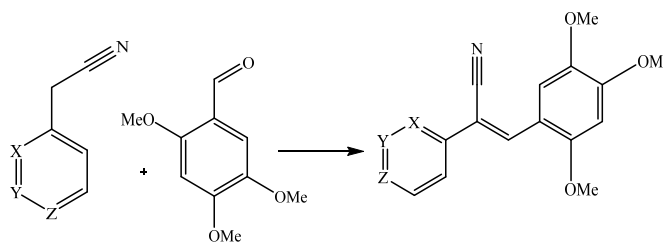
¹Unidad de Polímeros y Electrónica Orgánica, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Val3-Ecocampus Valsequillo, Independencia O2 Sur 50, San Pedro Zacachimalpa, Pue. México.

²Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla (BUAP). 14 Sur Esquina San Claudio, San Manuel, 72570, Puebla, México

³Biomolecular Crystallography Laboratory, Department of Bioinformatics, School of Chemical and Biotechnology, SASTRA University, Thanjavur 613 401, India

⁴Department of Chemistry, Johns Hopkins University, New Chemistry Building, 3400 N. Charles St. Baltimore, MD, 21218, USA.

SI 1.0. General procedure for the compounds (I-V)



I: X=Y=Z=CH; **II:** X=Y=CH Z=C and substituted with 2,4,5-TM(phenyl)CH=C(CN)-

III: X=N; Y=Z=CH; **IV:** X=Z=CH; Y=N; **V:** X=Y=CH; Z=N

Scheme S1. Reactions to obtain the compounds studied **I-V**.

I (Z)-2-(phenyl)-3-(2,4,5-trimethoxyphenyl)-acrylonitrile and **II** (2Z,2'Z)-2,2'-(1,4-phenylene)-bis(3-(2,4,5-trimethoxyphenyl)-acrylonitrile also is called as 1,4-bis- (α -cyano-(2,4,5-trimethoxystyryl)) benzene. **III**: (Z)-2-(pyridin-2-yl)-3-(2,4,5-trimethoxyphenyl) acrylonitrile, **IV** (Z)-2-(pyridin-3-yl)-3-(2,4,5-trimethoxyphenyl)-acrylonitrile and **V** (Z)-2-(pyridin-4-yl)-3-(2,4,5-trimethoxy-phenyl)acrylonitrile .

The general method used to obtain the compounds (**I**, **III**, **IV** and **V**): An amount of 2,4,5-TMB (5.0 mmol) dissolved in (6 ml) of methanol were added 5.0 mmol of the acetonitrile derivative (PhAcN or 2-, 3- 4-PyAcN) in a ball flask, The reaction mixture temperature was raised to reflux and KOH as catalyst was added. The resume of the reaction conditions is shown in Table S1. At the beginning of the reactions, the mixtures acquired different appearances as brown yellow, a darker color, orange color. After the reaction mixture time became dense up until the precipitate formation. The precipitates were filtered under vacuum to obtain the powders, which are washed several times with distilled water. The products **I-IV** were purified by double recrystallization from methanol obtaining a yellows powders with melting points and yields that are resume in the Table S1.

SI 1.1 Synthesis of II.

The molar ration between 2,4,5-TMB and 1,4-PhDAcN was of 2:1. The method synthesis was like former compounds. 0.251 g (1.2 mmol) was dissolved in 5 mL of methanol with 0.100g (6.0 mmol). The reaction mixture temperature was at reflux and an amount of 0.033 g of KOH as catalyst was used. The reaction mixture developed a yellow-orange color, after one hour it changed to an orange-red color until a precipitate of the same color was formed. The solution was vacuum filtered and after several washes with water to remove the catalyst an orange-red solid was obtained. Finally, the compound was purified twice by

recrystallization with DMF. The melting point of obtained product is of 273-275 ° C and yield of 91%.

Table S1. Reaction conditions used for obtaining **I-V**

Compound	Molar ratio 1:1:1 and 1. 2:1 (II)			Time h	T °C	yield (%)
I	PhAcN	2,4,5-TMB	KOH	18	54	85
II	1,4-PhDAcN			3	54	91
III	2-pyAcN;			18	58	70
IV	3-PyAcN			23	58	65
V	HCl de 4-PyAcN,			18	54	80

SI 1.2. Crystallization conditions of **I-V**. All crystals were obtained by slow evaporation at room temperature.

I crystals: 10 mg of powder was dissolved in 1 mL of ethyl acetate; the solution was kept at rest at RT for 72h. Crystals in the form of rectangular prisms with a melting point of 147-148 ° C were obtained. As well when acetone was used as solvent at RT and for 48h needle crystals with a melting point of 145-146 ° C were obtained.

II crystals.10 mg of the orange-red powder was dissolved in 5 ml of chloroform, the solution was kept at room temperature and after 16 h, needle-shaped orange-red crystals with a melting point of 273-275°C were obtained.

III crystals: 10 mg of the **I** powder was dissolved in 1 mL of ethanol; the solution was kept standing at room temperature (RT). After 8 hours yellow crystals were formed in the form of elongated needles with melting point from 135-136 ° C.

IV crystals, 10 mg of the yellow-green crystalline powder was dissolved in 1 mL of ethyl acetate, the solution was kept standing at RT for 48 hours until the formation of green crystals in the form of rectangular prisms with a point of melting 154-155 ° C.

V crystals: 10 mg of the dark-yellow powder was dissolved in 10 mL of ethanol; the solution could stand at RT for 8 h. Yellow needle-shaped crystals with a point of fusion of 155-157 ° C were obtained.

The compound **I** was crystallized in different solvents and under the following conditions.

- a) 10 mg of the compound **I** was placed in a 5 mL beaker, dissolved in 1 mL of ethyl acetate. It was left to stand at room temperature for 72 hours, obtaining yellow-white crystals in the shape of a rectangular prism.
- b) 10 mg of the compound **I** was placed in a 5 mL beaker and dissolved in 1 mL of acetone. It was left to stand at room temperature for 48 hours, obtaining white needle-shaped crystal.
- c) In a two-mouth flask, 50 mg of **I** was added and 5 mL of DMSO was added, the temperature was raised to 120 ° C and allowed to stir for 72 hours. The solution was changed from a yellow- white to a reddish orange. The orange liquid was transferred to a 10 ml beaker and left at room temperature for a week to obtain crystals in the form of long orange needles.
- d) In a two-mouth flask 50 mg of **I** was added and 5 mL of DMF was added, then the temperature was raised to 120 ° C and left under constant stirring for 48 hours, the color-changing solution from a yellow-white to A reddish orange. The orange liquid was transferred to a 10 mL beaker and allowed to crystallize at room temperature for a week obtaining orange crystals and in the form of orange needles.

SI 2.0. Characterization IR, ¹H-NMR and EI of the compounds (I-V)

The IR spectra of **I-II** and **III-V** are shown in Figure S1. The bands important are: in the raw materials the presence of the absorption band at 1689 cm^{-1} due to the vibration of the carbonyl group $\nu\text{C}=\text{O}$ is not observed, and if observe a new vibration bands such as: the elongation vibration of the double bond $\nu\text{C}=\text{C}$ conjugate (acrylonitrile group $-\text{HC}=\text{CCN}-$), in the range of $1612\text{-}1617\text{ cm}^{-1}$. Just as the band of greater intensity between $1575\text{-}1586\text{ cm}^{-1}$ typically corresponds to a double bond of a phenyl group. Another very intense vibration band due to the $-\text{C}\equiv\text{N}$ group attached to the conjugated double bond, which was observed between $2198\text{-}2204\text{ cm}^{-1}$ and the band assigned to the vibration $\delta\text{C-H}$ for the proton that is attached to the atom Carbon conjugated double bond in the range of $920\text{-}720\text{ cm}^{-1}$. The assignment of the signals of **I-V** $^1\text{H-NMR}$ are summarized in the Tables S2-S4 according to the protons assigned of the structures, Scheme S2 and Figure S3. The compound **I** was acquired in $\text{MeOH-d}_4/\text{acetone-d}_6$ mixture, acetone-d_6 and DMF-d_7 , Table S2. The ppm of the protons of phenylacrylonitrile and the proton H_9 (Table S2) are displaced to low field $\text{MeOH-d}_4/\text{acetone-d}_6$ mixture $>$. $\text{DMF-d}_7 \approx \text{acetone-d}_6$. Due to the compound **II** is a symmetrical molecule the proton of double bond and the phenyl do not appear at low field unlike pyridine compounds **III-V**, which is an indication that phenyl does not have a strong electro-attractant effect such as pyridine. The most important is the proton of α,β -unsaturated ($-\text{CH}=\text{CCN}-$) due to $-\text{CN}$, which is an electro attractor group. For the compound **III** corresponding to signal at 8.83, ppm, for the compound **IV** the proton was located at 7.97 ppm, for compound **V** the proton appears at 8.22 ppm, Finally, for compound **I** the proton attached to the carbon of the conjugated double bond $-\text{CH}=\text{CCN}-$ is shift to higher field, that could be the signal at 7.96 ppm.

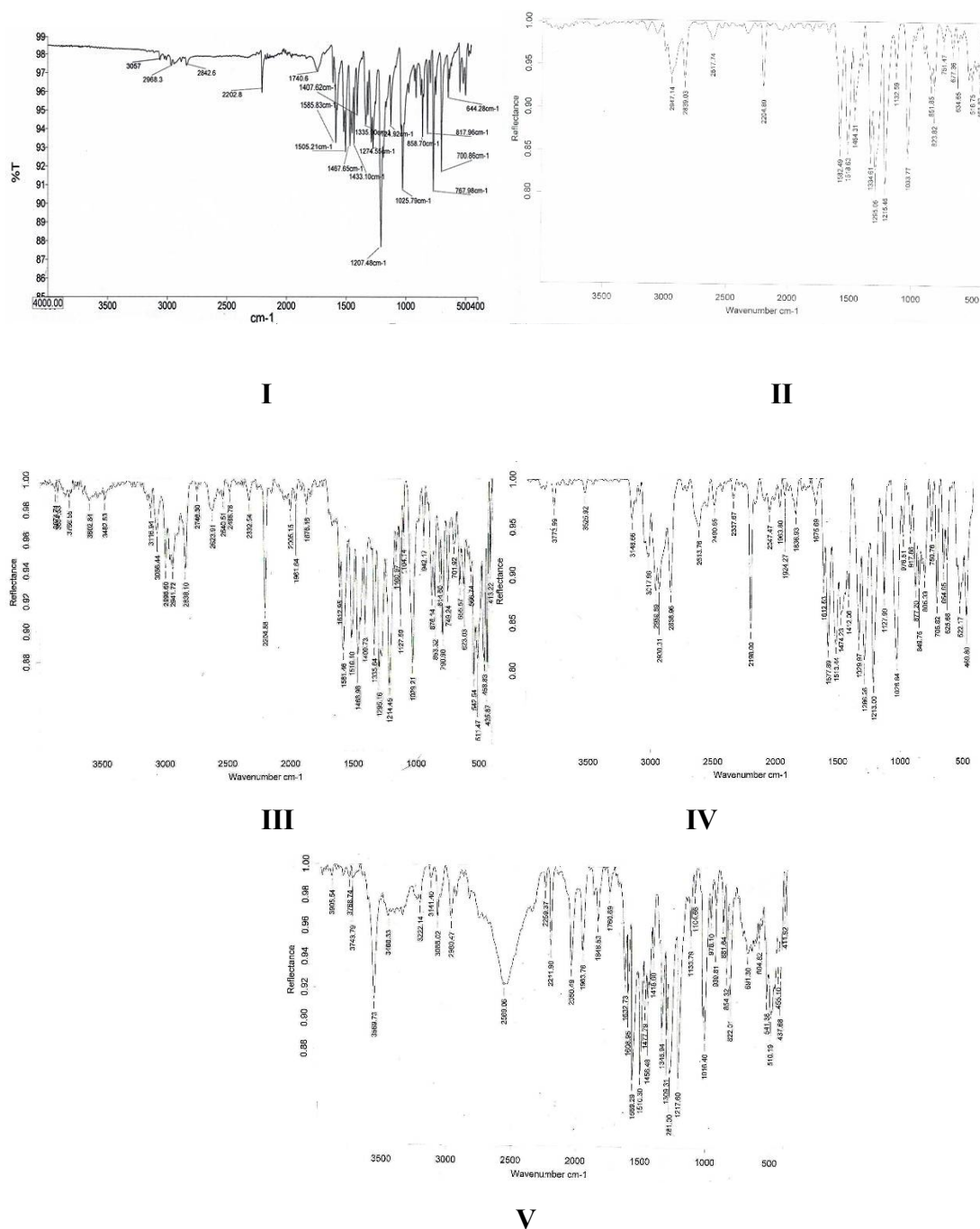
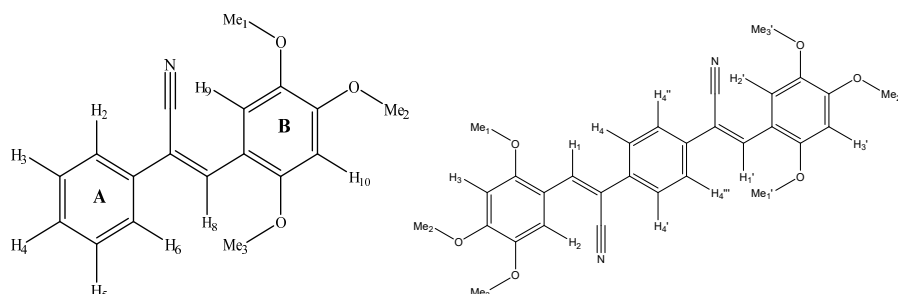
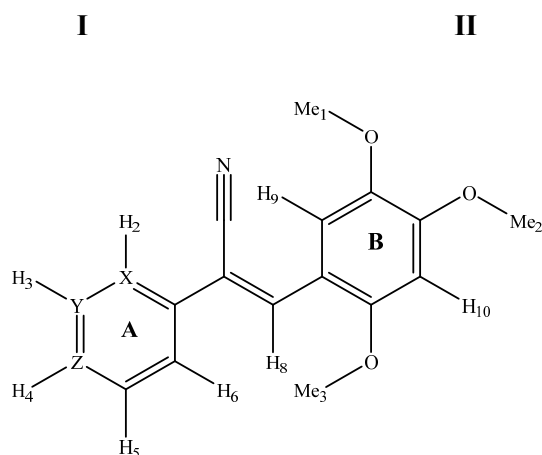


Figure S1. IR spectra of the compounds I, II, III, IV and V.





Scheme S2. **III** is when X=N; Y=C; and Z=C: **IV** is when X=C; Y=N; and Z=C: **V** is when X=C; Y=C; and Z=N.

Table S2. Chemical shift values (ppm) and coupling constant (J_{Hz}) values of compound compounds **I**.

Part	CDCl_3	MeOH-d_4 / acetone-d_6	acetone-d_6	DMF-d_7
Acry- H_8	7.96	9.37	7.98	8.05
H_2, H_6	7.68-7.66, $J=10$	d, 8.88-	d, 7.65-7.64 $J=5$	d, 7.92-7.91 $J=5$
$\text{H}_3, \text{H}_5, \text{H}_4$	7.44-7.41, $J=10, 5$ 7.37-7.32, $J=10, 5$	m, 8.71-8.69 $J=10$ m, 8.69-8.68 $J=5$	m, 7.47-7.46 $J=5$, 7.47-7.45; 7.45- 7.44 $J=10, 5$	m, 7.73-7.71 $J=10$ 7.71-7.70 $J=5$,
	7.94			
H_9	7.94	s, 9.10	s, 7.98	s, 8.27
H_{10}	6.52	s, 8.10	s, 6.77	s, 7.10
Me_1	4.03	s, 5.15	s, 3.90	s, 4.16
Me_2	3.96	s, 5.11	s, 3.85	s, 4.15
Me_3	3.88	s, 5.06	s, 3.81	s, 4.06

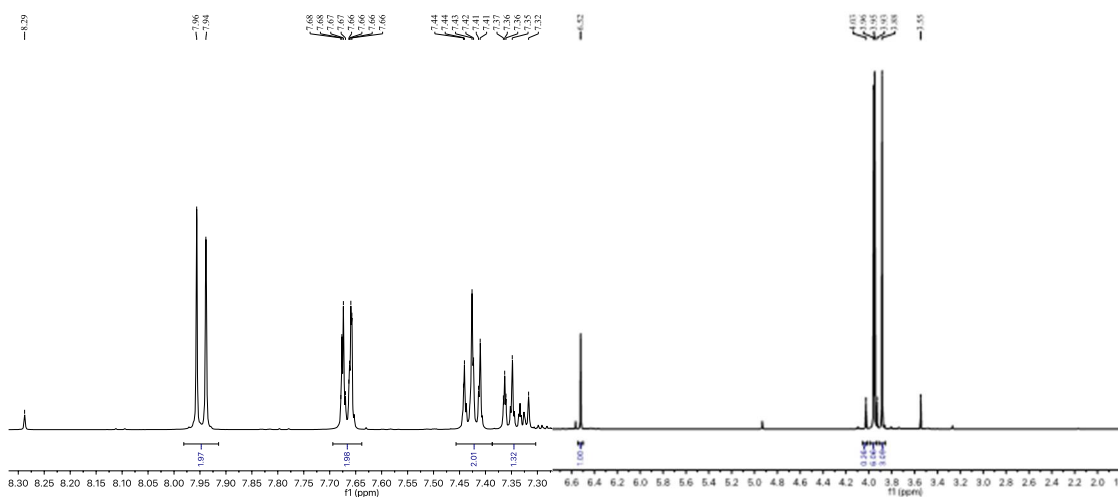
Table S3. Chemical shift values(ppm) and coupling constant (Hz) values of compound compounds **II**.

II	CDCl_3
	s7.95
H_1, H'_1	s,7.89
$2\text{H}_4, 2\text{H}'_4$	s7.65

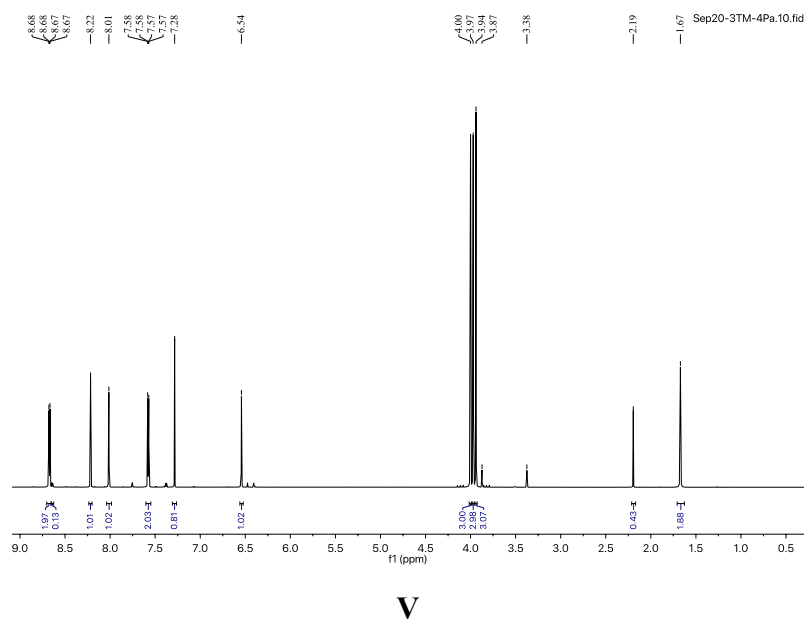
H ₂ , H' ₂	s, 7.89
H ₃ , H' ₃	s, 6.46
Me ₁ , Me' ₁	s, 3.90
Me ₂ Me' ₂	s, 3.88
Me ₃ Me' ₃	s, 3.82

Table S4 chemical shift values(ppm) and coupling constant (Hz) values of compounds **III-V**

Part	III		IV		V	
Acry-H ₈		8.83		7.97		8.22
A	H ₃	8.66-8.64; J=10	H ₂	8.93	H ₅ , H ₃	8.68-8.67 J=5.0
	H ₄ , H ₆	7.77-7.72, J=10	H ₄	8.61-8.60 J=5	H ₂ ; H ₆	7.58-7.57, J=5.0
	H ₅	7.25-7.23; J=10	H ₅ , H ₆	7.96-7.95, J=5		
B	H ₉	8.04		8.02		8.01
	H ₁₀	6.54		6.54		6.54
	Me1	3.97		3.99		4.00
	Me2	3.98		3.97		3.97
	Me3	3.93		3.92		3.94

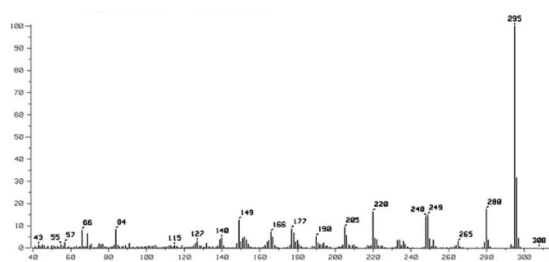


I

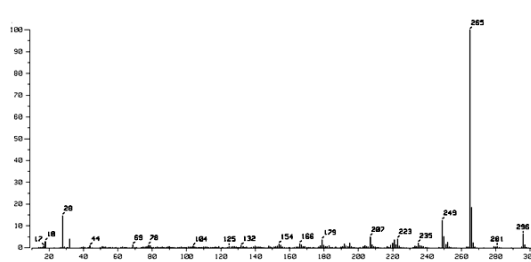


V

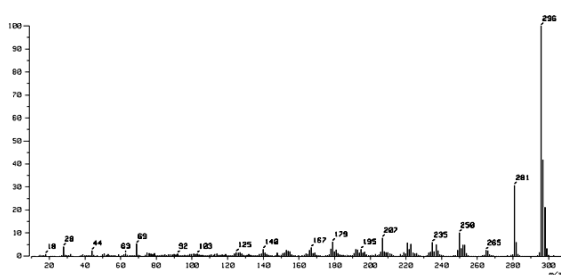
Figure S2. ^1H -NMR spectra of the compounds **I**, **II**, **III**, **IV** and **V** in CDCl_3 .



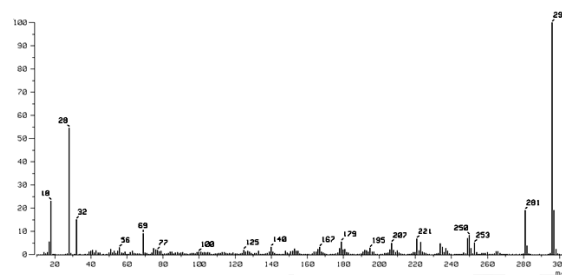
I



III



IV

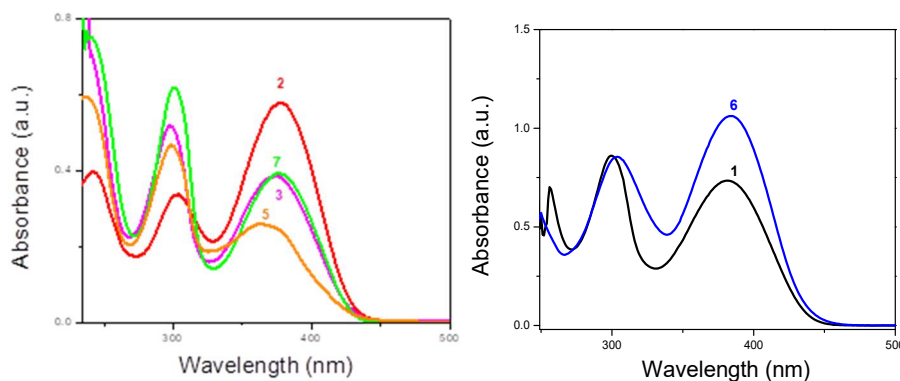


V

Figure S3. EI spectra of the compounds **I**, **II**, **III** and **IV**.

3.0 Absorption spectroscopy in solution.

The **I-V** compounds solutions at 0.001 mM concentration and at room temperature using (1) DMSO, (2) MeOH, (3) AcCN, (4) acetone, (5) THF, (6) EtOAc, (7) CHCl₃, and (8) MeOH:acetone (70:30) mixture were prepared. UV-Vis spectra were acquired, because the compounds solutions under UV lamp different emission were observed. The solvents were selected to evaluate the non-polar (non-HBD; no hydrogen bond-donor formation, “aprotic”; e.g. CHCl₃), polar non-HBD (“aprotic” solvents; e.g. acetone, DMF, DMSO, THF, EtOAc), and with a dipolar group HBD (“protic”; e.g. methanol) (Figure S11). i.e. in some solvents the fluorescence intensity decreased (quenching process) and in others the fluorescence wavelength showed a shift. The **I-V** absorbance values in the different solvents are shown in Figures S4-S7.



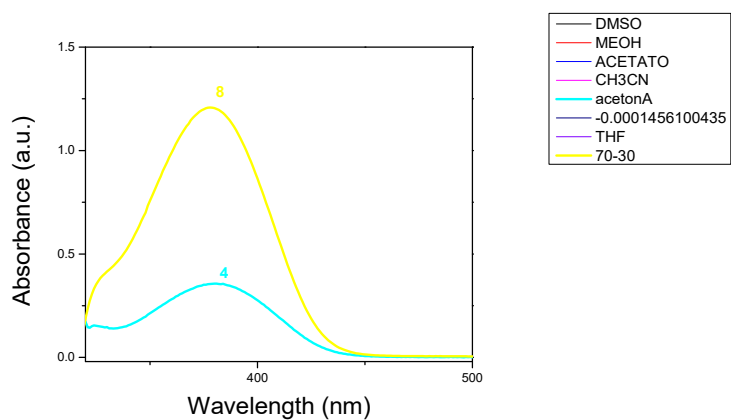


Figure S4. Absorption spectra of compound **I** in solvents 1-8

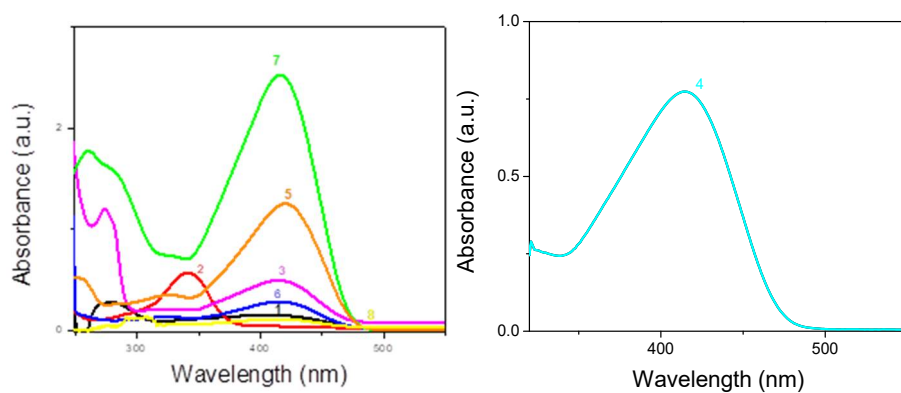


Figure S5. Absorption spectra of compound **II** in solvents 1-8

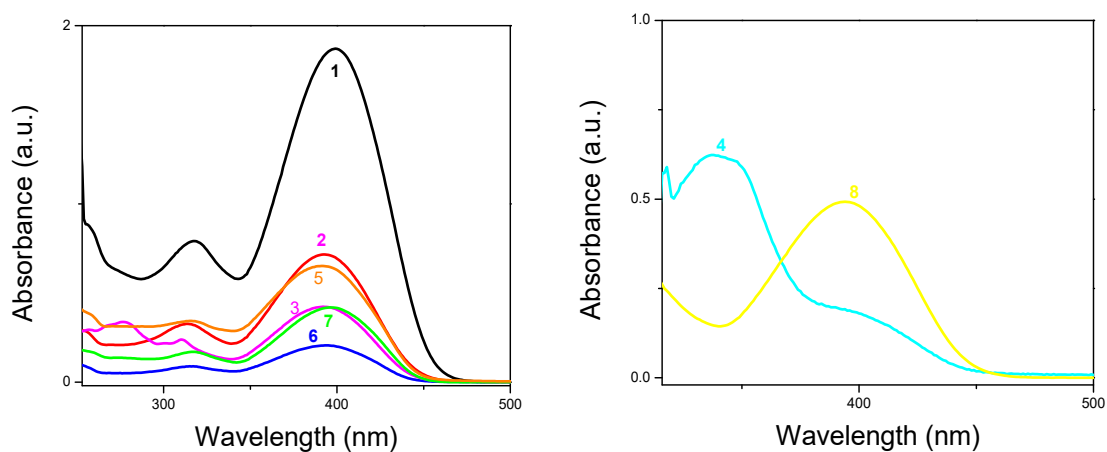


Figure S6. Absorption spectra of compound **III** in solvents 1-8

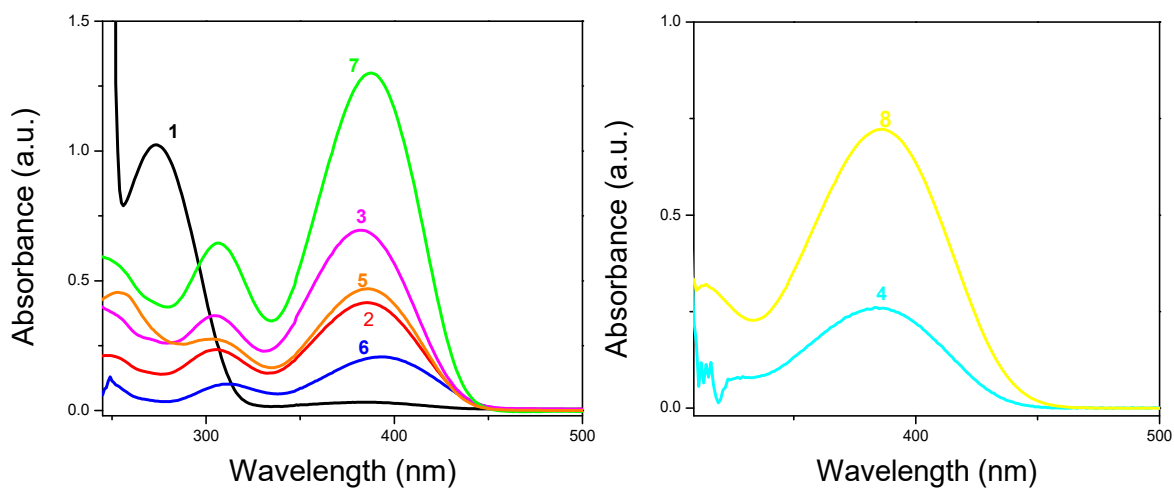


Figure S7. Absorption spectra of compound **IV** in solvents 1-8

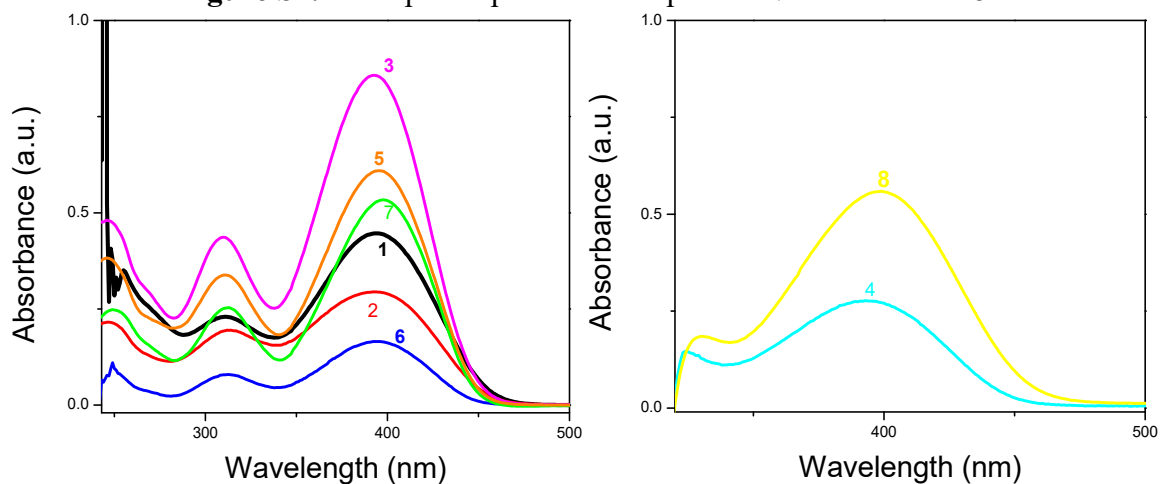


Figure S8. Absorption spectra of compound **V** in solvents 1-8

Table S5. Photophysical properties λ_{abs1} , λ_{abs2} , λ_{abs3} , (nm) and ϵ ($\text{M}^{-1} \text{cm}^{-1}$) of the **I-V** compounds in several solvents: 1= DMSO (46.68), 2= MeOH (32.70), 3= AcCN acetonitrile (37.5), 4= acetone (21.01), 5= THF (7.5), 6= EtOAc, (6.02), 7= CHCl_3 (4.81), and 8= mixture MeOH/Acetone(70:30). (23.21)

Solvent	λ_{abs1}	λ_{abs2}	λ_{abs3}	ϵ_1	ϵ_2	ϵ_3
I						
1	256	299	381	17525	21500	8350
2	242	303	376	9875	8425	14500
3	241	298	374	17650	12950	9625
4		324	380		4075	8825
5	235	298	366	14875	11675	6450
6	250	303	384	14225	21400	26500
7	241	299	375	27400	23075	14675
8		326	378		6400	18050
II						
1	278		415	6970		3773
2	243	341		5486	14247	
3	274		415	20007		8268
4			414			19350
5	251	324	415	8718	5858	20884
6	254	324	415	3937	3453	7244
7	261	281	416	14770	13190	21042
8		331	413		1587	2844
III						
1	256	315	396	10300	9000	21025
2	251	313	393	4900	5425	17900
3	276	310	392	5600	3950	7025
4	318	337	406	9825	10375	2750
5	243	315	391	7575	5700	10850
6	250	316	393	2040	1475	3425
7	258	316	396	2825	2800	6975
8			393			8205
IV						
1	274		383	19675		620
2	249	306	386	3700	4200	7500
3	252	306	383	6800	7022.5	13350
4		325	385		1827.5	6425
5	254	305	387	8725	5275	9675
6	250	314	394	2000	1495	3052.5
7	248	307	389	8625	9525	19225
8		315	387		8000	18050
V						
1	256	312	394	8750	5725	11150
2	248	313	390	5500	4825	7200

3	248	310	393	11725	10600	20800
4		324	395		3525	6875
5	247	313	397	9550	8425	15225
6	250	313	395	2750	1975	4125
7	253	313	398	6050	6325	13325
8		328	399		9800	30025

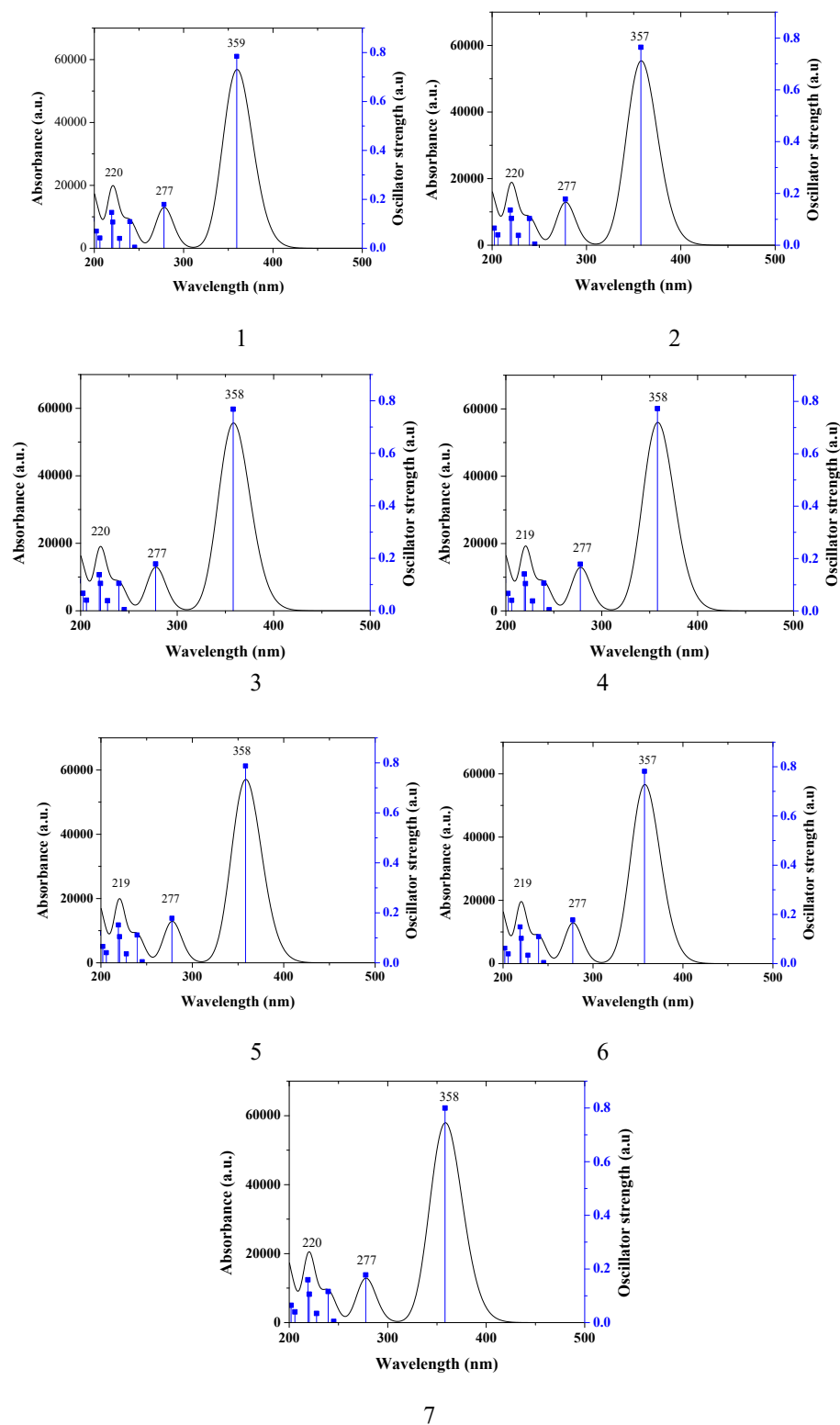
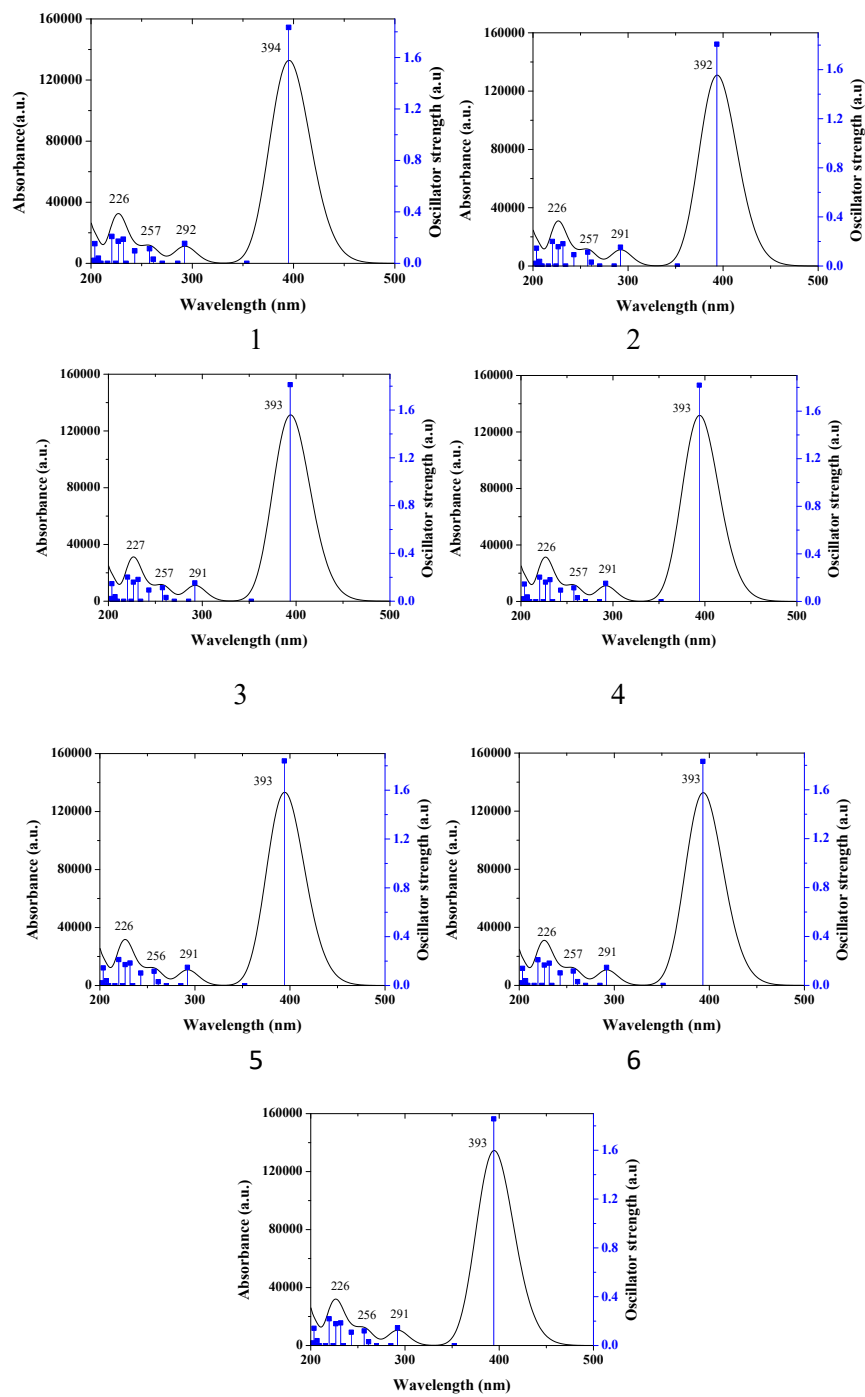


Figure S9. Absorption spectra of **I** calculated with at theoretical level of m062x / pVTZ in DMSO(1), Methanol(2), Acetonitrile(3), Acetone (4), THF(5), Ethyl Acetate (6), Chloroform (7).



7

Figure S10. Absorption spectra of **II**, calculated with at theoretical level of m062x / pVTZ in DMSO(1), Methanol(2), Acetonitrile(3), Acetone (4), THF(5), Ethyl Acetate (6), Chloroform (7).

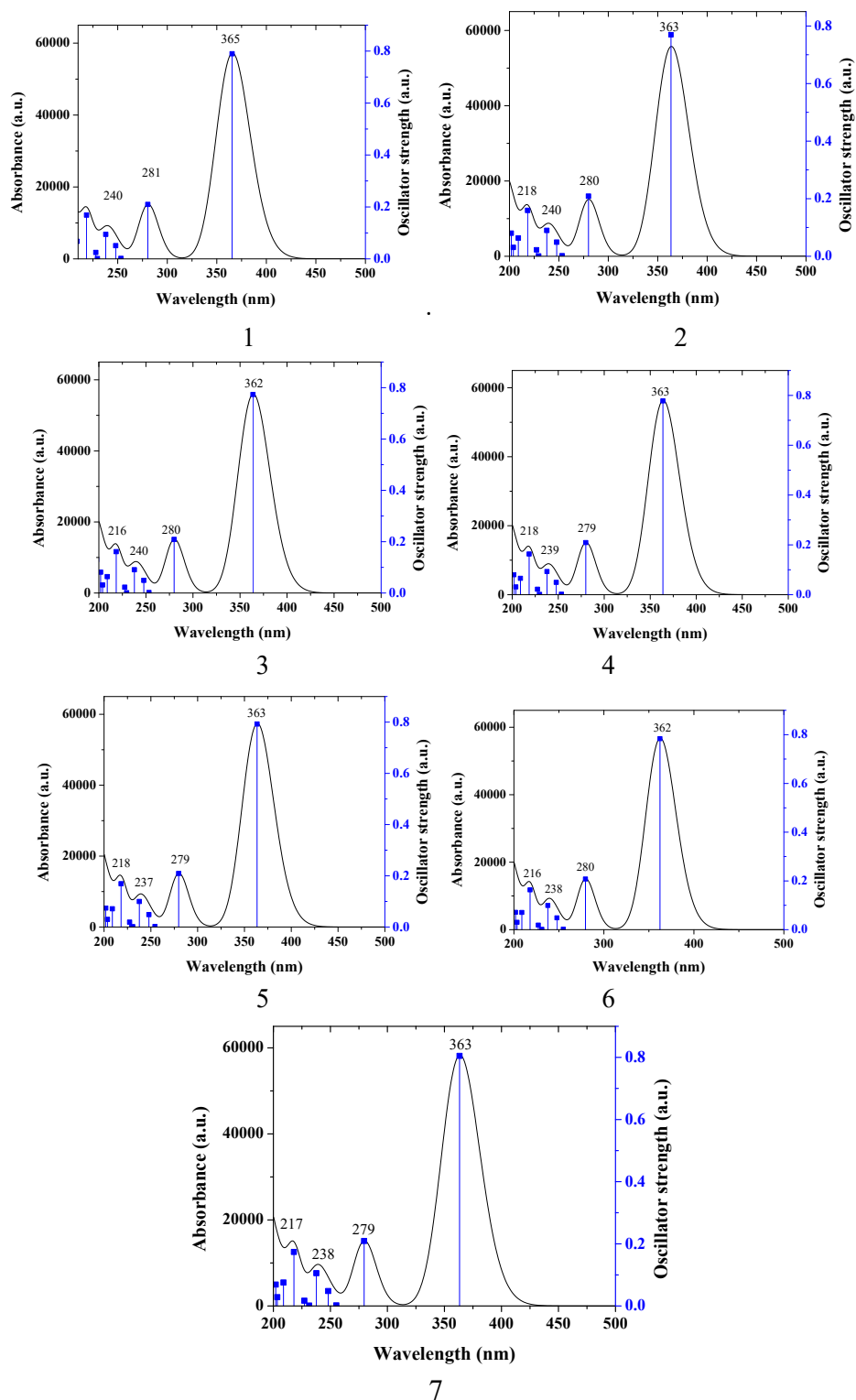
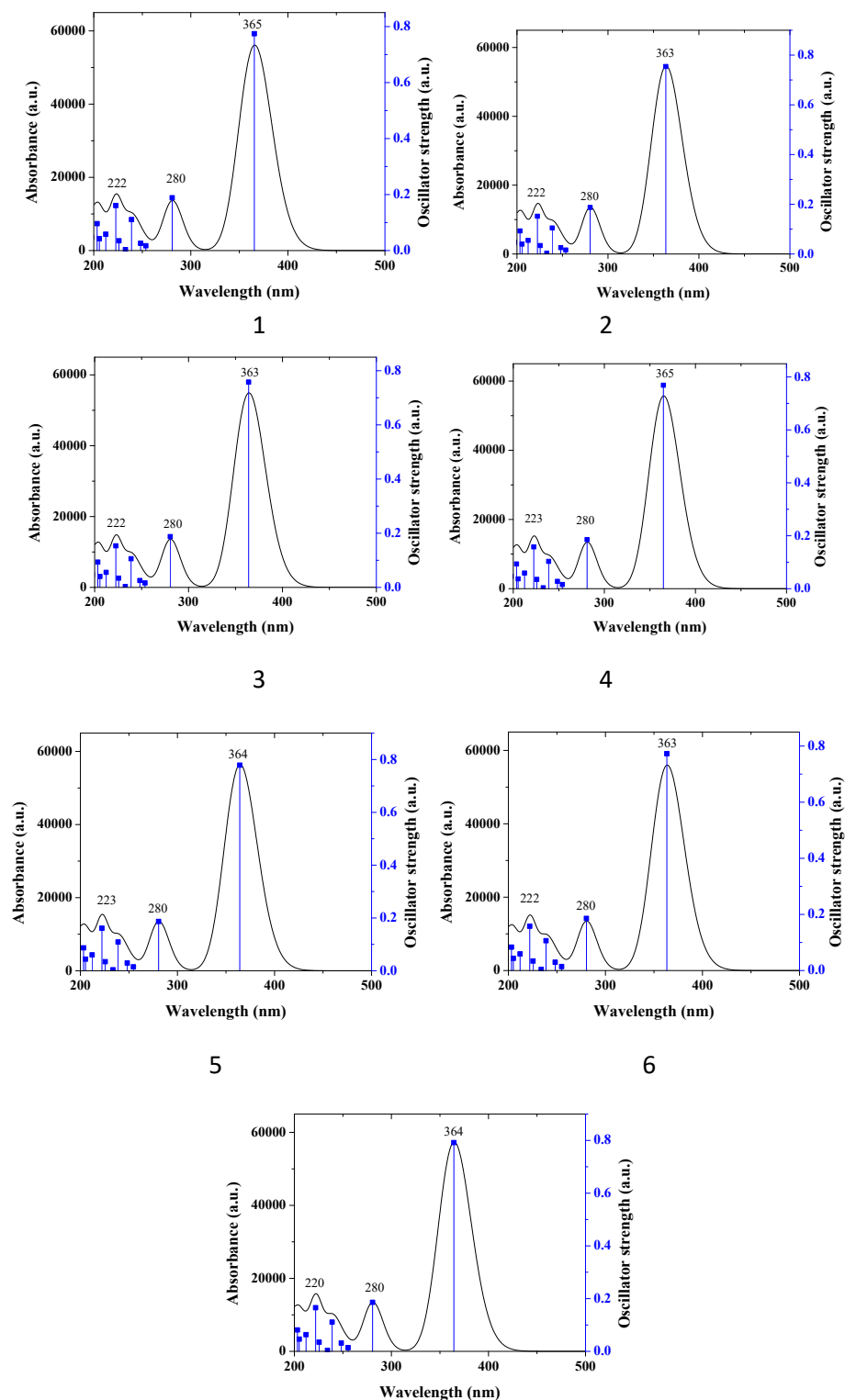


Figure S11. Absorption spectra of **III**, calculated with at theoretical level of m062x / pVTZ in DMSO(1), Methanol(2), Acetonitrile(3), Acetone (4), THF(5), Ethyl Acetate (6), Chloroform (7).



7

Figure S12. Absorption spectra of **IV**, calculated with at theoretical level of m062x / pVTZ in DMSO(1), Methanol(2), Acetonitrile(3), Acetone (4), THF(5), Ethyl Acetate (6), Chloroform (7).

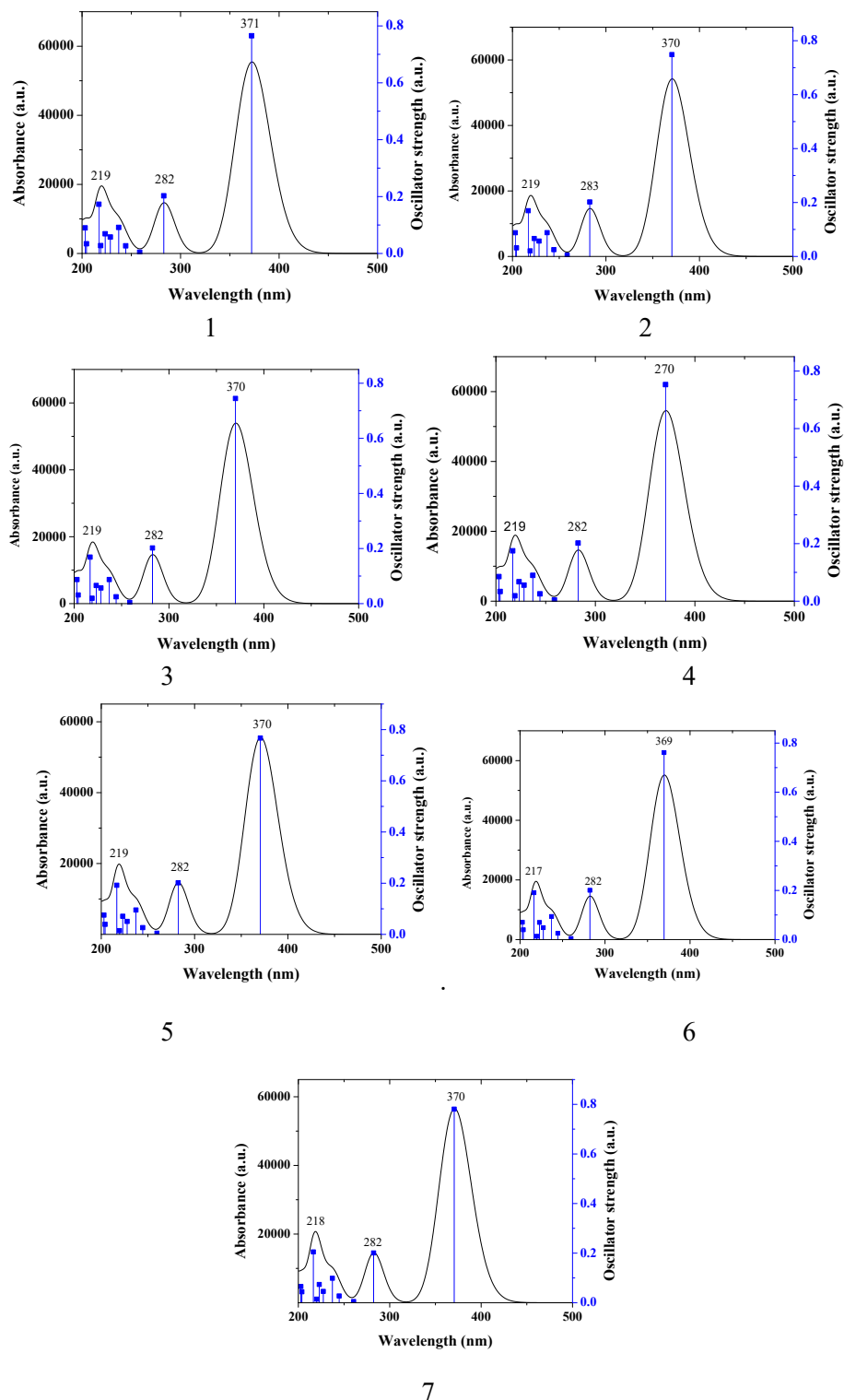


Figure S13. Absorption spectra of **V**, calculated with at theoretical level of m062x / pVTZ in DMSO(1), Methanol(2), Acetonitrile(3), Acetone (4), THF(5), Ethyl Acetate (6), Chloroform (7).

Table S6. Experimental and calculated at theory level of m062x/cc-pvtz for **I-V** compounds. Absorption wavelength (nm), excitation energy (eV) and oscillator strengths (*f*) in DMSO(1), Metanol(2), Acetonitrile(3), Acetone (4), THF(5), Ethyl Acetate (6), Chloroform (7).

I					II				
1									
λ (nm)	E (eV)	f	Major contribution (%)	λ_{exp} (nm)	λ (nm)	E (eV)	f	Major contribution (%)	λ_{exp} (nm)
359	3.44	0.784	HOMO→LUMO(97)		395	3.13	1.834	H-1→L+1(14) HOMO→LUMO(84)	
277	4.46	0.179	H-1→LUMO(88)		292	4.23	0.154	H-3→L+1(10) H-2→LUMO(60) H-1→L+1(21)	
239	5.17	0.109	H-3→LUMO(20) HOMO→L+2(11) HOMO→L+3(45)		257	4.80	0.114	H-3→L+1(11) H-2→LUMO(11) H-1→L+1(53) HOMO→LUMO(11)	
220	5.61	0.107	H-2→LUMO(18) HOMO→L+1(29) HOMO→L+2(30)		231	5.34	0.187	H-5→LUMO(33) H-4→LUMO(21) HOMO→L+2(31)	
219	5.64	0.146	H-3→LUMO(22) HOMO→L+1(17) HOMO→L+2(18) HOMO→L+3(20)		220	5.73	0.209	HOMO→L+3(40) HOMO→L+5(30)	
2									
357	3.46	0.764	HOMO→LUMO(97)		393	3.15	1.807	H-1→L+1(14) HOMO→LUMO(84)	
277	4.46	0.178	H-1→LUMO(88)		292	4.24	0.153	H-3→L+1(10) H-2→LUMO(60) H-1→L+1(20)	
239	5.17	0.103	H-3→LUMO(21) HOMO→L+2(11) HOMO→L+3(45)		257	4.81	0.112	H-3→L+1(11) H-2→LUMO(11) H-1→L+1(53) HOMO→LUMO(11)	
220	5.62	0.103	H-2→LUMO(17) HOMO→L+1(27) HOMO→L+2(32)		231	5.35	0.181	H-5→LUMO(33) H-4→LUMO(21) HOMO→L+2(31)	
219	5.65	0.135	H-3→LUMO(23) HOMO→L+1(19) HOMO→L+2(16) HOMO→L+3(20)		220	5.62	0.200	HOMO→L+3(39) HOMO→L+5(30)	
3									
358	3.46	0.768	HOMO→LUMO(97)		393	3.14	1.812	H-1→L+1(14) HOMO→LUMO(84)	
277	4.46	0.178	H-1→LUMO(88)		292	4.24	0.153	H-3→L+1(10) H-2→LUMO(60) H-1→L+1(21)	
239	5.17	0.104	H-3→LUMO(21) HOMO→L+2(11) HOMO→L+3(45)		257	4.81	0.113	H-3→L+1(11) H-2→LUMO(11) H-1→L+1(53) HOMO→LUMO(11)	
220	5.62	0.104	H-2→LUMO(17) HOMO→L+1(28)		231	5.35	0.182	H-5→LUMO(33) H-4→LUMO(21)	

			HOMO→L+2(31)					HOMO->L+2(31)	
219	5.65	0.137	H-3→LUMO(22) HOMO→L+1(19) HOMO→L+2(17) HOMO→L+3(20)		220	5.62	0.201	HOMO->L+3(39) HOMO->L+5(30)	
4									
358	3.46	0.772	HOMO→LUMO(97)		393	3.14	1.819	H-1->L+1(14) HOMO->LUMO(84)	
277	4.46	0.178	H-1→LUMO(88)		292	4.24	0.152	H-3->L+1(10) H-2->LUMO(60) H-1->L+1(21)	
239	5.17	0.105	H-3→LUMO(21) HOMO→L+2(12) HOMO→L+3(45)		257	4.81	0.113	H-3->L+1(11) H-2->LUMO(11) H-1->L+1(53) HOMO->LUMO(11)	
220	5.62	0.104	H-2→LUMO(18) HOMO→L+1(29) HOMO→L+2(30)		231	5.35	0.183	H-5->LUMO(33) H-4->LUMO(22) HOMO->L+2(31)	
219	5.65	0.141	H-3→LUMO(22) HOMO→L+1(17) HOMO→L+2(18) HOMO→L+3(21)		220	5.62	0.204	HOMO->L+3(39) HOMO->L+5(31)	
5									
358	3.46	0.787	HOMO→LUMO(97)		394	3.14	1.839	H-1->L+1(14) HOMO->LUMO(84)	
277	4.46	0.178	H-1→LUMO(88) HOMO→L+3(4%)		292	4.24	0.149	H-3->L+1(10) H-2->LUMO(60) H-1->L+1(21)	
239	5.17	0.111	H-3→LUMO(21) HOMO→L+2(13) HOMO→L+3(45)		257	4.82	0.117	H-3->L+1(11) H-2->LUMO(12) H-1->L+1(53) HOMO->LUMO(11)	
220	5.62	0.104 7	H-2→LUMO(22) HOMO→L+1(34) HOMO→L+2(24)		231	5.35	0.184	H-5->LUMO(30) H-4->LUMO(25) HOMO->L+2(32)	
219	5.62	0.104	H-3→LUMO(19) HOMO→L+1(13) HOMO→L+2(22) HOMO→L+3(25)		219	5.63	0.212	HOMO->L+3(37) HOMO->L+5(33)	
6									
357	3.47	0.781	HOMO→LUMO(97)		393	3.15	1.832	H-1->L+1(14) HOMO->LUMO(84)	
277	4.46	0.177	H-1→LUMO(87)		291	4.24	0.147	H-3->L+1(10) H-2->LUMO(60) H-1->L+1(21)	
239	5.17	0.109	H-3→LUMO(21) H-1→LUMO(10) HOMO→L+2(14) HOMO→L+3(44)		256	4.82	0.117	H-3->L+1(11) H-2->LUMO(12) H-1->L+1(53) HOMO->LUMO(11)	
220	5.62	0.102	H-2→LUMO(23) HOMO→L+1(34) HOMO→L+2(23)		231	5.35	0.181	H-5->LUMO(29) H-4->LUMO(26) HOMO->L+2(32)	
218	5.66	0.149	H-3→LUMO(18) HOMO→L+1(12) HOMO→L+2(22)		219	5.64	0.210	HOMO->L+3(36) HOMO->L+5(34)	

			HOMO→L+3(26)						
7									
358	3.46	0.80	HOMO→LUMO(97)		394	3.14	1.857	H-1->L+1(14) HOMO->LUMO(84)	
277	4.46	0.177	H-1→LUMO(87)		292	4.24	0.146	H-3->L+1(10) H-2->LUMO(60) H-1->L+1(21)	
239	5.17	0.115	H-3→LUMO(21) H-1→LUMO(10) HOMO→L+2(14) HOMO→L+3(44)		256	4.82	0.119	H-3->L+1(11) H-2->LUMO(12) H-1->L+1(53) HOMO->LUMO(11)	
220	5.62	0.105	H-2→LUMO(26) HOMO→L+1(37) HOMO→L+2(20)		231	5.34	0.185	H-5->LUMO(27) H-4->LUMO(28) HOMO->L+2(32)	
218	5.66	0.159	H-3→LUMO(17) HOMO→L+2(24) HOMO→L+3(28)		219	5.64	0.219	HOMO->L+3(36) HOMO->L+5(34)	

III					IV				
λ (nm)	E (eV)	f	Major contribution (%)	λ_{exp}	λ (nm)	E (eV)	f	Major contribution (%)	λ_{exp} (nm)
1									
365	3.40	0.778	HOMO→LUMO (97)		365	3.39	0.774	HOMO→LUMO(97)	
280	4.42	0.209	H-3→LUMO(52) H-3→L+1(33)		280	4.41	0.1885	H-1→LUMO(88)	
247	5.00	0.050	H-1→L+1(12) HOMO→L+1(61)		338	5.18	0.110	H-2→LUMO(19) HOMO→L+3(53)	
237	5.21	0.945	H-2→LUMO(23) HOMO→L+2(18) HOMO→L+3(41)		225	5.48	0.0349	H-2→LUMO(37) HOMO→L+2(41)	
218	5.67	0.168	H-1→L+2 (5%) HOMO→L+1(3)		222	5.56	0.160	H-2→LUMO(26) HOMO→L+2(22) HOMO→L+3(30)	
2									
363	3.41	0.769	HOMO→LUMO(97)		363	3.40	0.754	HOMO→LUMO(97)	
279	4.42	0.208	H-1→LUMO (89)		280	4.42	0.187	H-1→LUMO (88)	
247	5.00	0.049	H-1→L+1(12) HOMO→L+1(62)		238	5.19	0.104	H-2→LUMO(20) HOMO→L+3(52)	
237	5.21	0.09	H-2→LUMO(23) HOMO→L+2(19) HOMO→L+3(41)		225	5.49	0.034	H-2→LUMO(35) HOMO→L+2(43)	
218	5.67	0.159	HOMO→L+2(35) HOMO→L+3(33)		222	5.57	0.151	H-2→LUMO(27) HOMO→L+2(20) HOMO→L+3(31)	
3									
363	3.40	0.773	HOMO→LUMO(97)		363	3.40	0.7581	HOMO→LUMO(97)	
280	4.42	0.208	H-1→LUMO(89)		280	4.42	0.187	H-1→LUMO(88)	
247	5.00	0.049	H-1→L+1(12) HOMO→L+1(62)		238	5.19	0.105	H-2→LUMO(20) HOMO→L+3(52)	
237	5.21	0.090	H-2→LUMO(23) HOMO→L+2(19) HOMO→L+3(41)		225	5.49	0.034	H-2→LUMO(35) HOMO→L+2(43) HOMO→L+1(2)	

			HOMO→L+1(2)						
218	5.67	0.161	HOMO→L+2(35) HOMO→L+3(33)		222	5.57	0.153	H-2→LUMO(27) HOMO→L+2(21) HOMO→L+3(31)	
4									
363	3.40	0.778	HOMO→LUMO(97)		364	3.39	0.768	HOMO→LUMO(97)	
279	4.42	0.209	H-1→LUMO(89)		281	4.41	0.185	H-1→LUMO(88)	
247	5.00	0.049	H-1→L+1(13) HOMO→L+1(62)		238	5.19	0.103	H-2→LUMO(20) HOMO→L+2(10) HOMO→L+3(51)	
237	5.21	0.092	H-2→LUMO(23) HOMO→L+2(19) HOMO→L+3(41)		225	5.49	0.035	H-2→LUMO(37) HOMO→L+2(42)	
218	5.67	0.163	HOMO→L+2(35) HOMO→L+3(34)		222	5.57	0.157	H-2→LUMO(26) HOMO→L+2(21) HOMO→L+3(32)	
5									
363	3.41	0.792	HOMO→LUMO(97)		364	3.40	0.778	HOMO→LUMO(97)	
379	4.43	0.209	H-1→LUMO(89)		280	4.41	0.186	H-1→LUMO(88)	
247	5.00	0.0485	H-1→L+1(13) HOMO→L+1(63)		238	5.19	0.108	H-2→LUMO(19) HOMO→L+2(10) HOMO→L+3(52)	
237	5.21	0.099	H-2→LUMO(21) HOMO→L+2(21) HOMO→L+3(41)		225	5.49	0.034	H-2→LUMO(39) HOMO→L+2(41) HOMO→L+1(2)	
218	5.68	0.169	HOMO→L+2(33) HOMO→L+3(35)		222	5.58	0.161	H-2→LUMO(24) HOMO→L+2(22) HOMO→L+3(31)	
				6					
362	3.42	0.783	HOMO→LUMO(97)		363	3.41	0.772	HOMO→LUMO(97)	
279	4.43	0.207	H-1→LUMO(89)		280	4.42	0.185	H-1→LUMO(88)	
237	5.21	0.099	H-2→LUMO(20) HOMO→L+2(21) HOMO→L+3(41)		238	5.19	0.106	H-2→LUMO(19) HOMO→L+2(10) HOMO→L+3(51)	
227	5.46	0.018	H-2→LUMO(61) HOMO→L+2(25)		225	5.50	0.033	H-2→LUMO(39) HOMO→L+2(41)	
217	5.68	0.163	HOMO→L+2(33) HOMO→L+3(35)		221	5.58	0.158	H-2→LUMO(24) HOMO→L+2(21) HOMO→L+3(32)	
				7					
363	3.41	0.804	HOMO→LUMO(97)		364	3.40	0.791	HOMO→LUMO (97%)	
279	4.43	0.209	H-1→LUMO(89)		280	4.41	0.185	H-1→LUMO(88)	
248	4.99	0.048	H-1→L+1(13) HOMO→L+1(63)		338	4.85	0.110	H-2→LUMO(18) HOMO→L+2(11) HOMO→L+3(51)	
237	5.21	0.105	H-2→LUMO(19) HOMO→L+2(22) HOMO→L+3(41)		225	5.49	0.034	H-2→LUMO(41) HOMO→L+2(40)	
218	5.68	0.173	HOMO→L+2(32) HOMO→L+3(35)		221	5.58	0.165	H-2→LUMO(23) HOMO→L+2(23) HOMO→L+3(32)	

λ (nm)	E (eV)	f	Major contribution (%)	λ_{exp} (nm)	λ (nm)	E (eV)	f	Major contribution (%)	λ_{exp} (nm)
1					2				
372	3.33	0.765	HOMO→LUMO(97)		370	3.34	0.744	HOMO→LUMO(97)	
282	4.38	0.202	H-1→LUMO(90)		282	4.38	0.202	H-1→LUMO(90)	
237	5.22	0.091	HOMO→L+2(20) HOMO→L+3(54)		237	5.23	0.087	HOMO→L+2(20) HOMO→L+3(54)	
223	5.54	0.057	H-3→LUMO(16) H-2→LUMO(22) HOMO→L+1(42)		223	5.55	0.065	H-3→LUMO(15) H-2→LUMO(22) HOMO→L+1(42)	
217	5.71	0.173	H-3→LUMO(36) HOMO→L+2(16) HOMO→L+3(16)		216	5.71	0.168	H-3→LUMO(38) HOMO→L+2(16) HOMO→L+3(17)	
3					4				
370	3.34	0.748	HOMO→LUMO(97)		370	3.34	0.752	HOMO→LUMO(97)	
282	4.38	0.202	H-1→LUMO(90)		282	4.38	0.202	H-1→LUMO(90) HOMO→L+3(4)	
237	5.22	0.088	HOMO→L+2(20) HOMO→L+3(54)		237	5.22	0.089	HOMO→L+2(20) HOMO→L+3(54) HOMO→L+1(4)	
223	5.55	0.066	H-3→LUMO(15) H-2→LUMO(22) HOMO→L+1(42)		223	5.55	0.067	H-3→LUMO(15) H-2→LUMO(21) HOMO→L+1(43)	
216	5.71	0.020	H-3→LUMO(38) HOMO→L+2(16) HOMO→L+3(17)		216	5.71	0.175	H-3→LUMO(38) HOMO→L+2(16) HOMO→L+3(17)	
5					6				
370	3.34	0.767	HOMO→LUMO(97)		369	3.35	0.761	HOMO→LUMO(97)	
282	4.38	0.201	H-1→LUMO(90)		282	4.39	0.200	H-1→LUMO(90)	
237	5.22	0.095	HOMO→L+2(21) HOMO→L+3(53)		237	5.22	0.093	HOMO→L+2(22) HOMO→L+3(53)	
223	5.55	0.070	H-3→LUMO(14) H-2→LUMO(20) HOMO→L+1(45)		222	5.45	0.069	H-3→LUMO(13) H-2→LUMO(20) HOMO→L+1(45)	
216	5.72	0.192	H-3→LUMO(39) HOMO→L+2(17) HOMO→L+3(19)		216	5.72	0.190	H-3→LUMO(40) HOMO→L+2(16) HOMO→L+3(20)	
7									
370	3.34	0.780	HOMO→LUMO(97)						
282	4.39	0.200	H-1→LUMO(90)						
237	5.22	0.098	HOMO→L+2(23) HOMO→L+3(52)						
222	5.56	0.073	H-3→LUMO(12) H-2→LUMO(19) HOMO→L+1(46)						
216	5.72	0.204	H-3→LUMO(38) HOMO→L+2(17) HOMO→L+3(20)						

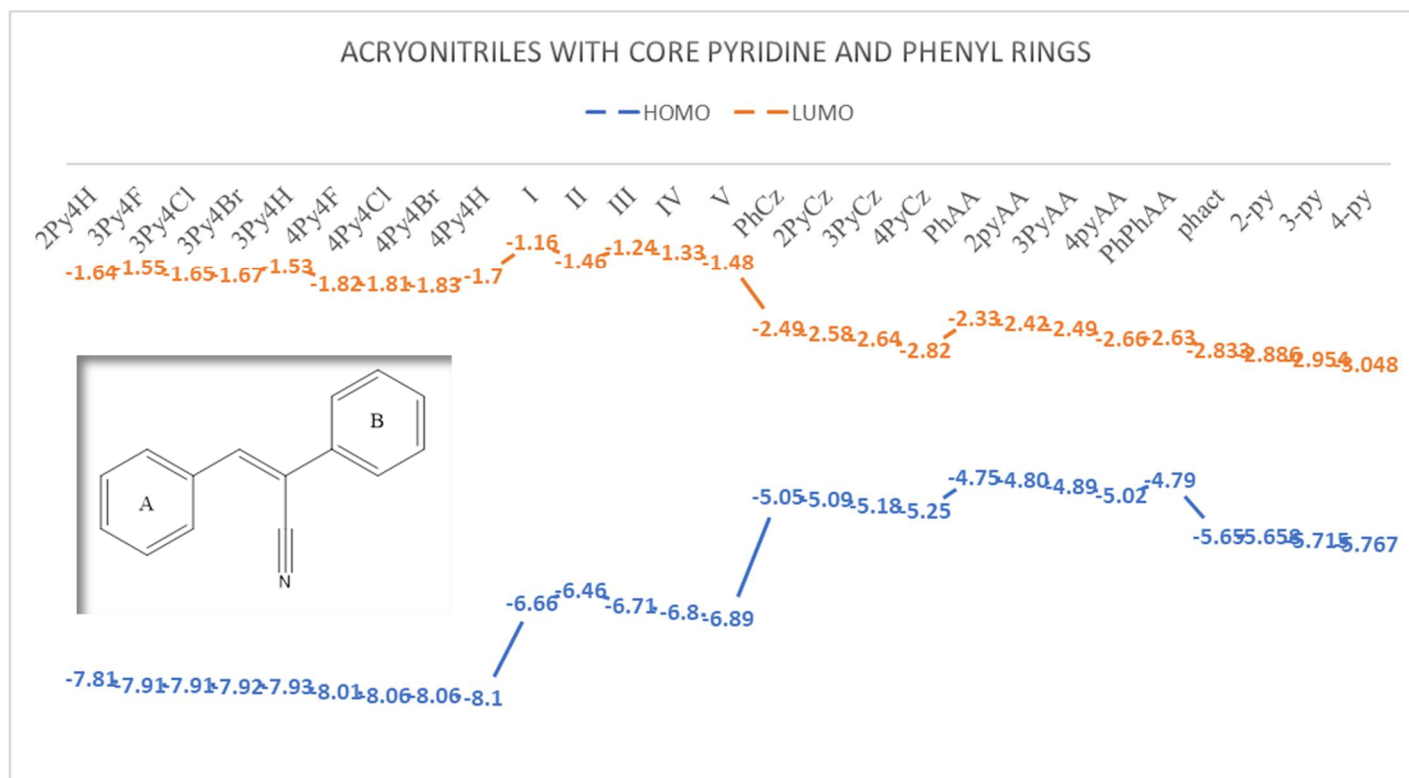


Figure S14. Schematic diagrams of HOMO and LUMO comparison by DFT calculations of acrylonitrile's compounds contain ring A substituted with F, Cl, Br, 2,4,5-TMO, -N(CH₃)₂, N(Ph)₂, Cz and ring (B) is a phenyl ring or pyridine ring in position *ortho*, *meta* and *para*.

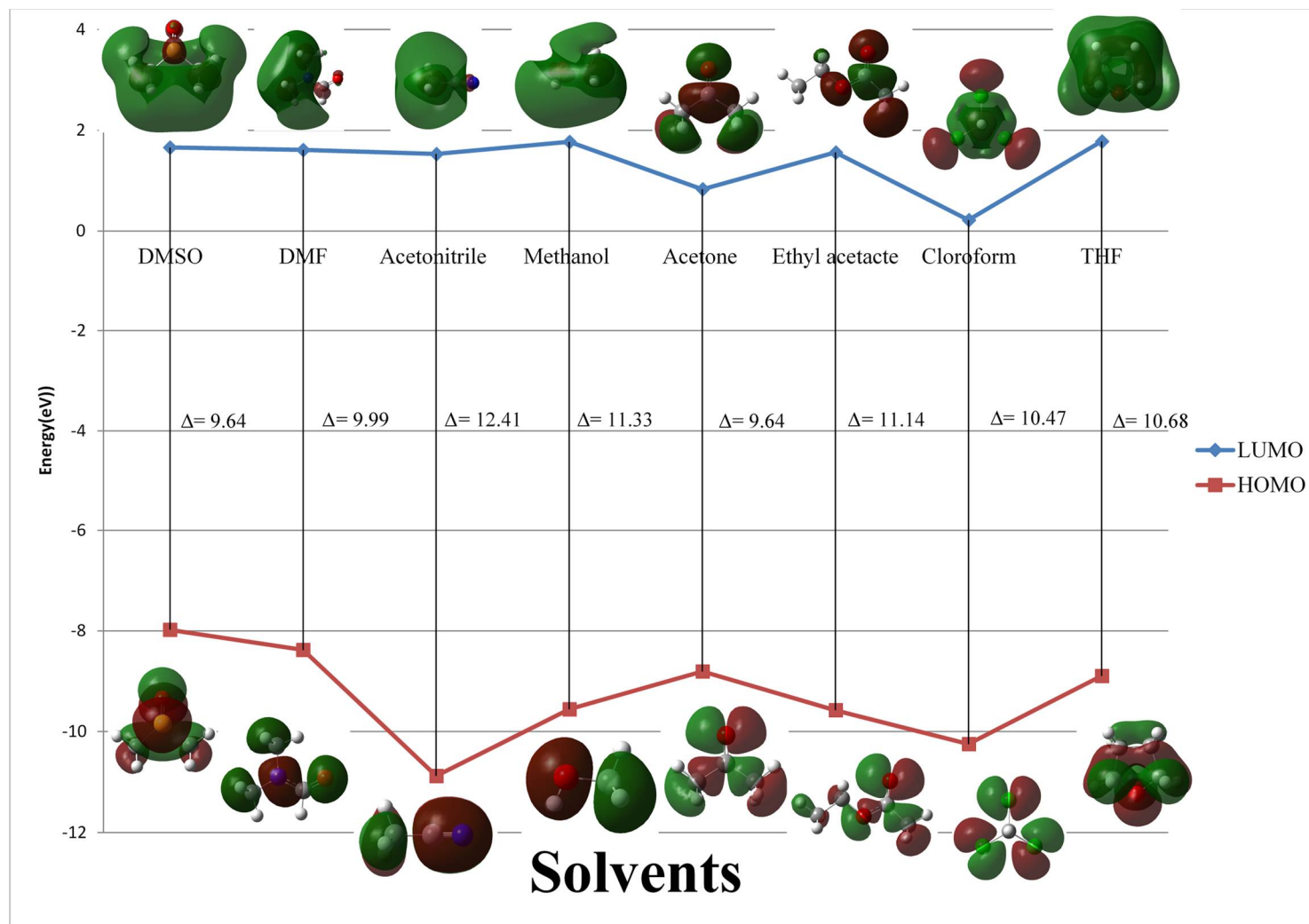
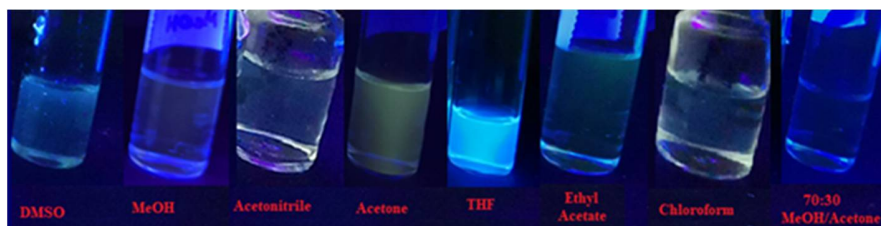


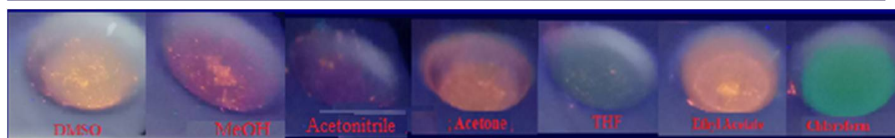
Figure S15. Graph of HOMO and LUMO calculations, energy gap with theory level of m062x / pVTZ

Table S7. DFT calculations of (1) DMSO, (2) MeOH, (3) AcCN, (4) Acetone (5) THF, (6) EtOAc, (7) Chloroform.

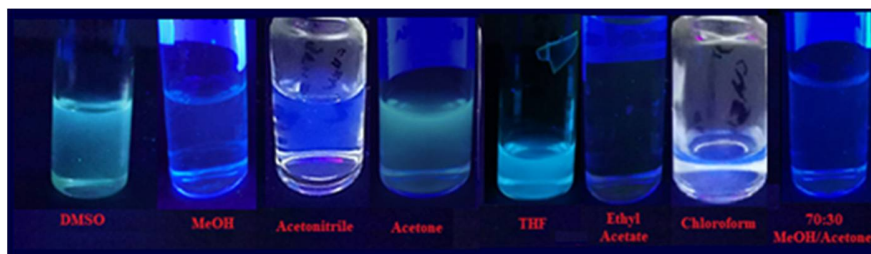
Solvent	Dielectric constant	LUMO	HOMO	Gap
		eV		
1	46.68	1.66	-7.98	9.64
2	32.7	1.77	-9.56	11.33
4	37.5	1.53	-10.88	12.41
5	21.04	0.83	-8.81	9.64
7	7.58	1.78	-8.9	10.68
3	6.02	1.56	-9.58	11.14
6	4.81	0.22	-10.25	10.47



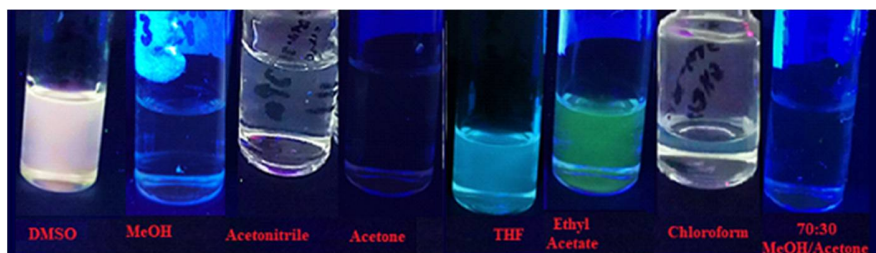
I



II



III



IV

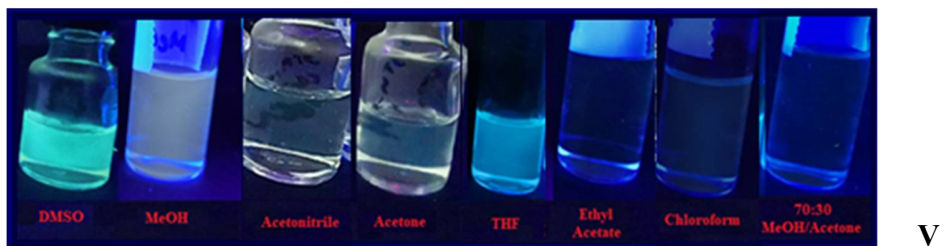


Figure S16. Images of the emission **I-V** solution under UV lamp.in (1)DMSO, (2) MeOH, (3) AcCN, (4) acetone, (5) THF, (6) EtOAc, (7) CHCl₃, and (8) MeOH:acetone (70:30).at concentration of 0.001 mM.

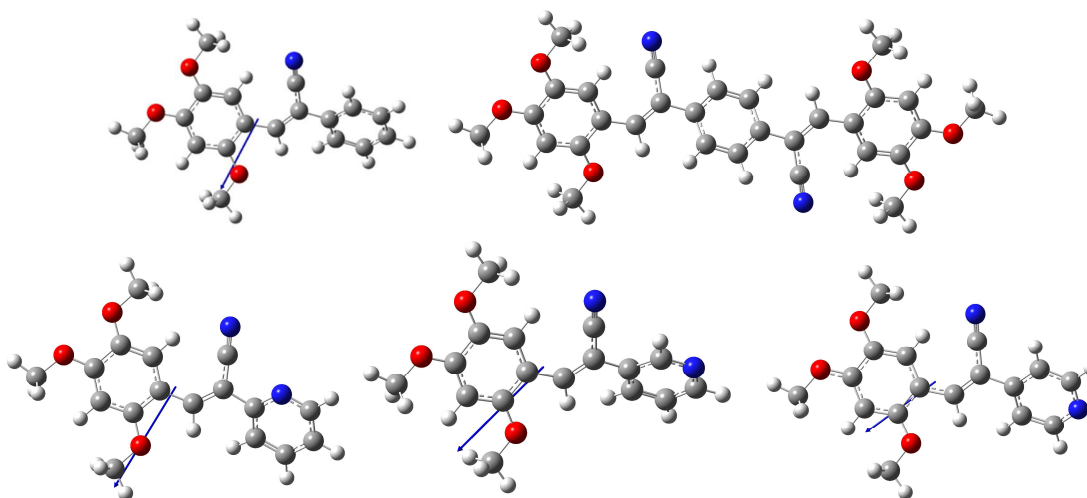


Figure S17. Dipole moment of **I-V** performed with a theory level at m062x / pVTZ.

Table S8. Wave numbers (cm^{-1}) for the absorption and fluorescence emission maxima of the 1-V in different solvents and the Stokes shift. (1) DMSO, (2) MeOH, (3) EtOAc, (4) AcCN, (5) Acetone, (6) Chloroform, (7) THF and (8) mixture MeOH/Acetone (70:30).

Solvent	λ_{abs} nm	$\bar{\nu}_a$ (cm^{-1})	λ_{em} nm	$\bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$1/2 \bar{\nu}_a + \bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a + \bar{\nu}_f$ (cm^{-1})
I							
1	381	26,246.72	468	21,367.52	4,879.2	23,807.12	47,614.24
2	376	26,595.74	---	--	--	--	--
3	374	26,737.97	513	19,493.18	6,548.48--	22,767.42	45,534.84--
4	380	26,315.79	---	18,281.54		---	---
5	366	27,322.40	547		8,034.25	22,298.66	44,597.33
6	384	26,041.66	---		---	---	---
7	375	26,666.66	504	19,841.27	7,481.13--	23,581.83	47,163.67--
8	378	26,455.03	---	--	--	--	--
II							
1	415	24,096.39	530	18,867.92	5,228.47	21,482.15	42,964.31
2	341	29,325.51	690	14,492.75	14,842.76	21,909.13	43,818.26
3	415	24,096.39	521	19,193.86	4,902.53	21,645.12	43,290.25
4	414	24,154.59	530	18,867.92	5,286.67	21,511.25	43,022.51
5	415	24,096.39	516	19,379.84	4,716.55	21,738.11	43,476.23
6	415	24,096.39	523	19,120.46	4,975.93	21,608.42	43,216.85
7	416	24,038.46	503	19,880.72	4,157.74	21,959.59	43,919.18
8	413	24,213.08	607	16,474.46	7,738.62	20,343.77	40,687.54
III							
1	396	25,252.52	498	20,080.32	5,171.21	22,666.41	45,332.83
2	393	25,445.29	442	22,624.43	2,820.86	24,034.86	48,069.72
3	392	25,510.20	---	22,988.50	2,521.69	24,249.35	48,498.7
4	406	24,630.54	---	18,797.00	5,833.54	21,713.78	43,427.54
5	391	25,575.45	435	20,576.13	4,999.32	23,075.79	46,151.58
6	393	25,445.29	532	--	--	--	--
7	396	25,252.52	486	--	--	--	--
8	393	25,445.29	440	22,727.27	2,718.02	24,086.28	48,172.56
IV							
1	383	26,109.66	584	17,123.29	8,986.38	21,616.47	43,232.94
2	386	25,906.74	---	--	--	--	--
3	383	26,109.66	525	19,047.62	6,333.09	22,214.16	44,428.33
4	385	25,974.03	---	--	--	--	--

5	387	25,839.79	---	----	---	---	---
6	394	25,380.71	--	---	---	---	---
7	389	25,706.94	540	18,518.52	7,321.27	21,179.15	44,358.31
8	387	25,839.79	---	--	--	--	--
				V			
1	394	25,380.71	507	19,723.87	5,656.84	22,552.29	45,104.58
2	390	25,641.03	553	18,083.18	7,557.85	21,862.1	43,724.21
3	393	25,445.29	---	---	---	---	---
4	395	25,316.46	519	19,267.82	6,177.47	22,356.55	44,713.11
5	397	25,188.92	510	19,607.84	5,708.62	22,462.15	44,924.3
6	395	25,316.46	---	--	--	--	--
7	398	25,125.63	506	19,762.85	5,426.07	22,475.88	44,951.77
8	399	25,062.66	---	--	--	--	--

Table S9. Dielectric constant and refractive index of various solvents, as well as Lippert's, Bakhshiev's and Kawasaki-Chamma-Violet's polarity parameters.

	Solvent	ϵ_r	n	Δf	$f(\epsilon, n) + 2g(n)^*$	$f(\epsilon, n)$	$\mu (D)$	F (ϵ, n)	F₁ (ϵ, n)¹	F₂ (ϵ, n)
1	DMSO	46.68	1.479	0.263	1.488	0.84	3.9	0.2632	0.8404	0.628
2	MeOH	32.7	1.329	0.308	1.302	0.854	1.7	0.3062	0.8545	0.5622
3	AcCN	37.5	1.344	0.138	1.331	0.8631	3.45	0.3054	0.3536	0.3851
4	Acetone	21.04	1.359	0.203	1.281	0.792	2.87	0.2847	0.4892	0.3999
5	THF	7.58	1.407	0.21	1.102	0.5491	1.75	0.2096	0.5491	0.4468
6	EtOAc	6.02	1.372	0.305	0.9954	0.4891	1.88	0.1998	0.863	0.535
7	CHCl ₃	4.81	1.48	0.284	1.002	0.3709	1.15	0.1375	0.7924	0.5453
8	MeOH/Acetone	23.21	1.334	0	-	-	-	0.2974	0.8139	0.5442

*Experimental and theoretical values of different references of $(\epsilon, n) + 2g(n)$ and $f(\epsilon, n)$

¹ Experimental parameters according to the equations of Lippert's $F(\epsilon, n)$, Bakhshiev's $F_1(\epsilon, n)$ y Kawski – Chamma – Viallet $F_2(\epsilon, n)$

Table S10. Wave numbers (cm^{-1}) for the absorption and fluorescence emission maxima of the 1-V in solid state and the Stokes shift.

Sample	λ_{abs} nm	ν_{a} cm^{-1}	λ_{em} nm	ν_{f} cm^{-1}	$\nu_{\text{a}}-\nu_{\text{f}}$ cm^{-1}	$1/2 \bar{\nu}_{\text{a}}+\bar{\nu}_{\text{f}}$ (cm^{-1})	$\bar{\nu}_{\text{a}}+\bar{\nu}_{\text{f}}$ (cm^{-1})
(I)	438	22,831.05	472	21,186.44	1,644.61	22,008.74	44,017.49
(II)	604	16,556.29	616	16,233.77	322.52	16,395.03	32,790.06
III	463	21,598.27	501	19,960.08	1,638.19	20,779.17	41,558.35
IV	478	20,920.50	518	19,305.02	1,615.48	20,112.76	40,225.52
V	488	20,491.82	502	19,920.32	571.5	20,206.07	40,412.14

Table S11. Crystallographic data for the structures of **I** and **II**

Parameters	Ia and Ib	II
Empirical formula	$\text{C}_{18}\text{H}_{17}\text{N}_1\text{O}_3$	$\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_6$
M_r	295.32	512.54
Color, habit	Colorless, block	Orange
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	293	110
a (Å)	14.5858(2)	4.4283 (2),
b (Å)	7.37534(14)	18.0006 (11),
c (Å)	14.6835(2)	15.5766 (7)
α (°)	90	9093.627 (4)
β (°)	103.7001(14)	90
γ (°)	90	
V (Å ³)	1534.65(4)	1239.16 (11)
Z	4	2
Dc(g cm ⁻³)	1.278	1.374
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	0.707	0.79
Crystal size (mm)	0.557 x 0.20 x 0.111	0.22 × 0.08 × 0.03
$T_{\text{min}}, T_{\text{max}}$	0.943, 0.985	0.891, 0.977
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37305, 3259, 2680	8104, 2437, 1936
R_{int}	0.048	0.041
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.633	0.616
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0421, 0.1132, 1.030	0.055, 0.160, 1.05
No. of reflections	3259	2437
No. of parameters	203	175

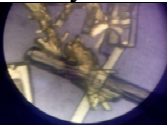
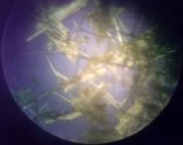
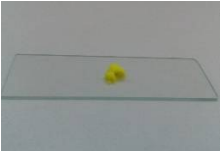
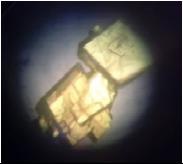
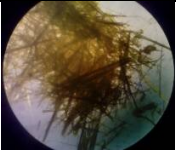
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.17, -0.22	0.33, -0.25

Table S12. Crystallographic data for the structures of III-V

Parameters	III	IV	V
Empirical formula	C ₁₇ H ₁₆ N ₂ O ₃	C ₁₇ H ₁₆ N ₂ O ₃	C ₁₇ H ₁₆ N ₂ O ₃
M_r	296.32	296.32	296.32
Color, habit	Yellow, needle	Yellow, block	Orange, needle
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	110	293(2)	110(2)
a (Å)	7.13613 (18),	7.9756(4)	3.92005(11)
b (Å)	17.5199 (5),	9.1759(4)	21.5815(7)
c (Å)	23.2243 (5)	10.7900(4)	8.3715(3)
α (°)	90	81.523(3)	90
β (°)	90	75.072(4)	92.609(3)
γ (°)	90	76.392(4)	90
V (Å ³)	2903.60 (13)	738.40(6)	707.50(4)
Z	1	2	2
Dc(g cm ⁻³)	1.356	1.333	1.391
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	0.77	0.758	0.791
Crystal size (mm)	0.43 × 0.09 × 0.05	0.43 × 0.22 × 0.18	0.23 × 0.07 × 0.03
$T_{\min}, T_{\max}$	0.830, 0.967	0.967, 0.928	0.881, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22286, 2843, 2455	28355, 3124, 2395	8996, 2769, 2660
R_{int}	0.041	0.0461	0.031
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.616	0.633	0.616
$R[F^2 > 2\sigma F^2]$, $wR(F^2)$, S	0.035, 0.096, 1.05	0.046, 0.143, 1.04	0.032, 0.087, 1.09
No. of reflections	2843	3124	2769
No. of parameters	203	202	202
H-atom treatment	H-atom parameters	H-atom parameters	H-atom parameters

	constrained	constrained	constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.23, -0.17	0.26, -0.14	0.18, -0.17

Table S13. Crystal morphology for **I-V**

Compound	Appearance		m.p.
	Powder	Crystal	°C
Ia			147-148
Ib			145-146
III			134-135
IV			152-153
V			165-166

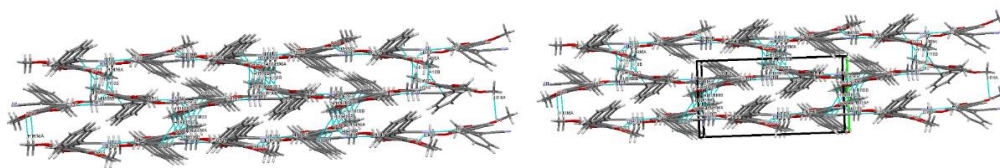


Figure S18. herringbone packing or **I** slipped stacking without π - π overlap between adjacent molecules

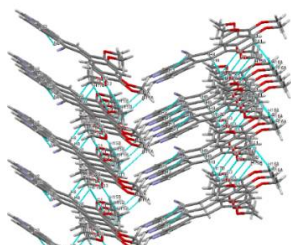


Figure S22. Herringbone packing or **V** slipped stacking without π - π overlap occurring between adjacent molecules

Table S14. Second order perturbation theory analysis of Fock matrix in NBO basis for **I** and **II**.

Donor (i)	ED (e)	Acceptor (j)	ED (e)	E ²	E(j)-E(i) ^c (a.u.)	F(i,j) ^d (a.u.)	Donor (i)	ED (i)(e)	Acceptor (j)	ED e	E ²	E(j)- E(i) ^c (a.u.)	F(i,j) ^d (a.u.)
I							II						
Phenylacrylonitrile													
π C3-C4	1.65884	π^* C5-C6	0.32111	29.35	0.35	0.092	π C2-C3	1.63204	π^* C1-C3	0.37678	30.21	0.35	0.092
π C1-C2	1.63887	π^* C3-C4	0.33096	29.13	0.35	0.091	π C1-C3	1.97317	π^* C2-C3	0.38016	30.05	0.35	0.092
π C5-C6	1.67548	π^* C1-C2	0.36746	28.56	0.36	0.091	π C1-C2	1.67465	π^* C1-C3	0.37678	28.03	0.36	0.090
π C7-C8	1.84453	π^* C15-N1	0.07588	22.14	0.50	0.095	π C4-C5	1.8419	π^* C12-N1	0.07595	22.16	0.49	0.095
π C15-N1	1.96788	π^* C7-C8	0.18159	8.60	0.48	0.060	π C12-N1	1.96827	π^* C4-C5	0.18414	8.54	0.48	0.060
σ C7-C15	1.97797	σ^* C15-N1	0.00962	5.53	1.77	0.089	C4-C12	1.97793	σ^* C12-N1	0.00958	5.50	1.77	0.088
σ C1-C7	1.95783	σ^* C8-C9	0.02188	4.78	1.25	0.069	σ C3-C4.	1.95804	σ^* C12-N1	0.00958	4.89	1.70	0.082
σ C2-C3	1.98005	σ^* C1-C7	0.03202	4.70	1.27	0.069	σ C5-C6	1.97384	σ^* C3-C4	0.03173	4.04	1.24	0.063
σ C8-C9	1.97391	σ^* C1-C7	0.03202	4.03	1.24	0.063	σ C2-C3	1.97317	σ^* C1-C3	0.02262	3.24	1.37	0.060
σ C1-C6	1.97352	σ^* C1-C2	0.02253	3.29	1.37	0.060							
trimethoxyphenyl													
π C11-C12	1.71197	π^* C9-C10	0.43053	32.15	0.37	0.101	π C9-C10	1.71158	π^* C6-C11	0.43068	32.24	0.37	0.101
π C13-C14	1.71931	π^* C11-C12	0.40085	28.19	0.35	0.092	π C7-C8	1.72032	π^* C9-C10	0.40033	28.09	0.35	0.091
π C9-C10	1.64051	π^* C13-C14	0.34048	27.98	0.36	0.090	π C6-C11	1.63935	π^* C7-C8	0.34079	28.03	0.36	0.090
σ C9-C14	1.96902	σ^* O3-C13	0.02651	5.23	1.22	0.071	σ C6-C7	1.96897	C8-O1	0.02648	5.25	1.22	0.071
σ C10-C11	1.9782	σ^* O2-C12	0.0256	4.97	1.25	0.070	σ C11-C12	1.97822	C9-O2	0.02557	4.97	1.25	0.070
σ C12-C13	1.96882	σ^* O2-C17	0.00977	4.51	1.12	0.064	σ C8-C9	1.96879	C14-O2	0.00978	4.51	1.12	0.064
σ O3-C18	1.99057	σ^* C2-C13	0.0357	4.04	1.48	0.069	σ C13-O1	1.99057	C8-C9	0.03572	4.04	1.48	0.069
σ O1-C16	1.99168	σ^* C9-C10	0.02915	3.84	1.52	0.069	C15-O3	1.99165	C6-C11	0.02935	3.86	1.52	0.069
σ O2-C17	1.99109	σ^* C12-C13	0.0357	3.80	1.50	0.068	C14-O2	1.99107	C8-C9	0.03572	3.80	1.50	0.068
σ O1-C10	1.98925	σ^* C9-C14	0.0203	2.15	1.59	0.052	C11-O3	1.98926	C6-C7	0.02029	2.16	1.59	0.052
σ O3-C13	1.98917	σ^* C11-C12	0.02519	1.93	1.58	0.049	C8-O1	1.98914	C9-C10	0.02519	1.93	1.58	0.049
σ O2-C12	1.98989	σ^* C13-C14	0.02504	1.78	1.63	0.048	C9-O2	1.98991	C7-C8	0.02501	1.78	1.63	0.048
LP O2	1.83456	π^* C11-C12	0.40085	41.32	0.44	0.128	O2	1.83428	C9-C10	0.40033	41.40	0.44	0.128
LP O3	1.85537	π^* C13-C14	0.34048	36.01	0.44	0.119	O1	1.85552	C7-C8	0.34079	35.97	0.44	0.119
LP O1	1.85509	π^* C9-C10	0.43053	33.59	0.45	0.119	O3	1.85417	C6-C11	0.43068	33.81	0.45	0.119
LP N1	1.96388	σ^* C7-C15	0.03968	15.86	1.14	0.120	N1	1.96393	C4-C12	0.03966	15.85	1.14	0.120

ED: Electron Density

E⁽²⁾: means energy of hyperconjugative interaction

Table S15. Second order perturbation theory analysis of Fock matrix in NBO basis for **III** and **IV**

Donor (i)	ED (e)	Acceptor (j)	ED (e)	E ²	E(j)- E(i) ^c (a.u.)	F(i,j) ^d (a.u.)	Donor (i)	ED (e)	Acceptor (j)	ED (e)	E(2) Kcal/mol	E(j)-E(i) ^c (a.u.)	F(i,j) ^d (a.u.)
III							IV						
Pyridilacrylonitrile													
π C5-N1	1.70153	π* C1-C2	0.30278	37.87	0.40	0.110	π N1-C2	1.70781	π* C1-C5	0.34145	37.12	0.40	0.110
π C3-C4	1.6657	π* C5-N1	0.4293	37.70	0.35	0.104	π C3-C4	1.66343	π N1-C2	0.37406	36.94	0.35	0.102
π C1-C2	1.6336	π* C3-C4	0.30181	33.33	0.35	0.098	π C1-C5	1.60241	π* C3-C4	0.30758	31.52	0.35	0.096
π C6-C8	1.84079	π* C7-N2	0.06976	20.84	0.51	0.094	π C6-C8	1.84522	π* C7-N2	0.0753	21.99	0.50	0.095
π C7-N2	1.96582	π* C6-C8	0.17976	8.92	0.47	0.060	π C7-N2	1.96771	π* C6-C8	0.18325	8.66	0.48	0.060
σ C6-C7	1.97826	σ* C7-N2	0.00943	5.72	1.77	0.090	σ C6-C7	1.97783	σ* C7-N2	0.00956	5.57	1.77	0.089
σ C5-C6	1.96089	σ* C8-C9	0.02203	4.99	1.25	0.071	σ C5-C6	1.95892	σ* C7-N2	0.00956	4.81	1.71	0.082
σ C1-N1	1.98587	σ* C5-C6	0.03986	4.82	1.40	0.074	σ C4-C5	1.97402	σ* C1-C5	0.03624	2.77	1.37	0.055
σ C3-C4	1.97992	σ* C5-C6	0.03986	4.72	1.28	0.070	σ C2-C3	1.9872	σ* C3-C4	0.01368	1.95	1.39	0.047
σ C8-C9	1.97438	σ* C5-C6	0.03986	3.79	1.23	0.061	-	-	-	-			
σ C2-C3	1.98211	σ* C3-C4	0.01377	2.14	1.39	0.049	-	-	-	-			
trimethoxyphenyl Grup													
π C11-C12	1.71028	π* C9-C10	0.4331	32.56	0.37	0.101	C11-C12	1.71063	C9-C10	0.43116	32.42	0.37	0.101
π C13-C14	1.71738	π* C11-C12	0.4005	28.53	0.35	0.092	C13-C14	1.71973	C11-C12	0.39935	28.14	0.35	0.091
π C9-C10	1.63906	π* C13-C14	0.33544	27.65	0.36	0.090	C9-C10	1.64097	C13-C14	0.33965	27.89	0.36	0.090
σ C9-C14	1.96911	σ* C13-O3	0.02657	5.23	1.22	0.071	C9-C14	1.96882	O3-C13	0.0264	5.24	1.22	0.071
σ C10-C11	1.9782	σ* C12-O2	0.0256	4.96	1.25	0.070	C10-C11	1.97823	O2-C12	0.0255	4.95	1.25	0.070
σ C12-C13	1.9689	σ* C16-O2	0.00984	4.54	1.12	0.064	C12-C13	1.96882	O2-C16	0.00978	4.51	1.12	0.064
σ C17-O3	1.9905	σ* C12-C13	0.03588	4.08	1.48	0.070	O3-C17	1.99052	C12-C13	0.0358	4.05	1.48	0.070
σ C15-O1	1.99168	σ* C9-C10	0.02901	3.85	1.52	0.069	O1-C15	1.99165	C9-C10	0.0294	3.86	1.52	0.069
σ C16-O2	1.99109	σ* C12-C13	0.03588	3.80	1.50	0.068	O2-C16	1.99104	C12-C 13	0.0358	3.81	1.50	0.068
σ C10-O1	1.98929	σ* C9-C14	0.02035	2.12	1.59	0.052	C8-C9	1.97384	C10-C11	0.02632	3.47	1.33	0.061
σ C13-O3	1.98922	σ* C11-C12	0.02528	1.93	1.58	0.049	O1-C10	1.98926	C9-C14	0.0202	2.17	1.59	0.052
σ C12-O2	1.98995	σ* C13-C14	0.02502	1.76	1.64	0.048	C14-O2	1.98991	C13-C 14	0.02507	1.78	1.63	0.048
							C13-O3	1.98916	C13-C 14	0.02507	1.49	1.61	0.044
LP O2	1.83306	π* C11-C12	0.4005	41.72	0.44	0.128	O2	1.83326	C11-C12	0.39935	41.69	0.44	0.128
LP O3	1.85486	π* C13-C14	0.33544	36.18	0.44	0.119	O3	1.85476	C13-C14	0.33965	36.24	0.44	0.119
LP O1	1.85558	π* C9-C10	0.4331	33.57	0.45	0.119	O1	1.85453	C9-C10	0.43116	33.74	0.45	0.119
LP N2	1.96442	σ* C6-C7	0.03854	15.78	1.13	0.119	N2	1.96408	C6-C7	0.03966	15.91	1.13	0.120
LP N1	1.91169	σ* C5-C4	0.03719	14.13	0.99	0.107	N1	1.91499	C2-C3	0.02827	12.83	1.00	0.103

Table S16. Second order perturbation theory analysis of Fock matrix in NBO basis for **V**.

Donor (i)	ED (e)	Acceptor (j)	ED (e)	E ²	E(j)-E(i) ^c (a.u.)	F(i,j) ^d (a.u.)
V						
Pyridilacrylonitrile						
π C1-C5	1.63101	C2-N1	0.37048	39.64	0.35	0.104
π C2-N1	1.71245	C3-C4	0.29592	38.14	0.40	0.111
π C3-C4	1.6516	C1-C5	0.35599	33.45	0.36	0.098
π C6-C8	1.83532	C7-N2	0.07622	22.35	0.50	0.096
π C7-N2	1.96801	C6-C8	0.18582	8.55	0.48	0.059
σ C6-C7	1.97796	σ^* C7-N2	0.00959	5.56	1.77	0.089
σ C1-C2	1.98513	σ^* C5-C6	0.03324	5.24	1.27	0.073
σ C5-C6	1.95935	σ^* C7-N2	0.00959	4.93	1.70	0.082
σ C8-C9	1.97418	σ^* C5-C6	0.03324	4.02	1.24	0.063
σ C4-C5	1.97378	σ^* C1-C5	0.02169	3.17	1.37	0.059
σ C3-N1	1.98746	σ^* C3-C4	0.02733	1.58	1.51	0.044
trimethoxyphenyl Group						
π C11-C12	1.70886	π^* C9-C10	0.43341	32.87	0.37	0.101
π C13-C14	1.7217	π^* C11-C12	0.39718	28.15	0.35	0.092
π C9-C10	1.63689	π^* C13-C14	0.33505	27.63	0.36	0.090
σ C9-C14	1.96905	σ^* C13-O3	0.02645	5.25	1.22	0.072
σ C10-C11	1.97828	σ^* C12-O2	0.02545	4.94	1.25	0.070
σ C12-C13	1.96883	σ^* C16-O2	0.00985	4.55	1.12	0.064
σ C17-O3	1.99048	σ^* C12-C13	0.03599	4.08	1.48	0.070
σ C15-O1	1.9916	σ^* C9-C10	0.02928	3.89	1.52	0.069
σ C16-O2	1.991	σ^* C11-C12	0.03599	3.84	1.50	0.068
σ C10-O1	1.98934	σ^* C9-C14	0.02036	2.14	1.59	0.052
σ C13-O3	1.98919	σ^* C11-C12	0.02528	1.92	1.58	0.049
σ C12-O2	1.98999	σ^* C13-C14	0.02503	1.76	1.64	0.048
O2	1.83095	C11-C12	0.39718	42.31	0.44	0.129
O3	1.85423	C13-C14	0.33505	36.46	0.44	0.119
O1	1.85317	C9-C10	0.43341	34.29	0.45	0.120
N2	1.96392	C6-C7	0.03931	15.90	1.13	0.120
N1	1.91675	C3-C4	0.02733	13.04	1.01	0.104

Table S17. Geometrical parameters for intermolecular interactions exist in different dimers of **I-V** and the intermolecular interaction energies for these dimers (in kcal mol⁻¹).

Dimer	Important interactions	Geometry (Å, °)			Symmetry operator	Distance (Å)	E _{coul}	E _{pol}	E _{dis}	E _{rep}	E _{tot}
		d(H⋯A)	d(D⋯A)	<D⋯A							
I											
1	C17-H17 <i>B</i> ⋯C14	2.89	3.949	165	-x+3/2, y-1/2, -z+1/2	8.247	-4.2	-1.6	-9.1	5.8	-9.1
	C16-H16 <i>A</i> ⋯O3	2.571	3.660	179							
2	C3-H3⋯O3	2.675	3.525	134	-x+2, -y+1, -z	6.378	-2.5	-1.3	-10.2	5.8	-8.2
3	C16-H16 <i>B</i> ⋯O3	2.506	3.481	148	x+1/2, -y+1/2, z+1/2	9.040	-4.4	-1.5	-5.1	4.4	-6.7
	C5-H5⋯N1	2.452	3.469	155							
4	C6-H6⋯C3	2.89	3.969	171	-x+5/2, y-1/2, -z+1/2	8.770	-1.8	-0.7	-7.2	3.6	-6.1
	C6-H6⋯C4	2.893	3.934	160							
5	C18-H18 <i>B</i> ⋯C1	2.715	3.560	134	-x+2, -y, -z	6.355	-2.4	-1.5	-9	7	-5.9
	C18-H18 <i>B</i> ⋯C2	2.819	3.764	145							
6	H16 <i>C</i> ⋯C1		2.347		x-1/2, -y-3/2, z+1/2	11.509	-1.8	-0.7	-3.7	2	-4.2
II											
1	C2⋯C5		3.232		x+1, y, z	4.428	-6.6	-4.2	-38	30.1	-18.8
	C2⋯C5		3.389								
	C2⋯C5		3.346								
	C14-C14 <i>A</i> ⋯ C10	2.789	3.712	142							
	C13-H13 <i>C</i> ⋯ N1	2.666	3.728	164							
2	C1-H1⋯C14	2.775	3.698	171	-x+3, y+1/2, -z+3/2	14.539	-3.8	-1.8	-6.7	6.1	-6.3
	C15-H15 <i>B</i> ⋯C13	2.791	3.407	116							
	C10-H10⋯N1	2.615	3.696	173							
	C15-H15 <i>A</i> ⋯N1	2.739	3.372	115							
3	C1-H1⋯C14	2.775	3.698	142	-x-1, y+1/2, -z+1/2	14.539	-3.8	-1.9	-6.7	6.2	-6.2
	C15-H15 <i>B</i> ⋯C13	2.789	3.407	115							

	C10-H10...N1	2.613	3.696	172							
	C15-H15A...N1	2.739	3.372	116							
4	C14-H14B...O3	2.693	3.759	166	-x+2, y-1/2, -z+3/2	12.526	-1.8	-0.8	-4.2	2	-4.9
	H14B... H15B		2.357								
5	C13-H13B...O1	2.431	3.353	141	x-3, y, z-1	19.823	-3.7	-1.1	-3.3	3.3	-4.8
6	C14-H14B...O3	2.693	3.759	166	-x+2, y+1/2, -z+3/2	12.526	-1.8	-0.8	-4.2	2	-4.8
III											
1	C16-H16A...C1	2.864	3.759	139	x+1/2, y, -z+1/2	3.907	-7.5	-3.5	-20.3	16.1	-15.2
	C16-H16A...C7	2.735	3.605	136							
	C17-H17C...N2	2.525	3.572	160							
	C18-H18C...C13	2.815	3.707	139							
	C18-H18A...O3	2.718	3.649	143							
	C16-H16C...C1	2.651	3.692	159							
	C16-H16C...N1	2.659	3.716	163							
	C16-H16C...C3	2.859	3.848	151							
2	C5-H5...N2	2.257	3.232	147	-x+1/2, y+1/2, z	8.808	-5.4	-2.3	-6.5	7.7	-6.6
	C18-H18A...C6	2.807	3.483	120							
3	C18-H18B...O1	2.566	3.477	140	-x, y+1/2, -z+1/2	9.289	-3.1	-1	-5.1	3.1	-6
4	C3...C3		3.624		x-1/2, -y+1/2, -z+1	11.689	-2.6	-0.9	-4.8	3.5	-4.8
	C4-H4...N2	3.045	4.117	174							
	C4-H4...C15	3.125	4.123	154							
5	C17-H17B...N1	2.877	3.947	167	-x+1/2, -y, z+1/2	12.288	-2.7	-0.5	-1.6	0.5	-4.2
6	C3-H3...C16	3.062	3.688	117	x, -y+1/2, z+1/2	12.584	-0.1	-0.4	-2.7	1.2	-2
IV											
1	C18-H18C...O1	2.712	3.688	149	-x+1, -y, -z+1	4.057	-7.2	-2.4	-20.2	12	-17.8
2	C17-H17A...C14	2.807	3.709	140	-x, -y, -z+1	6.924	-2.2	-1.6	-12.2	6.9	-9.1
3	C5-H5...N2	2.676	3.64	147	x, y-1, z	9.176	-4.1	-1.6	-5.7	5.1	-6.4
	C6-H6...C18	2.865	3.715	135							
	H18B...H8		2.225								
	C18-H18B...O1	2.506	3.465	146							
	C16-H16A...O3	2.484	3.464	149							
4	C18-H18A...N2	2.624	3.579	146	-x+1, -y, z	7.769	-3.1	-1.5	-5.8	4	-6.3

5	C16-H16C···N1	2.726	3.346	116	x-1, y, z+1	11.649	-3.5	-1.1	-4.9	3.5	-6
	H17A···H2		2.388								
6	C16···C16		3.569		-x, -y+1, -z+1	8.767	-0.9	-0.3	-2.8	1	-3.1
V											
1	C18-H18C···N2	2.743	3.829	175	x-1, y, z	3.920	-1.2	-2.8	-20.7	14.4	-10.3
	C18-H18A···C18	2.848	3.92	168							
	C17-H17A···C11	2.792	3.583	129							
	C16-H16C···C16	2.854	3.92	166							
2	H17C···H3		2.282		-x+2, y+1/2, -z	11.936	-3.7	-1.5	-5.2	4.9	-5.6
	C11-H11···N1	2.698	3.786	177							
	C16-H16C···C5	2.865	3.404	110							
3	C3-H3···N2	2.583	3.474	138	x, y, z-1	8.372	-2.8	-1	-5.3	3.5	-5.5
4	H18B···H8		2.182		x-1, y, z-1	9.081	-2.7	-1.4	-5.5	4.8	-4.8
	C18-H18B···O1	2.482	3.419	143							
	C16-H16B···O3	2.457	3.407	145							
5	C6-H6···C17	2.859	3.707	135	-x+2, y+1/2, -z+1	11.344	-1.4	-0.6	-2.9	1.7	-3.2
6	C17-H17B···N2	2.797	3.525	124	-x+3, y-1/2, -z+1	11.631	-1.1	-0.4	-2	1.1	-2.4

Table S18. Second order perturbation theory analysis of Fock matrix in NBO basis for I-V.

Compound	<i>Donor</i> (<i>i</i>)	<i>ED</i> (<i>e</i>)	<i>Acceptor</i> (<i>j</i>)	<i>ED</i> (<i>e</i>)	<i>E</i> (2)	<i>E</i> (<i>j</i>)- <i>E</i> (<i>i</i>) ^c (<i>a.u.</i>)	<i>F</i> (<i>i,j</i>) ^d (<i>a.u.</i>)
I	π C5-C6	1.67548	π^* C1-C2	0.36746	28.56	0.36	0.091
	π C7-C8	1.84453	π^* C15-N1	0.07588	22.14	0.50	0.095
	σ C7-C15	1.97797	σ^* C15-N1	0.00962	5.53	1.77	0.089
	σ C2-C3	1.98005	σ^* C1-C7	0.03202	4.70	1.27	0.069
	σ C8-C9	1.97391	σ^* C1-C7	0.03202	4.03	1.24	0.063
	σ C1-C6	1.97352	σ^* C1-C2	0.02253	3.29	1.37	0.060
II	π C2-C3	1.63204	π^* C1-C3	0.37678	30.21	0.35	0.092
	π C4-C5	1.8419	π^* C12-N1	0.07595	22.16	0.49	0.095
	σ C3-C4.	1.95804	σ^* C12-N1	0.00958	4.89	1.70	0.082
	σ C2-C3	1.97317	σ^* C1-C3	0.02262	3.24	1.37	0.060
III	π C1-C2	1.6336	π^* C3-C4	0.30181	33.33	0.35	0.098
	π C6-C8	1.84079	π^* C7-N2	0.06976	20.84	0.51	0.094
	σ C6-C7	1.97826	σ^* C7-N2	0.00943	5.72	1.77	0.090
	σ C1-N1	1.98587	σ^* C5-C6	0.03986	4.82	1.40	0.074
	σ C3-C4	1.97992	σ^* C5-C6	0.03986	4.72	1.28	0.070
	σ C8-C9	1.97438	σ^* C5-C6	0.03986	3.79	1.23	0.061
	σ C2-C3	1.98211	σ^* C3-C4	0.01377	2.14	1.39	0.049
	LP O2	1.83306	π^* C11-C12	0.4005	41.72	0.44	0.128
	LP O3	1.85486	π^* C13-C14	0.33544	36.18	0.44	0.119
	LP O1	1.85558	π^* C9-C10	0.4331	33.57	0.45	0.119
	LP N2	1.96442	σ^* C6-C7	0.03854	15.78	1.13	0.119
	LP N1	1.91169	σ^* C5-C4	0.03719	14.13	0.99	0.107
	π N1-C2	1.70781	π^* C1-C5	0.34145	37.12	0.40	0.110
	π C6-C8	1.84522	π^* C7-N2	0.0753	21.99	0.50	0.095

IV	σ C6-C7	1.97783	σ^* C7-N2	0.00956	5.57	1.77	0.089
	σ C5-C6	1.95892	σ^* C7-N2	0.00956	4.81	1.71	0.082
	σ C4-C5	1.97402	σ^* C1-C5	0.03624	2.77	1.37	0.055
V	π C2-N1	1.71245	π^* C3-C4	0.29592	38.14	0.40	0.111
	π C3-C4	1.6516	π^* C1-C5	0.35599	33.45	0.36	0.098
	π C6-C8	1.83532	π^* C7-N2	0.07622	22.35	0.50	0.096
	σ C6-C7	1.97796	σ^* C7-N2	0.00959	5.56	1.77	0.089
	σ C5-C6	1.95935	σ^* C7-N2	0.00959	4.93	1.70	0.082
	σ C4-C5	1.97378	σ^* C1-C5	0.02169	3.17	1.37	0.059
	σ C3-N1	1.98746	σ^* C3-C4	0.02733	1.58	1.51	0.044

^a $E(2)$ means energy of hyper conjugative interactions (stabilization energy in kJ/mol). ^b $E_j - E_i$ is energy difference between donor and acceptor i and j NBO orbitals. ^c $F(i,j)$ is the Fock matrix element between i and j NBO orbitals.