Electronic supplementary information (ESI)

Green light-emitting 2-(*1H*-indol-3-yl)acetonitrile based D-A fluorophores – A combined theoretical and experimental study

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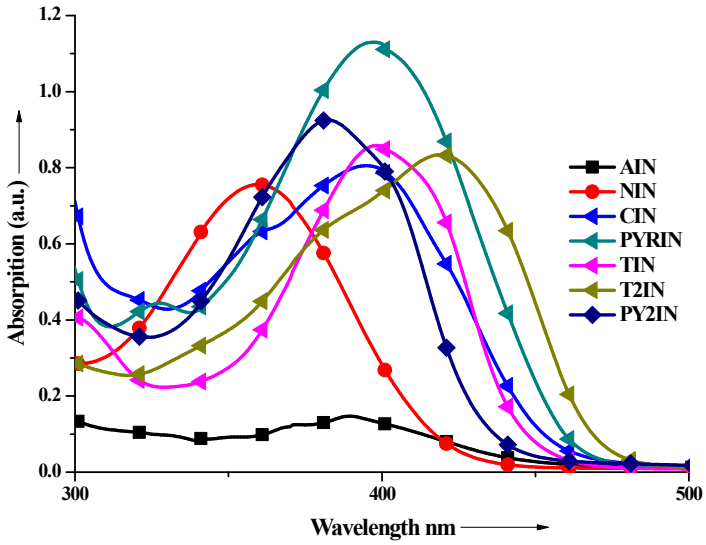


Figure S1: Absorption spectra of all the compounds in **THF** solvent.

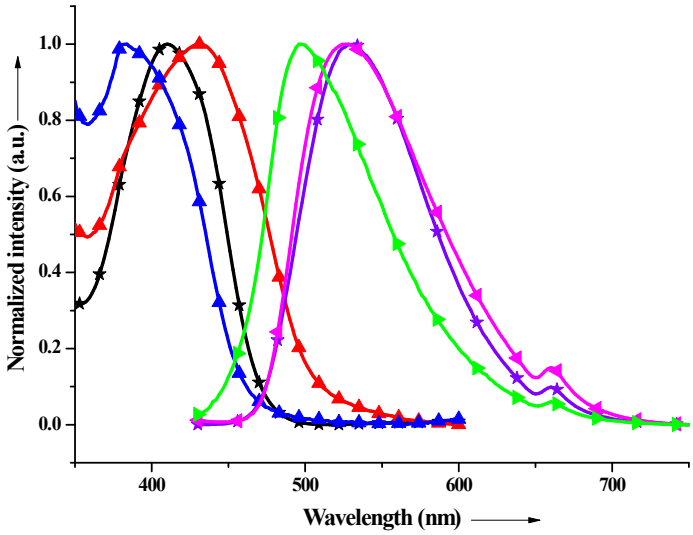


Figure S2: Absorption and Emission spectra of **TIN, T2IN** and **PY2IN** for thin film.

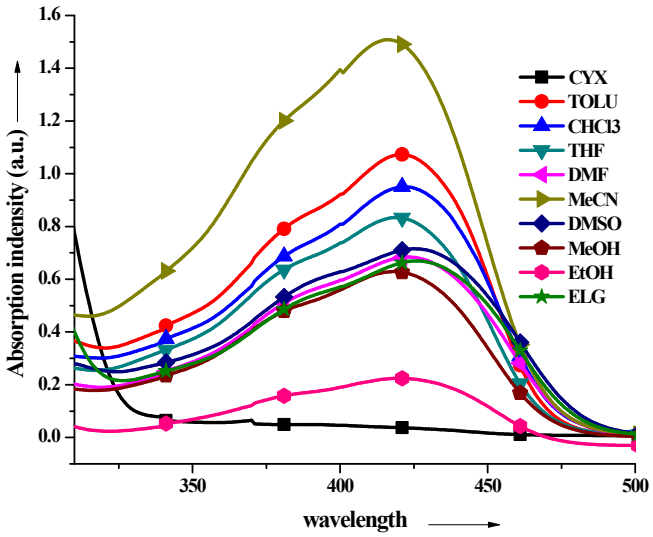


Figure S3: Absorption spectra of **T2IN** in different solvents

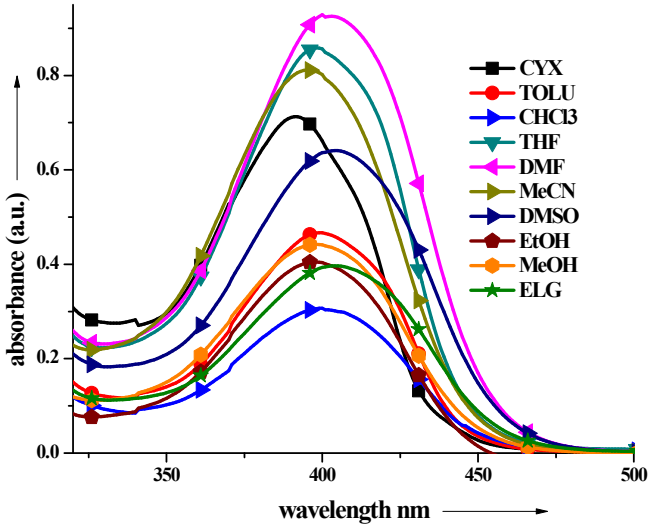
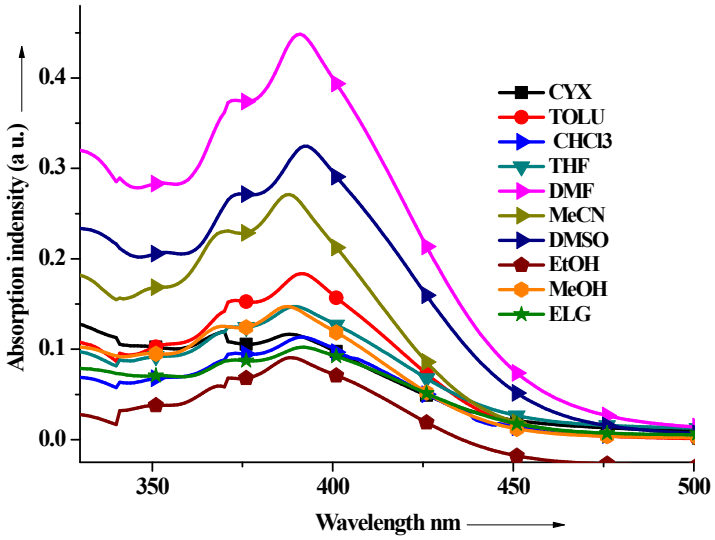


Figure S4: Absorption spectra of **TIN** in different solvents



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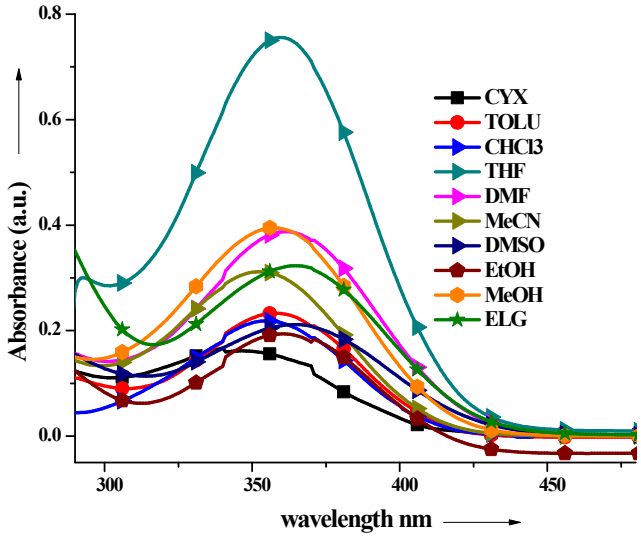


Figure S6: Absorption spectra of **NIN** in different solvents

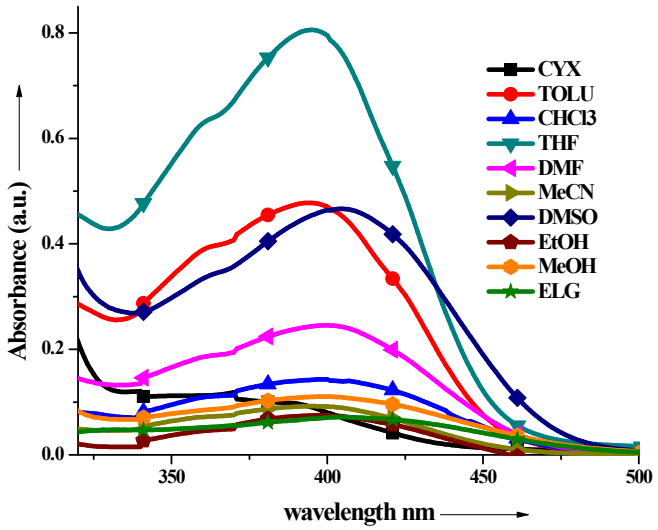
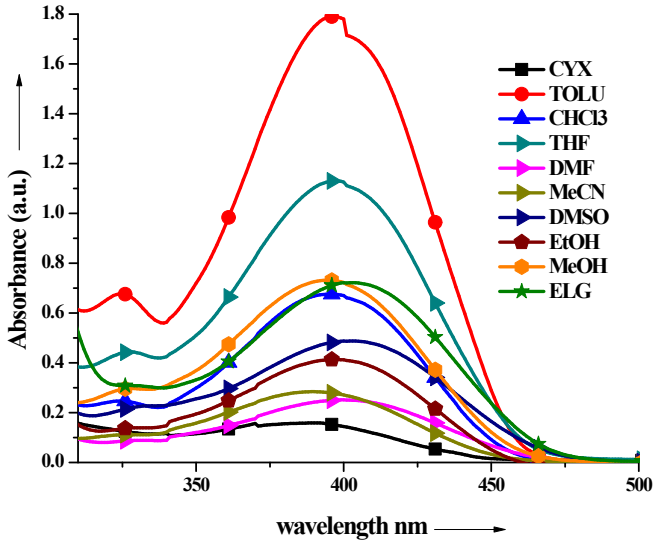


Figure S7: Absorption spectra **CIN in** different solvents



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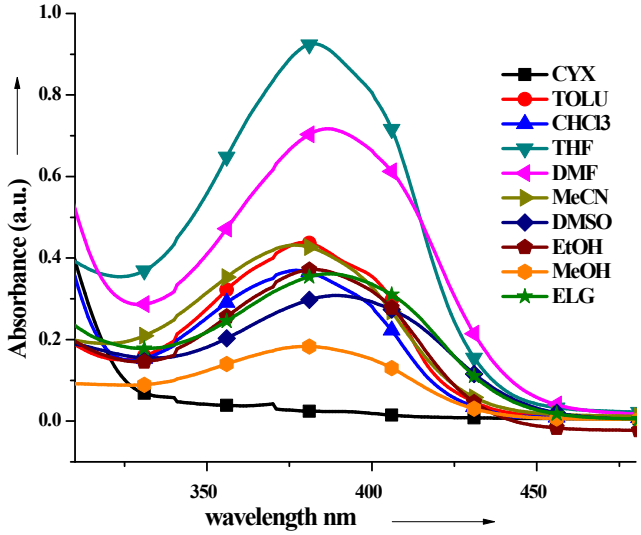

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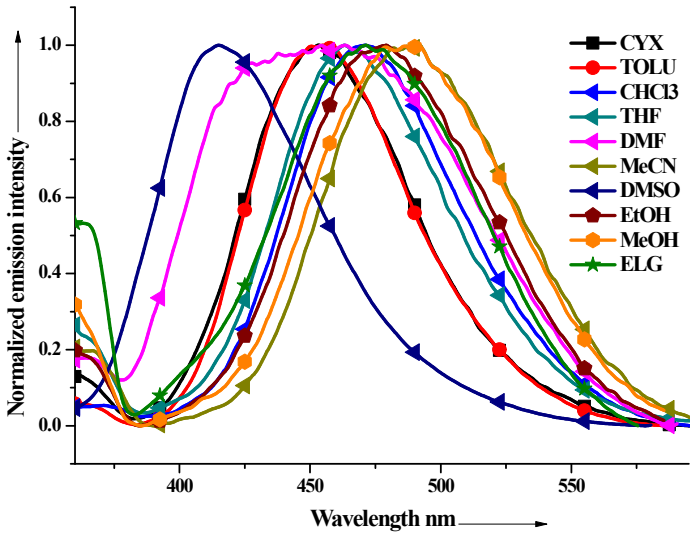

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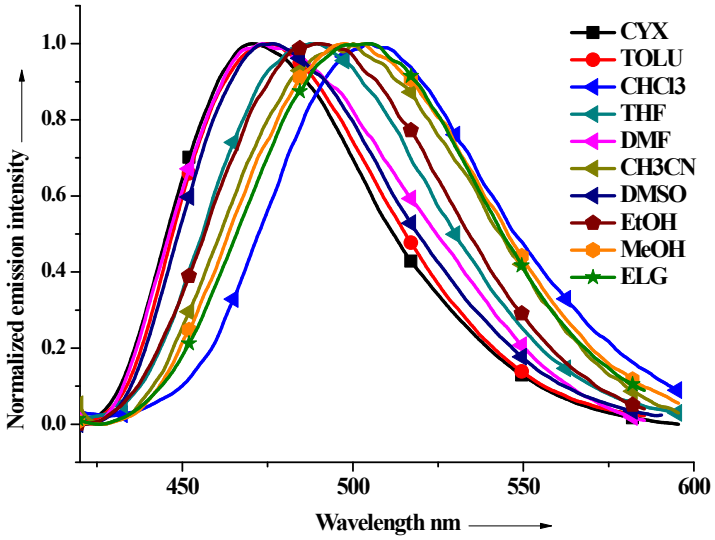
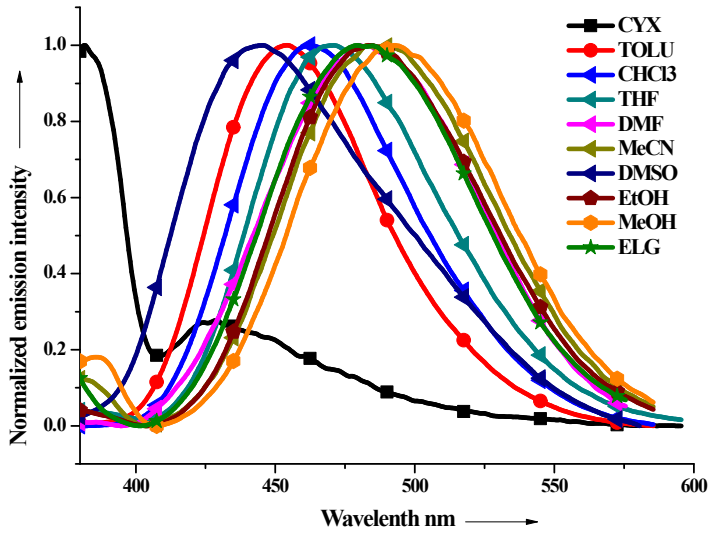


Figure S11: Emission spectra of **PYRIN** in different solvents.



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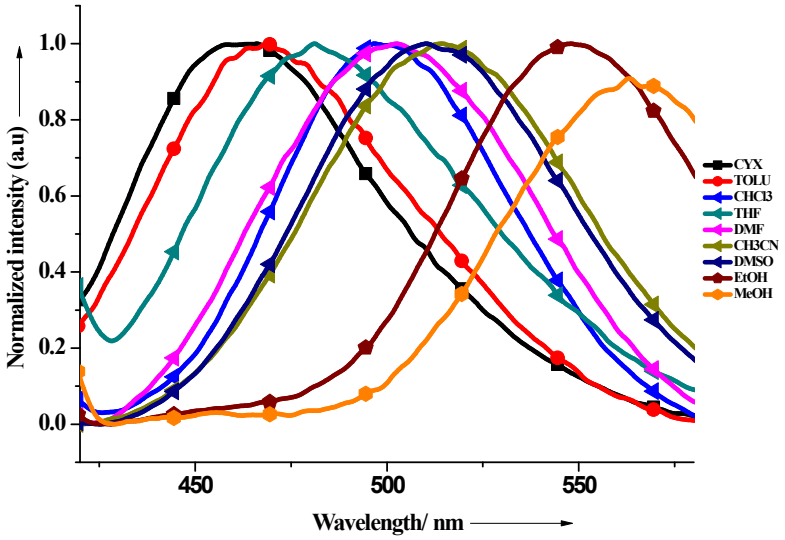

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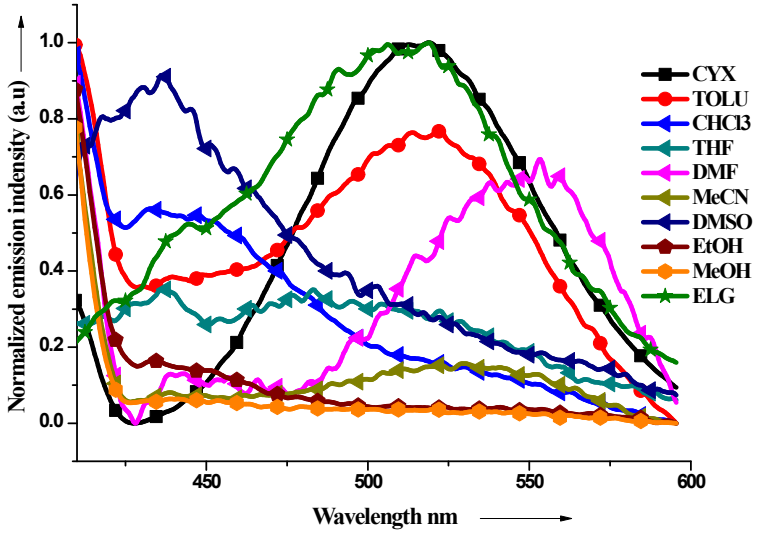

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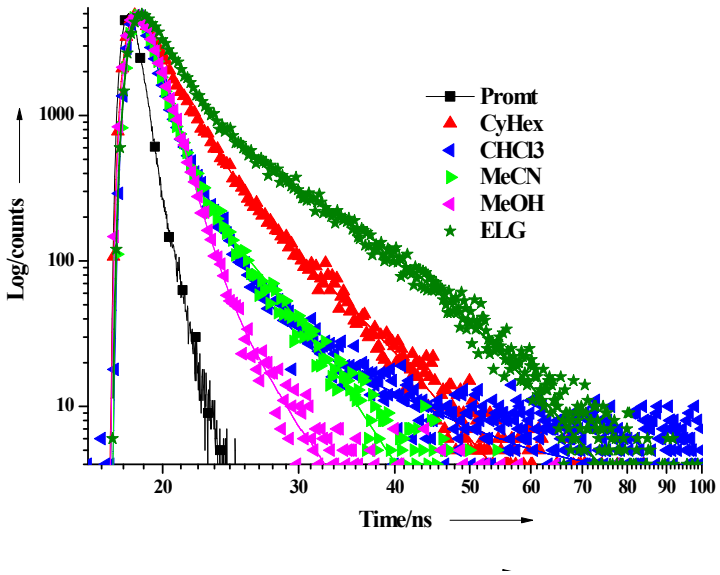
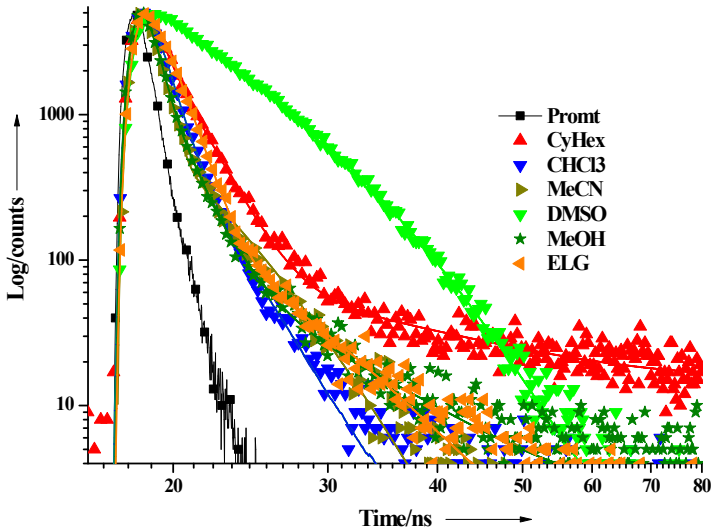


Figure S15: Fluorescence decay curves of **CIN** in all of the solvents studied.



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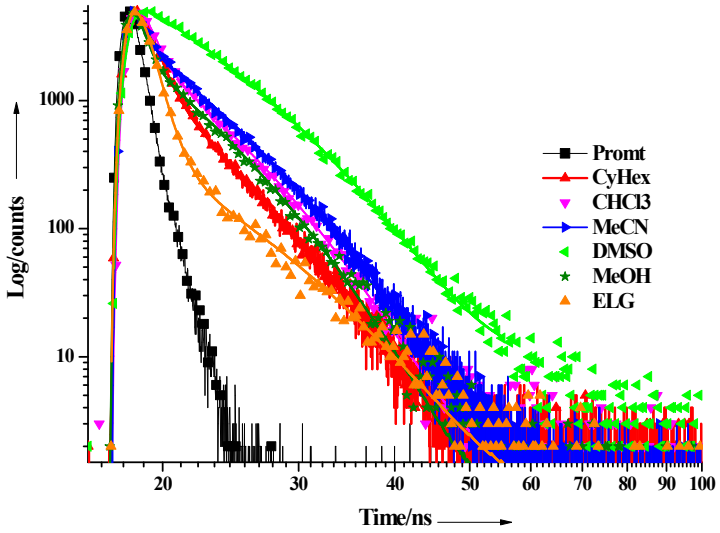

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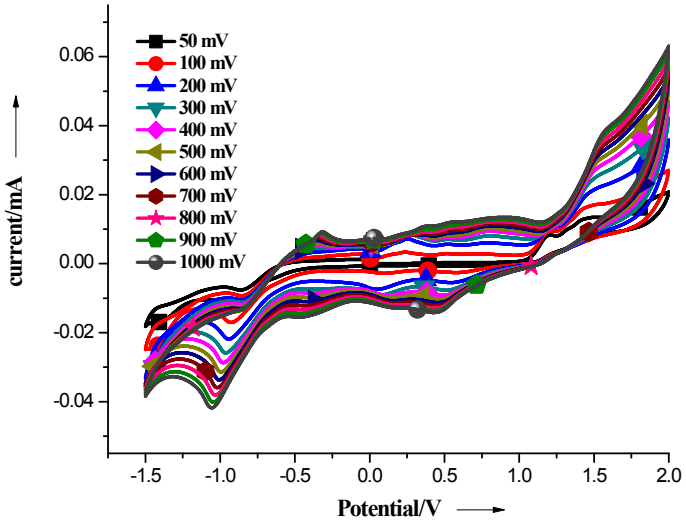
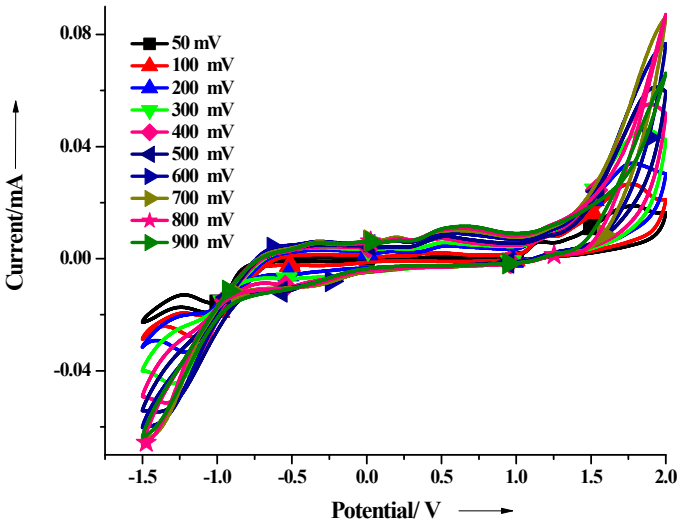


Figure S18: Cyclic volatamogram of **AIN** with multi scan rate in DMF.



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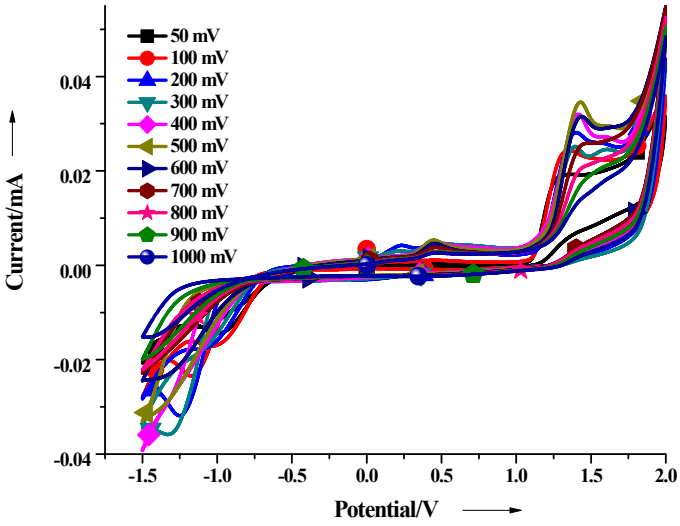

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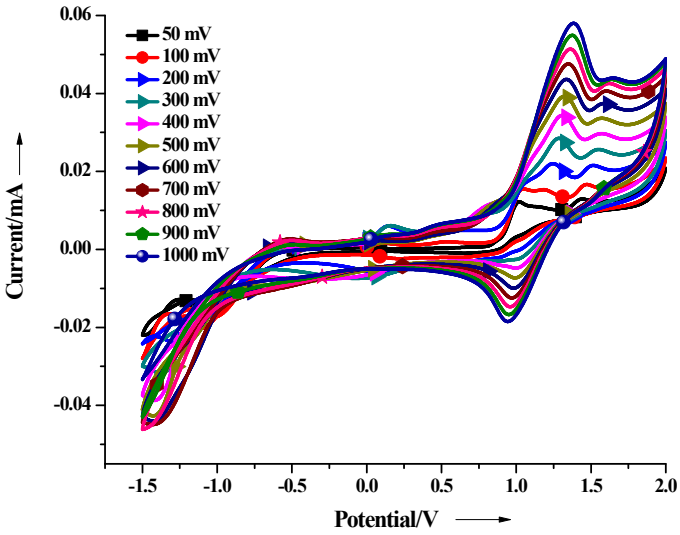

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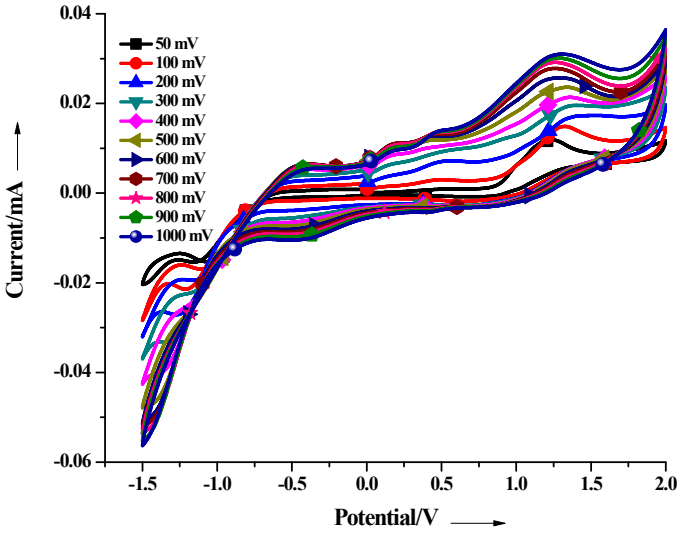

Figure S22: Cyclic volatamogram of **T2IN** with multi scan rate in DMF.

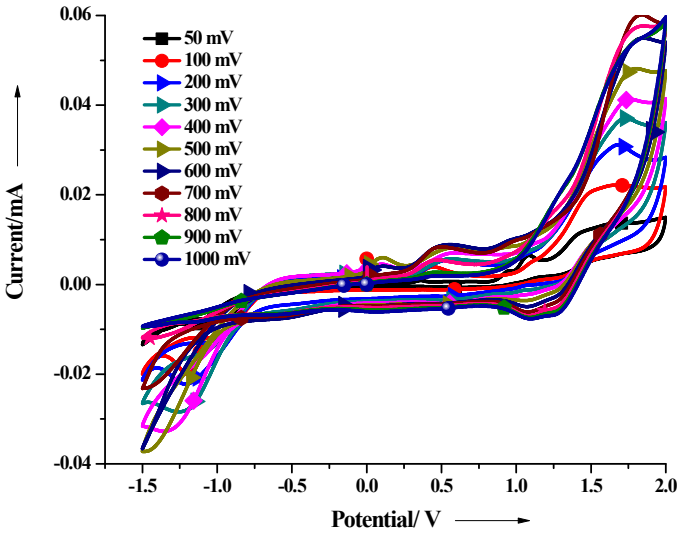

Figure S23: Cyclic volatamogram of **CIN** with multi scan rate in DMF.

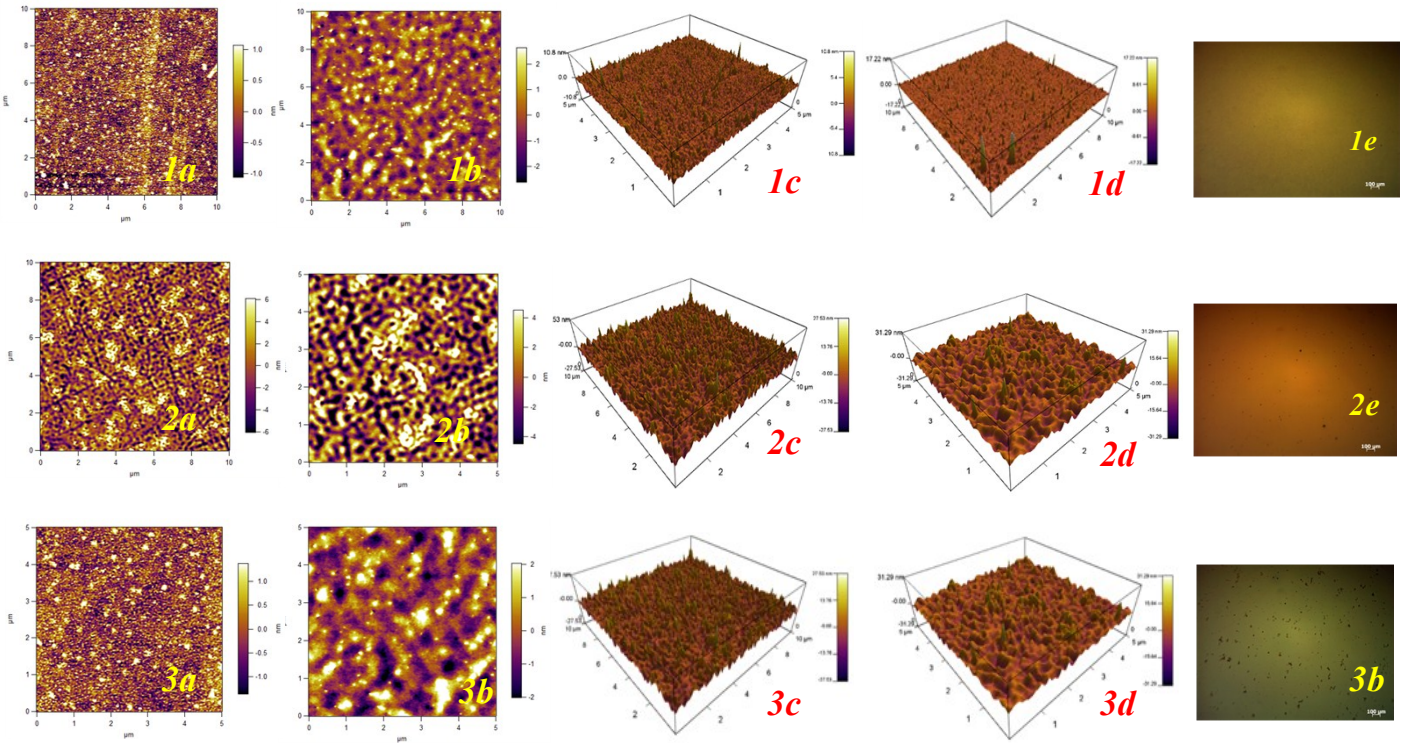

Figure S24 AFM image of PY2IN (1), T2IN (2) and TIN (3) in thin films. a) Non annealed 2D View (10ηm) b) annealed 2D view (5 ηm) c) Non annealed at 100 ˚C in 3D view (10 ηm) d) annealed at 100 ˚C in 3D view (5 ηm).

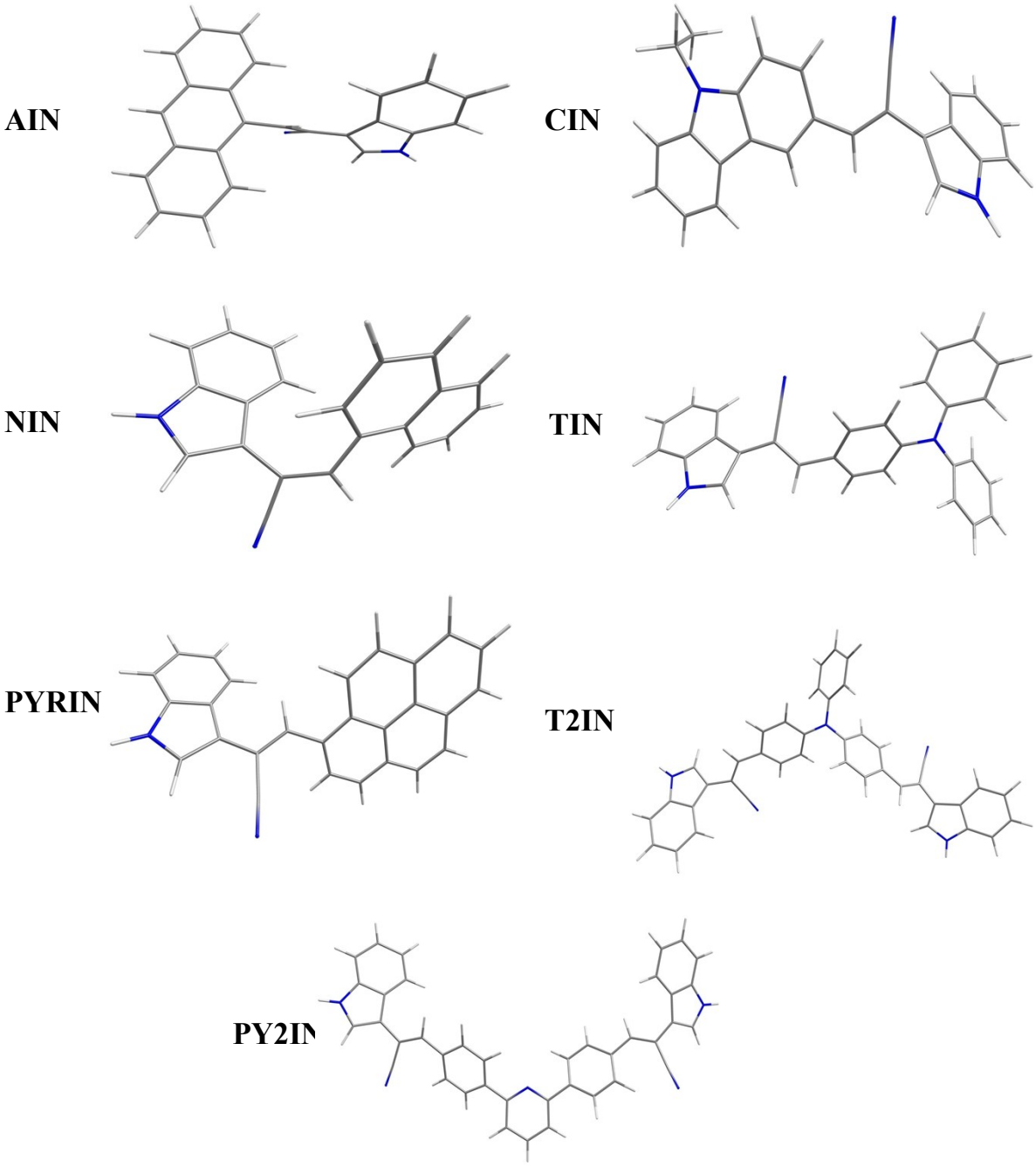

Figure S25: B3LYP/6-311G(d,p) optimized structures of chosen flurophores.

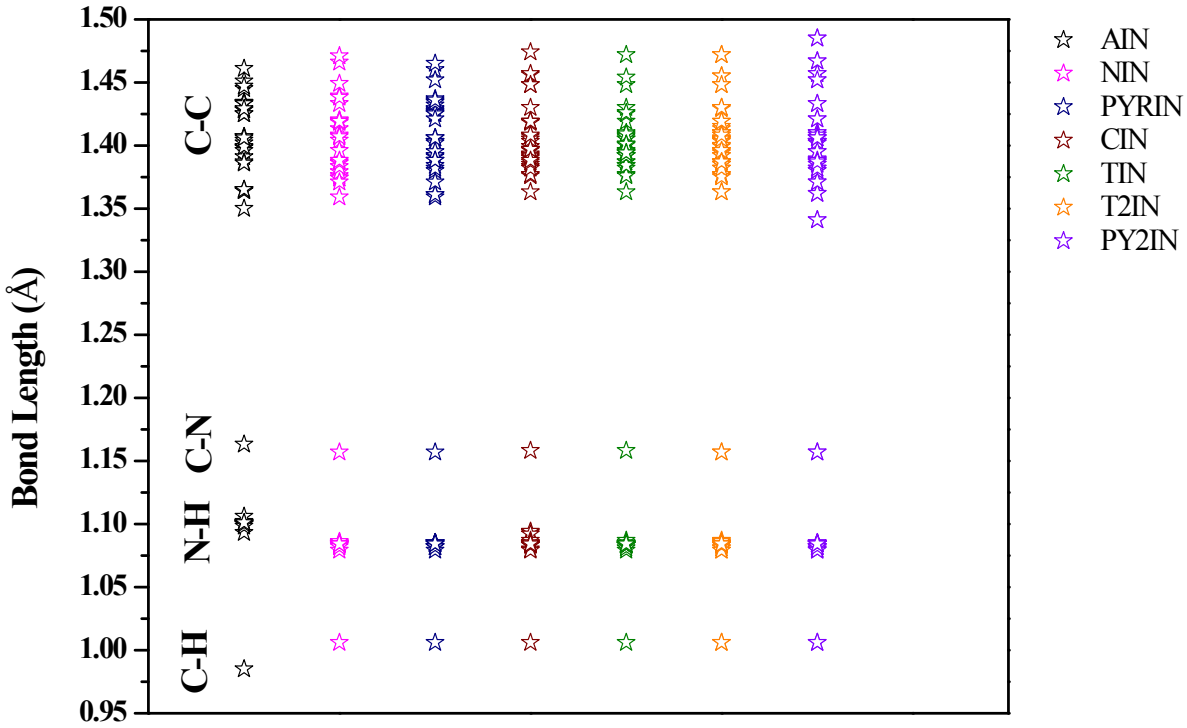

Figure S26: Illustration of π-delocalization from calculated C-C bond lengths of the chosed molecules at B3LYP/6-311G(d,p) level.

Table S1: life time data for all the solvents in **TIN**

SOLVENT	TIN							
	τ_1 [ns]	α_1 [%]	τ_2 [ns]	α_2 [%]	<τ> ns	χ^2	K_r ($10^7 s^{-1}$)	K_{nr} ($10^7 s^{-1}$)
CYHEX	3.81	62.75	2.40	37.25	---	0.88	----	----
$CHCl_3$	8.14	28.54	3.45	71.46	8.92	1.17	1.12	10.08
MeOH	1.33	26.35	4.51	73.65	4.20	0.95	0.47	23.33
ELG	6.12	39.08	5.76	60.92	5.90	1.10	5.76	11.18
MeCN	2.59	49.61	4.27	50.39	3.64	1.29	0.54	26.92
DMSO	2.62	44.39	5.71	55.61	4.88	1.00	1.63	18.85

Table S2: Life time data for all the solvents in **T2IN**

SOLVENT	T_2IN									
	τ_1 [ns]	α_1 [%]	τ_2 [ns]	α_2 [%]	τ_3 [ns]	α_3 [%]	<τ> ns	χ^2	K_r ($10^7 s^{-1}$)	K_{nr} ($10^7 s^{-1}$)
CYHEX	1.11	74.30	3.56	25.70	-	-	------	0.93	------	-------
MeOH	1.73	50.73	2.90	49.27	-	-	2.45	1.43	0.40	40.40
$CHCl_3$	2.09	27.95	1.15	5.30	4.92	66.75	4.44	1.22	2.92	19.59
MeCN	2.21	69.62	3.82	30.38	-	-	2.90	1.02	0.34	34.13
DMSO	2.91	74.86	5.93	25.14	-	-	4.13	1.02	0.48	23.72
ELG	5.23	78.88	5.03	21.12	-	-	5.18	1.29	3.47	15.83

Table S3: life time data for all the solvents in **PY2IN**

SOLVENT	PY$_2$IN									
	τ_1 [ns]	α_1 [%]	τ_2 [ns]	α_2 [%]	τ_3 [ns]	α_3 [%]	<τ> ns	χ^2	K_r ($10^7 s^{-1}$)	K_{nr} ($10^7 s^{-1}$)
CYHEX	1.93	61.58	1.63	8.09	4.44	30.33	---	1.09	----	-----
$CHCl_3$	6.59	80.95	2.73	19.05	-	-	6.24	1.19	7.85	8.17
MeOH	1.82	25.31	9.38	7.08	3.32	67.61	4.30	1.22	3.95	19.30
ELG	9.69	89.92	6.13	10.08	-	-	9.45	1.19	3.59	6.98
MeCN	3.67	70.93	3.50	29.07	-	-	3.62	1.07	1.93	25.69
DMSO	8.32	5.13	5.41	94.87	-	-	5.63	1.10	3.55	14.20

Table S4: life time data for all the solvents in **PYRIN**

SOLVENT	PYRIN							
	τ_1 [ns]	α_1 [%]	τ_2 [ns]	α_2 [%]	<τ> ns	χ^2	K_r ($10^7 s^{-1}$)	K_{nr} ($10^7 s^{-1}$)
CYHEX	6.25	57.57	4.17	42.43	-----	0.86	------	------
$CHCl_3$	4.88	39.25	4.27	60.75	4.52	1.19	1.09	98.90
MeOH	1.85	40.62	4.11	59.38	3.57	0.95	1.06	26.94
ELG	5.24	79.53	5.96	20.47	5.40	0.96	2.96	15.55
MeCN	1.47	31.89	4.47	68.11	4.06	1.12	0.93	23.69
DMSO	5.23	100	-	-	5.23	1.20	3.25	15.86

Table S5: life time data for all the solvents in **CIN**

SOLVENT	CIN									
	τ_1 [ns]	α_1 [%]	τ_2 [ns]	α_2 [%]	τ_3 [ns]	α_3 [%]	$<\tau>$ ns	χ^2	K_r ($10^7 s^{-1}$)	K_{nr} ($10^7 s^{-1}$)
CYHEX	3.64	23.47	1.94	54.33	7.02	22.20	-----	0.86	------	------
$CHCl_3$	3.81	59.39	2.01	33.97	1.15	6.11	3.34	1.23	6.58	23.35
MeOH	8.67	92.84	3.09	7.16	-	-	8.51	1.11	1.64	10.10
ELG	1.57	54.09	9.63	45.91	-	-	8.33	1.18	6.72	5.28
MeCN	6.02	77.67	4.28	22.33	-	-	5.72	0.99	6.11	16.95

Table S6. Frontier molecular orbital energies (eV) of chosen molecules computed at the B3LYP/6-311+G(d,p) level.

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	Band Gap
AIN	-6.82	-6.71	-6.13	-5.48	-2.25	-1.54	-1.00	-0.77	3.22
NIN	-7.09	-6.62	-6.37	-5.85	-2.22	-1.21	-0.85	-0.85	3.63
PYRIN	-6.68	-6.66	-6.18	-5.48	-2.40	-1.43	-1.06	-0.97	3.08
CIN	-6.40	-6.28	-6.09	-5.46	-1.87	-1.35	-0.74	-0.31	3.59
TIN	-6.88	-6.43	-5.95	-5.30	-2.05	-1.06	-0.92	-0.78	3.25
T2IN	-6.47	-6.13	-5.80	-5.32	-2.31	-2.00	-1.16	-0.88	3.01
PY2IN	-6.68	-6.61	-5.77	-5.68	-2.36	-2.34	-1.17	-1.12	3.32

Table S7. Molecular orbital composition (%) of various fragments of **AIN** in the ground state.

	Energy (eV)	Donor	π-Spacer	Acceptor
HOMO-3	-6.824	39.35	51.22	9.42
HOMO-2	-6.71	17.53	35.8	46.67
HOMO-1	-6.126	21.15	42.4	36.45
HOMO	-5.477	70.25	9.75	20
LUMO	-2.252	49.82	31.57	18.61
LUMO+1	-1.545	29.08	19.95	50.97
LUMO+2	-0.996	54.45	7.62	37.94
LUMO+3	-0.775	60.2	29.18	10.63

Table S8. Molecular orbital composition (%) of various fragments of **NIN** in the ground state

	Energy (eV)	Donor	π-Spacer	Acceptor
HOMO-3	-7.093	82.71	7.68	9.61
HOMO-2	-6.622	32.02	35.47	32.51
HOMO-1	-6.371	45.52	12.56	41.91
HOMO	-5.852	57.16	23.86	18.98
LUMO	-2.217	64.9	12.23	22.87
LUMO+1	-1.21	58.87	17.73	23.4
LUMO+2	-0.879	42.16	40.63	17.21
LUMO+3	-0.849	52.8	30.95	16.25

Table S9. Molecular orbital composition (%) of various fragments of **PYRIN** in the ground state.

	Energy (eV)	Donor	π-Spacer	Acceptor
HOMO-3	-6.684	24.52	26.82	48.66
HOMO-2	-6.665	34.28	26.43	39.28
HOMO-1	-6.184	42.44	24.62	32.94
HOMO	-5.477	61.09	8.26	30.66
LUMO	-2.401	56.86	18.34	24.81
LUMO+1	-1.434	40.95	26.7	32.36
LUMO+2	-1.061	49.14	11.11	39.75
LUMO+3	-0.973	37.21	15.78	47.01

Table S10. Molecular orbital composition (%) of various fragments of **CIN** in the ground state.

	Energy (eV)	Donor	π-Spacer	Acceptor
HOMO-3	-6.397	31.78	5.82	62.4
HOMO-2	-6.281	17.62	12.55	69.84
HOMO-1	-6.09	42.96	35.93	21.1
HOMO	-5.462	58.72	24.46	16.83
LUMO	-1.874	44.63	16.96	38.4
LUMO+1	-1.347	61.33	4.57	34.11
LUMO+2	-0.743	68.56	7.53	23.91
LUMO+3	-0.314	75.7	5.81	18.49

Table S11. Molecular orbital composition (%) of various fragments of **TIN** in the ground state.

	Energy (eV)	Donor	π-Spacer	Acceptor
HOMO-3	-6.878	46.2	20.05	33.75
HOMO-2	-6.428	14.96	4.77	80.26
HOMO-1	-5.955	39.55	36.46	23.99
HOMO	-5.3	67.26	11.84	20.9
LUMO	-2.051	30.29	20.97	48.73
LUMO+1	-1.062	93.78	0.8	5.42
LUMO+2	-0.919	94.85	2.36	2.79
LUMO+3	-0.783	46.2	12.77	41.02

Table S12. Molecular orbital composition (%) of various fragments of **T2IN** in the ground state.

	Energy (eV)	Donor	π-Spacer	π-Spacer	Acceptor	Acceptor
HOMO-3	-6.467	14.53	1.44	4.54	0.56	78.93
HOMO-2	-6.132	30.71	20.21	18.81	16.41	13.86
HOMO-1	-5.801	49.21	13.39	17.58	10.62	9.2
HOMO	-5.322	54.98	8.15	5	18.16	13.71
LUMO	-2.31	36.93	13.83	11.14	19.93	18.17
LUMO+1	-1.996	24.16	9.77	9.78	30.07	26.23
LUMO+2	-1.159	85.99	1.2	1.01	5.44	6.36
LUMO+3	-0.879	55.72	6.59	3.54	30.18	3.97

Table S13. Molecular orbital composition (%) of various fragments of **PY2IN** in the ground state.

	Energy (eV)	Donor	π-Spacer	π-Spacer	Acceptor	Acceptor
HOMO-3	-6.684	25.96	7.56	7.56	29.45	29.46
HOMO-2	-6.614	33.59	13.58	13.58	19.62	19.62
HOMO-1	-5.767	65.48	6.56	6.56	10.7	10.7
HOMO	-5.681	70.18	7.19	7.19	7.72	7.72
LUMO	-2.362	59.14	9.57	9.57	10.86	10.86
LUMO+1	-2.339	51.98	11.52	11.53	12.48	12.48
LUMO+2	-1.171	37.76	6.32	6.32	24.8	24.8
LUMO+3	-1.122	51.51	6.84	6.84	17.41	17.41