Electronic Supporting Information

A Convenient Route to Vinylogous Dicyano Aryl Based AIEgen with Switchable Mechanochromic Luminescence Property

Saurajit Ghosh[a], Himanshi Bhambri[b], Ajeet Kumar Singh[c], Sanjay K. Mandal[b], Lisa Roy[c] and Partha Sarathi Addy[a*]

[a] *Birla Institute of Technology and Science Pilani, Pilani Campus, Department of Chemistry, Pilani, Rajasthan 333031, India.*
**E-mail: partha.sarathi@pilani.bits-pilani.ac.in; ORCID: 0000-0002-0516-7307*
[b] *Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Mohali, Punjab 140306, India*
[c] *Institute of Chemical Technology Mumbai, IOC Odisha Campus Bhubaneswar, IIT Kharagpur Extension Centre, Bhubaneswar 751013, India*

Contents

1. Supplementary Tables

Table S.1.1: Solvatochromic information of DCPV and BIDCPV

Compound	**Solvent**	**$\lambda_{abs.}$ (UV-VIS) (nm)**	**ϵ ($Mol^{-1}L\ cm^{-1}$)**
DCPV	Toluene	425	11377
	Chloroform	420	37310
	Acetonitrile	440	18663
	DMF	475	14233
	Methanol	450	10780
	Water	430	10646
BIDCPV	Toluene	375	13700
	Chloroform	350	20300
	Acetonitrile	320	23613
	DMF	380	11460
	Methanol	365	13433
	Water	390	9150

Table S.1.2. Crystallographic Data and Structure Refinement Parameters for DCPV and BIDCPV.

Compound	**DPCV**	**BIDCPV·0.5(C_6H_{14})**
Chemical formula	$C_{16}H_{12}N_4$	$C_{26}H_{21}N_4$
Formula weight (g/mol)	260.30	389.47
Temperature (K)	102(2)	100(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	18.742(2)	9.9540(15)
b (Å)	5.2346(5)	27.051(4)
c (Å)	14.0627(14)	7.6877(12)
α (°)	90	90
β (°)	105.787(3)	95.868(6)
γ (°)	90	90
Z	4	4
V ($Å^3$)	1327.6(2)	2059.2(5)
Density (g/cm^3)	1.302	1.256
μ (mm^{-1})	0.644	0.591
F(000)	544	820
θ (°) Range for data coll.	2.45 to 66.70	4.465 to 66.734
Reflections collected	19721	29626
Independent reflections	2344	3638
Reflections with I >2σ(I))	2237	3253
R_{int}	0.0722	0.0838
No. of parameters refined	197	244
GOF on F^2	1.075	1.056
Final R_1[a]/wR_2[b] (I >2σ(I))	0.0422/0.1031	0.0496/0.1378
R_1[a]/wR_2[b] (all data)	0.0486/0.1045	0.0535/0.1435
Largest diff. peak and hole ($eÅ^{-3}$)	0.318 and -0.26	0.259 and -0.212

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma 2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S.1.3. Hydrogen Bonding Parameters for DCPV.

D-H···A (Å)	r(D-H) (Å)	r(H···A) (Å)	r(D···A) (Å)	∠D-H···A (deg)
N(1)-H(1a)···N(3)	1.009	2.191	3.156	159.33
N(1)-H(1b)···N(3)	1.013	2.278	3.207	151.84
C(6)-H(6)···N(3)	1.072	2.731	3.613	139.38
N(2)-H(2a)···N(1)	1.020	2.574	3.521	154.29
N(2)-H(2b)···N(2)	1.008	2.478	3.444	160.42
C(3)-H(3)···N(2)	1.077	2.702	3.648	146.32

Table S.1.4. Theoretical and Experimental HOMO - LUMO Energy gap of DCPV and BIDCPV

	DCPV			BIDCPV		
	HOMO (eV)	**LUMO (eV)**	**ΔE (eV)**	**HOMO (eV)**	**LUMO (eV)**	**ΔE (eV)**
Experimental	**- 5.60**	**- 3.35**	**2.25**	**- 5.50**	**- 2.40**	**3.10**
B3LYP / 6-31+G**	**- 5.56**	**- 2.60**	**2.96**	**- 6.22**	**- 2.74**	**3.48**
M06 / 6-31+G**	**- 5.85**	**- 2.45**	**3.40**	**- 6.50**	**- 2.58**	**3.92**
PBE1PBE / 6-31+G**	**- 5.79**	**- 2.54**	**3.25**	**- 6.48**	**- 2.67**	**3.81**

2. Supplementary Figures

2.1 Solid State Fluorescence Spectra and Images

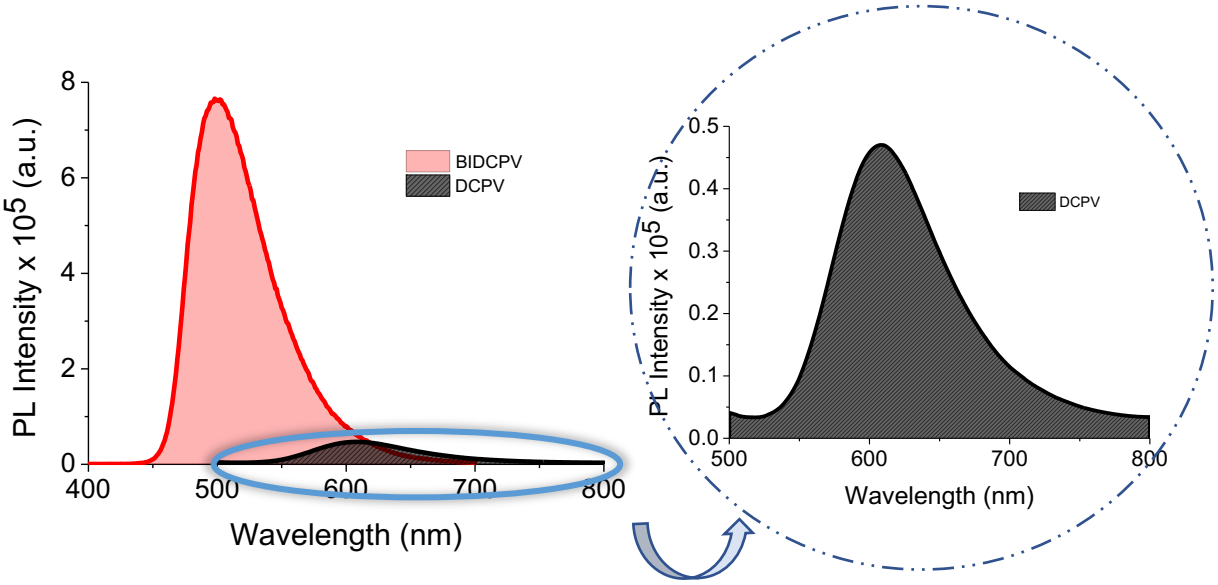


Figure S.2.1.1: Solid State Fluorescence comparison of DCPV and BIDCPV.

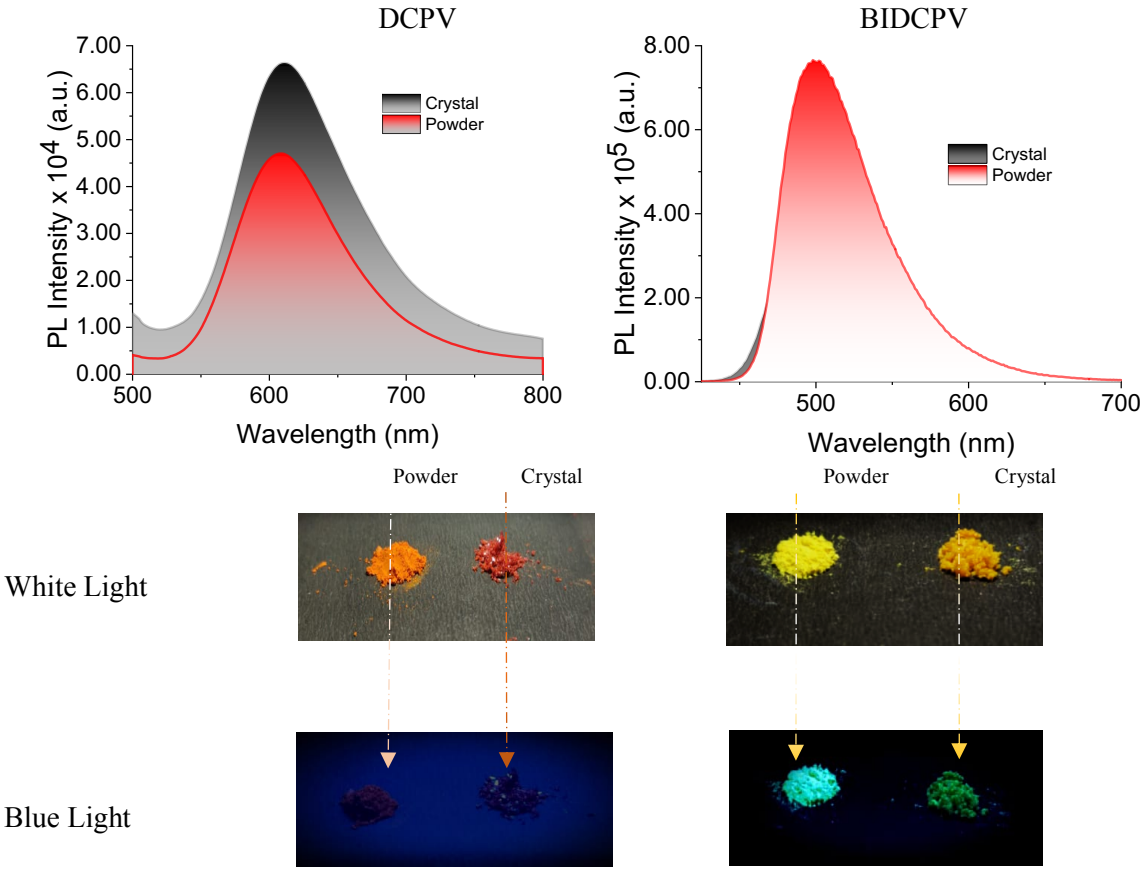


Figure S.2.1.2: Crystal and Powder form Solid State Fluorescence comparison of DCPV and BIDCPV.

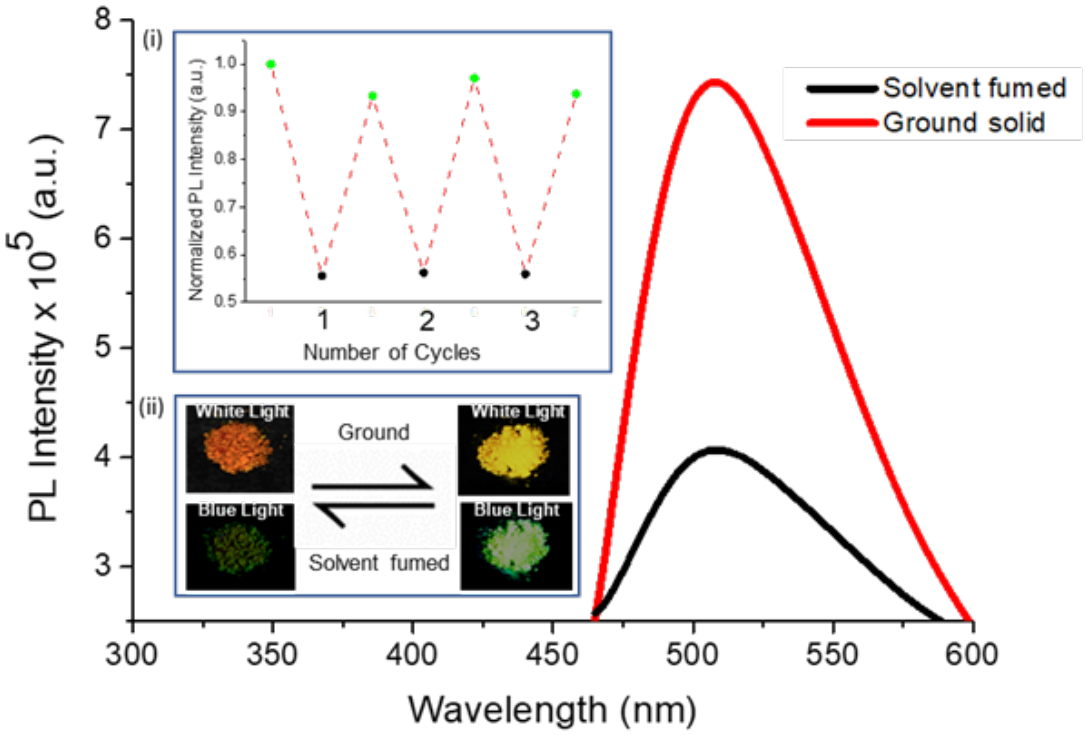


Figure S.2.1.3: Comparison of solid state fluorescence of BIDCPV in solvent fumed crystalline and ground form. Inset – (i) Fluorescence switchability of BIDCPV by solvent fuming / ground and (ii) White and Blue light pictures of Dark and Bright fluorescence states of BIDCPV tuned by Solvent Vapour.

2.2 AIE Assay Plots

- DCPV (Graph legends represents Water %) :

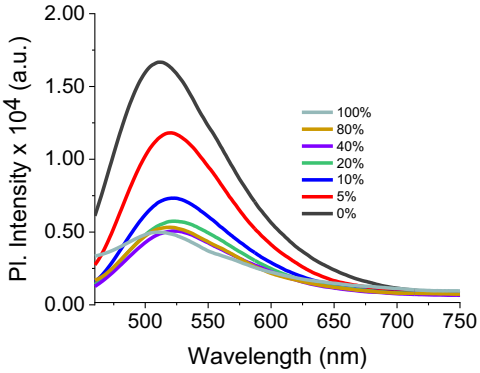


Figure S.2.2.1: DCPV AIE study in Fluorescence

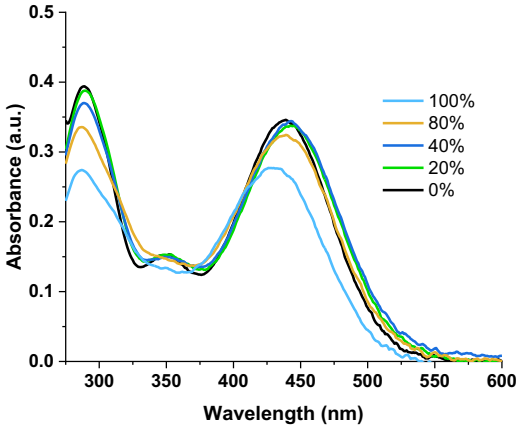


Figure S.2.2.2: DCPV AIE Study in UV

- BIDCPV (Graph legends represents Water %)

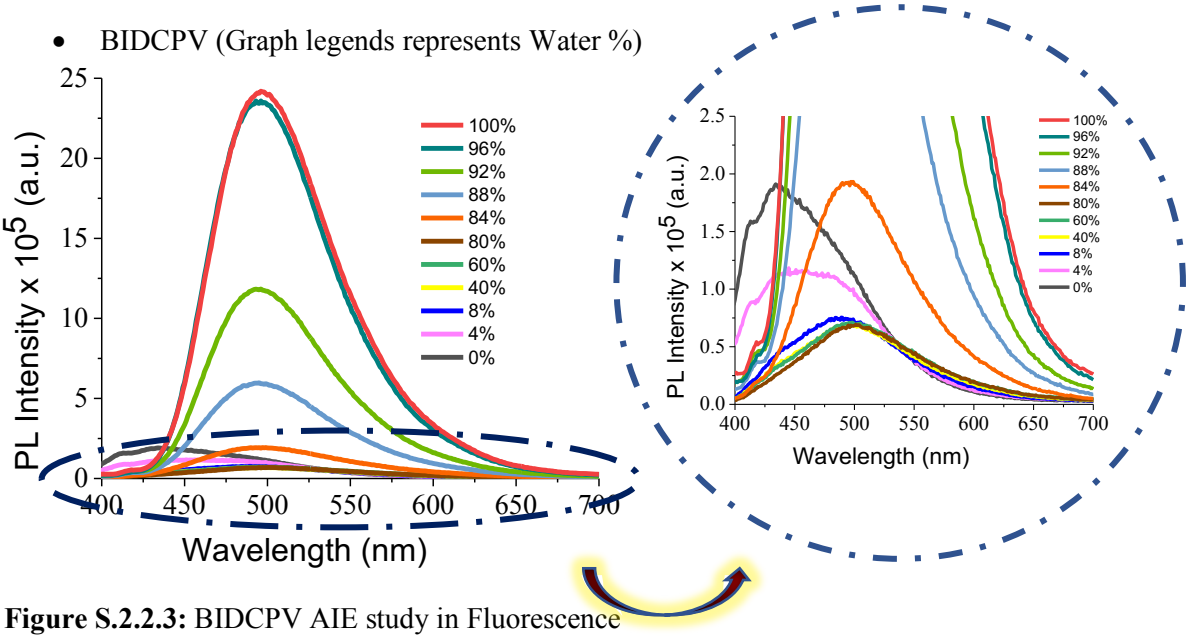


Figure S.2.2.3: BIDCPV AIE study in Fluorescence

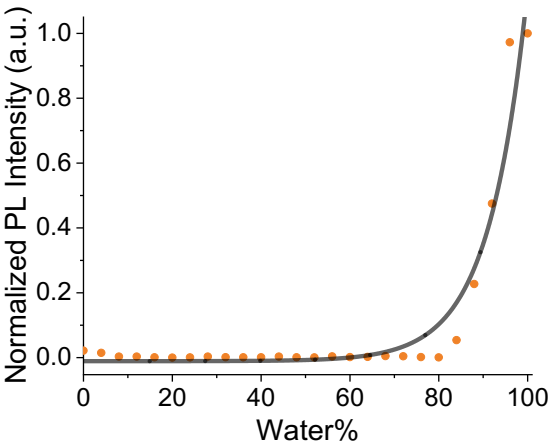


Figure S.2.2.4: Relative increase in Fluorescence due to Aggregation

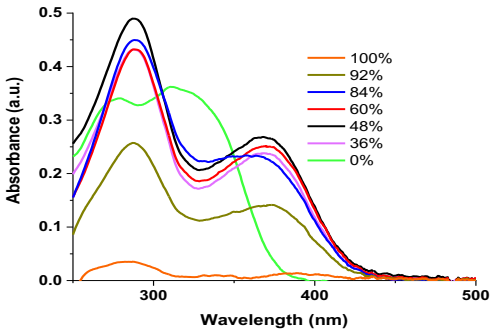
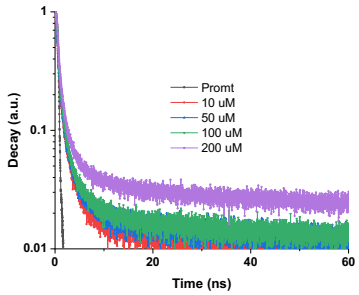


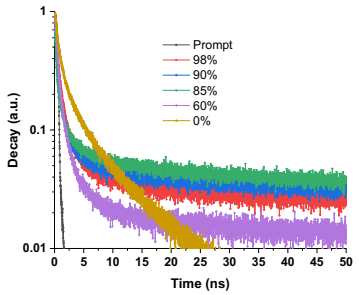
Figure S.2.2.5: BIDCPV AIE study in UV

2.3 Fluorescence Lifetime (TCSPC) Plots



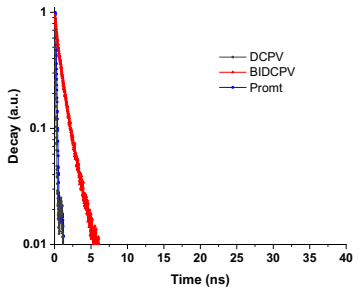
Conc. (µM)	Average Lifetime (ns)
	T_1
10	0.3
50	0.3
100	0.95
200	11.9

Figure S.2.3.1: Fluorescence lifetime data of BIDCPV in water at different concentrations



% Of water	Average Lifetime (ns)
	T_1
0	1.1
60	0.18
85	2.5
90	10
98	11.9

Figure S.2.3.2: Fluorescence lifetime data of BIDCPV in different percentages of Acetonitrile -Water Solvent system (Legends represents percentage of Water)



Compound	Average Lifetime (ns)	
	T_1	T_2
DCPV	1.0	0.1
BIDCPV	0.9	4.1

Figure S.2.3.3: Solid State Fluorescence lifetime data of DCPV and BIDCPV

2.4 PXRD Plots:

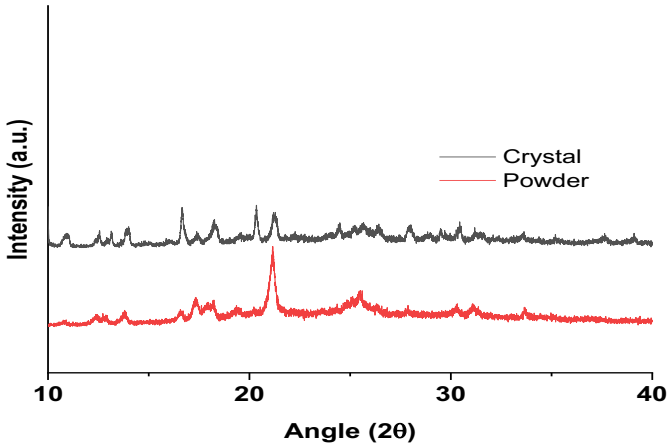


Figure S.2.4.1: PXRD data of Crystal and powdered samples of DCPV

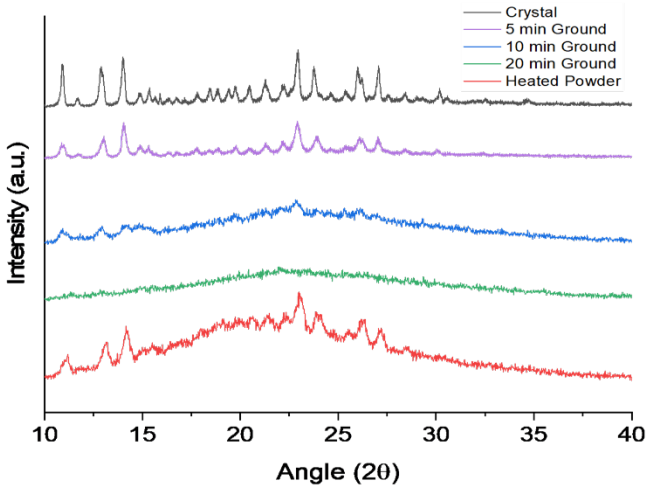


Figure S.2.4.2: PXRD data for confirmation of heat reversibility of crystallinity for BIDCPV

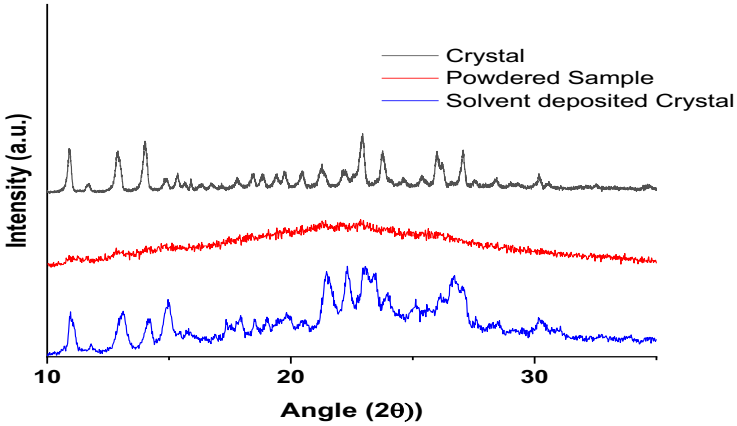


Figure S.2.4.3: PXRD data of BIDCPV for confirmation of reversibility of crystallinity by DCM vapour deposition

2.5 Field Emission Scanning Electron Microsocopy (FESEM) Images

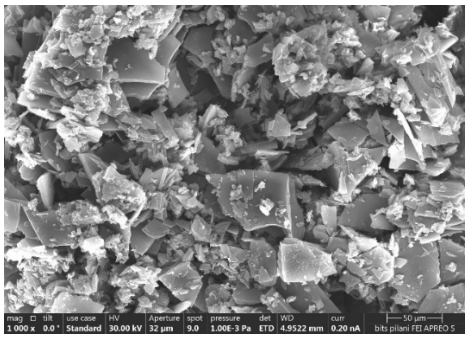


Figure S.2.5.1: DCPV Crystalline sample

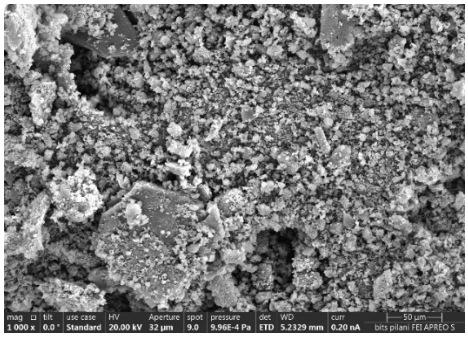


Figure S.2.5.2: DCPV powdered sample

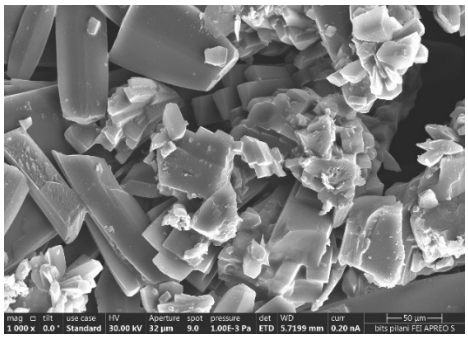


Figure S.2.5.3: BIDCPV Crystalline sample

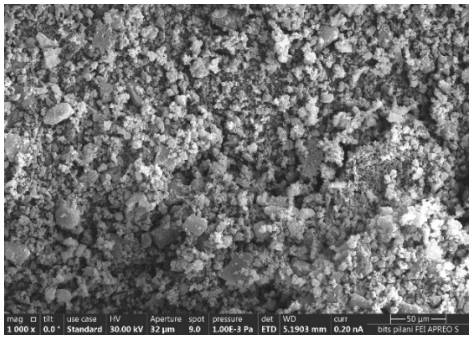


Figure S.2.5.4: BIDCPV powdered sample

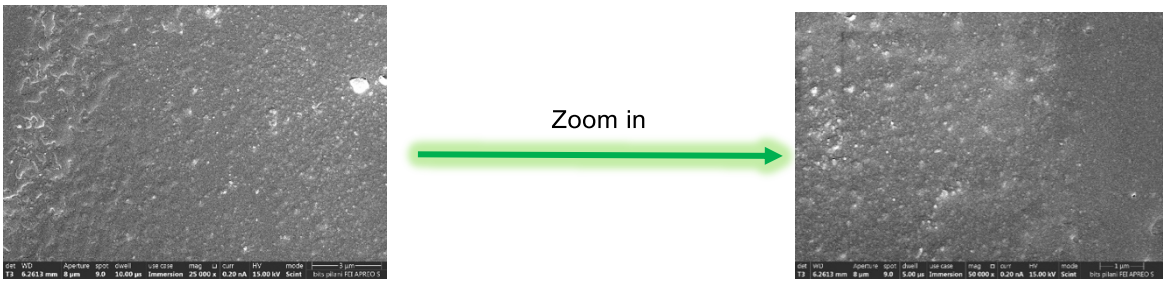


Figure S.2.5.5: Solvent evaporated BIDCPV FESEM image in Chloroform

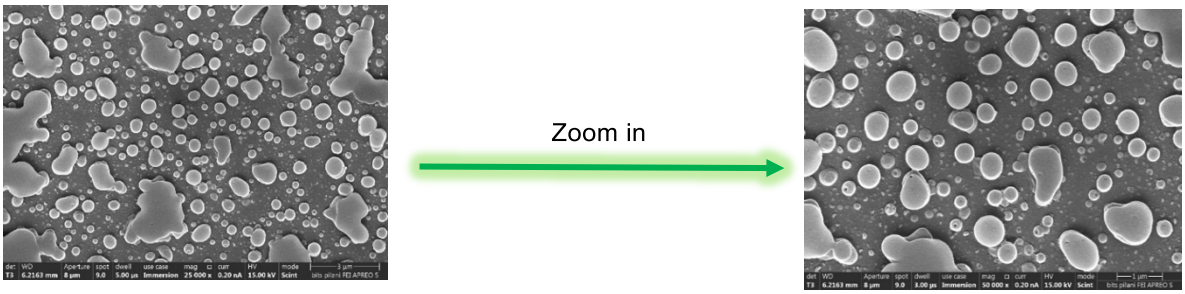


Figure S.2.5.6: Solvent evaporated BIDCPV FESEM image in Water

- BIDCPV FESEM images in different Phases

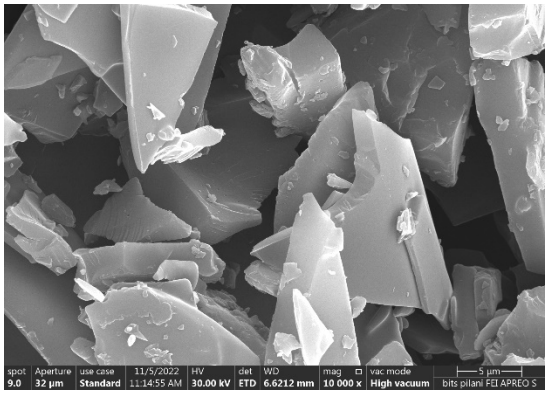


Figure S.2.5.7: Pristine

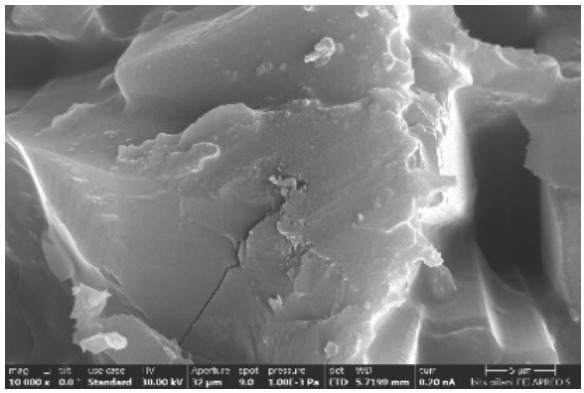


Figure S.2.5.8: Crystal

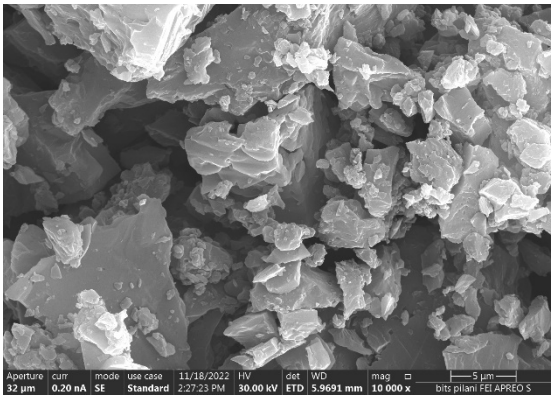


Figure S.2.5.9: Sheared

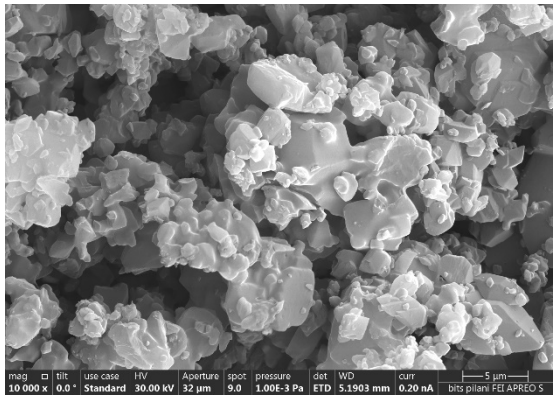


Figure S.2.5.10: Powdered by 20 mins grinding

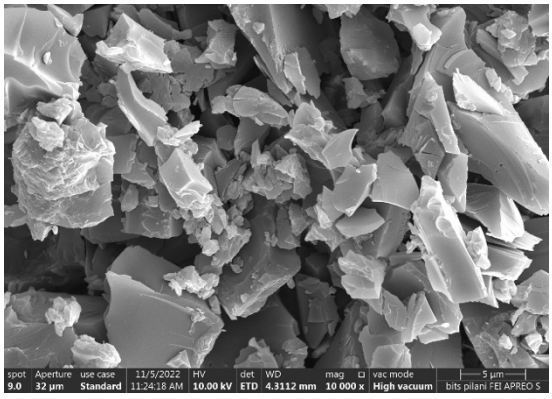


Figure S.2.5.11: Heated powder

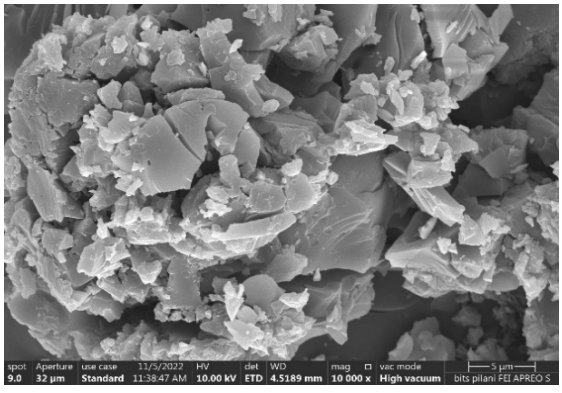


Figure S.2.5.12: Solvent vaporised powder

2.6 DLS Graphs and Data of BIDCPV

Plot of BIDCPV in Chloroform

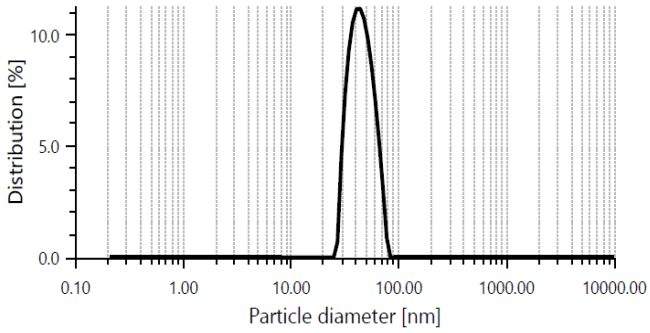


Figure S.2.6.1: Particle Size Distribution (Intensity) plot in Chloroform

Plot of BIDCPV in Water

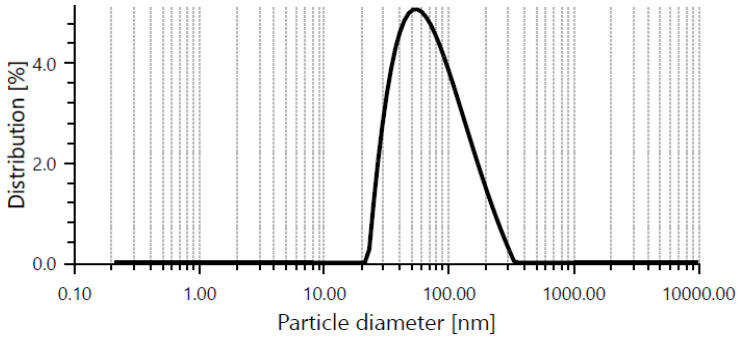


Figure S.2.6.2: Particle Size Distribution (Intensity) plot in Water

Solvent(s)	Parameter(s)		
	Hydrodynamic Diameter (nm)	**Polydispersity Index (%)**	**Diffusion Coefficient ($\mu m^2/s$)**
Chloroform	45.52	9.4	10.8
Water	141.80	971.9	3.5

2.7 Solid State UV-VIS spectra:

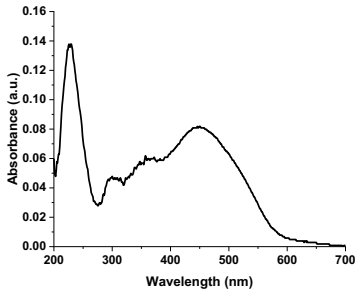


Figure S.2.7.1: Solid state UV spectra for DCPV

Compound	Solid State UV λ_{max} (nm)
DCPV	450
BIDCPV	370

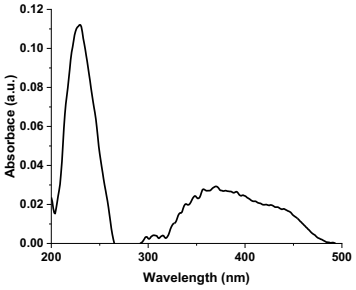


Figure S.2.7.2: Solid state UV spectra for BIDCPV

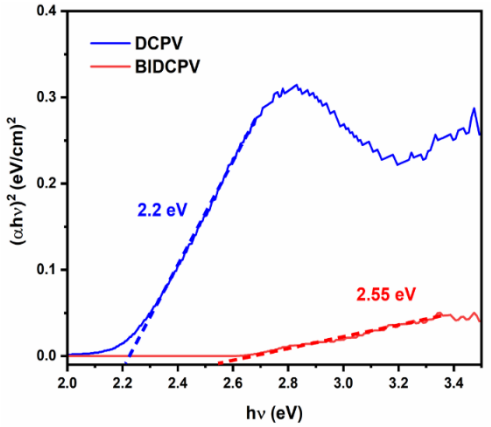


Figure S.2.7.3: In Solid state HOMO-LUMO energy gap of DCPV (blue) and BIDCPV (red) from DRS data.

2.8 Pl. Spectra for BIDCPV in water having varied concentration

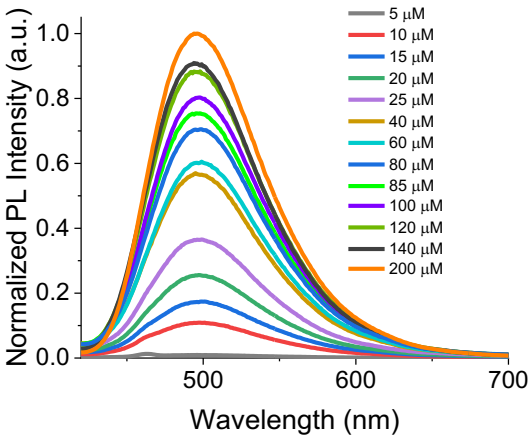


Figure S.2.8.1: Normalized Pl. spectra of BIDCPV in water having different concentration

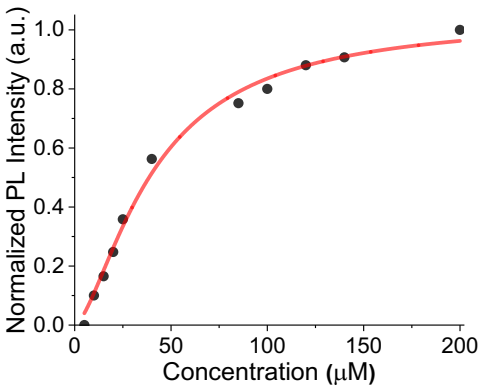


Figure S.2.8.2: Relative enhancement of Fluorescence with inc. in concentration of BIDCPV in Water

2.9 Thermogravimetric Analysis (TGA) Plots:

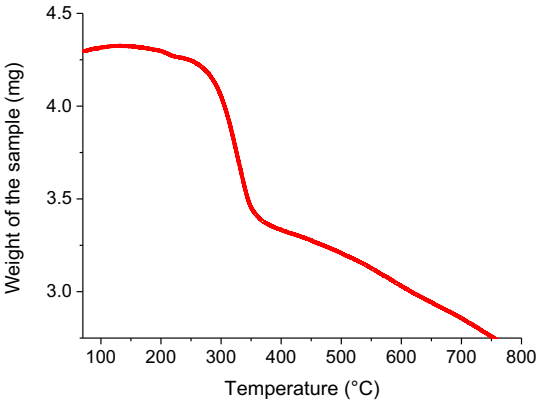


Figure S.2.9.1: Representative TGA graph of DCPV

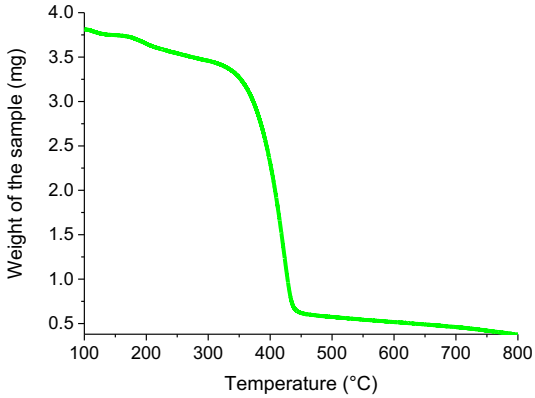


Figure S.2.9.2: Representative TGA graph of BIDCPV

2.10 Cyclic Voltametry (CV) Curves:

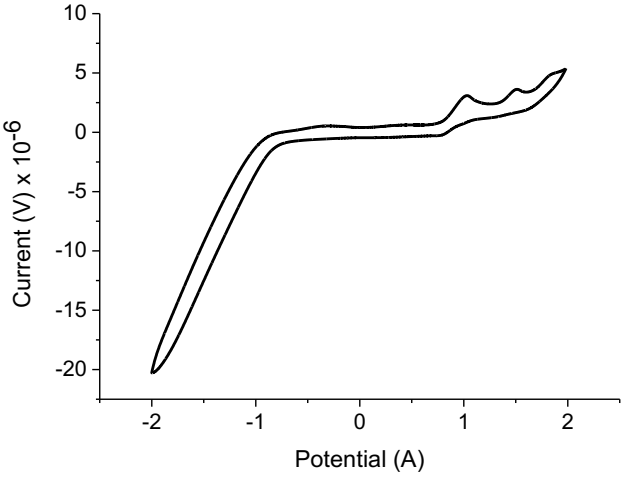


Figure S.2.10.1: Representative CV Plot of DCPV

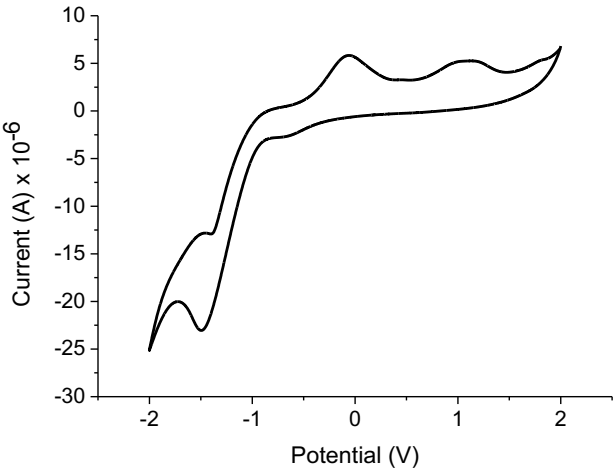


Figure S.2.10.2: Representative CV Plot of BIDCPV

2.11 UV-vis Plots of DCPV and BIDCPV in different solvents:

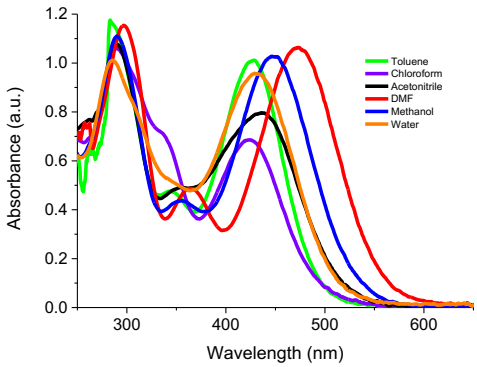


Figure S.2.11.1: UV-Vis Absorbance spectra of DCPV in different solvents

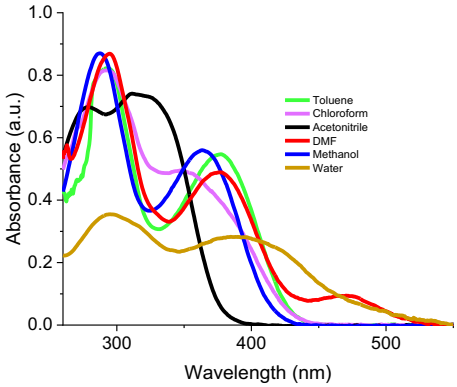
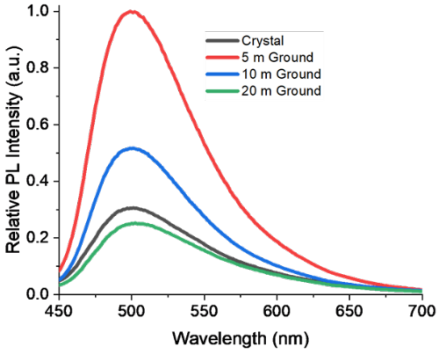


Figure S.2.11.2: UV-Vis Absorbance spectra of BIDCPV in different solvents

2.12 Solid state PL. spectra and PLQY values of different states of BIDCPV during grinding



Time of grinding	PLQY
0 min	0.17
5 min	0.52
10 min	0.26
20 min	0.14

Figure S.2.12.1: Fluorescence Emission spectra of different states of BIDCPV during grinding.

3. Single Crystal X-ray Diffraction Study

In each case, a suitable crystal was chosen with the help of a light microscope and was mounted in a nylon loop to attach to a goniometer head, which was then placed under nitrogen gas flow for slow cooling to 100 K. A Kappa APEX II diffractometer equipped with sealed-tube monochromated Cu Kα radiation was used for the entire measurement (centering, initial crystal evaluation, and data collection) by the program APEX3.[S1] All data were integrated, and reflections were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by using the program SAINT.[S1] Finally, data were also corrected for the Lorentz and polarization effects. Using the subroutine XPREP[S1] the space group was determined, and an absorption correction (SADABS)[S1] and merging of data were performed to generate the necessary files for solution and refinement. A structure solution was obtained by direct methods using the SHELXS program of the SHELXTL package and was refined using SHELXL.[S2] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, unless otherwise stated, were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. Non-spherical form factors were used in the refinement of **DCPV**. [S3] The disordered guest methanol molecules (1.25 molecules per molecule of BIDCPV) in **BIDCPV** were modelled appropriately.[S4] All figures were drawn using Mercury V 3.10.2[S5] The hydrogen bonding parameters were generated using PLATON.[S6] The final positional and thermal parameters of the non-hydrogen atoms for all structures are given in the CIF files.

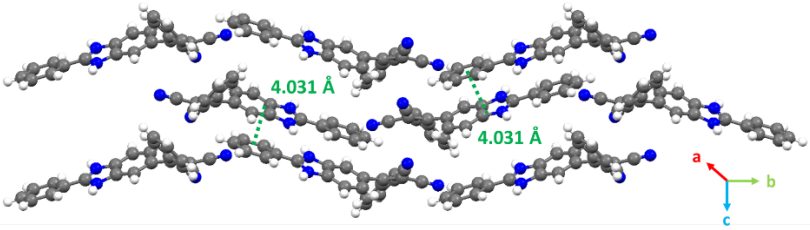


Figure S.3.1.1: Stacking pattern of layers in BIDCPV.

References

[S1] APEX3, SADABS, and SAINT, Bruker AXS Inc., Madison, WI, USA, 2015.

[S2] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2015, **71**, 3-8.

[S3] F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, M. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkoetter-Stock, S. Steinhauer, D. Lentz, H. Puschmann, S. Grabowsky, *Chem. Sci.*, 2021, **12**, 1675-1692.

[S4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement, and analysis program. *J. Appl. Cryst.* 2009, **42**, 339-341.

[S5] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Crystallogr.*, 2008, **41**, 466–470.

[S6] A. L. Spek, *Acta Cryst.* 2009, **D65**, 148-155.

4. Characterization of Compounds

4.1 Characterization of DCPV :

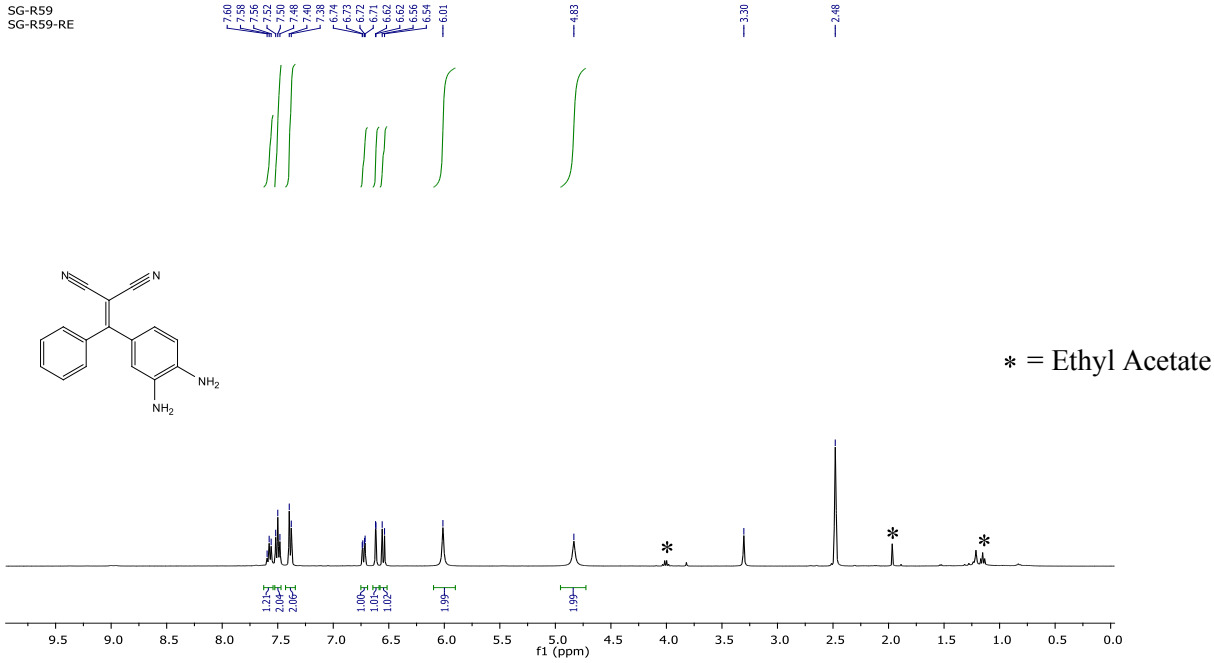


Figure S.4.1.1: ^{1}H NMR data of DCPV

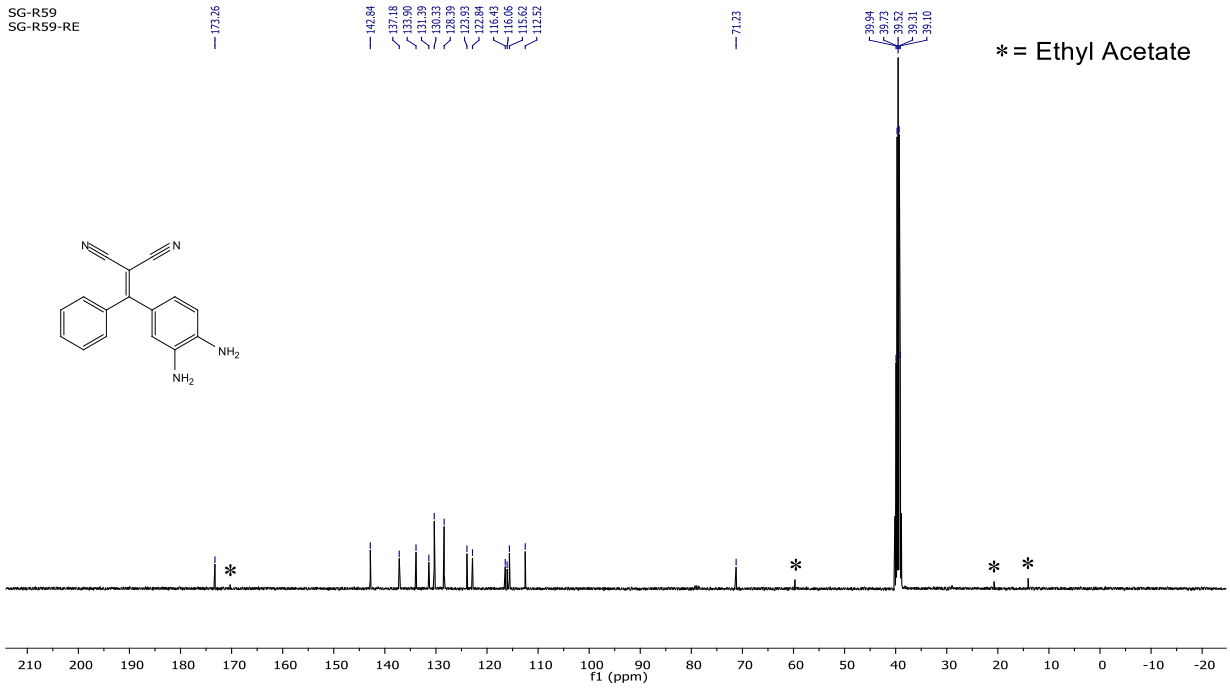
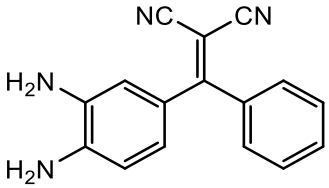


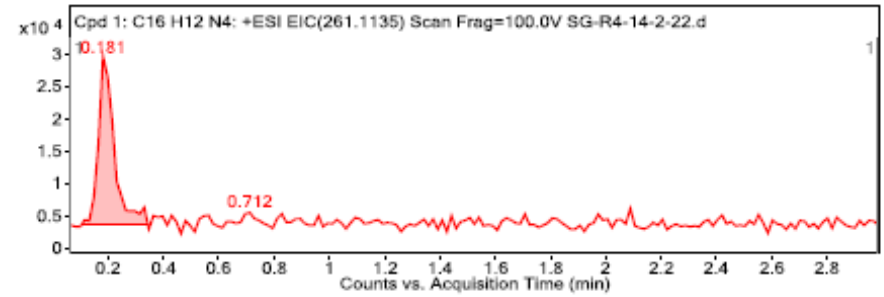
Figure S.4.1.2: ^{13}C NMR data of DCPV

Compound Table

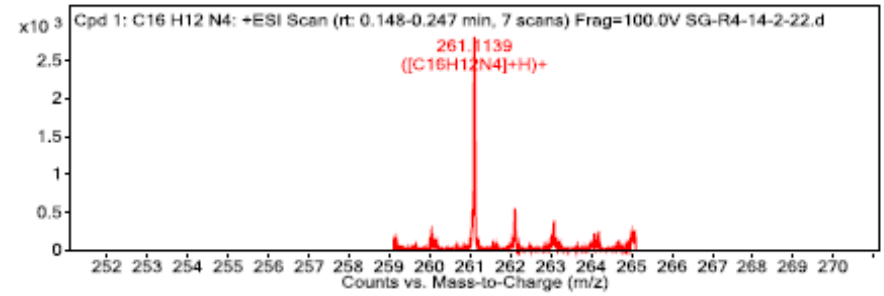
Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C16 H12 N4	0.181	260.1066	2824	C16 H12 N4	260.1062	1.49

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C16 H12 N4	261.1139	0.181	Find By Formula	260.1066





MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
261.1139	261.1135	-1.62	1	2824.13	C16H12N4	(M+H)+
262.1176	262.1164	-4.78	1	559.19	C16H12N4	(M+H)+
263.1147	263.1192	17.16	1	119.86	C16H12N4	(M+H)+

Figure S.*4.1.3:* High Resolution Mass Spectrometry (HRMS) data of DCPV

^{1}H NMR (400 MHz, d_6-DMSO) : δ (ppm) 7.58 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 6.73 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.62 (d, *J* = 1.3 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H), 4.83 (s, 2H).

^{13}C NMR (100 MHz, d_6-DMSO) : δ (ppm) 173.26, 142.84, 173.18, 133.90, 131.39, 130.33, 128.39, 123.93, 122.84, 116.43, 116.06, 115.62, 112.52, 71.23.

HRMS (ESI) for $C_{16}H_{12}N_4$: Calculated $(M+H)^+$ - 261.1135, Found – 261.1139.

Melting Point : 185°C

4.2 Characterization of BIDCPV

NMR of Pristine Compound

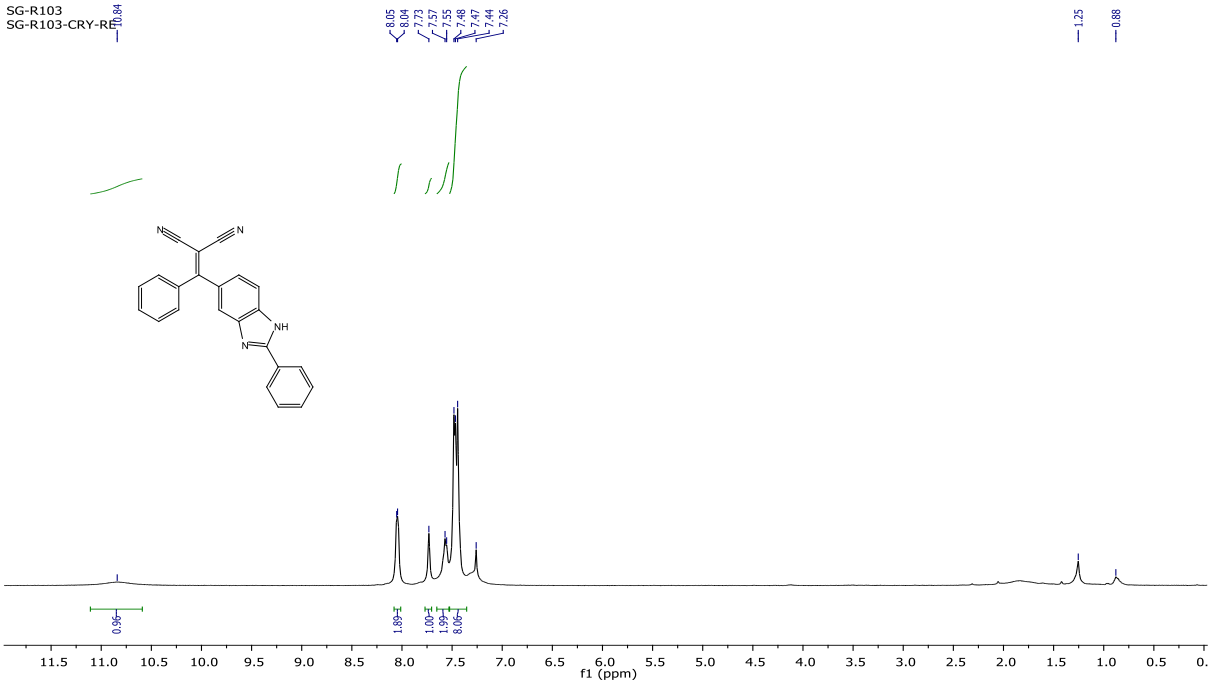


Figure S.4.2.1: ^{1}H NMR data of BIDCPV (Pristine)

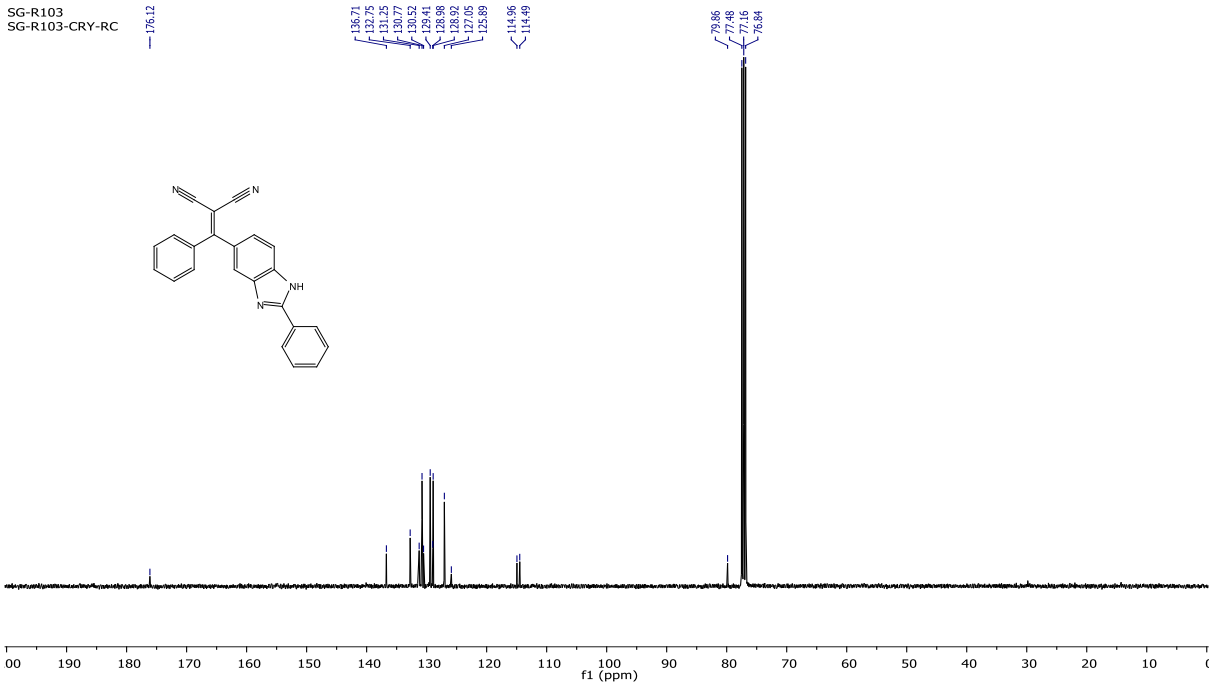


Figure S.4.2.2: ^{13}C NMR data of BIDCPV (Pristine)

NMR of Crystalline compound

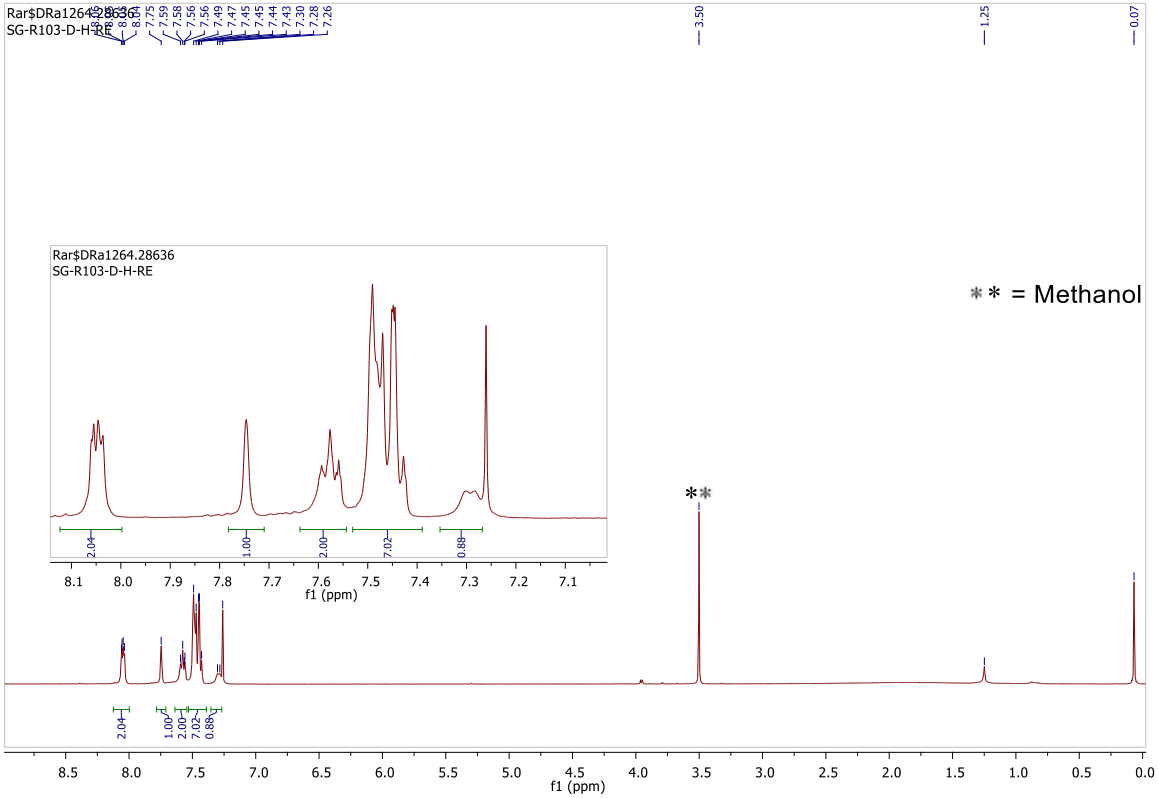


Figure S.4.2.3: ^{1}H NMR data of BIDCPV (Crystalline)

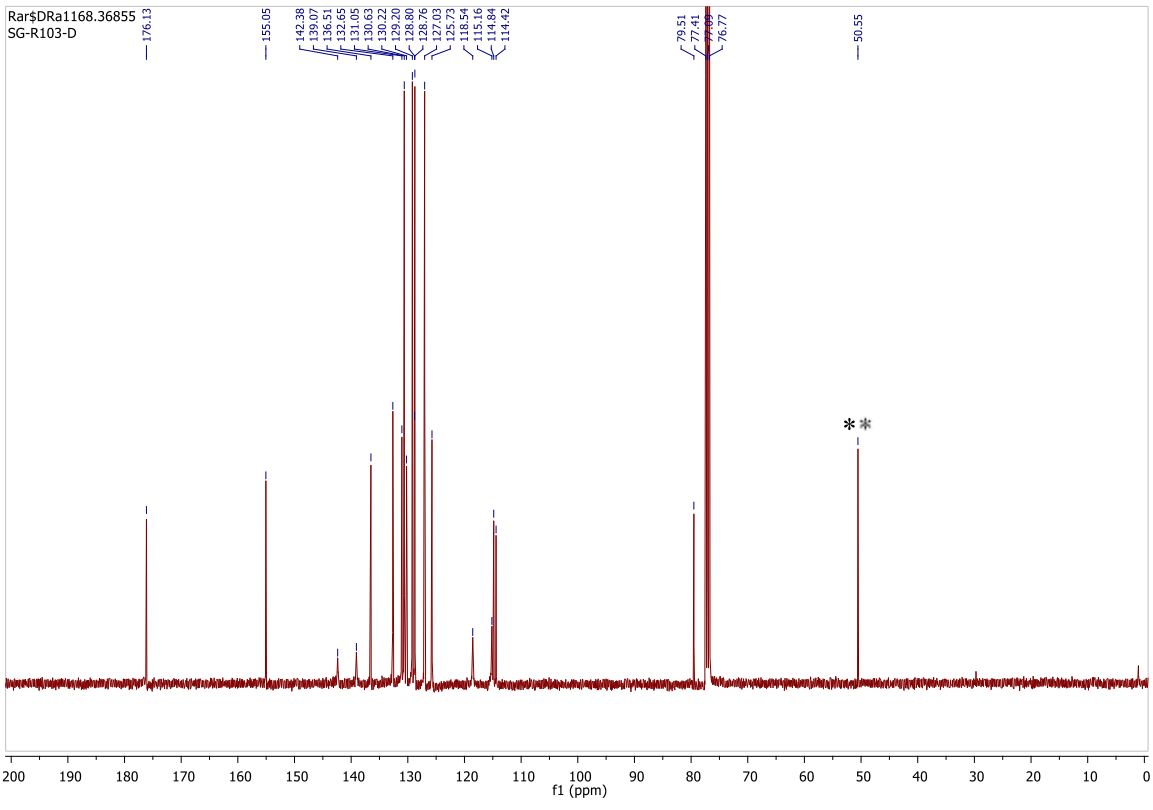
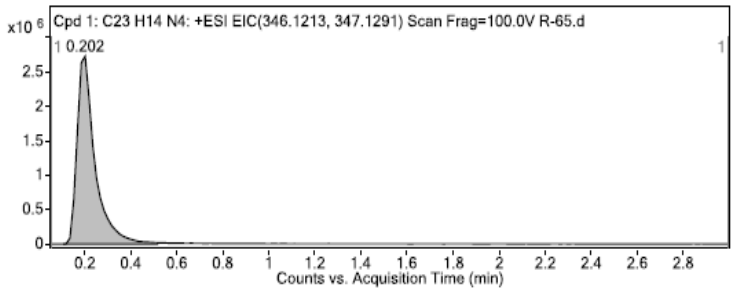


Figure S.4.2.4: ^{13}C NMR data of BIDCPV (Crystalline)

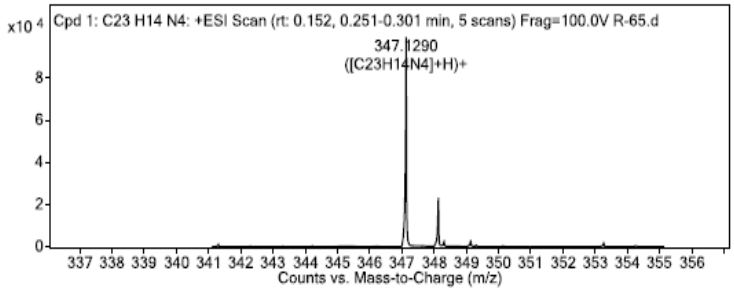
Compound Table

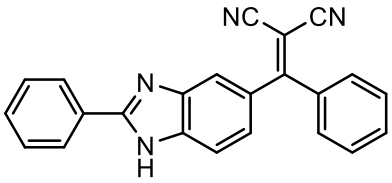
Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C23 H14 N4	0.202	346.1216	99898	C23 H14 N4	346.1218	-0.83

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C23 H14 N4	347.129	0.202	Find By Formula	346.1216



MS Zoomed Spectrum





MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
346.1082	346.1213	37.81	1	103.62	C23H14N4	M+
347.129	347.1291	0.43	1	99898.37	C23H14N4	(M+H)+
348.1314	348.1321	2.02	1	23302.34	C23H14N4	(M+H)+
349.134	349.1352	3.37	1	2812.23	C23H14N4	(M+H)+
350.1371	350.1381	2.98	1	319.78	C23H14N4	(M+H)+

Figure S.4.2.5: High Resolution Mass Spectrometry (HRMS) data of BIDCPV

^{1}H NMR (400 MHz, d-Chloroform) : δ (ppm) 10.84 (s, 1H), 8.05 (d, *J* = 3.5 Hz, 2H), 7.73 (s, 1H), 7.65 – 7.53 (m, 2H), 7.52 – 7.38 (m, 8H).

^{13}C NMR ((100 MHz, d-Chloroform) : δ (ppm) 176.12, 136.71, 132.75, 131.25, 130.77, 130.52, 129.41, 128.98, 128.92, 127.05, 125.89, 114.96, 114.49, 79.86.

HRMS (ESI) for $C_{23}H_{14}N_4$: Calculated $(M+H)^+$ - 347.1291, Found – 347.1290

Melting Point : 122°C

5. Computational Details

All DFT calculations were performed with the Gaussian 09 software.[S7] We selected the hybrid B3LYP functional[2] with 6-31+G** Pople basis set[3] on all atoms. Solvent effects were incorporated using the SMD (Solvation Model based on Density) solvation model[S8] and acetonitrile as solvent. TD-DFT calculations were conducted with optimized geometries, together with the long-range corrected hybrid exchange-correlation functional CAM-B3LYP in acetonitrile solvent, with n states =10 and root =1, as implemented in the Gaussian 09 software using 6-31+G** Pople basis set on all atoms.

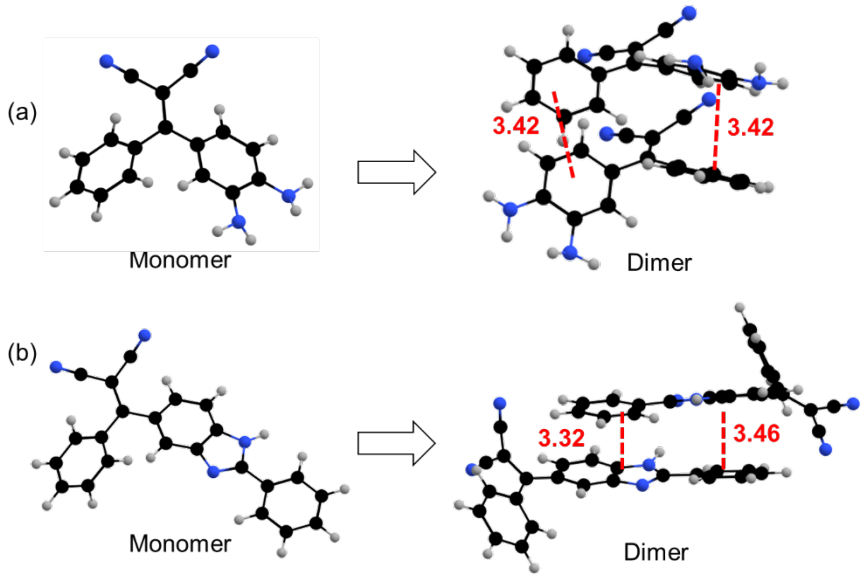


Figure S.5.1: Optimized geometries of all calculated conformers of (a) DCPV and (b) BIDCPV.

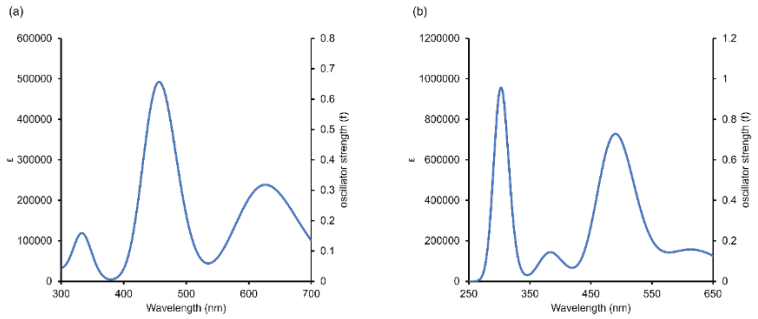


Figure S.5.2: TD-DFT calculated emission spectrum for monomer of (a) DCPV and (b) BIDCPV.

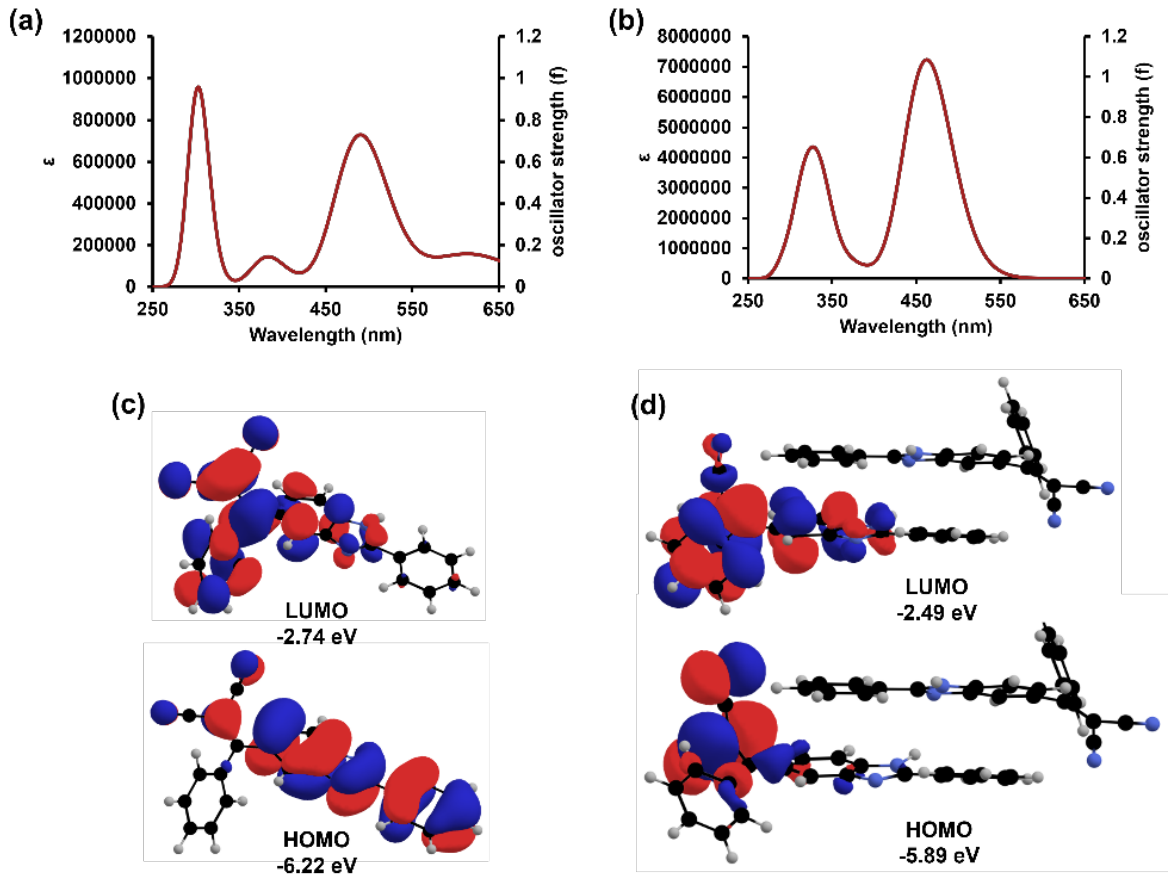


Figure S.5.3: TD-DFT calculated emission spectrum for BIDCPV (a) monomer, (b) dimer and their corresponding frontier molecular orbital for (c) monomer and (d) dimer the ground singlet S_0 state. Notably, as expected the HOMO-LUMO energy gap reduces by 0.08 eV in the optimized dimer of BIDCPV.

References:

[S7] Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al, Gaussian, Inc., Wallingford CT, 2009.
[S8] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.*, **2009**, *113*, 6378-6396.

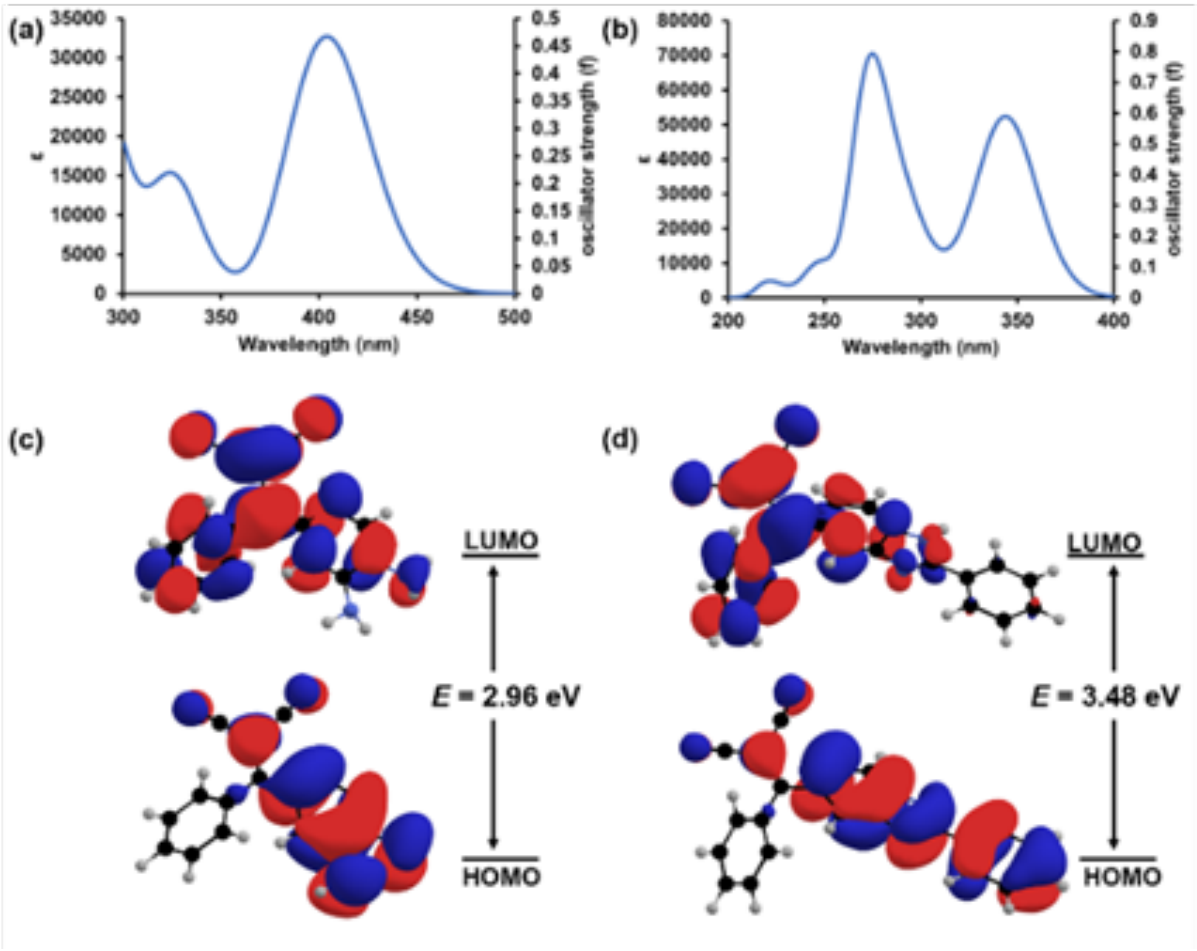


Figure S.5.4: TD-DFT calculated absorption spectrum of (a) DCPV, (b) BIDCPV and their corresponding frontier molecular orbitals in the ground state (c) and (d).

XYZ Coordinates:

DCPV

C	-1.631101000	1.258596000	0.750424000
C	-2.992238000	0.997767000	0.798740000
C	-0.753476000	0.358725000	0.102821000
C	-3.541195000	-0.147378000	0.186652000
C	-1.301299000	-0.821107000	-0.461091000
C	-2.665407000	-1.083847000	-0.439306000
H	-3.663068000	1.683559000	1.309857000
H	-0.647778000	-1.537623000	-0.949100000
H	-1.243920000	2.135761000	1.255716000
C	0.679789000	0.591349000	0.036014000
C	1.584006000	-0.579957000	0.067957000
C	2.655852000	-0.695818000	-0.836890000
C	1.365410000	-1.604551000	1.009757000
H	2.811545000	0.072795000	-1.587302000
H	0.537168000	-1.520867000	1.706262000
C	3.494950000	-1.810907000	-0.796124000
C	2.219373000	-2.707123000	1.062051000
H	4.309050000	-1.897908000	-1.510057000
H	2.052735000	-3.483244000	1.803631000
C	3.283954000	-2.814357000	0.157686000
H	3.942080000	-3.678240000	0.192406000
N	-3.210937000	-2.210985000	-1.074811000
H	-3.944280000	-2.676082000	-0.545752000
H	-2.507763000	-2.884609000	-1.361825000
N	-4.893159000	-0.400229000	0.240440000
H	-5.295909000	-0.970216000	-0.495001000
H	-5.484080000	0.370675000	0.529068000
C	1.228825000	1.870803000	-0.058559000
C	0.473040000	3.037132000	-0.380968000
N	-0.093964000	4.013194000	-0.675821000
C	2.619111000	2.128372000	0.138712000
N	3.743296000	2.386564000	0.313742000

BIDCPV

C	-0.943959000	-1.911134000	0.913793000
C	0.388770000	-2.221216000	1.153374000
C	-1.327439000	-0.738421000	0.200884000
C	1.344730000	-1.334520000	0.644185000
C	-0.351500000	0.158380000	-0.273986000
C	0.991462000	-0.154651000	-0.062831000
H	0.669992000	-3.103226000	1.719973000
H	-0.633753000	1.058245000	-0.809945000
H	-1.713401000	-2.557094000	1.321586000
C	-2.744682000	-0.428099000	-0.024633000
C	-3.171762000	0.979394000	0.092607000
C	-4.063180000	1.553126000	-0.835092000
C	-2.661416000	1.774889000	1.138833000
H	-4.427502000	0.963445000	-1.670011000
H	-1.968373000	1.339859000	1.851520000
C	-4.443539000	2.889901000	-0.710989000
C	-3.062117000	3.104499000	1.271880000
H	-5.117058000	3.327231000	-1.442410000
H	-2.676860000	3.703594000	2.091980000
C	-3.951592000	3.665634000	0.346418000
H	-4.253135000	4.704926000	0.443755000
N	2.132791000	0.533200000	-0.435456000
N	2.715333000	-1.321749000	0.682287000
C	-3.664078000	-1.418757000	-0.339505000
C	-3.288562000	-2.746042000	-0.715050000
N	-3.027595000	-3.829850000	-1.055107000
C	-5.077401000	-1.202915000	-0.325692000
N	-6.236211000	-1.080371000	-0.301783000
C	3.144622000	-0.185795000	0.025071000
H	3.300855000	-2.012569000	1.135415000
C	4.563095000	0.157982000	-0.128315000
C	5.582989000	-0.735118000	0.249648000
C	4.913022000	1.412232000	-0.664305000
H	5.341615000	-1.715058000	0.650633000
H	4.127613000	2.102193000	-0.955147000
C	6.924804000	-0.377416000	0.096647000
C	6.254537000	1.764458000	-0.815342000
H	7.702472000	-1.076894000	0.390034000
H	6.511812000	2.736138000	-1.227803000
C	7.265767000	0.872274000	-0.433990000
H	8.310072000	1.148495000	-0.55082700

DCPV (dimer)

C	2.584703000	0.599281000	0.106557000
C	3.734257000	-0.067344000	-0.265190000
C	1.851492000	0.192154000	1.258500000
C	4.222377000	-1.148544000	0.489895000
C	2.320072000	-0.923916000	1.987051000
C	3.479906000	-1.592128000	1.630192000
H	4.272247000	0.227402000	-1.160148000
H	1.769077000	-1.267400000	2.855123000
H	2.214511000	1.375080000	-0.554174000
C	0.609572000	0.843244000	1.638083000
C	-0.508330000	0.037455000	2.157318000
C	-1.383804000	0.548116000	3.133140000
C	-0.747149000	-1.255260000	1.651422000
H	-1.197078000	1.526160000	3.562228000
H	-0.074415000	-1.659305000	0.907763000
C	-2.473922000	-0.201499000	3.568388000
C	-1.839723000	-1.999859000	2.083459000
H	-3.135298000	0.204731000	4.326527000
H	-2.017205000	-2.985792000	1.666782000
C	-2.711699000	-1.473597000	3.039989000
H	-3.566380000	-2.051731000	3.375836000
N	3.986191000	-2.658064000	2.381280000
H	4.360385000	-3.436006000	1.841003000
H	3.364367000	-2.990664000	3.112996000
N	5.360849000	-1.822614000	0.123040000
H	5.888289000	-2.293984000	0.851870000
H	5.943080000	-1.391650000	-0.587323000
C	0.445793000	2.231911000	1.500196000
C	-0.832860000	2.844406000	1.442451000
N	-1.881810000	3.358506000	1.361306000
C	1.537876000	3.138218000	1.480834000
N	2.434169000	3.890125000	1.502644000
C	-2.599388000	0.554378000	-0.200548000
C	-3.763565000	-0.057878000	0.222791000
C	-1.855744000	0.014542000	-1.284613000
C	-4.252190000	-1.211255000	-0.413500000
C	-2.322235000	-1.175516000	-1.886586000

C	-3.497582000	-1.786526000	-1.481020000
H	-4.312585000	0.339624000	1.070227000
H	-1.759961000	-1.622864000	-2.698724000
H	-2.228123000	1.392690000	0.378631000
C	-0.601436000	0.609570000	-1.719120000
C	0.528051000	-0.260152000	-2.087245000
C	1.433647000	0.109888000	-3.098022000
C	0.742746000	-1.471638000	-1.401986000
H	1.263687000	1.017580000	-3.665792000
H	0.044324000	-1.771220000	-0.632738000
C	2.532359000	-0.693257000	-3.392608000
C	1.844278000	-2.269314000	-1.693748000
H	3.217375000	-0.396346000	-4.179773000
H	2.003143000	-3.189796000	-1.142034000
C	2.747626000	-1.879889000	-2.685964000
H	3.608945000	-2.499625000	-2.912753000
N	-4.005012000	-2.926204000	-2.119324000
H	-4.398204000	-3.632184000	-1.499788000
H	-3.371328000	-3.348678000	-2.791961000
N	-5.405478000	-1.831306000	0.009407000
H	-5.928474000	-2.371228000	-0.673096000
H	-5.993472000	-1.315898000	0.655257000
C	-0.441598000	1.999940000	-1.775177000
C	0.835836000	2.619696000	-1.794558000
N	1.879894000	3.148222000	-1.772352000
C	-1.537727000	2.894410000	-1.901811000
N	-2.434054000	3.630374000	-2.051337000

BIDCPV (dimer)

C	5.076319000	-0.656217000	1.611915000
C	3.914405000	-0.687283000	2.377765000
C	5.104477000	-0.050459000	0.330415000
C	2.781743000	-0.086332000	1.828247000
C	3.950623000	0.510878000	-0.227460000
C	2.780263000	0.508558000	0.541005000
H	3.898479000	-1.149301000	3.359783000
H	3.954027000	0.937816000	-1.224627000
H	5.989727000	-1.090421000	2.006458000
C	6.413264000	0.006258000	-0.384754000
C	7.120698000	1.299017000	-0.483564000
C	8.522391000	1.354864000	-0.326567000
C	6.417444000	2.506626000	-0.671830000
H	9.081501000	0.452897000	-0.105283000
H	5.338945000	2.504475000	-0.760637000
C	9.198190000	2.571630000	-0.392432000
C	7.101135000	3.717505000	-0.760960000
H	10.275100000	2.593193000	-0.251948000
H	6.542931000	4.634419000	-0.927484000
C	8.492561000	3.756088000	-0.623782000
H	9.020547000	4.704022000	-0.680169000
N	1.531903000	1.034106000	0.259544000
N	1.503202000	0.099031000	2.297996000
C	6.952802000	-1.162794000	-0.867620000
C	8.144917000	-1.244090000	-1.658298000
N	9.089348000	-1.361886000	-2.327582000
C	6.326512000	-2.433307000	-0.656237000
N	5.874978000	-3.495298000	-0.507306000
C	0.802276000	0.789657000	1.339243000
H	1.160495000	-0.155235000	3.216085000
C	-0.587360000	1.206482000	1.537509000
C	-1.414255000	0.564239000	2.475343000
C	-1.101450000	2.270681000	0.779158000
H	-1.037660000	-0.278601000	3.047715000
H	-0.458290000	2.757522000	0.052922000
C	-2.732199000	0.985921000	2.650045000
C	-2.418177000	2.690209000	0.958891000
H	-3.368216000	0.476506000	3.368767000
H	-2.814856000	3.507378000	0.364694000
C	-3.237259000	2.049362000	1.893861000
H	-4.265771000	2.373409000	2.023766000
C	-4.113483000	1.221363000	-1.752451000
C	-2.753529000	1.032258000	-1.945755000
C	-4.876761000	0.370866000	-0.903516000
C	-2.156736000	-0.025282000	-1.253605000
C	-4.266875000	-0.718541000	-0.253577000
C	-2.895773000	-0.903865000	-0.417293000
H	-2.180810000	1.679930000	-2.601651000
H	-4.841143000	-1.372707000	0.393140000
H	-4.615477000	2.018521000	-2.288855000
C	-6.305589000	0.614529000	-0.676967000
C	-7.200385000	-0.554994000	-0.580232000
C	-8.203077000	-0.631951000	0.405270000
C	-7.034735000	-1.629944000	-1.475839000
H	-8.310522000	0.169511000	1.128850000
H	-6.258337000	-1.578811000	-2.232235000
C	-9.029167000	-1.752218000	0.481750000
C	-7.876433000	-2.738561000	-1.408161000
H	-9.788614000	-1.808139000	1.256536000
H	-7.751692000	-3.553450000	-2.115634000
C	-8.873898000	-2.803067000	-0.428853000
H	-9.522653000	-3.672838000	-0.370270000
N	-2.054926000	-1.847424000	0.145687000
N	-0.865654000	-0.476972000	-1.181915000
C	-6.809779000	1.899224000	-0.540846000
C	-8.209292000	2.190711000	-0.531185000
N	-9.338390000	2.476312000	-0.538634000
C	-5.982118000	3.053341000	-0.377617000
N	-5.346828000	4.015361000	-0.210485000
C	-0.854368000	-1.558662000	-0.323281000
H	-0.038782000	0.036486000	-1.468671000
C	0.381510000	-2.271493000	-0.000817000
C	1.493399000	-2.199109000	-0.855054000
C	0.461499000	-3.038709000	1.174207000
H	1.437113000	-1.620689000	-1.772328000
H	-0.400523000	-3.087712000	1.832357000
C	2.664884000	-2.885466000	-0.541541000
C	1.639353000	-3.714580000	1.489145000
H	3.517250000	-2.829513000	-1.208984000
H	1.697308000	-4.297008000	2.404822000
C	2.744925000	-3.639146000	0.632641000
H	3.667133000	-4.159463000	0.873867000

6. Other Experimental Details

All reagents and solvents of commercial grade were used as received unless otherwise stated. The spectroscopic grade solvents were bought from Spectrochem. All the reagents were purchased from SRL chemicals, Sigma Aldrich and Spectrochem. Reaction progress was monitored by Thin Layer Chromatography (TLC) analysis using Merck TLC Silica gel F254 Aluminium Sheets. Reaction components were detected by UV-absorption (254 or 365 nm). Purifications by column chromatography were performed by using Silica gels (60-120 or 230-400 mesh) eluting with the mentioned solvent system. ^{1}H and ^{13}C characterization of isolated products were done using a Bruker 400 MHz NMR instrument in chloroform-d (CDCl3) or d6-dimethylsulfoxide (DMSO-d6). Chemical shifts (d) are reported relative to a tetramethylsilane (TMS) standard (δ 0.00 ppm) or to that of the solvent residual peak. Coupling constants (J) are reported in Hz. All 13C-NMR spectra are reported as proton decoupled. All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.
Mass spectra were recorded by electrospray ionization (ESI) method on a Q-TOF Micro with lock spray source. High resolution mass spectrometry (HRMS) was completed with a Agilent technologies 6545 Q-TOF LC/MS Mass Spectrometer instrument.

Synthesis of DCPV (2-((3,4-diaminophenyl) (phenyl)methylene) malononitrile). A 25 mL ethanolic solution of 3,4-diaminobenzophenone (5 g. ,23.5 mmol) and malononitrile (3.1 g. ,47 mmol) was taken in a 100 ml single necked RB fitted with a condenser. To this reaction mixture pyridine (1.9 mL, 23.5 mmol) was added and the reaction mixture was refluxed for 48 h at 80°C. The progress of the reaction was monitored by TLC. After 48 h, another equivalent of pyridine (1.9 mL, 23.5 mmol) was added to it and the reaction was continued for another 24 h at 80°C. After completion, the reaction mixture was concentrated under reduced pressure and the product was extracted in ethyl acetate (300 mL). The ethyl acetate solution was washed with 200 mL water twice followed by 200 mL saturated brine solution. The separated organic layer then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The desired product was purified by silica gel column chromatography. The product was eluted by 50% ethyl acetate in hexane solution. Product was further recrystallized from methanol and the desired product was obtained as dark orange crystalline solid (4.4 g, Yield ~ 72%). ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) 7.58 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 6.73 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.62 (d, *J* = 1.3 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H), 4.83 (s, 2H). ^{13}C NMR (100 MHz, d_6-DMSO): δ (ppm) 173.26, 142.84, 173.18,

133.90, 131.39, 130.33, 128.39, 123.93, 122.84, 116.43, 116.06, 115.62, 112.52, 71.23. HRMS (ESI) for $C_{16}H_{12}N_4$: Calculated $(M+H)^+$ - 261.1135, Found – 261.1139. Melting point is 185°C.

Synthesis of BIDCPV (2-(phenyl(2-phenyl-1H-benzo[d]imidazol-5-yl)methylene)malononitrile). DCPV (160 mg, 0.62 mmol) was dissolved in 3 mL ethanol in a 50 mL one- neck round bottomed flask fitted with a condenser. Benzaldehyde (75 µL, 0.74 mmol) was added to it followed by the addition of 3 mL 10% (W/V) Aq. $Na_2S_2O_5$. The reaction was set at reflux for next 18 h and the consumption of starting material was monitored by TLC. After the completion of the reaction, it was diluted with 20 mL ethyl acetate and quenched with 20 mL water. Then the organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Desired product was purified by silica gel column chromatography. The product was eluted by 60% ethylacetate in hexane. The product was further purified by recrystallization from methanol and obtained as yellow crystalline solid (158 mg, Yield ~ 75%). ^{1}H NMR (400 MHz, d-Chloroform): δ (ppm) 10.84 (s, 1H), 8.05 (d, *J* = 3.5 Hz, 2H), 7.73 (s, 1H), 7.65 – 7.53 (m, 2H), 7.52 – 7.38 (m, 8H). ^{13}C NMR ((100 MHz, d-Chloroform) : δ (ppm) 176.12, 136.71, 132.75, 131.25, 130.77, 130.52, 129.41, 128.98, 128.92, 127.05, 125.89, 114.96, 114.49, 79.86. HRMS (ESI) for $C_{23}H_{14}N_4$: Calculated $(M+H)^+$ - 347.1291, Found – 347.1290. Melting point is 122°C.

Absorbance (UV) and Emission (Fluorescence) Assay. To record the absorbance and emission spectra of DCPV and BIDCPV, 2 mM stock solutions of both the compounds in acetonitrile were prepared. These two stock solutions were serially diluted to prepare different samples. Absorbance spectra were recorded using Jasco V-650 UV-VIS Spectrophotometer and fluorescence emission spectra were recorded in Horiba Fluoromax-4 spectrofluorometer.

Solid State Fluorescence Studies. Solid state fluorescence data of DCPV and BIDCPV were recorded in Horiba Fluoromax-4 instrument. 20 mg of the solid samples were taken in a specific plate for recording the fluorescence emission.

Fluorescence Based AIE Study. To study the Aggregation Induced Emission (AIE) property of DCPV and BIDCPV, a series of samples were prepared maintaining different percentage of acetonitrile-water solvent system (0% water-100% acetonitrile, 10% water-90% acetonitrile, ……., 98% water-2% acetonitrile) and fixed concentration of compounds (50 µM) in it. Fluorescence data of these solutions were recorded using Horiba FluoroMax-4 spectrofluorometer for both the compounds separately. The UV-Vis spectra of these prepared solution were recorded in Jasco V-650 UV-VIS spectrophotometer.

Fluorescence Lifetime Measurement of DCPV and BIDCPV. Fluorescence lifetime data of DCPV and BIDCPV were measured in both solution and solid phase in Fluorohub TCSPC instrument with TDM monochromator and PPD-850 detector. In case of solution phase measurements, a stock 5 mM stock solution of both DCPV and BIDCPV was serially diluted to the mentioned strength sample solutions in mentioned solvent systems. The solutions poured in a quartz cuvette and placed in the machine for recording of data. In case of solid phase measurements, a suspension of powdered DCPV and BIDCPV was prepared in acetone. This suspension was drop casted to a glass cover slip to create a thin layer of compound on it. The Compound coated coverslip was placed in the instrument to record its lifetime results.

Powder X-Ray Diffraction (PXRD). DCPV and BIDCPV was recrystallized from methanol. Crystallised compounds were subjected for X-Ray Diffraction analysis. As well as the PXRD data of 5 min, 10 min, 20 min grinded samples were also taken in a Rigaku Miniflex X-Ray Diffractometer.

Sample preparation for FESEM Images. The samples of DCPV and BIDCPV were taken and placed in a carbon tape. A coating of gold was done before the sample imaging. After coating, the sample was placed in the specified place and subjected for imaging. To verify the aggregation property of BIDCPV previously prepared 2 mM stock solution of BIDCPV in acetonitrile was serially diluted with chloroform and water to afford 100 μM solutions in both solvents. The samples were drop casted in coverslips and left in open air at 25°C for 18 hr for complete evaporation of solvents. Sample loaded cover slips was coated by gold plating and The SEM images were taken. The data was recorded in FEI/Thermo Fischer instrument, model no. Apreo S, using Quorum Tech. coating unit, model no. Q150TES.

Solid State UV-vis. The Solid-State UV-vis spectra of DCPV and BIDCPV were recorded in Shimadzu UV-2450 UV-VIS spectrophotometer instrument. 5 mg of the compounds were measured. These measured compounds were mixed and grinded well with 50 mg solid Barium Sulfate. This mixture was placed in a specific cavity of the instrument and solid-state UV-vis data was recorded.

Dynamic Light Scattering (DLS) studies. BIDCPV solutions of conc. 50 μM were prepared in chloroform and water respectively from a mother stock solution of BIDCPV 2 mM in acetonitrile. The DLS data were recorded of the solutions using Anton Paar Particle Size Analyzer (PSA) instrument. Analytical report generated by the machine were directly reported without further modification.

Reversibility of Crystallinity and Fluorescence of BIDCPV. BIDCPV was recrystalized from hot methanol. These crystalline compounds were dried well and thoroughly powdered in a mortar pestle. The powdered samples were placed in a glass vial and subjected for heat for 40 s at 120°C in a preheated oil bath. Formerly powdered samples were clustered in effect of heat. These clustered compounds were sheared to generated the powdered form of BIDCPV. These reversed crystals and re-powdered forms of this reversed crystals were subjected for Fluorescence (Horiba Fluoromax 4) and PXRD (Rigaku Miniflex) analysis. Similarly, the powdered samples from the methanol crystals were taken in a glass plate and slowly dichloromethane solvent vapour was deposited upon them. The powdered samples recovered their crystal form. These solvent deposited crystals and its powdered form were also subjected for Fluorescence and PXRD analysis respectively using the same instruments mentioned above.

Concentration Dependent AIE Study. BIDCPV stock solution of 2 mM in acetonitrile was serially diluted to prepare solutions having strength 5 μM, 10 μM, ……., 200 μM in water. The fluorescence of these freshly prepared solutions were recorded in Horiba Fluorolog 3 spectrofluorometer.