Halogen-bonded Co-Crystals with AIE active α-cyanostilbenes

Rahul Dahiwadkar[a#], Gurudutt Dubey[a#], Althaf Shaik[a], Palash Jana[a], Vijay Thiruvenkatam[b] and Sriram Kanvah[a,*]

[a]Department of Chemistry, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar, Gujarat – 382055

[b]Department of Biological Engineering, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar, Gujarat -382055

sriram@iitgn.ac.in

# The authors contributed equally

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S1: Absorption and Emission

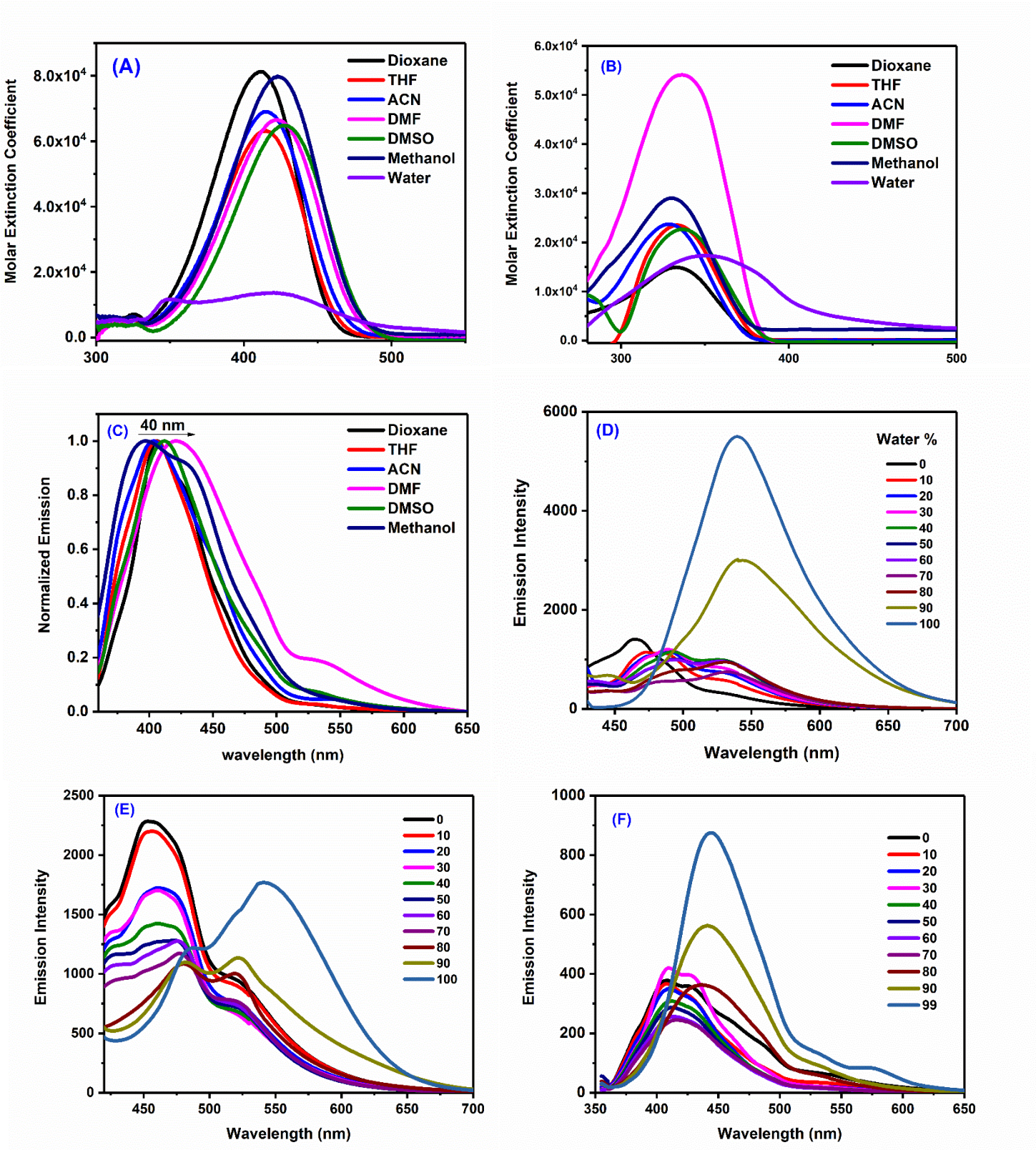


Figure S1: A) & B) Absorption spectra of Py and DI in all solvents. C) Emission spectra of DI in all solvents (excitation wavelength used is the absorption maxima). D), E) & F) Emission spectra of Py, MI, and DI in water/dioxane binary solvent mixture mixtures revealing enhanced emission in water. Concentration [10μM].

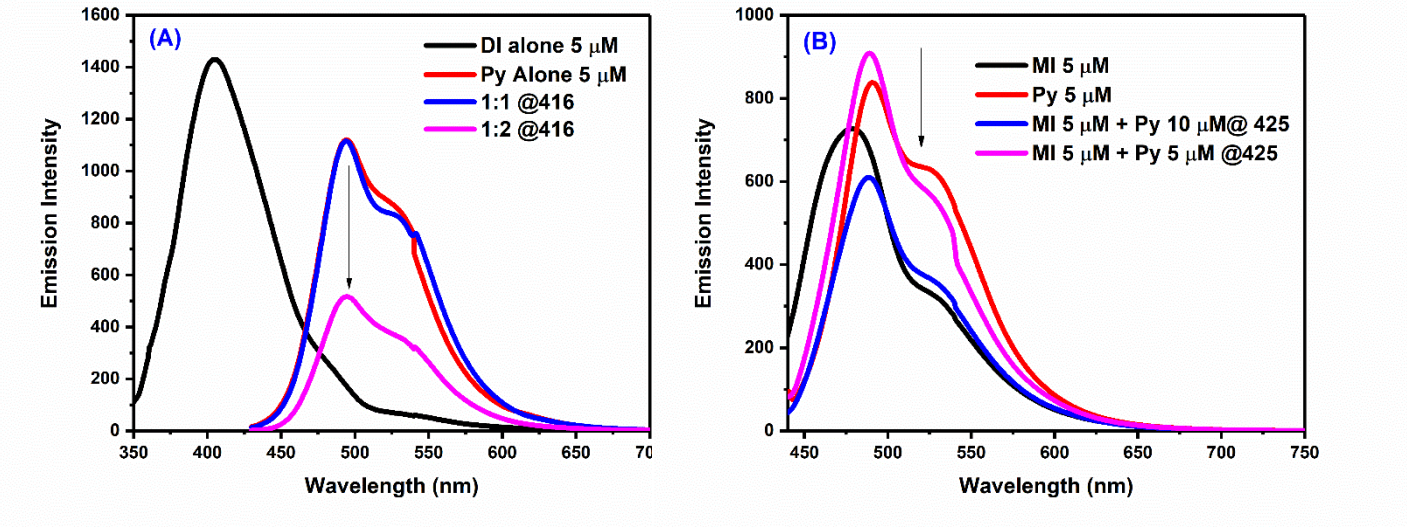


Figure S2: A) Emission spectra of DI and Py in different molar equivalents. B) Emission spectra of MI and Py in different molar mixtures

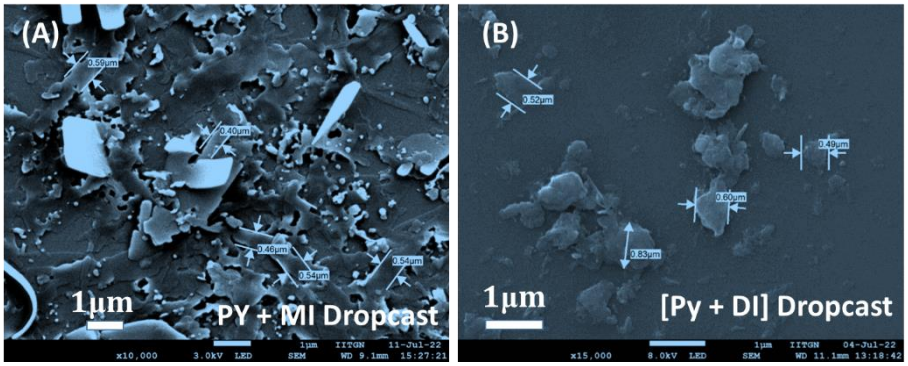


Figure S3: A) Drop-cast SEM images of molar mixtures of solution in water of Py-MI (5μM:5 μM) and B) Py-DI (10μM:5 μM) respectively.

Table S1: Lifetime Data for Py, MI and DI in dioxane and water									
Components		τ_1 (ns)	A1	τ_2 (ns)	A2	τ_3 (ns)	A3	Average Lifetime (τ) (ns)	χ^2
Py	Dioxane	-	-	-	-	-	-	-	-
	Water	2.19	22%	8.64	22%	0.11.	56%	**2.44**	1.13
MI	Dioxane	0.0016	100%	0.96	0.12%	-	-	0.0016	1.24
	Water	0.064	79%	0.35	21%	-	-	**0.12**	1.12
DI	Dioxane	-	100%	0.86	0.0%	-	-	-	0.98
	Water	0.058	46%	0.20	54%	-	-	**0.13**	1.00

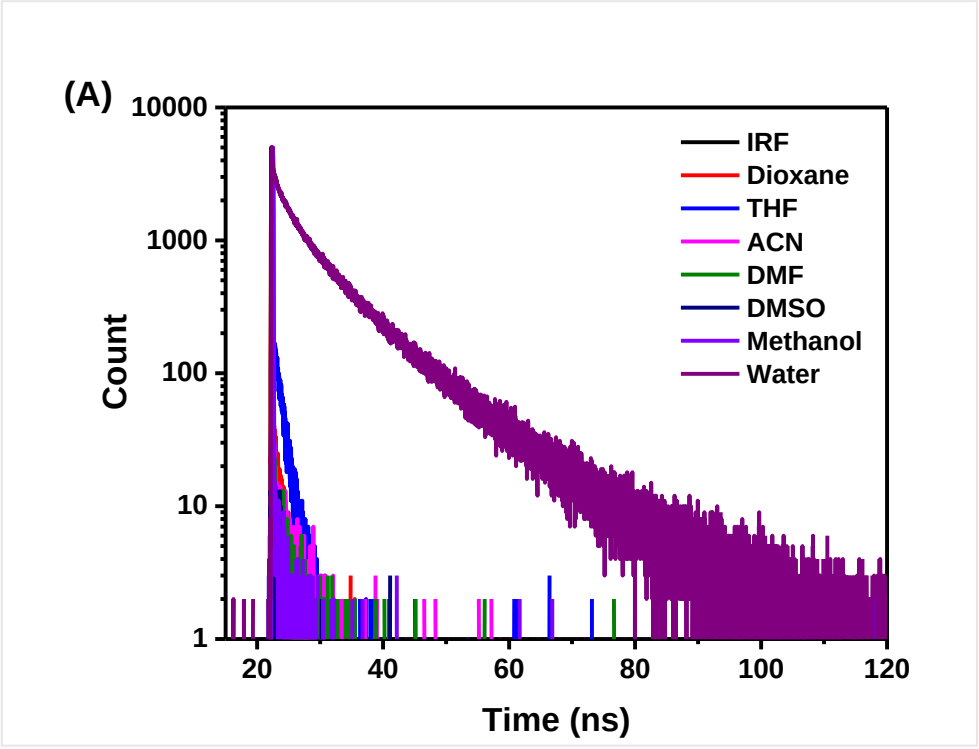


Figure S4a: Lifetime decay of Py in all solvents

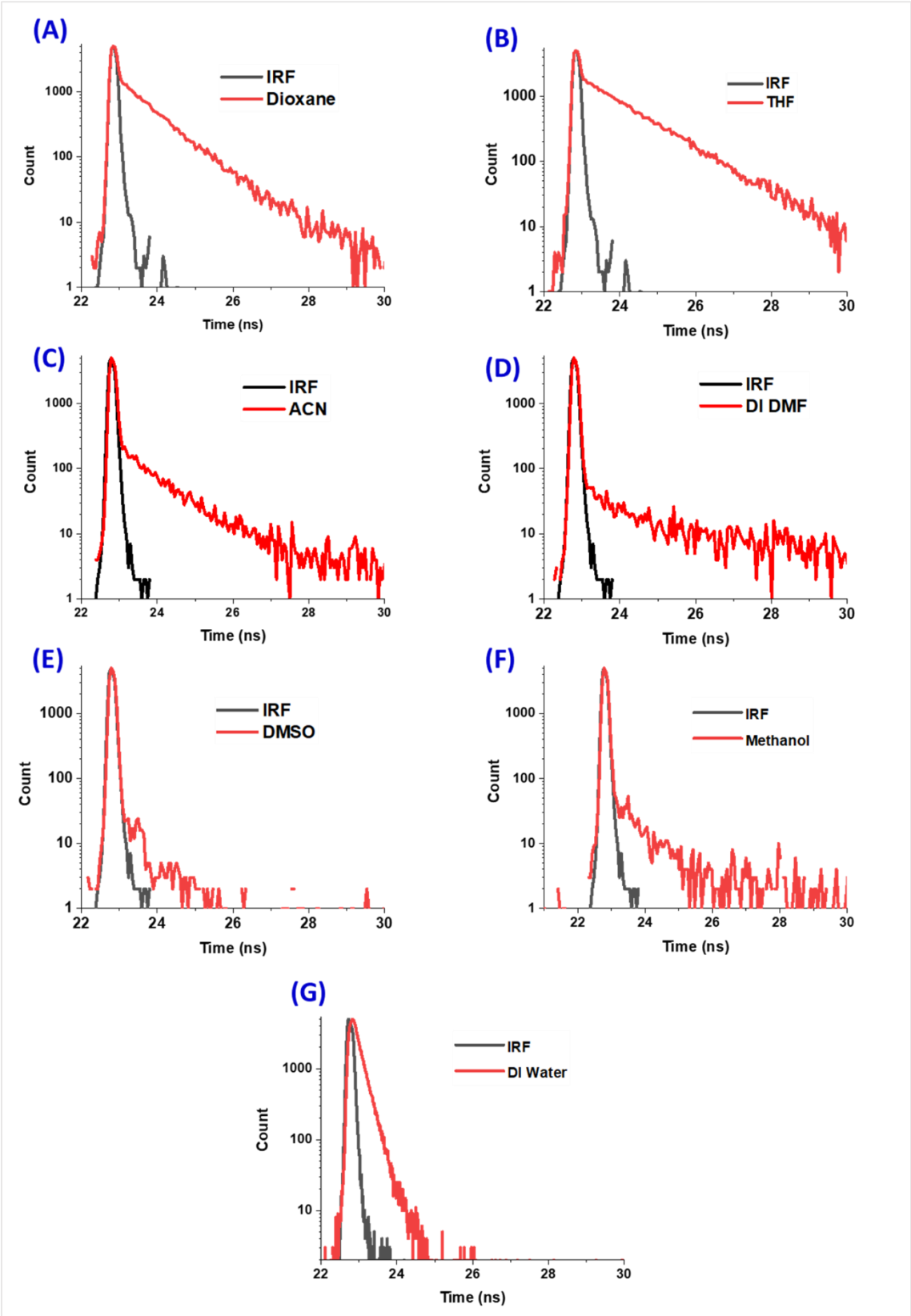


Figure S4b: Lifetime decay of DI in all solvents

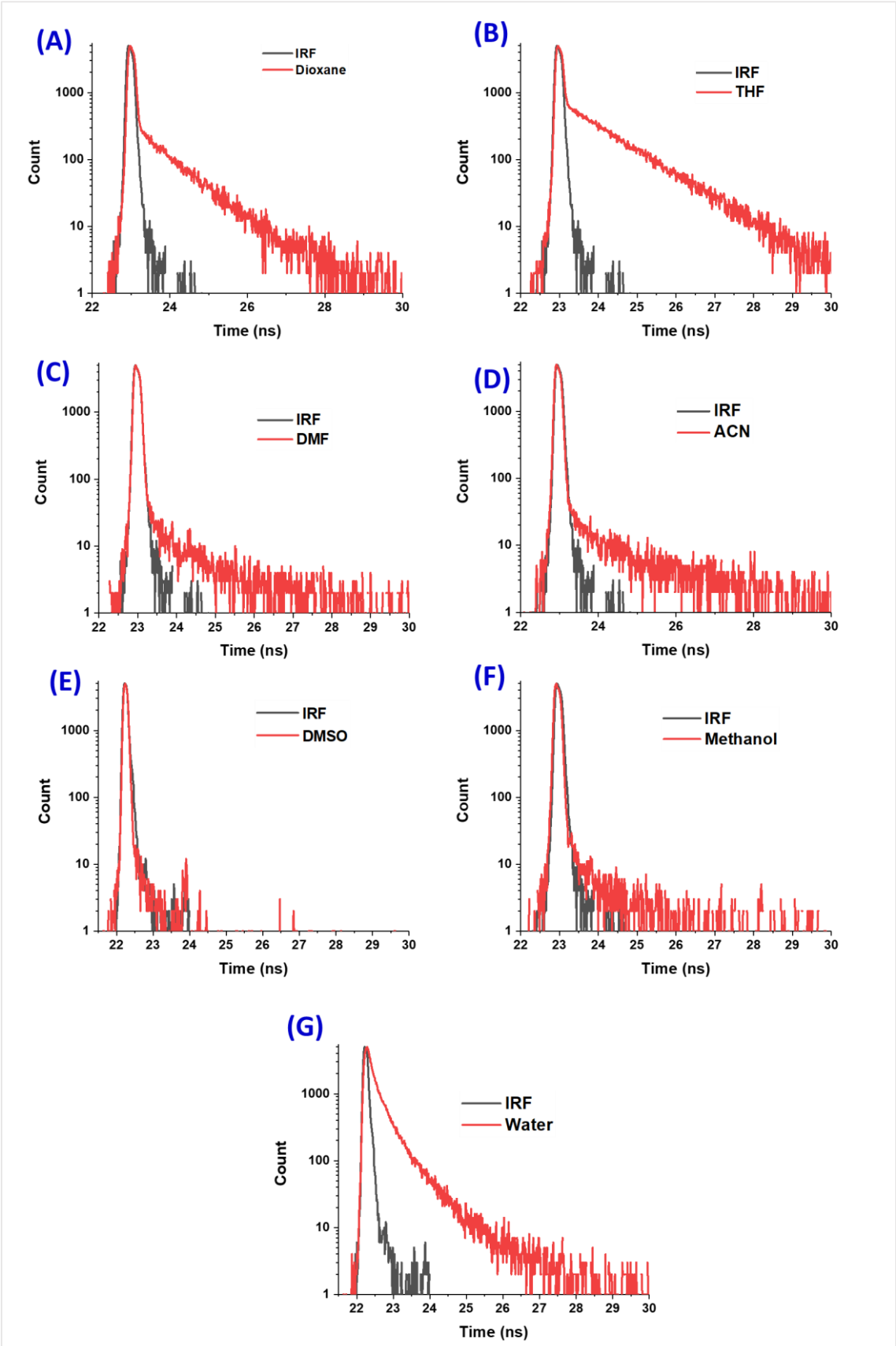


Figure S4c: Lifetime decay of MI in all solvents

S5: Microscopic Images of Single Crystal Under Nikon – TIRF Microscope

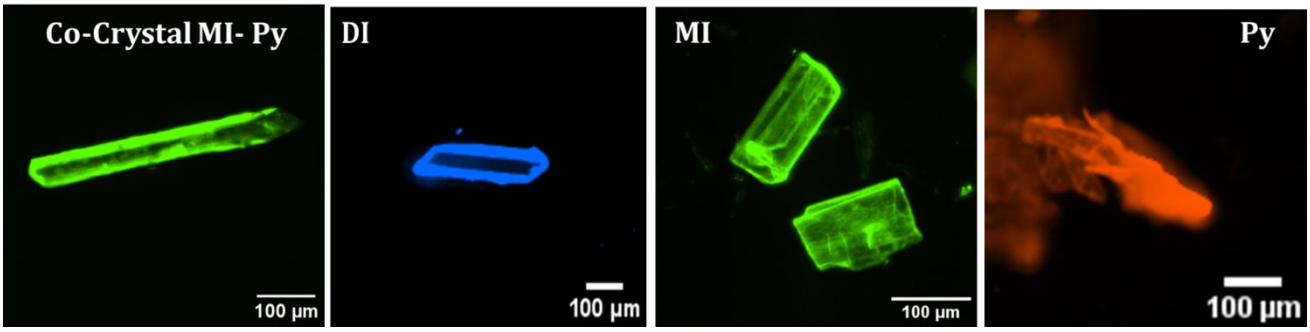


Figure S5: Images of single crystals of co-crystal Py-MI, DI, MI, and Py, respectively under a TIRF microscope (exciting at 515nm for co-crystal Py-MI, MI and Py and 350nm for DI.

S6: 2D Fingerprint Plots highlighting interactions.

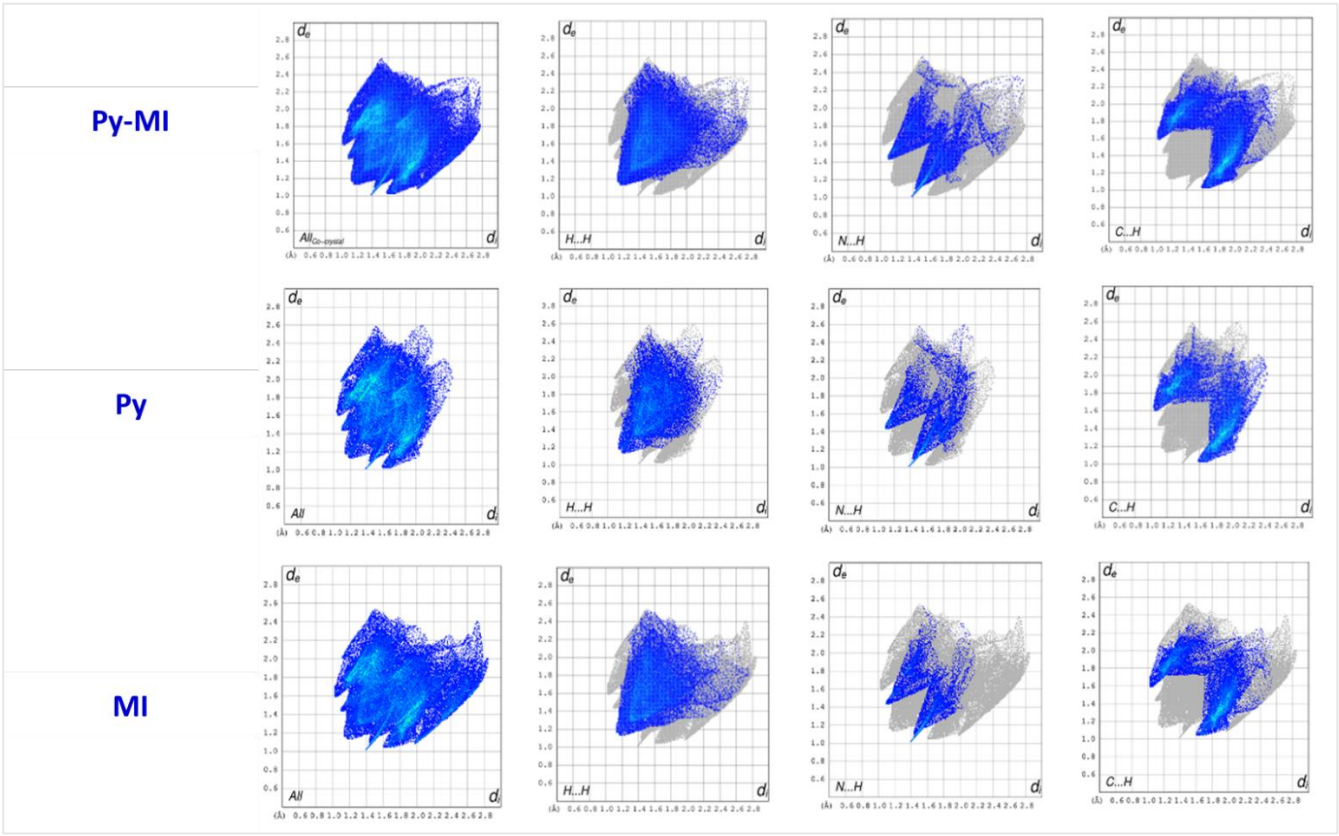


Figure S6: 2D fingerprint plots of MI, Py**,** Py-MI in co-crystal. Highlighting H···H, N···H and C···H interactions.

S7: Simulated UV absorption Spectra

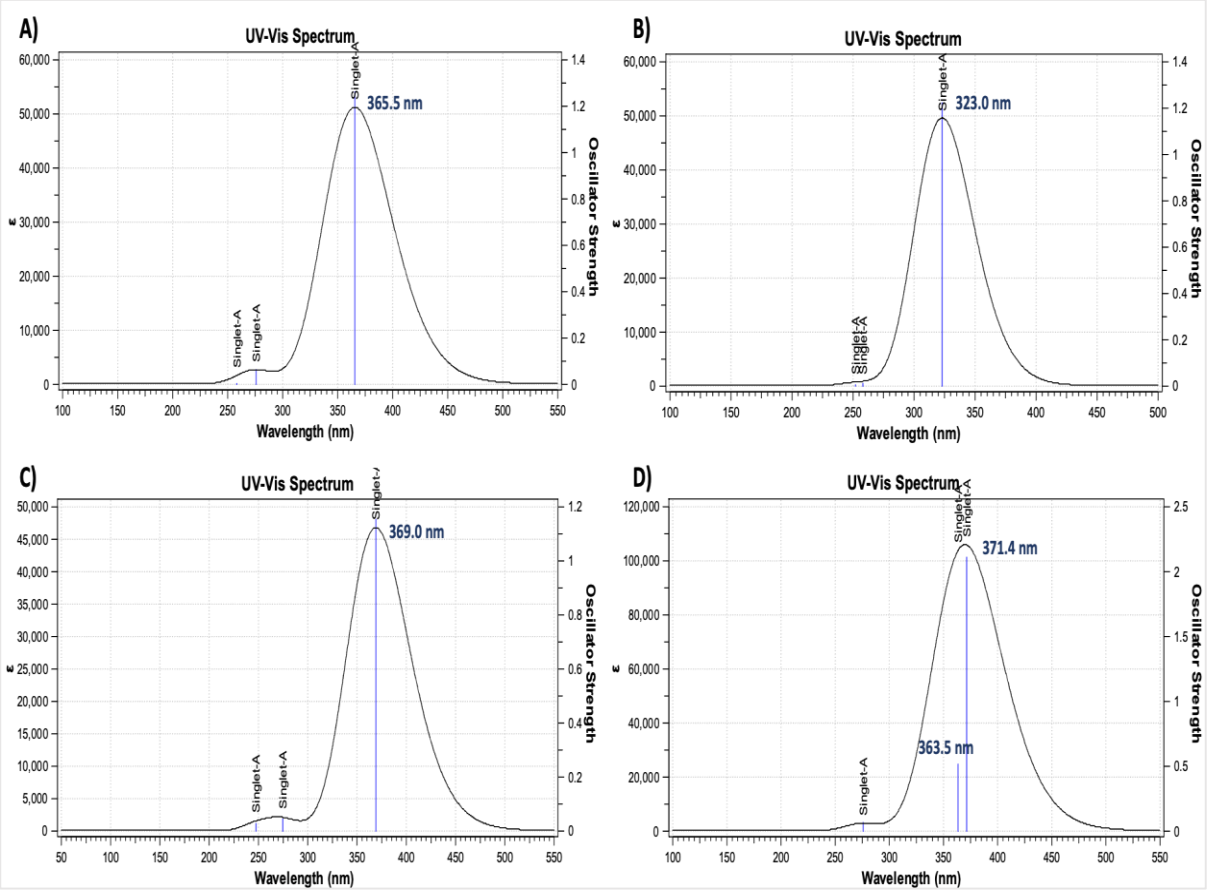


Figure S7: Simulated UV absorption spectra of MI (A), DI (B), Py (C) and Py-MI (D) obtained using at CAM-B3LYP method.

S8: Energy Framework Analysis:

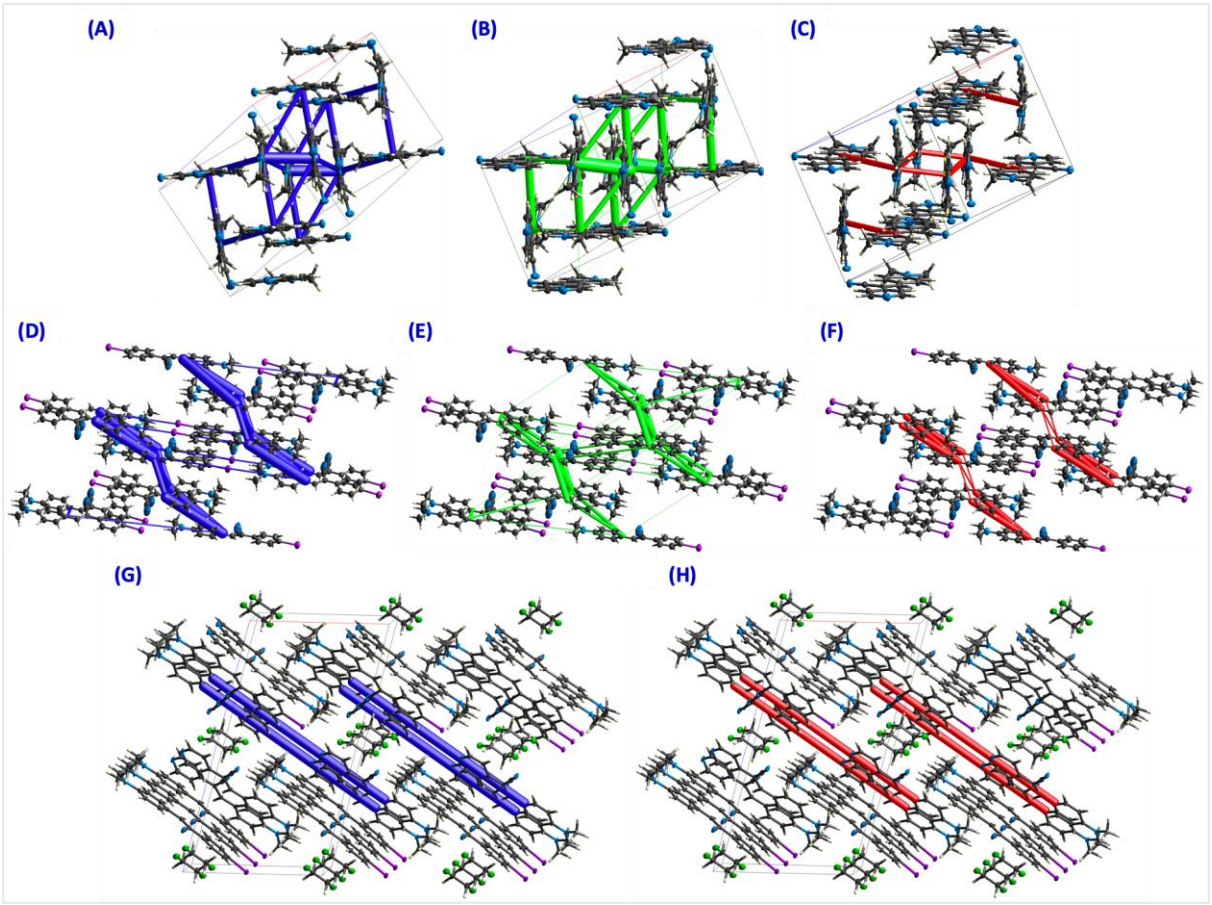


Figure S8: Energy framework analysis: (A) total energy component of Py, (B) Coulomb energy component of Py, (C) dispersion energy component of Py, (D) total energy component of MI, (E) Coulomb energy component of MI, (F) dispersion energy component of MI, (G) total energy component of Py-MI cocrystal, and (H) Coulomb energy component of Py-MI. The thickness of tubes is proportional to the interaction energy

S9: Solid state absorption spectra:

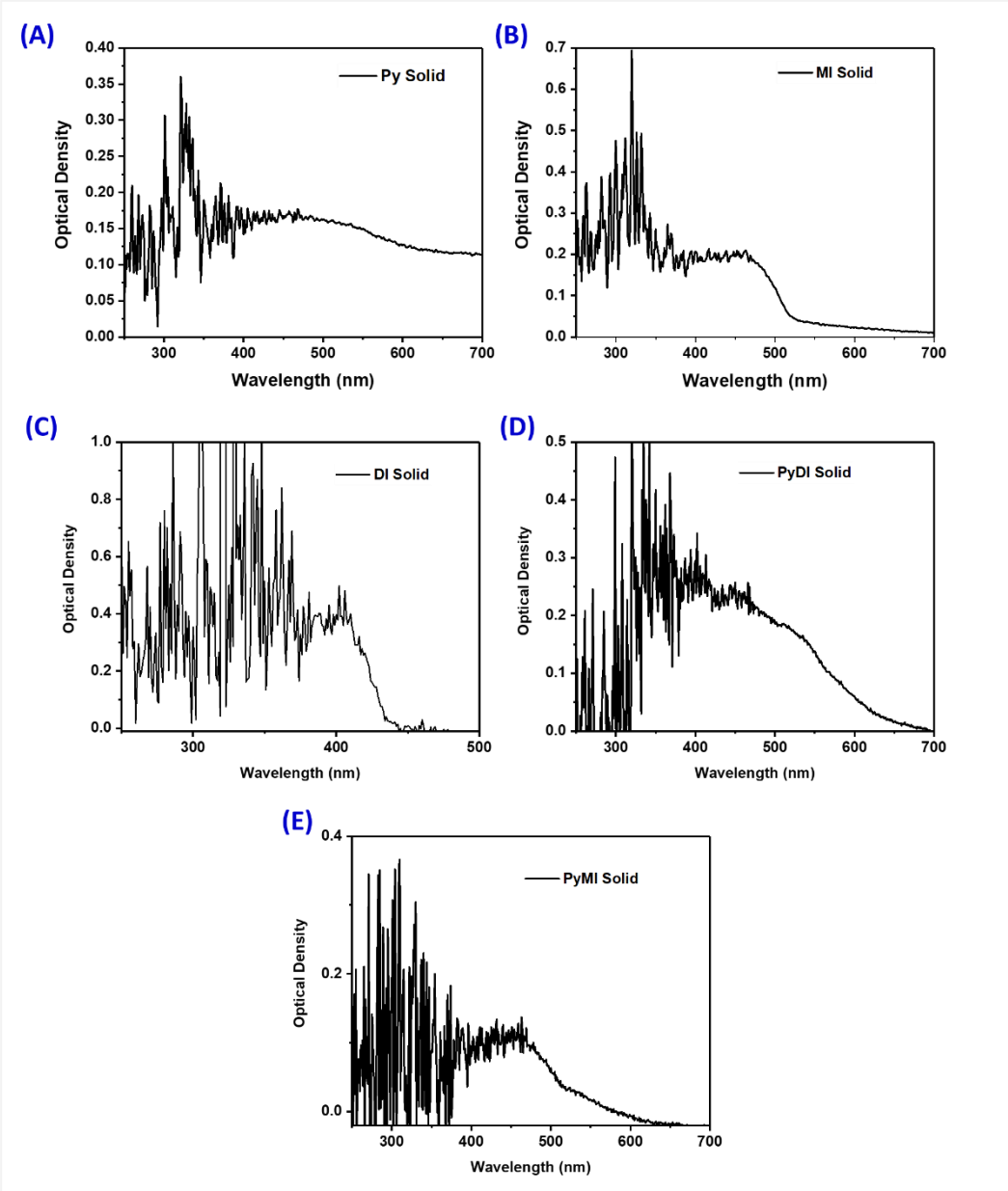


Figure S9: Solid state absorption spectra of A) Py B) MI C) DI D) Py+DI & E) Py+MI respectively.

S10: Gelation Methodology

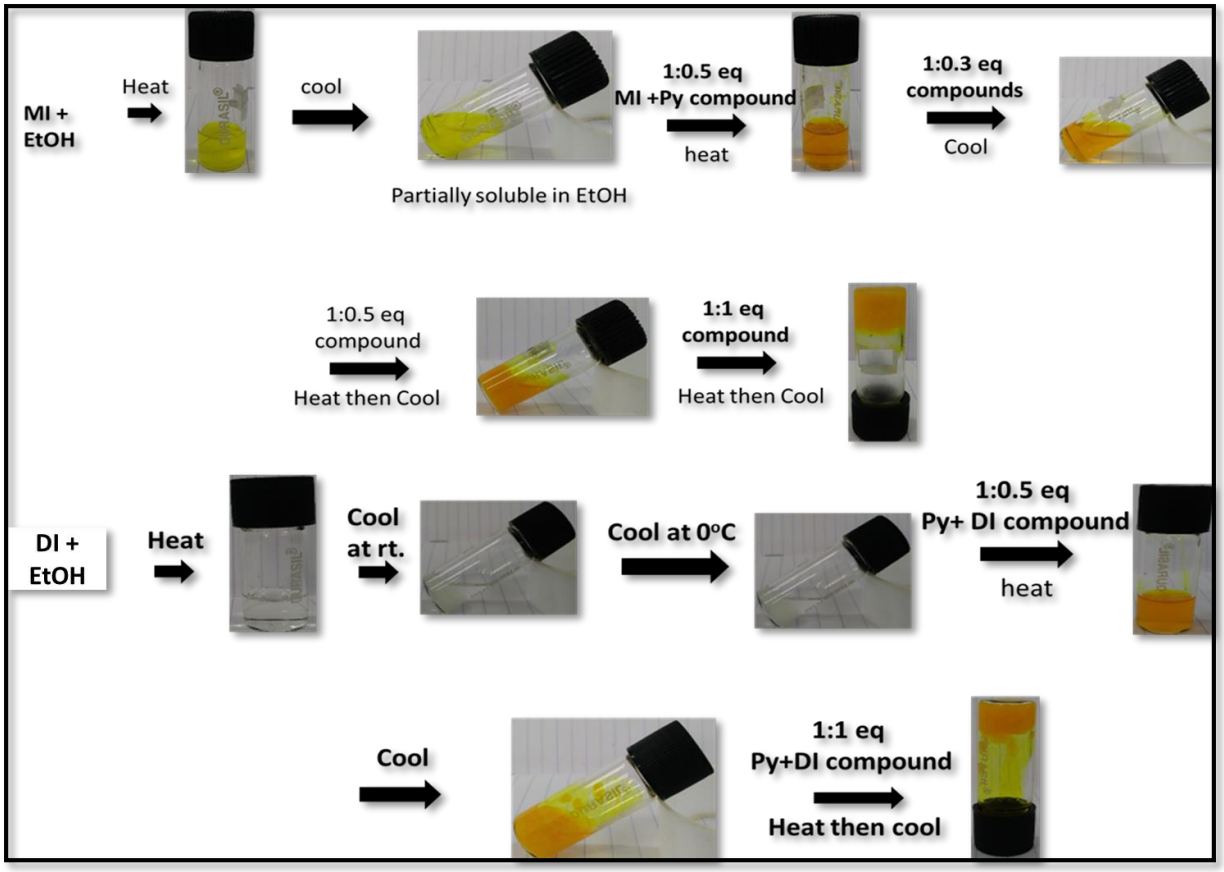


Figure S10: Gelation methodology; for Py along with DI and MI in different molar ratios in ethanol.

S11: Rheology Data

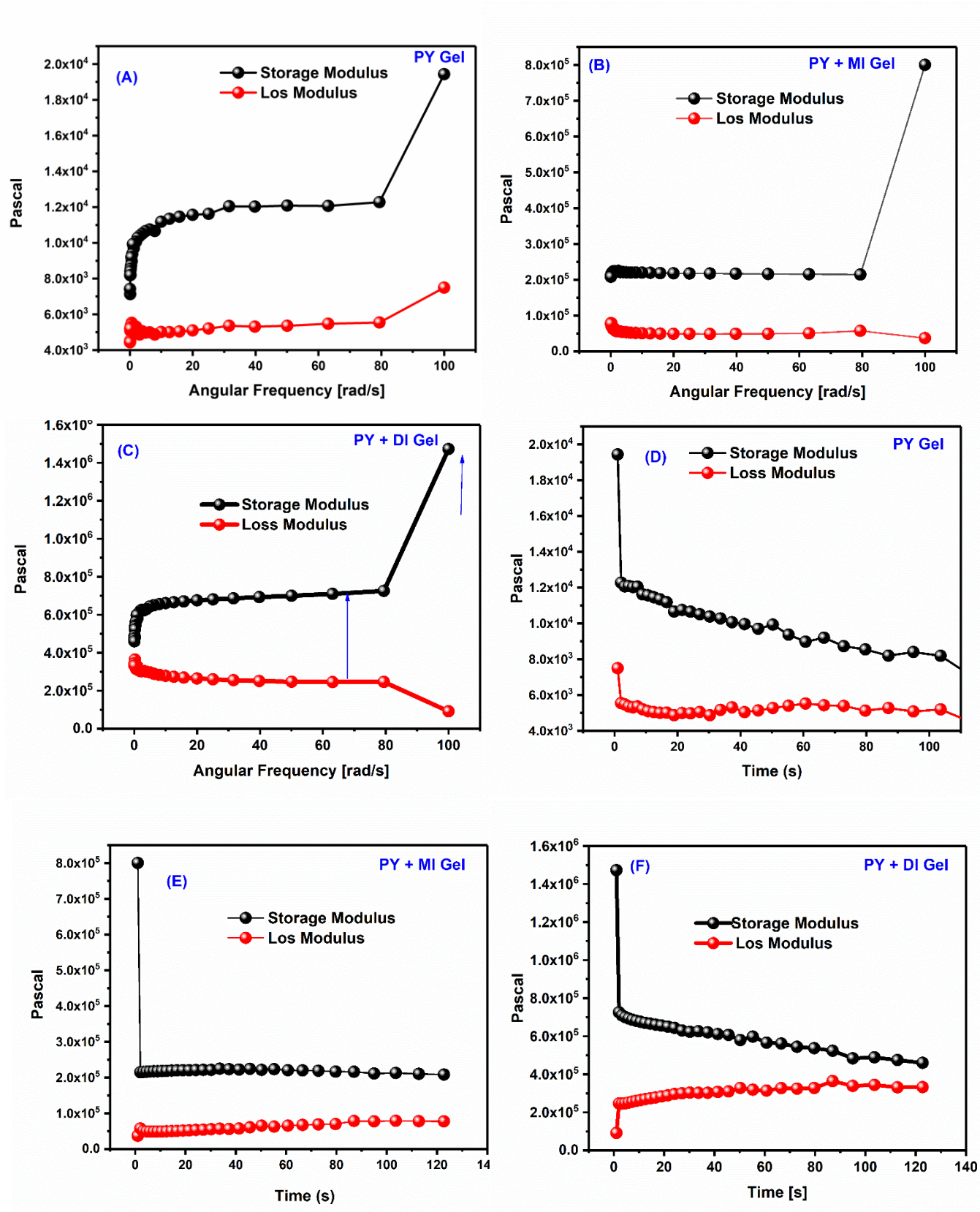
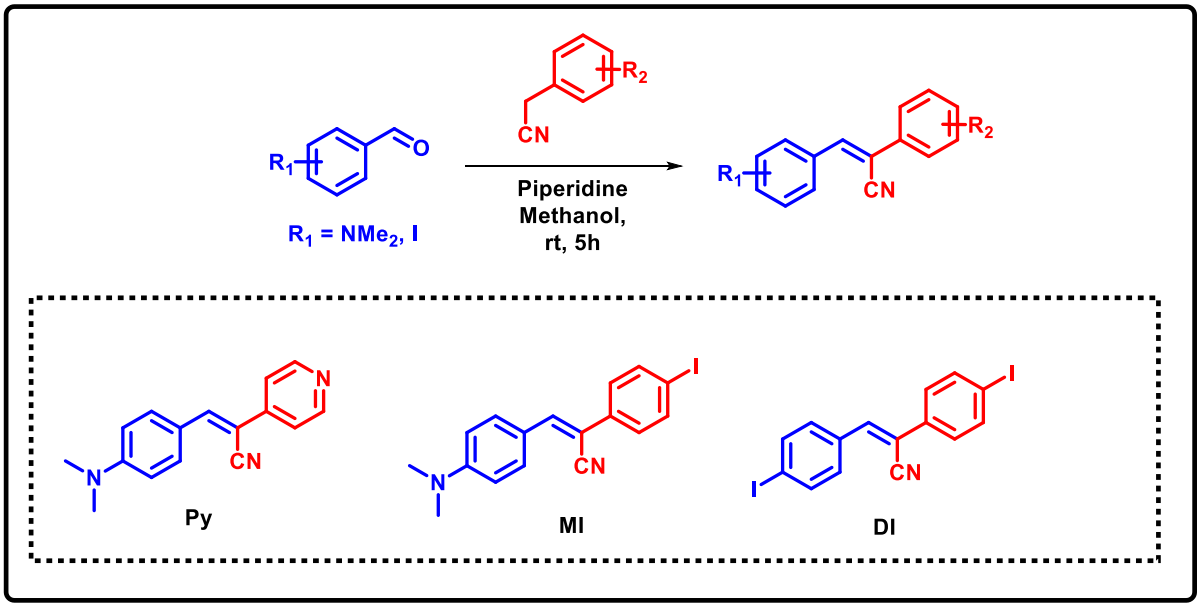


Figure S11 : A), B) & C) Angular Sweep measurements of Py, Py+MI, and Py+DI, respectively. D), E) & F) Time sweep measurements of Py, Py+MI, and Py+DI, respectively.

S12: Detailed Synthetic Procedures

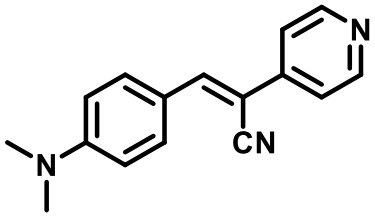


General procedure for Knoevenagel condensation reaction for all three compounds:

The respective phenyl acetonitrile was charged with piperidine in methanol and allowed to stir for 15 min, followed by the addition of respective benzaldehyde for 5h at room temperature to yield the desired α-cyanostilbenes in good yields (Py = 81%, Mi = 90% and DI = 91%). The spectral characterization and spectral copies are given below.

S13: Characterization data ^{1}H, ^{13}C, Mass Spectra

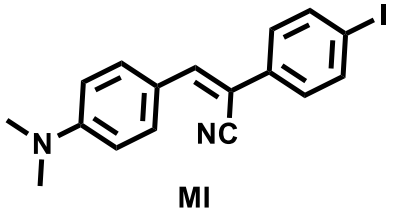
Compound Py:



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.49 (s, 1H), 7.42 (dd, *J* = 4.6, 1.6 Hz, 2H), 6.62 (t, *J* = 6.0 Hz, 2H), 3.00 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.36, 149.25, 143.94, 142.04, 131.22, 119.53, 118.26, 110.54, 99.95, 76.30, 76.05, 75.79, 38.97. Mass- [M+H] Observed: 250.1332

Compound MI:

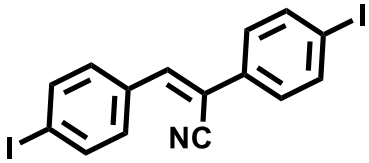


MI

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.22 (m, 3H), 6.60 (d, *J* = 9.0 Hz, 2H), 2.96 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.77, 141.74, 136.84, 134.15, 130.44, 126.00, 120.16, 118.04, 110.53, 102.05, 92.19, 76.28, 76.03, 75.77, 38.99. Mass – [M+H] observed – 375.0342

Compound DI:

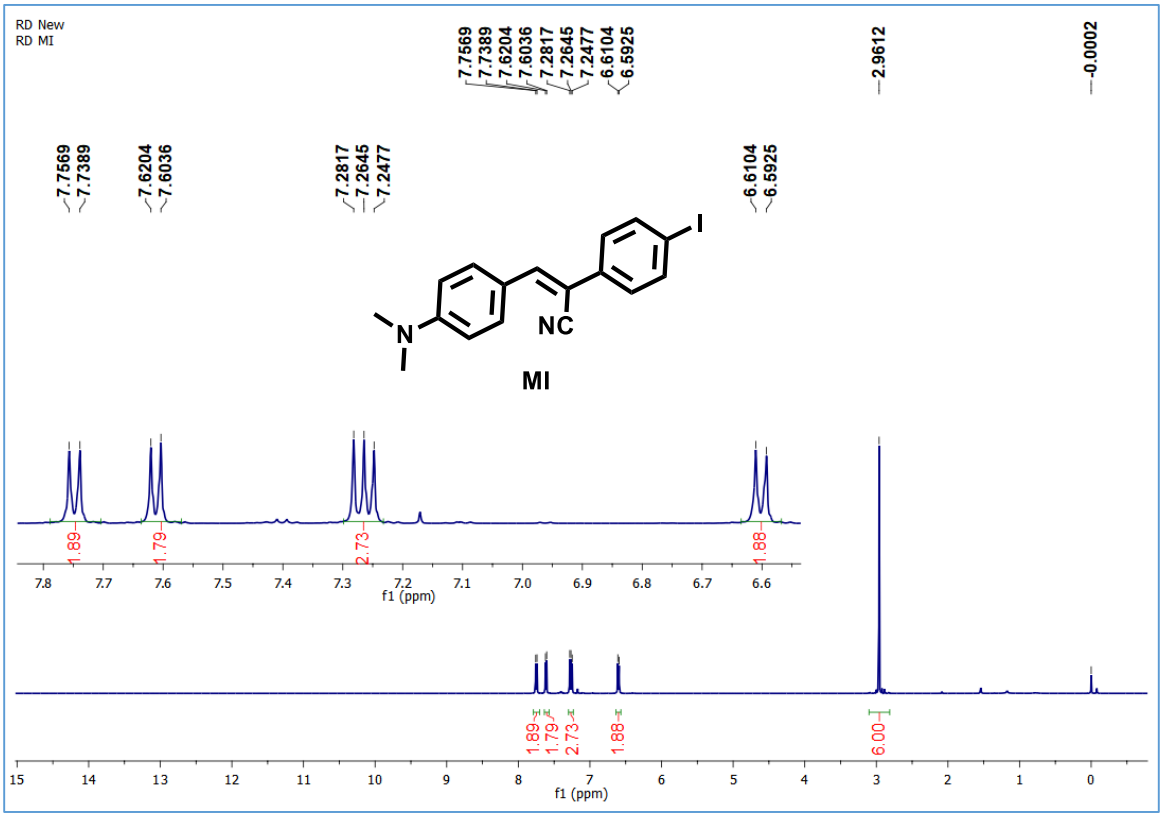


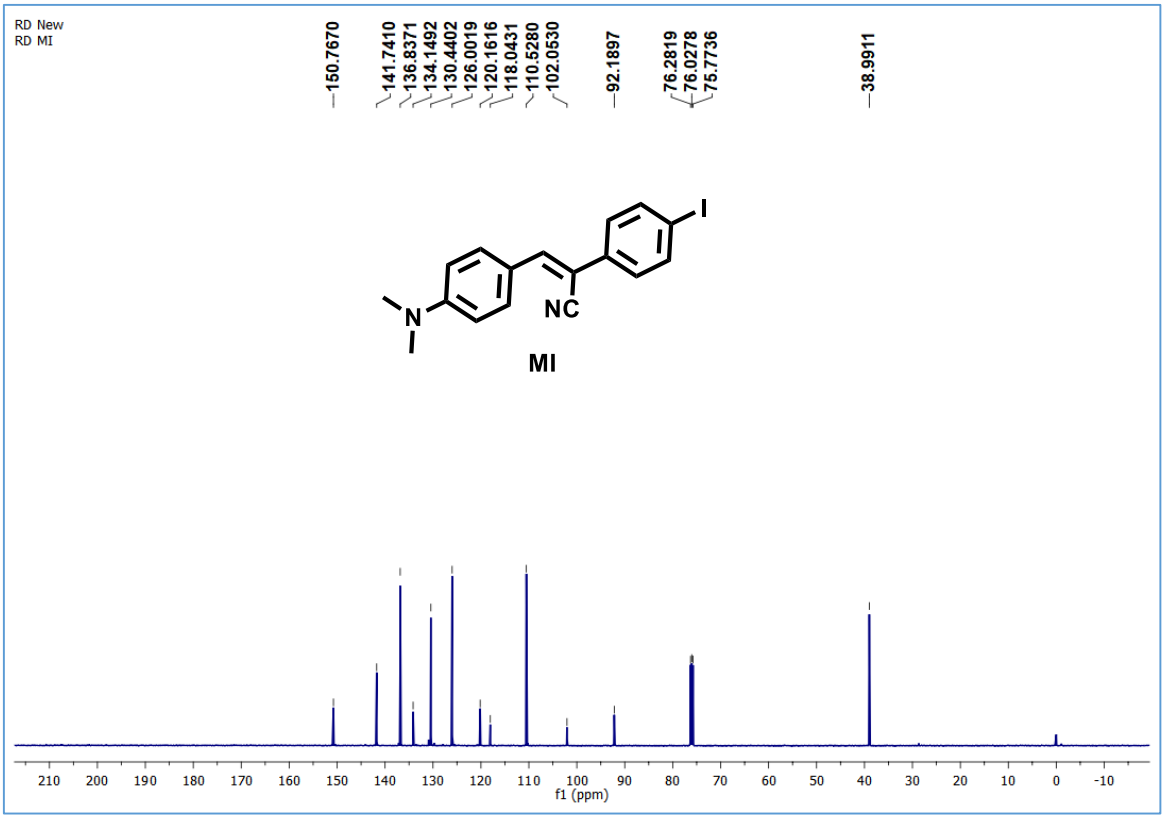
DI

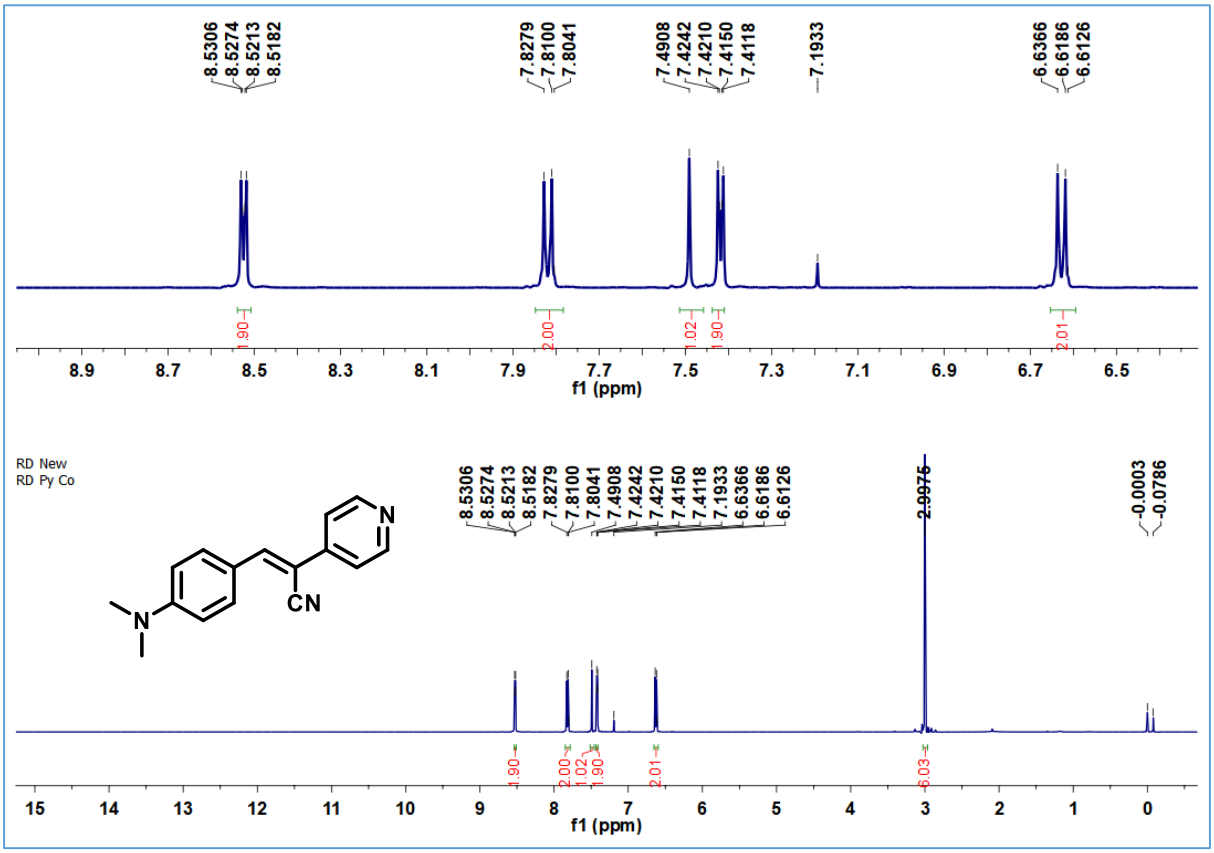
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 15.1, 8.4 Hz, 4H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.34 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.08, 137.21, 137.19, 132.58, 131.72, 129.61, 126.48, 116.23, 110.37, 96.42, 94.46, 76.28, 76.03, 75.78. Mass- [M+H] Observed:457.00

S14: Spectral copies



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1.02
1.90
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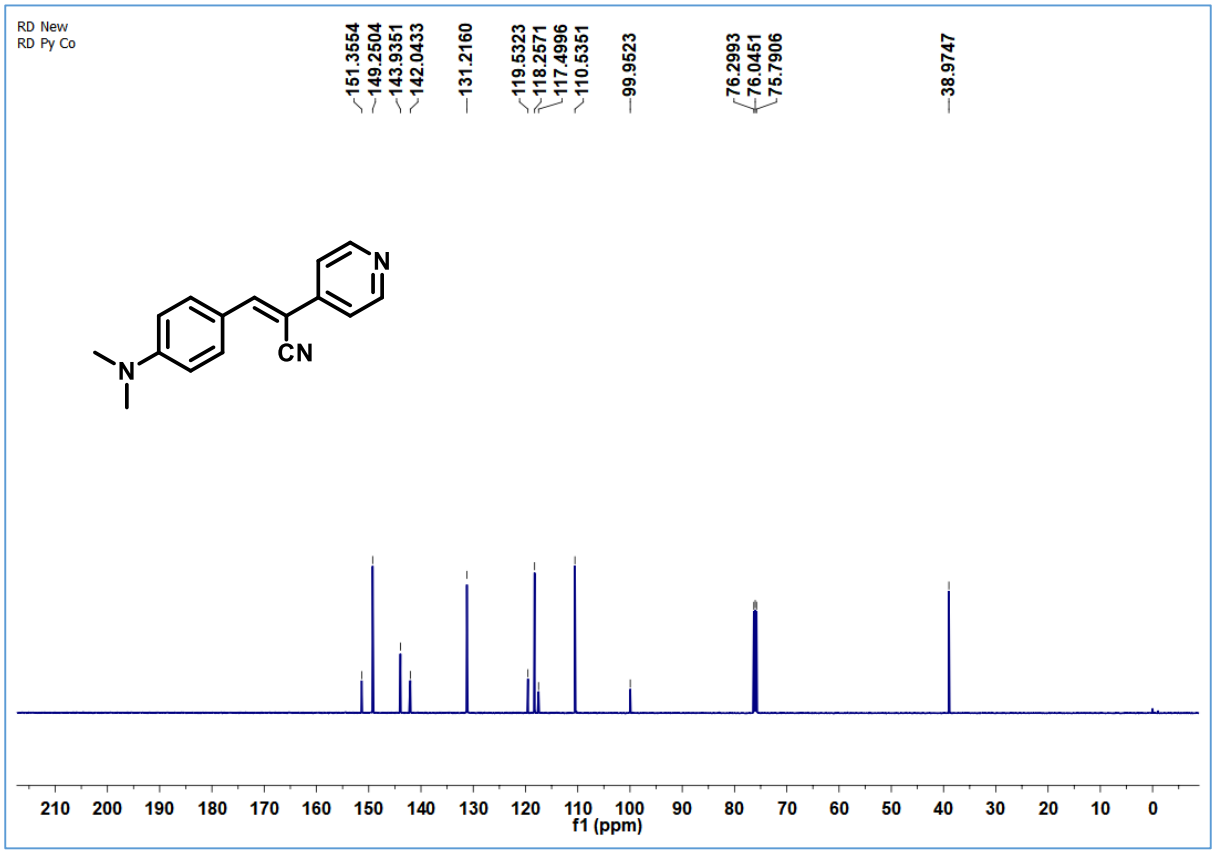
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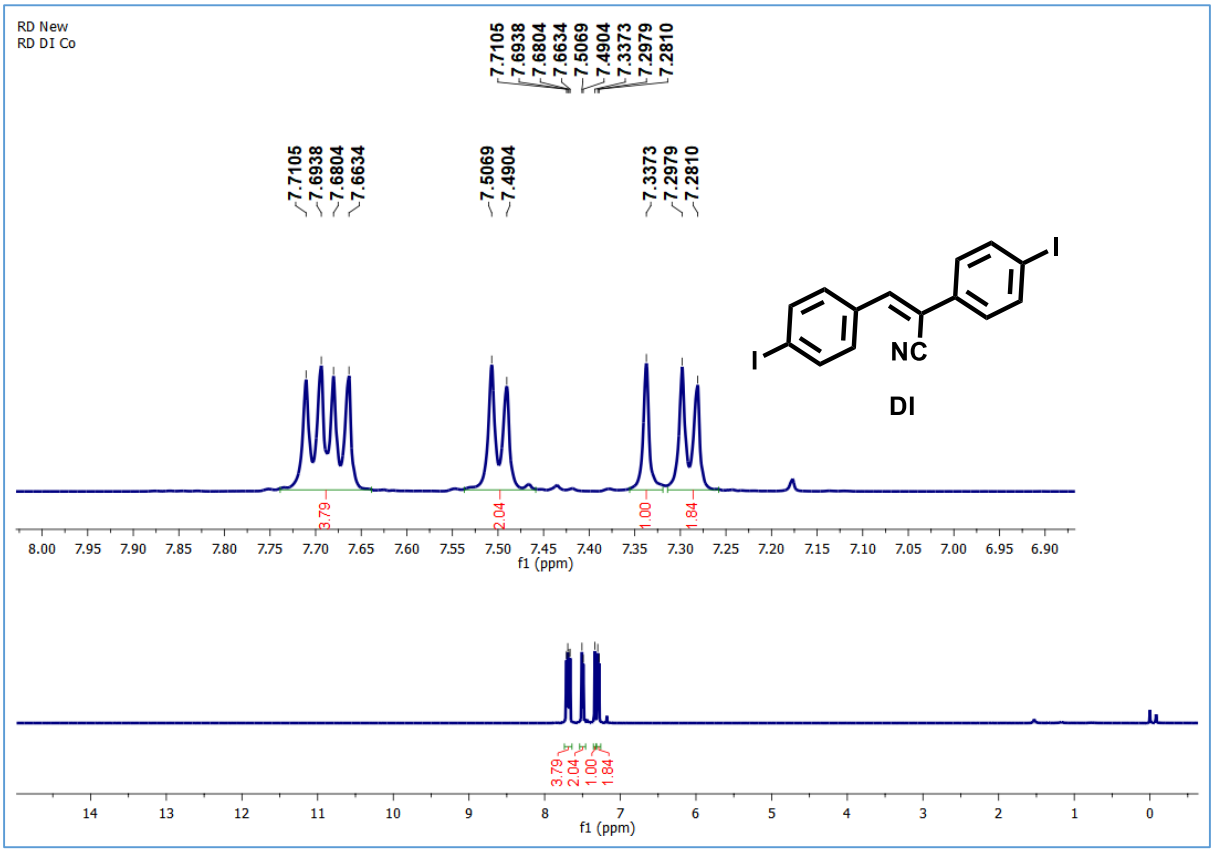
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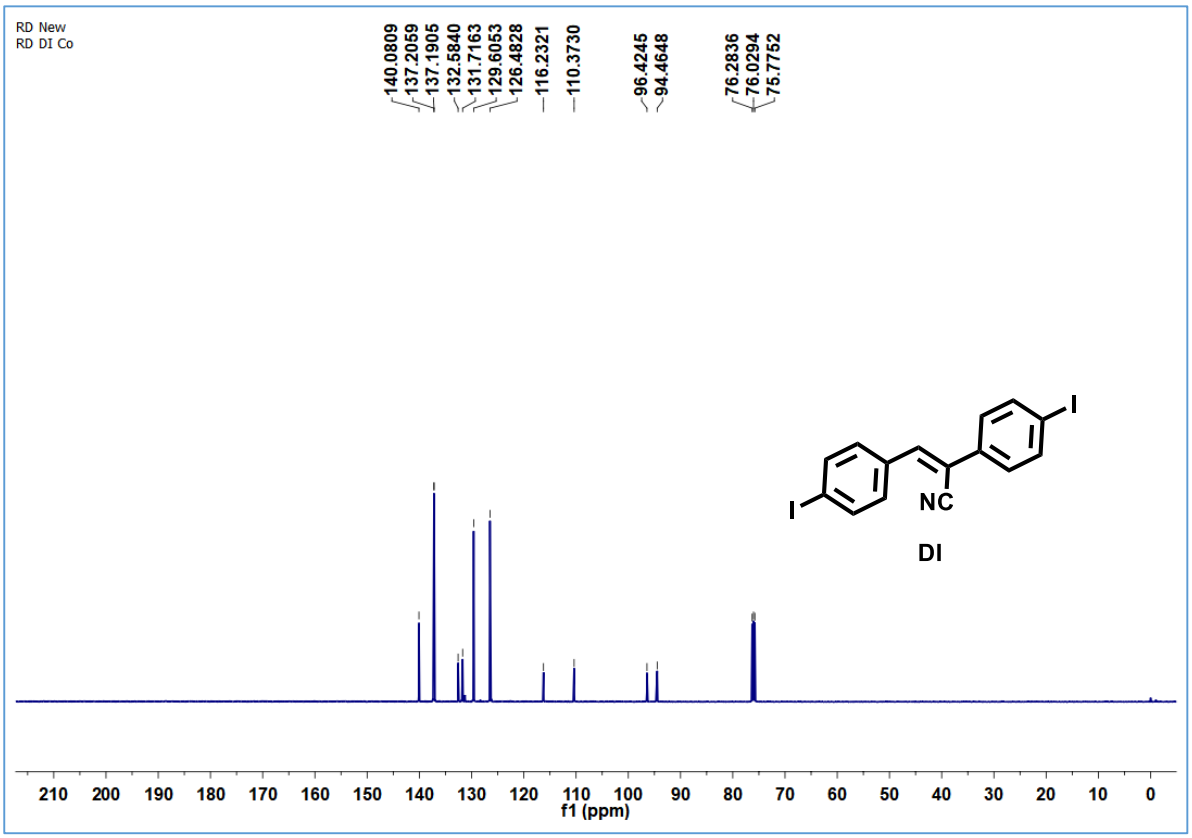
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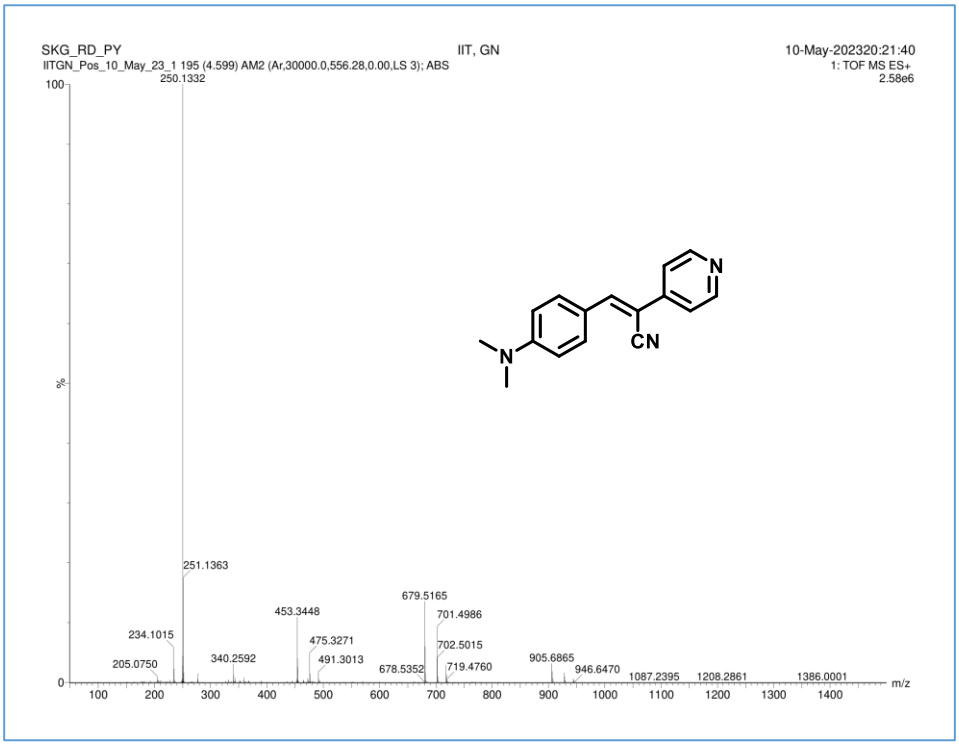
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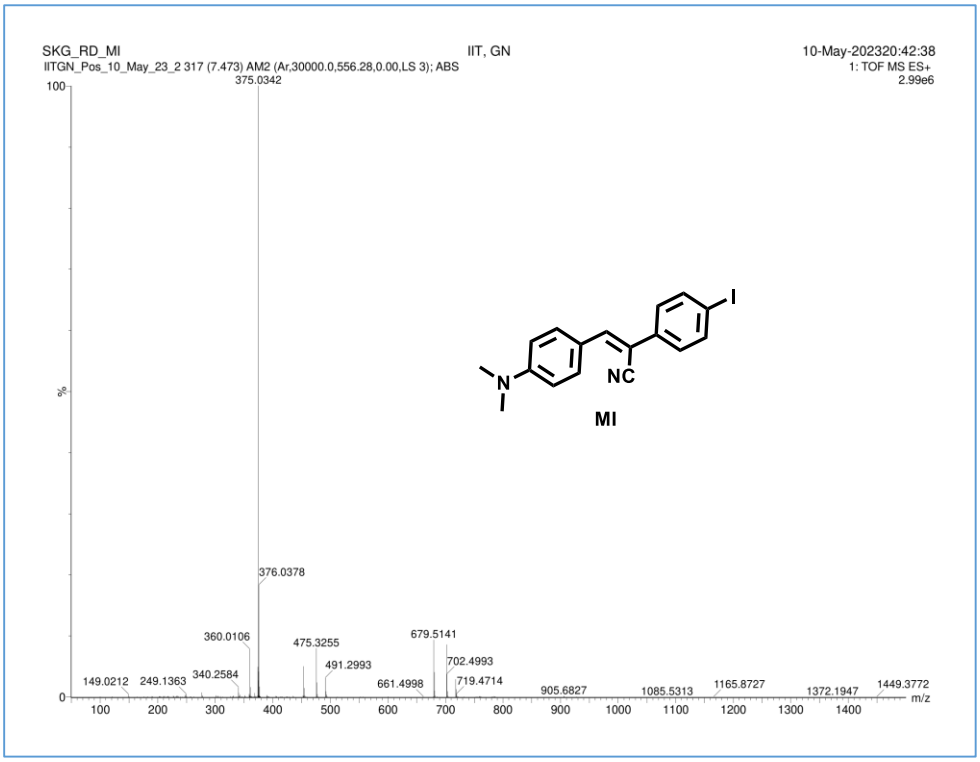
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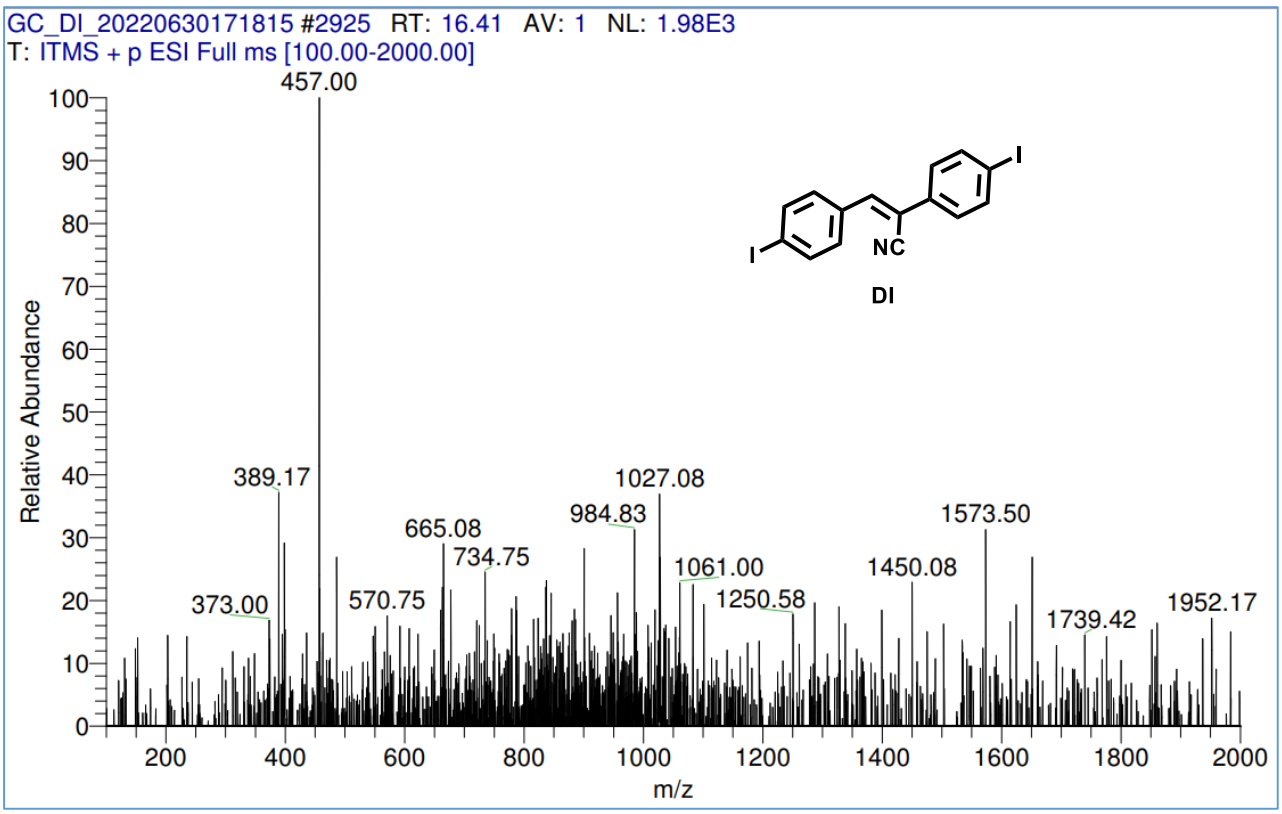
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