Electronic Supplementary Information (ESI)

Polymorphism in novel symmetric and asymmetric bis-hydrazone derivatives

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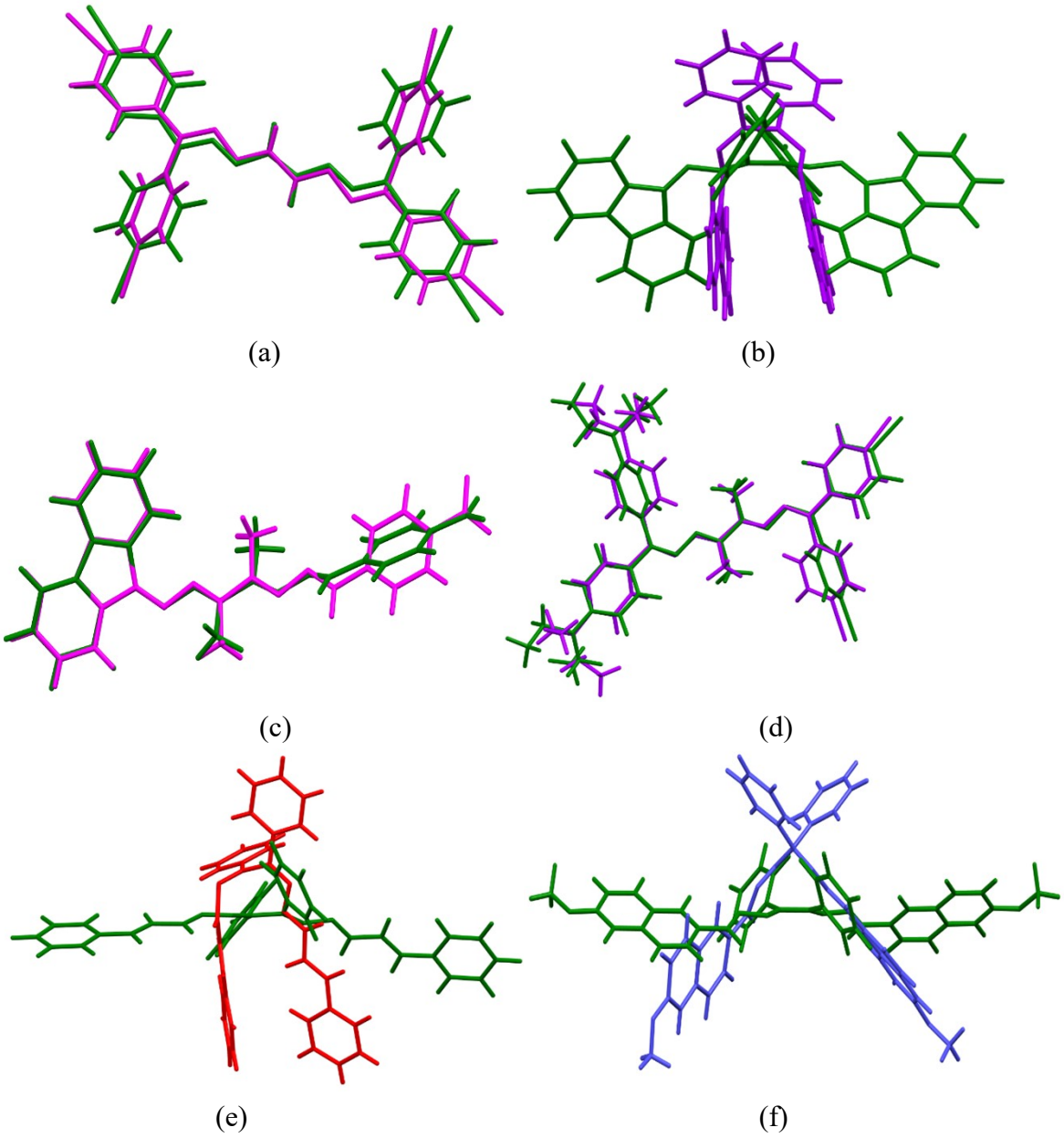
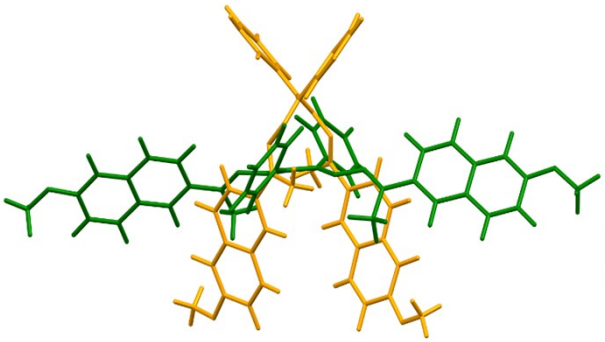
TABLE OF CONTENT

1. **Molecular overlay**

(a) The optimization calculation were performed with the Gaussian 09 package.[1] The molecular structure of compound **1-7** was drawn in Chemdraw. The structures were optimized with default symmetry using density functional theory (DFT) with the hybrid exchange-correlation functional (B3LYP), and using B3LYP/6-311,G(d,p) basis set for **FBB**, **FNBHB**, **NBB**, **NMBB**, and B3LYP/3-21G basis set for **DIBHG** and **EIBHB** respectively. The optimized structure obtained using Gaussian 09[1] (shown in green colour) is overlaid with the structure obtained from single-crystal X-ray diffraction using *Mercury Software*.



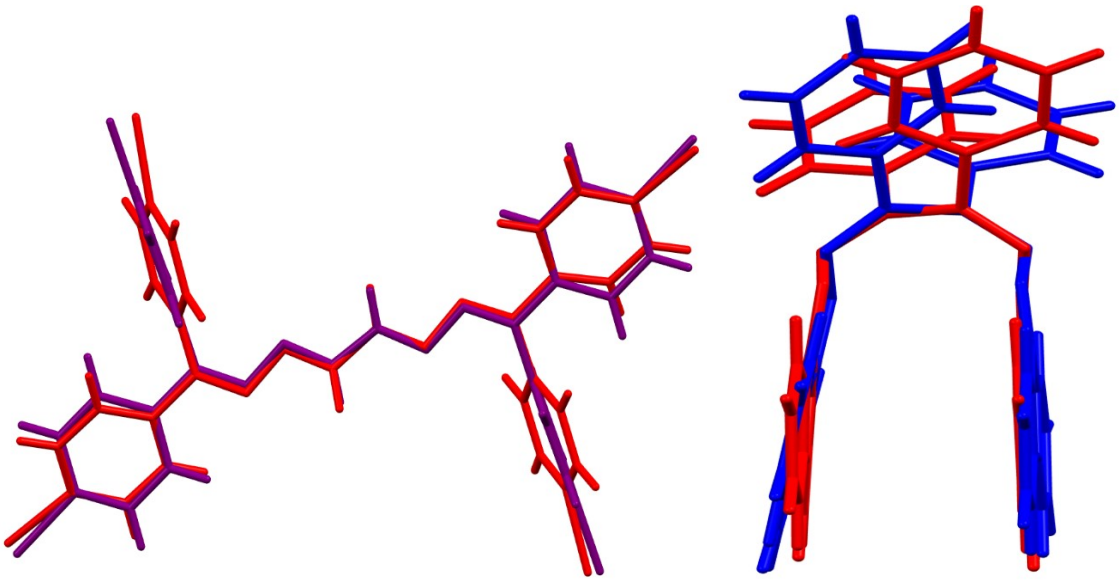
(a) (b) (c) (d) (e) (f)



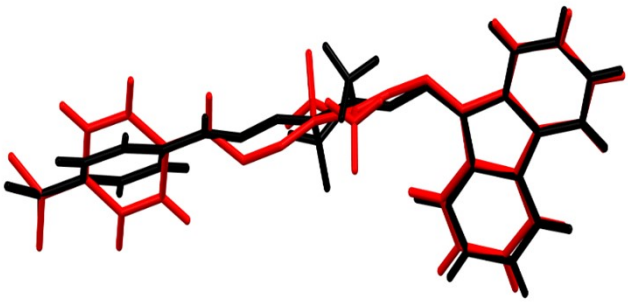
(g)

Fig. S1 The molecular overlay diagram of optimized and the molecular structure obtained from SC-XRD for (a)**DIBHG**, (b) **FBB**, (c) **FNBHB**, (d) **EIBHB**, (e) **CBHBz ,** (f)**NBB** and (g) **NMBB** respectively. In all the cases, the optimized structure is shown in green colour while the crystal structure obtained are shown in other colours.

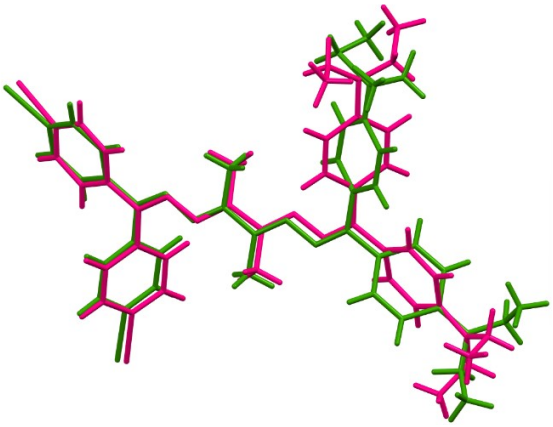
(b) The molecular overlay diagram between the polymorphs showing conformational differences are given below



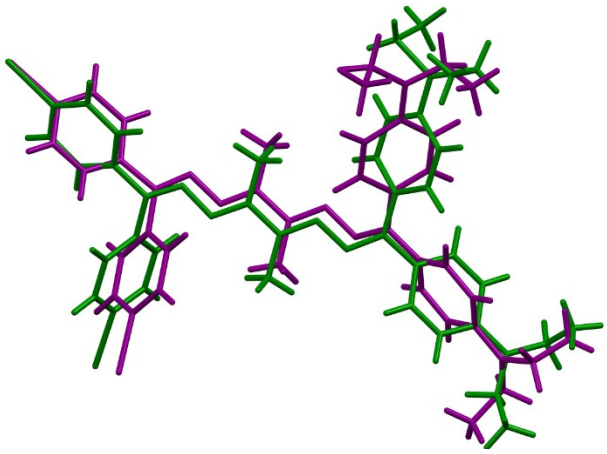
(a) (b)



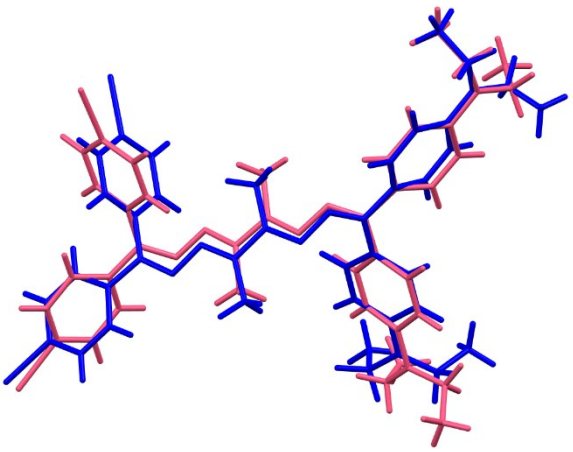
(c)



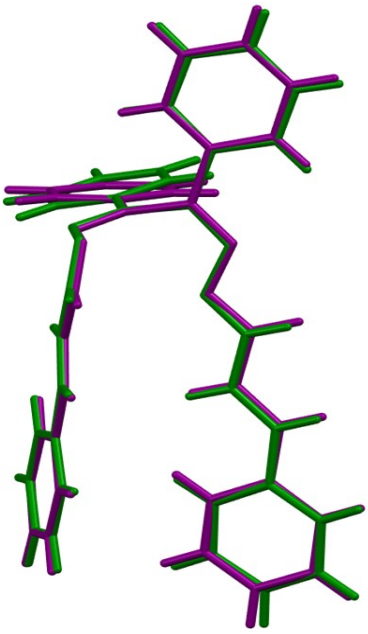
(d)



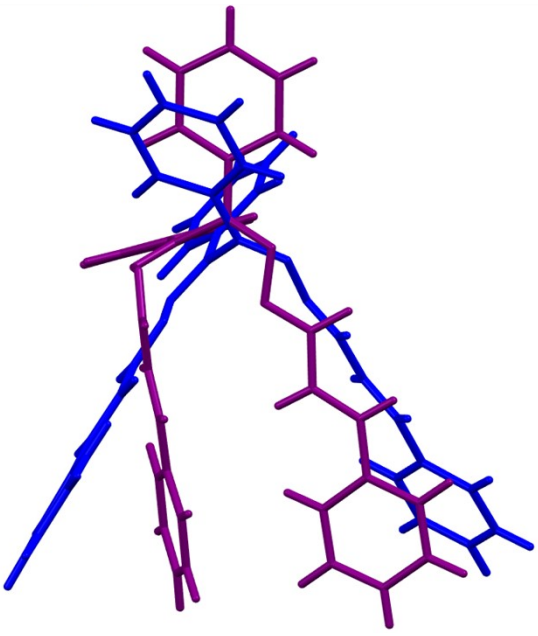
(e)



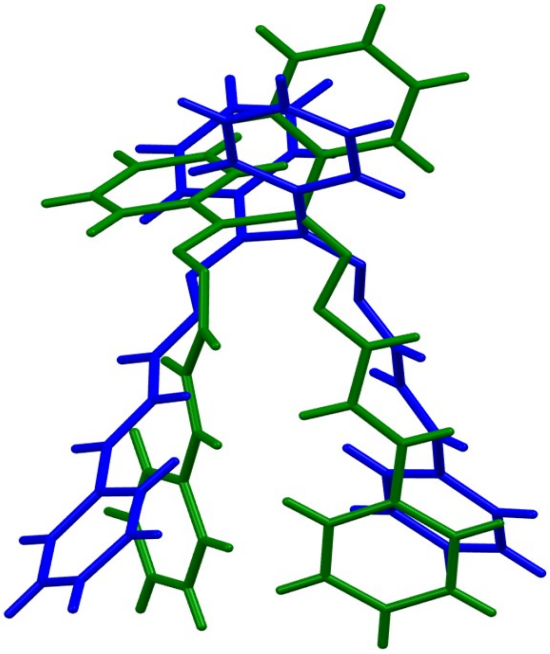
(f)



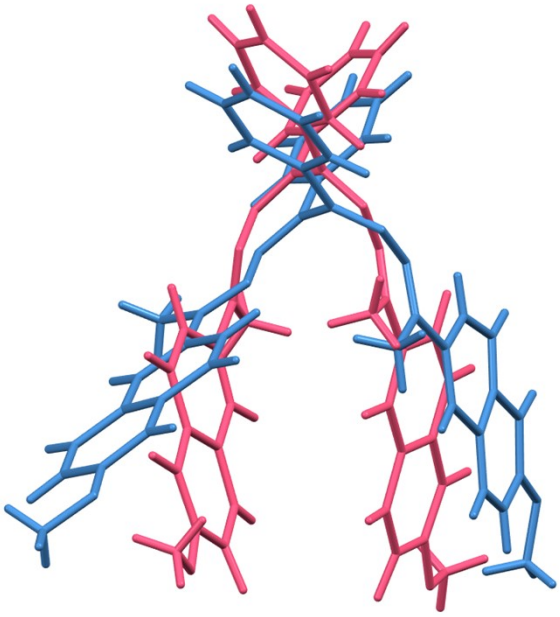
(g)



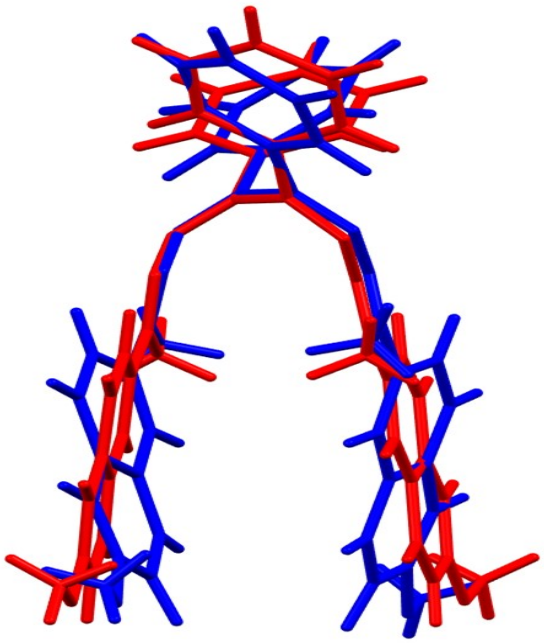
(h)



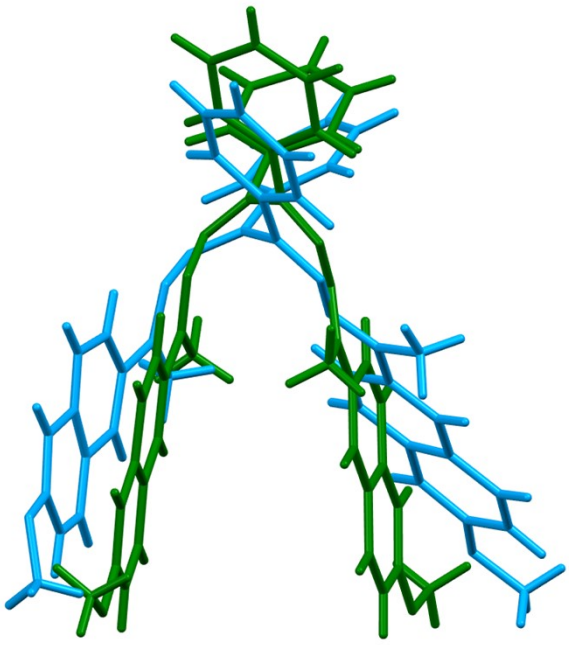
(i)



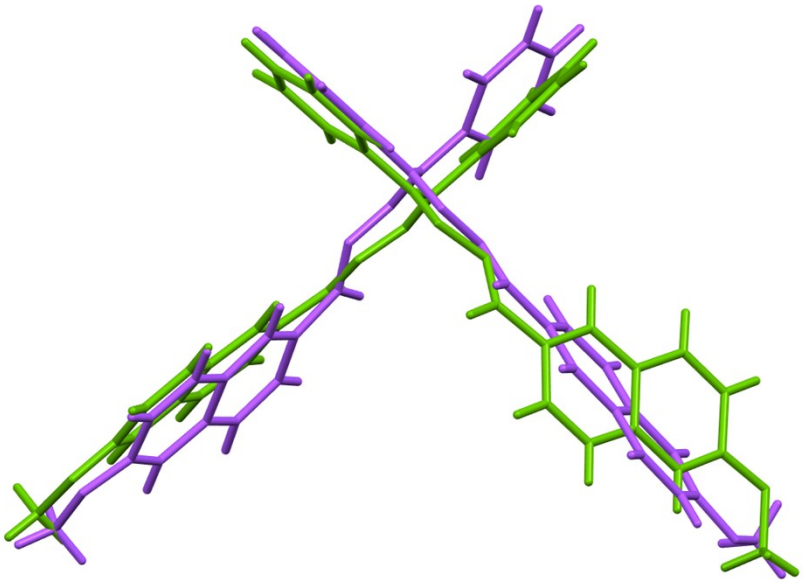
(j)



(k)



(l)



(m)

Fig. S2 Overlay diagram of pair of molecular structure obtained from SC-XRD and prepared in *Mercury software* with showing (a)**DIBHG-I** red and **DIBHG-II** black, (b) **FBB-I** blue and **FBB-II** red, (c) **FNBHB-I** black and **FNBHB-II** red, (d)**EIBHB**-I pink and **EIBHB-II** light green, (e) **EIBHB-II** green and **EIBHB-III** purple, (f) **EIBHB-I** pink and **EIBHB-III** blue, (g)**CBHBz-I** green and **CBHBz-II** purple, (h) **CBHBz-II** purple and **CBHBz-III** blue, (i)**CBHBz-I** green and **CBHBz-III** blue, (j) **NMBB-I** blue and **NMBB-II** pink, (k) **NMBB-II** blue and **NMBB-III** red, (l) **NMBB-I** blue and **NMBB-III** green, (m) **NBB-I** green and **NBB-II** violet, respectively

Table S1 The *rmsd [r]* values of overlaid structure of optimized and structure obtained from crystal structure.

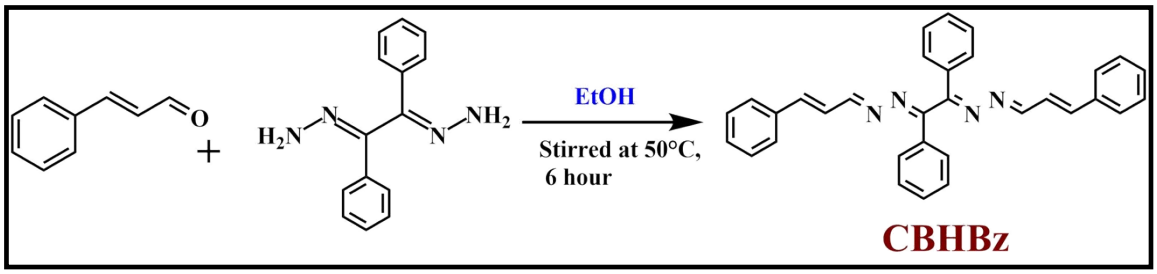
Molecular overlay between optimized and structure obtained from SCXRD	**Bais set used for optimization**	***rmsd[r]***
DIBHG (optimized) and **DIBHG-II**	B3LYP/3-21G	0.5223
FBB (optimized) and **FBB-I**	B3LYP/6-311,G(d,p)	3.6306
FNBHB (optimized) and **FNBHB-I**	B3LYP/6-311,G(d,p)	0.5125
EIBHB (optimized) and **EIBHB-I**	B3LYP/3-21G	1.1045
CBHBz (optimized) and **CBHBz-I**	B3LYP/6-311,G(d,p)	5.2176

NBB (optimized) and **NBB-I**	B3LYP/6-311,G(d,p)	4.7035
NMBB (optimized) and **NMBB-II**	B3LYP/6-311,G(d,p)	5.8201

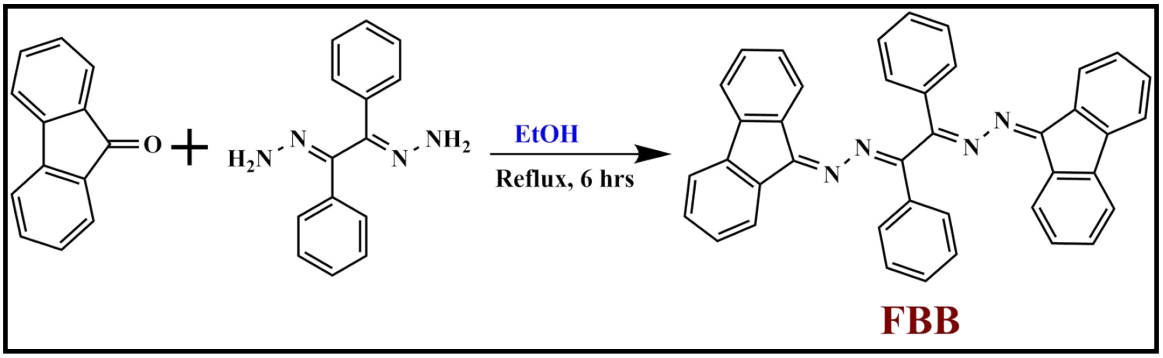
2. Experimental Section

(a) Synthesis

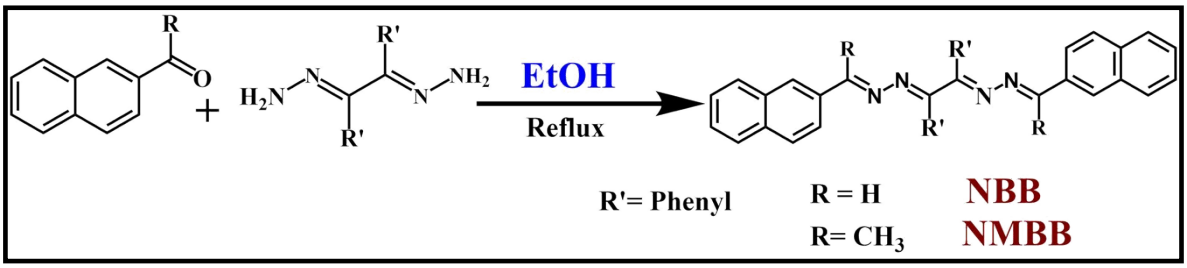
All the chemicals and solvents of reagent grade used for synthesizing and crystallizing compounds **1-7** were purchased from commercial sources such as Sigma –Aldrich, TCI and Alfa Aesar. Benzil, 4,4′-bis(diethylamino)benzophenone, 9-fluorenone, 4-nitro benzaldehyde, glyoxal (40% w/w aq. Solution) has been purchased from Alfa Aeser. Trans-cinnamaldehyde has been purchased from TCI. 6-methoxy-2-napthaldehyde, 6′-methoxy-2′-acetonaphthone, bis(4-iodophenyl)methanone and 2,3-butanedione has been purchased from Sigma Aldrich. All these chemicals and solvents have been used as such without further purification, except ethyl acetate, methanol, dichlormethane and hexane were distilled before use. All the compounds were prepared using a Schiff-based condensation reaction with slight modification of the reported literature.[2]



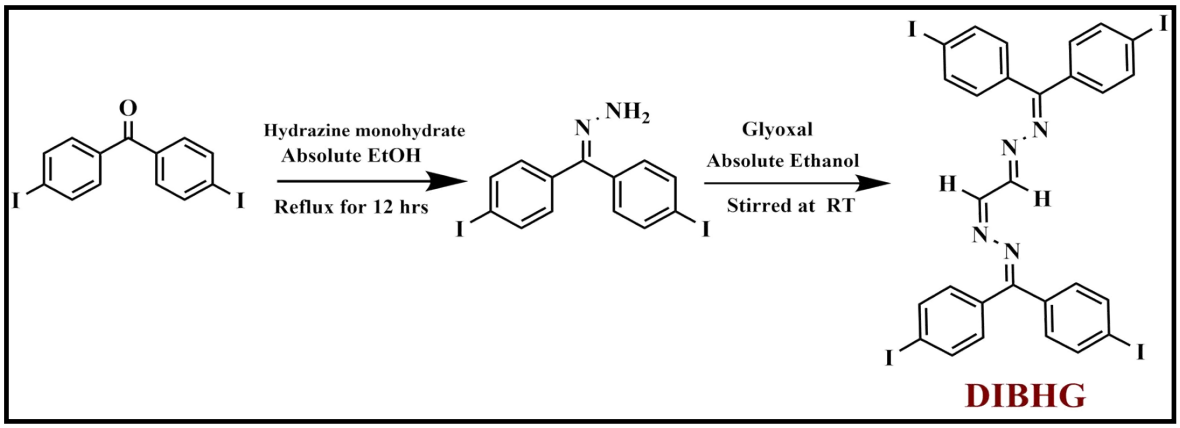
(a)



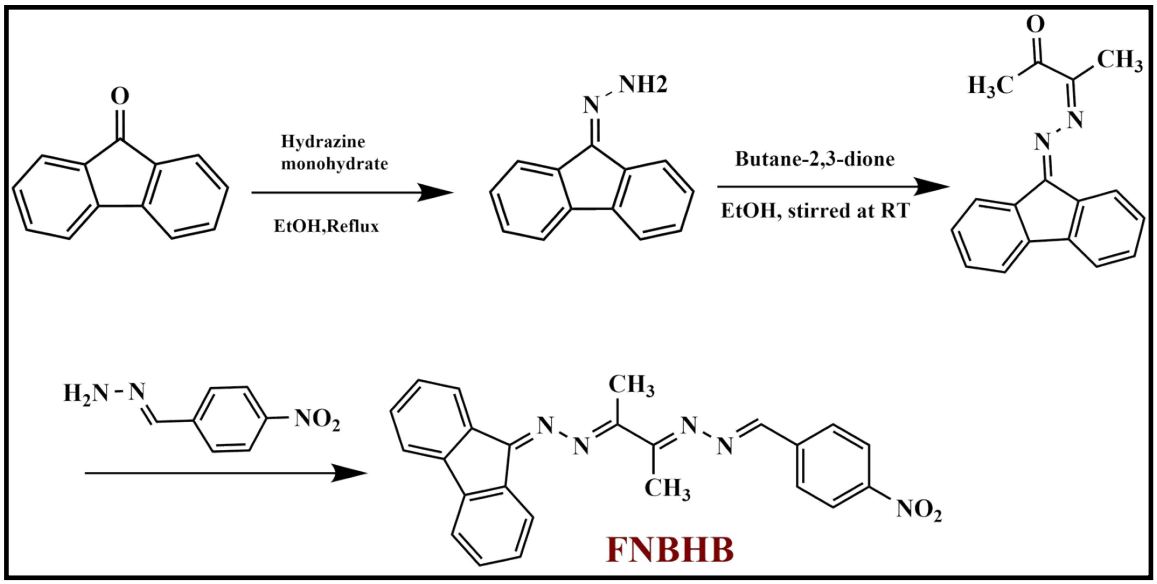
(b)


EtOH
Reflux
R'= Phenyl
R = H
NBB
R= CH3
NMBB

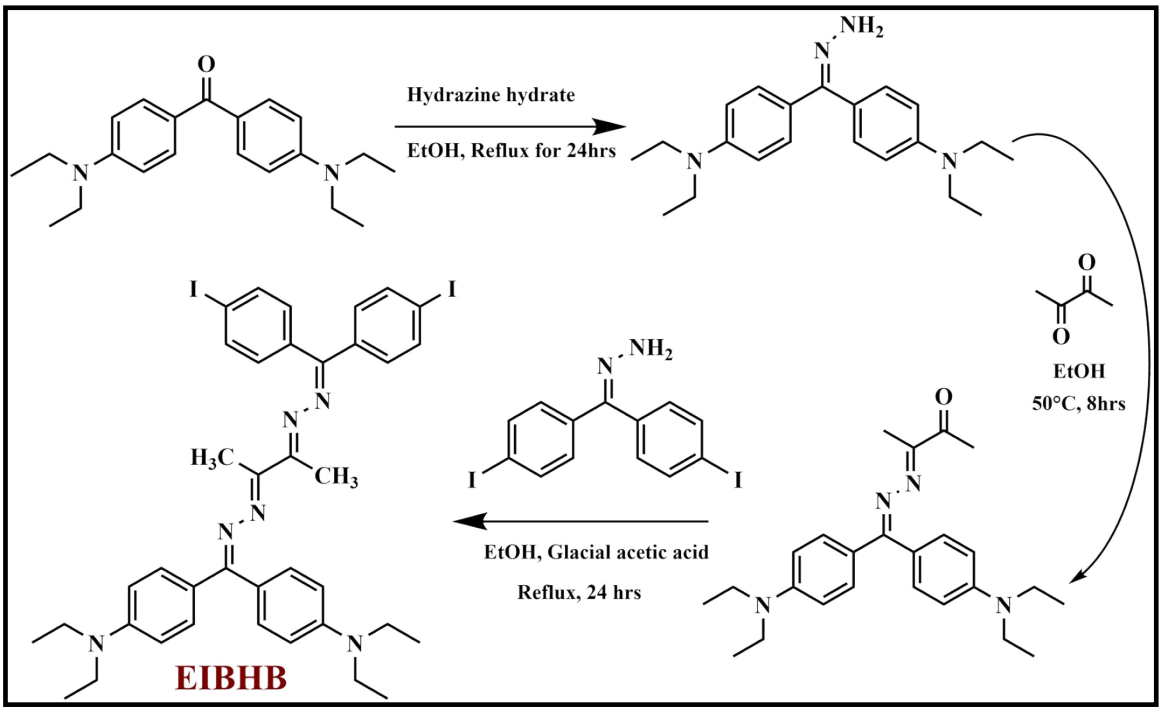
(c)


Hydrazine monohydrate
Absolute EtOH
Reflux for 12 hrs
Glyoxal
Absolute Ethanol
Stirred at RT
DIBHG

(d)


Hydrazine monohydrate
EtOH,Reflux
Butane-2,3-dione
EtOH, stirred at RT
FNBHB

(e)

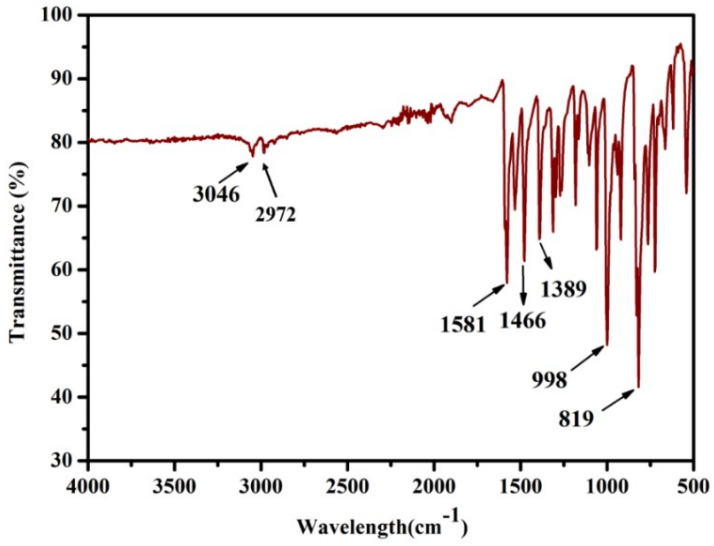


(f)

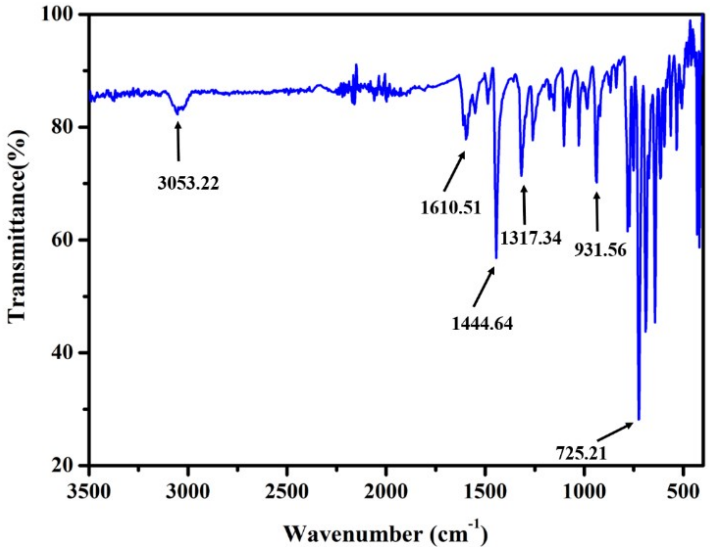
Fig. S3 The synthetic procedure for the preparations of **CBHBz**, **FBB**, **NBB**, **NMBB**, **DIBHG**, **FNBHB** and **EIBHB** respectively.

(b) FTIR spectra

The FT-IR spectra of each compounds **1-7** were collected using a Fourier-transform infrared spectrometer (Shimadzu).



(a)


Transmittance(%)
Wavenumber (cm-1)
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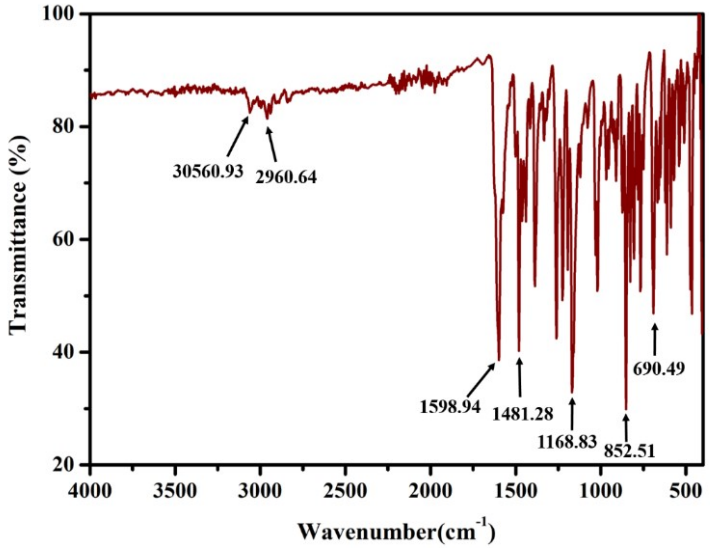
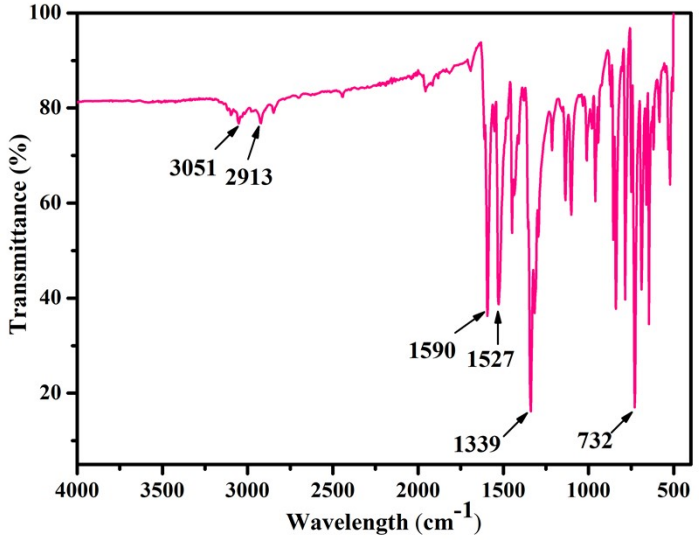
1610.51
1317.34
931.56
1444.64
725.21

(b)


Transmittance (%)
Wavenumber(cm-1)
30560.93
2960.64
1598.94
1481.28
1168.83
852.51
690.49

(b)


Transmittance (%)
Wavelength (cm-1)
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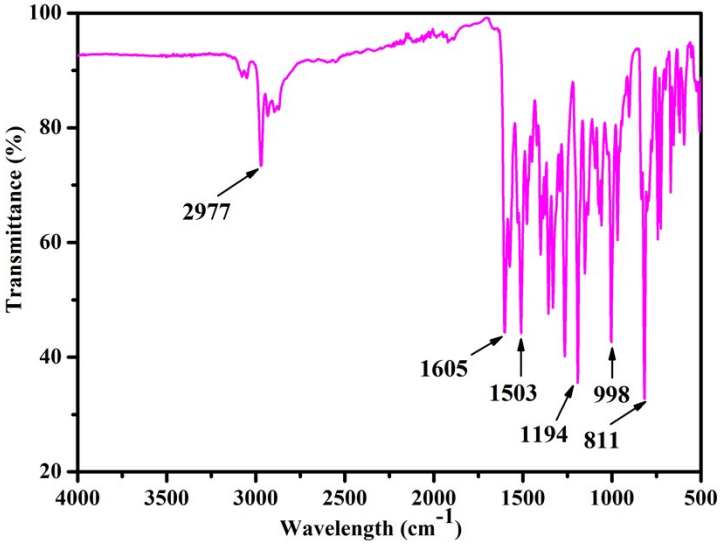
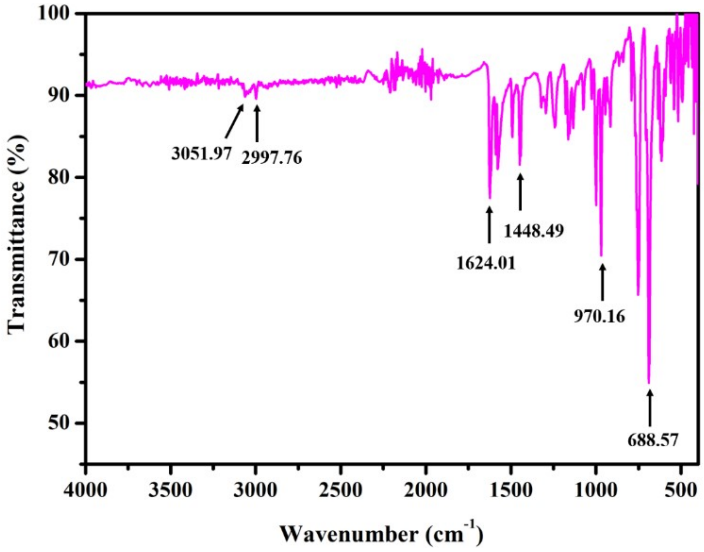
2913
1590
1527
1339
732

(c)


Transmittance (%)
Wavelength (cm-1)
2977
1605
1503
1194
998
811

(d)


Transmittance (%)
Wavenumber (cm-1)
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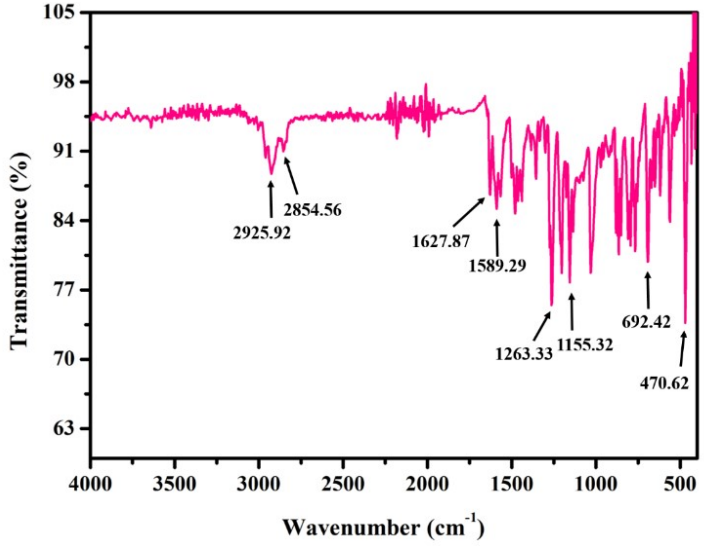
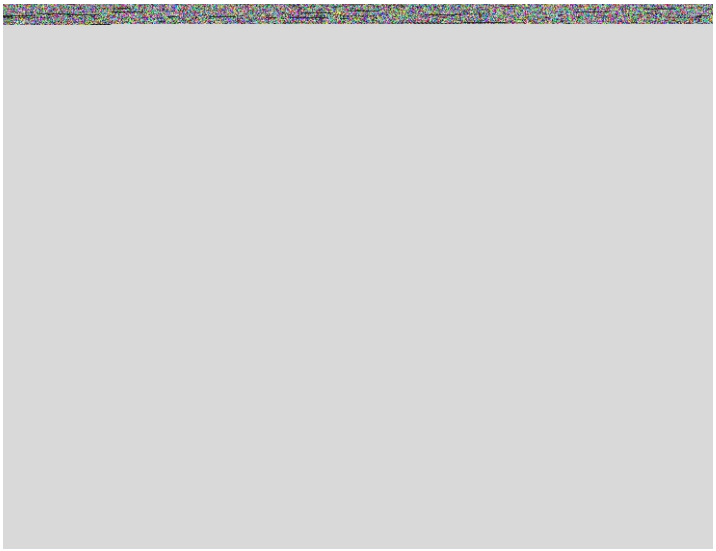
2997.76
1624.01
1448.49
970.16
688.57

(e)


Transmittance (%)
Wavenumber (cm-1)
2925.92
2854.56
1627.87
1589.29
1263.33
1155.32
692.42
470.62

(f)

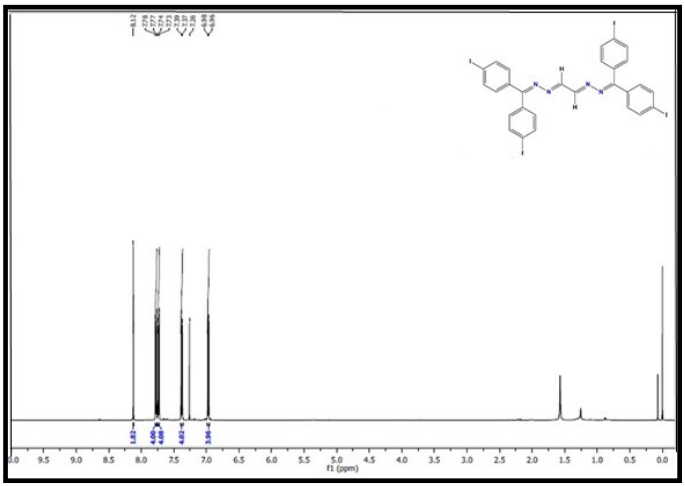


(g)

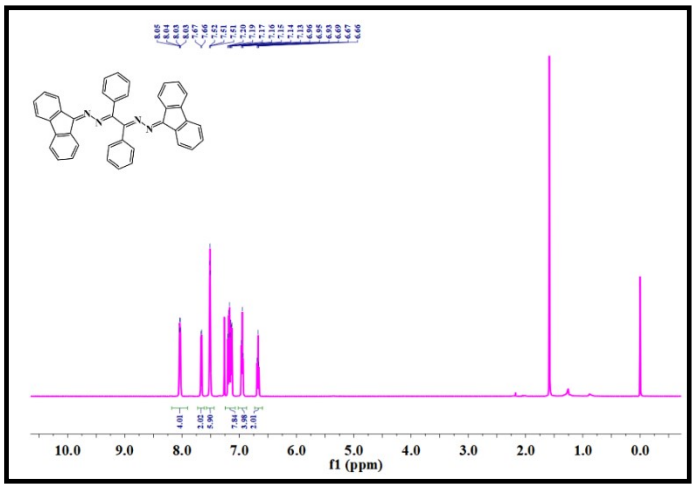
Fig. S4 FT-IR spectra of as-synthesized material of compounds (a) **DIBHG**, (b)**FBB**, (c) **FNBHB**, (d) **EIBHB**, (e) **CBHBz**, (f) **NMBB** and (g) **NBB** respectively, recorded in Shimadzu (IR Affinity-1SWL).

(c) ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of compounds **1-7** are given below



(a)



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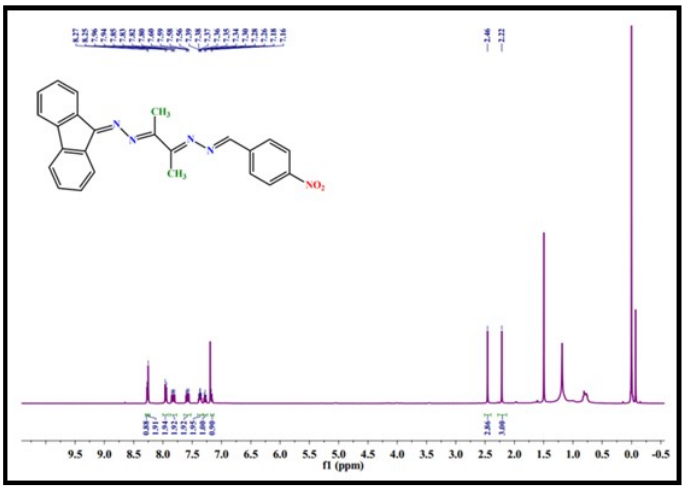
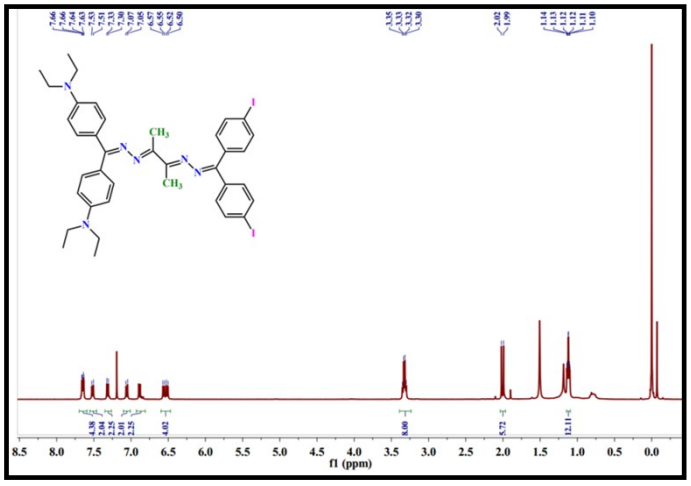
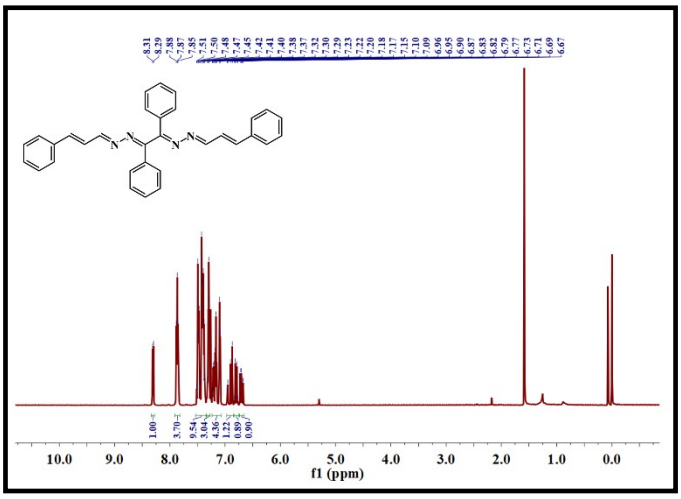


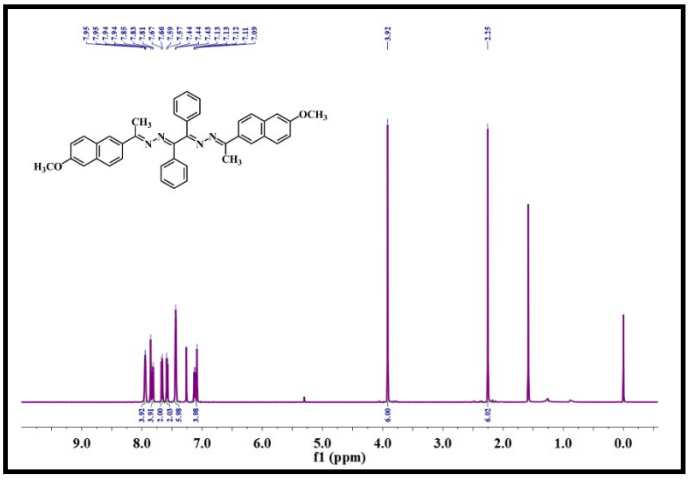
(c)



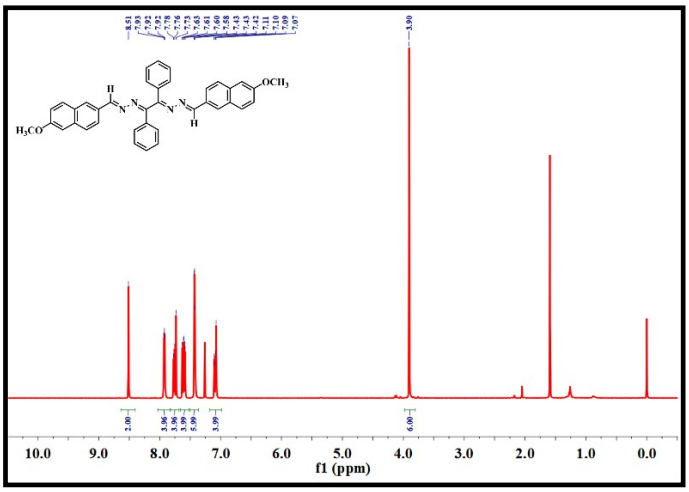
(d)



(e)



(f)



(g)

Fig. S5 ^{1}H-NMR spectra of (a) **DIBHG**, (b) **FBB,** (c) **FNBHB,** (d) **EIBHB**, (e) **CBHBz**, (f) **NMBB**, and (g)**NBB**, respectively.

^{1}H-NMR data of compounds

DIBHG: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 2H), 7.78(d, J = 15Hz, 4H), 7.74(d, 4H), 7.39(d, 4H), 6.98(d, 4H)

FBB: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.67(2H, m), δ 6.95 (4H, m), δ 7.16 (8H,m),δ 7.52 (6H,m), δ 7.67 (2H,d), δ 8.04 (4H,m).

FNBHB:^{1}H NMR (400 MHz, $CDCl_3$): δ2.22 (3H, s), δ2.46 (3H, s), δ7.16 (1H, d), δ7.26 (1H, m), δ7.34 (2H, m), δ7.56 (2H, m), δ7.80 (2H, m), δ7.94 (2H, d), δ8.25 (2H, s), δ8.27 (1H, s).

EIBHB: ^{1}H NMR (400 MHz, $CDCl_3$): δ1.10 (12H, m), δ1.99 (6H, d), δ3.30 (8H, q), δ6.50 (4H, q), δ6.86 (2H, d), δ7.05 (2H, d), δ7.39 (2H, d), δ7.51 (2H, d), δ7.63 (4H, m).

CBHBz: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.69 (1H, m), δ 6.82 (1H, m), δ 6.90 (1H, m), δ 7.18 (4H, m), δ 7.30 (4H, m), δ 7.42 (10H, m), δ 7.87 (4H, t), δ 8.31(1H, d).

NMBB: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.25 (6H, s),δ 3.92 (6H, s), δ 7.12 (4H, m), δ 7.44 (6H, m), δ 8.57 (2H,d), δ 7.66 (2H,d), δ 7.85 (4H, m), δ 7.66 (2H, d), δ 7.85 (4H, m), δ 7.95 (4H,m).

NBB: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.90 (6H, s), δ 7.09(4H, m),δ 7.42(6H, m),δ 7.61(4H, m), δ 7.76(4H, m), δ 7.92(4H,m), δ 8.51(2H, s).

3. **List of solvents used for crystallization**

Table S2 List of solvent used for the crystallization of **NMBB.**

The solvent used for crystallization of NMBB	**Outcomes of crystallization**
DCM + Hexane (1:1)	NMBB-I and NMBB-II
DCM +Hexane (1:2)	NMBB-III
Ethylacetate	NMBB-I
ortho-xylene (*o*-XY)	NMBB-I
meta-xylene (*m*-XY)	NMBB-I
para-xylene (*p*-XY)	NMBB-I
1,4-dioxane (DIOX)	NMBB-I
Carbon tetrachloride (CCl_4)	NMBB-I
Mesitylene (Ms)	NMBB-I

Acetronitrile (ACN)	NMBB-I
Chloroform ($CHCl_3$)+Hexane [(CH)]	NMBB-I
Toluene (TOL)	NMBB-I
Anisole (ANS)	NMBB-I
Dimethylformamide (DMF)	NMBB-I
Ethylbenzene (EBz)	NMBB-I
2-methyl pyridine	NMBB-I
3-methyl pyridine	NMBB-II
4-methyl pyridine	NMBB-I
Cyclohexanone (CHX)	NMBB-I
Bromo benzene	NMBB-I
Morpholine (MOR)	NMBB-I
DCM	NMBB-I
Benzene + Toluene	NMBB-I

Table S3 List of solvent used for the crystallization of **EIBHB.**

The solvent used for crystallization of EIBHB	**Outcomes of crystallization**
Ethylacetate	EIBHB-I and EIBHB-II
Nitrobenzene	EIBHB-I and EIBHB-II
DCM	EIBHB-III
THF	EIBHB-III
$CHCl_3$	EIBHB-III
1,4-Dioxane	EIBHB-III
Nitromethane	EIBHB-III
Toluene	EIBHB-III
Benzene	EIBHB-III
o-Xylene(*o*-XY)	EIBHB-III
m-Xylene(*m*-XY)	EIBHB-III
p-Xylene(*p*-XY)	EIBHB-III
Cyclohexanone	EIBHB-III
EtOH+$CHCl_3$	EIBHB-III
Isopropanol +$CHCl_3$	EIBHB-III
Mesitylene	EIBHB-III
Cyclohexane+$CHCl_3$	EIBHB-III
Chlorobenzene	EIBHB-III
Bromobenzene	EIBHB-III

Morpholine	EIBHB-III
Anisole	EIBHB-III

Table S4 List of solvent used for the crystallization of **DIBHG**.

The solvent used for crystallization of DIBHG	**Outcomes of crystallization**
Dichloromethane (DCM)	DIBHG-I and DIBHG-II
Ethylacetate	DIBHG-II
Nitromethane	DIBHG-II
Toluene	DIBHG-II
Mesitylene	DIBHG-II
o-Xylene(*o*-XY)	DIBHG-II
m-Xylene(*m*-XY)	DIBHG-II
p-Xylene(*p*-XY)	DIBHG-II
Cyclohexane	DIBHG-II
Anisole	DIBHG-II
Chlorobenzene	DIBHG-II
Bromobenzene	DIBHG-II
MeOH+$CHCl_3$	DIBHG-II
EtOH+$CHCl_3$	DIBHG-II
Iso propanol +$CHCl_3$	DIBHG-II
Tertiary butanol+$CHCl_3$	DIBHG-II
Acetonitrile + $CHCl_3$	DIBHG-II

Table S5 List of solvent used for the crystallization of **FNBHB**.

The solvent used for crystallization of FNBHB	**Outcomes of crystallization**
Ethylacetate	FNBHB-I and FNBHB-II
Sublimation	FNBHB-II
$CHCl_3$	FNBHB-I
DCM	FNBHB-I
THF	FNBHB-I
1,4-Dioxane	FNBHB-I
o-Xylene(*o*-XY)	FNBHB-I
m-Xylene(*m*-XY)	FNBHB-I
p-Xylene(*p*-XY)	FNBHB-I
Nitrobenzene	FNBHB-I

Anisole	FNBHB-I
Mesitylene	FNBHB-I
Chlorobenzene	FNBHB-I
Bromobenzene	FNBHB-I
Morpholine	FNBHB-I
MeOH + DCM	FNBHB-I
EtOH + DCM	FNBHB-I
Benzene+DCM	FNBHB-I
Toluene +DCM	FNBHB-I
Cyclohexane+DCM	FNBHB-I
Nitromethane +DCM	FNBHB-I
Cyclohexanone + $CHCl_3$	FNBHB-I

Table S6 List of solvent used for the crystallization of **CBHBz**.

The solvent used for crystallization of CBHBz	**Crystallization outcomes**
o-Xylene (*o*-XY)	CBHBz-I
p-Xylene (*p*-XY)	CBHBz-I
DCM	CBHBz-I
Mesitylene	CBHBz-I
m-Xylene	CBHBz-II
1,4-Dioxane	CBHBz-II
Ethylbenzene	CBHBz-II
Benzene	CBHBz-II
Pyridine	CBHBz-II
DMF	CBHBz-II
2-Methyl pyridine	CBHBz-II
$CHCl_3$ (on fast evaporation)	CBHBz-III

Table S7 List of solvent used for the crystallization of **NBB.**

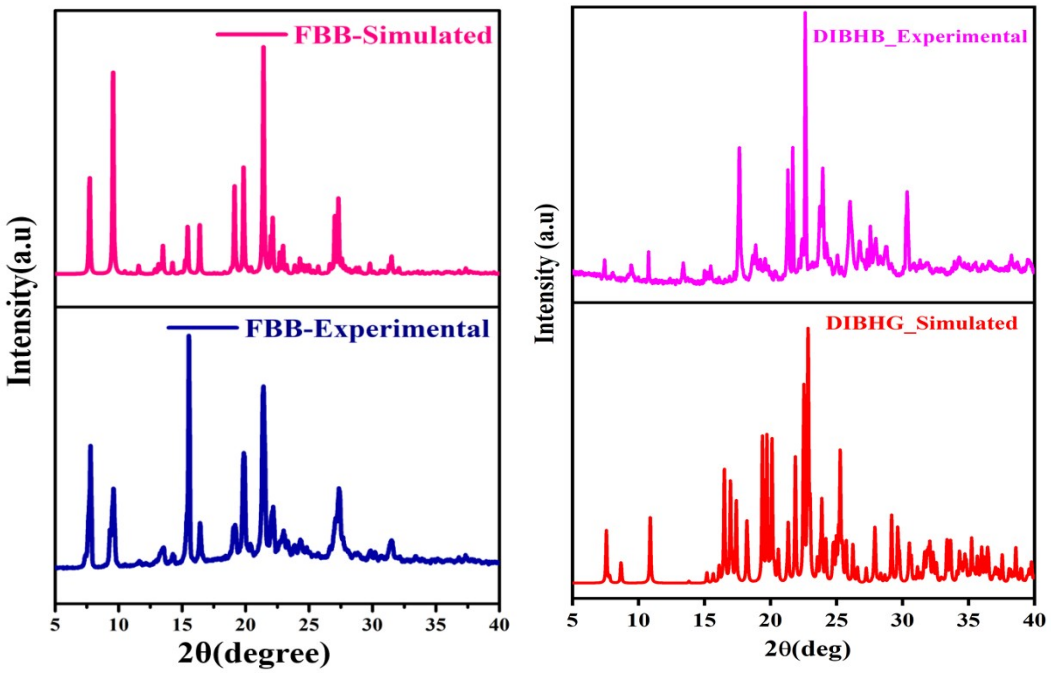
The solvent used for crystallization of NBB	**Outcomes of crystallization**
Ethylacetate	NBB-I
2-Methyl pyridine	NBB-I
Mesitylene	NBB-I
Bromo benzene	NBB-II

Table S8 List of solvents used for the crystallization of **FBB.**

Solvents used for crystallization of NBB	Outcomes of crystallization
meta-xylene (*m*-XY)	FBB-I
ortho-xylene (*o*-XY)	FBB-I
para-xylene	FBB-I
Mesitylene (Ms)	FBB-I
Toluene (TOL)	FBB-II
Sublimation	FBB-II

4. **Powder X-ray Diffraction**

The phase purity of bulk materials was analyzed by taking the Powder X-ray Diffraction Pattern (PXRD) using a Rigaku Miniflex-600 powder X-ray Diffractometer using CuKα radiation. The Data was collected from 5° to 40° at a scan rate of 2°/min by pasting the powder material of each samples at room temperature and compared with the simulated patterns extracted from single-crystal X-ray diffraction data.



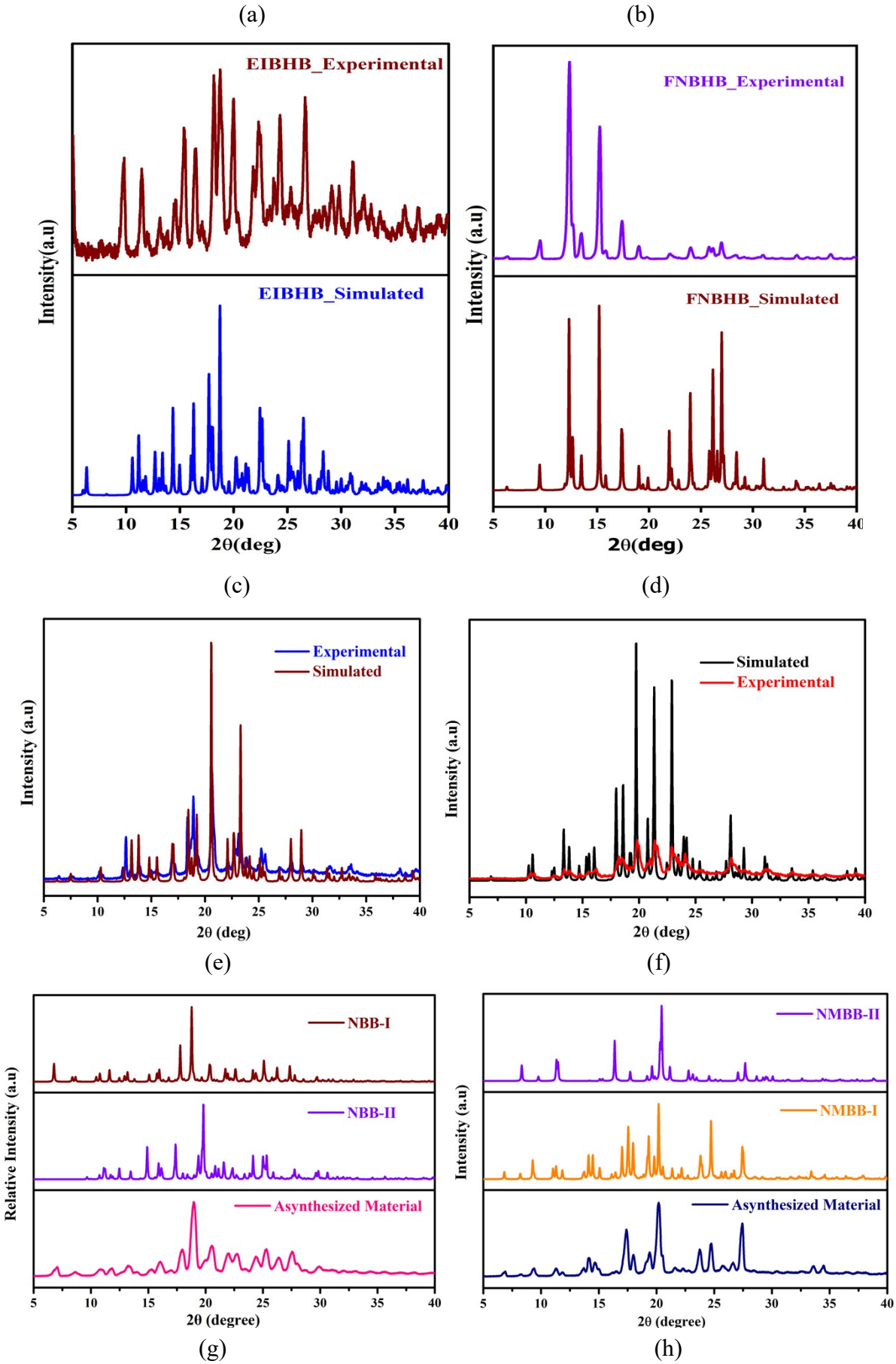

(a)
(b)
EIBHB_Experimental
EIBHB_Simulated
Intensity(a.u)
2θ(deg)
FNBHB_Experimental
FNBHB_Simulated
Intensity (a.u)
2θ(deg)
(c)
(d)
Experimental
Simulated
Intensity (a.u)
2θ (deg)
Simulated
Experimental
Intensity (a.u)
2θ (deg)
(e)
(f)
NBB-I
NBB-II
Asynthesized Material
Relative Intensity (a.u)
2θ (degree)
NMBB-II
NMBB-I
Asynthesized Material
Intensity (a.u)
2θ (degree)
(g)
(h)

Fig. S6 PXRD pattern for (a) **FBB**, (b) **DIBHG**, (c) **EIBHB**, **NMBB**, (d) **FNBHB,** (e) **CBHBz-I**, (f) **CBHBz-II**, (g)**NBB**, and (h)**NMBB** respectively

5. **Single X-ray diffraction data**

The crystal structure of all the compounds were determined in Bruker D8 Quest single crystal X-ray diffractometer equipped with a microfocus anode (MoKα) and a PHOTON 100 CMOS detector. The integration and scaling of data were performed using the Bruker suite programs[3] and the structures was solved by direct methods and refined by full-matrix least-squares on F2 using SHELX[4-6] and X-Seed software.[7] All non–hydrogen atoms were refined anisotropically. All the aromatic hydrogen atoms were placed using calculated positions on riding models. Crystallographic data and final refinement details for compounds are given below.

Table S9 Crystallographic data and structure refinement parameters of **FBB-I**, **FBB-II**, **NBB-I**, **NBB-II**, **DIBHG-I** and **DIBHG-II.**

	FBB-I	**FBB-II**	**NBB-I**	**NBB-II**	**DIBHG-I**	**DIBHG-II**
Moiety formula	$C_{40}\,H_{26}\,N_4$	$C_{40}\,H_{26}\,N_4$	$C_{38}\,H_{30}\,N_4\,O_2$	$C_{38}\,H_{30}\,N_4\,O_2$	$C_{28}\,H_{18}\,I_4\,N_4$	$C_{28}\,H_{18}\,I_4\,N_4$
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*C*2/c	$P2_1/n$	$P2_1/c$	$P2_1/c$	$Pna2_1$	*P*-1
a (Å)	26.8941(16)	9.3691(13)	10.5848(16)	15.271(2)	22.6243(16)	7.9279(7)
b(Å)	13.4775(8)	10.7182(15)	26.074(4)	9.8156(13)	5.5145(4)	9.8606(9)
c(Å)	18.9193(12)	29.938(4)	11.1341(19)	20.758(3)	23.3125(18)	10.2238(8)
α (°)	90	90	90	90	90	103.116(2)
β (°)	121.399(2)	94.932(4)	94.403(5)	98.675(6)	90	111.147(2)
γ (°)	90	90	90	90	90	98.956(3)
V/Å^3	5853.4(6)	2995.3(7)	3063.8(9)	3075.9(8)	2908.5(4)	700.70(11)
Z	8	4	4	4	4	1
D_{cal}/g cm^{-3}	1.277	1.248	1.246	1.241	2.097	2.176
T/K	298(2)	298(2)	300(2)	298(2)	293(2)	100(2)
μ/mm^{-1}	0.076	0.074	0.078	0.078	4.309	4.471
F_{000}	2352	1176	1208	1208	1704	426
Reflection measured	57036	46324	75825	84400	29890	18921

Unique reflections	7252	7470	6661	7687	5927	3487
Observed reflections	5737	4089	4168	4132	5495	3093
Parameters	397	398	407	399	335	167
R_{int}	0.0456	0.0759	0.0763	0.1311	0.0391	0.0302
Final R (I>2σ(I))	0.0448	0.0745	0.0589	0.0529	0.0247	0.0205
Final R(all data)	0.0589	0.1435	0.1027	0.1227	0.0317	0.0260
GOF on F2	1.038	1.064	1.064	1.069	1.078	1.059
CCDC No.	2425025	2425026	2425029	2425030	2123543	2425021

Table S10 Crystallographic data and structure refinement parameters of **NMBB-I**, **NMBB-II**, **NMBB-III, CBHBz-I, CBHBz-II** and **CBHBz-III**.

	NMBB-I	**NMBB-II**	**NMBB-III**	**CBHBz-I**	**CBHBz-II**	**CBHBz-III**
Moiety formula	$C_{40}H_{34}N_4O_2$	$C_{40}H_{34}N_4O_2$	$C_{40}H_{34}N_4O_2$	$C_{32}H_{26}N_4$	$C_{32}H_{26}N_4$	$C_{32}H_{26}N_4$
Crystal System	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	*P*-1	*C*cc2	*P*bcn	$P2_1$	$P2_12_12_1$	*P-1*
a (Å)	11.111(3)	9.9995(9)	18.426(7)	11.8378(18)	7.7573(5)	10.3829(7)
b(Å)	11.120(4)	21.219(2)	14.516(6)	7.6253(13)	17.2615(9)	10.6700(7)
c(Å)	13.583(4)	15.4151(14)	24.976(11)	14.277(3)	19.0749(10)	13.3452(8)
α (°)	75.672(9)	90	90	90	90	100.606(2)
β (°)	74.720(8)	90	90	96.549(6)	90	94.261(2)
γ (°)	83.333(11)	90	90	90	90	113.760(2)
V/Å^3	1566.1(8)	3270.8(5)	6681(5)	1280.4(4)	2554.2(3)	1311.79(15)
Z	2	4	8	2	4	2
D_{cal}/g cm^{-3}	1.278	1.224	1.198	1.210	1.213	1.181
T/K	100(2)	298(2)	298(2)	298(2)	298(2)	298(2)
μ/mm^{-1}	0.080	0.076	0.075	0.072	0.072	0.071
F_{000}	636	1272	2544	492	984	492
Reflection measured	32520	33864	216308	27445	55807	27627
Unique reflections	7777	4055	8201	6322	6356	6480
Observed reflections	6631	3325	5665	5153	4955	4644
Parameters	592	254	420	325	333	325

R_{int}	0.0442	0.1084	0.0810	0.0466	0.0613	0.0424
Final R (I>2σ(I))	0.587	0.0557	0.0551	0.0413	0.0431	0.0636
Final R(all data)	0.0685	0.0660	0.0842	0.0557	0.0639	0.0887
GOF on F2	1.124	1.053	1.050	1.059	1.040	1.018
CCDC No.	2425031	2425032	2425033	2425019	2425020	2427349

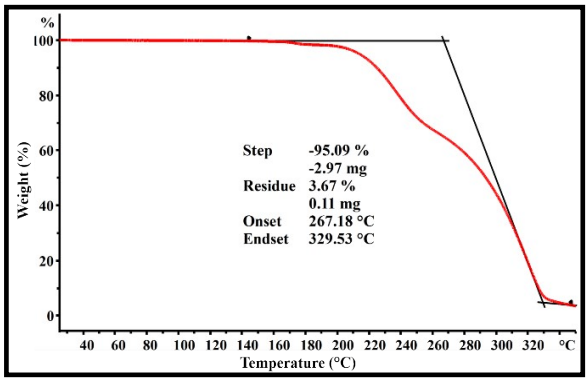
Table S11 Crystallographic data and structure refinement parameters of **FNBHB-I**, **FNBHB-II**, **EIBHB-I**, **EIBHB-II** and **EIBHB-III**.

	FNBHB-I	**FNBHB-II**	**EIBHB-I**	**EIBHB-II**	**EIBHB-III**
Moiety formula	$C_{24}H_{19}N_5O_2$	$C_{24}H_{19}N_5O_2$	$C_{38}H_{42}I_2N_6$	$C_{38}H_{42}I_2N_6$	$C_{38}H_{42}I_2N_6$
Crystal System	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	$P2_1/n$	P-1	P-1
a (Å)	28.913(4)	8.9156(12)	7.9713(7)	10.325(4)	11.4420(9)
b(Å)	4.8255(5)	9.8977(14)	15.8311(14)	11.902(5)	11.5769(9)
c(Å)	14.858(2)	12.0300(17)	29.590(3)	16.282(6)	14.7255(12)
α (°)	90.00	78.532(4)	90	83.689(12)	105.644(3)
β (°)	104.627(5)	88.488(4)	95.268(3)	72.592(13)	95.194(3)
γ (°)	90.00	83.005(4)	90	77.625(12)	90.202(3)
V/Å^3	2005.7(4)	1032.6(2)	3718.3(6)	1862.7(12)	1869.8(3)
Z	4	2	4	2	2
D_{cal}/g cm^{-3}	1.356	1.317	1.494	1.492	1.485
T/K	300(2)	300(2)	293(2)	298(2)	298(2)
μ/mm^{-1}	0.090	0.087	1.726	1.722	1.715
F_{000}	856	428	1672	836	836
Reflection measured	52280	34488	109878	47537	56555
Unique reflections	5014	5228	9247	9207	9351
Observed reflections	3509	2891	5242	6412	6559
Parameters	287	287	421	443	437
R_{int}	0.0645	0.0472	0.0525	0.0272	0.0291
Final R (I>2σ(I))	0.0542	0.0473	0.0651	0.0478	0.0626
Final R(all data)	0.0840	0.1038	0.1161	0.0726	0.0886
GOF on F2	1.035	1.032	1.032	1.055	1.044

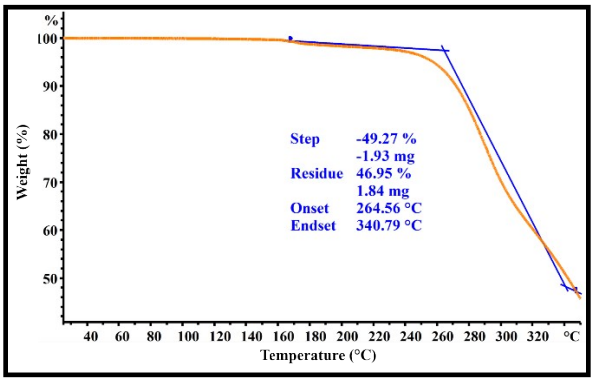
CCDC No.	2425027	2425028	2425022	2425023	2425024

6. Thermogravimetric analysis (TGA)

The thermal stability of a compounds was checked by TGA thermogram. The TGA of a compounds **1-7** was carried out by using Mettler Toledo equipped with Minichiller MT/230 under nitrogen atmosphere at a flow rate of 20ml/minute at a scan rate of 5°C/minute.



(a)



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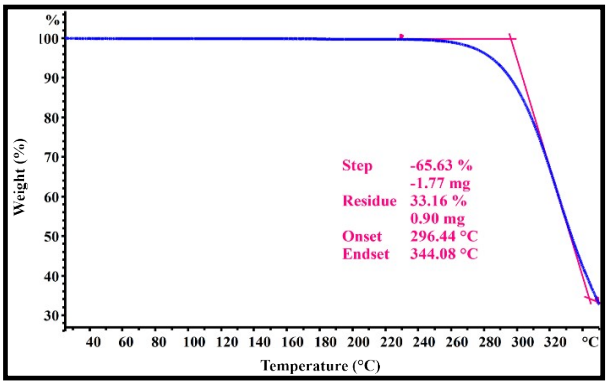

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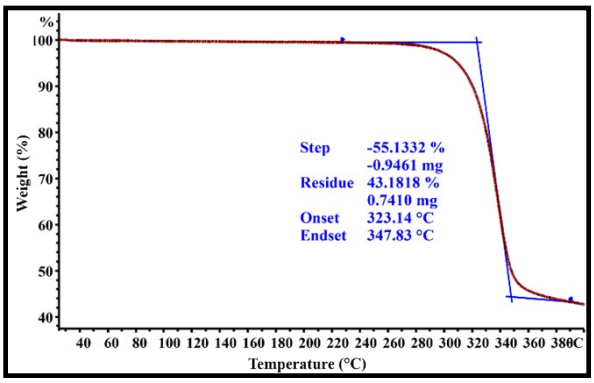

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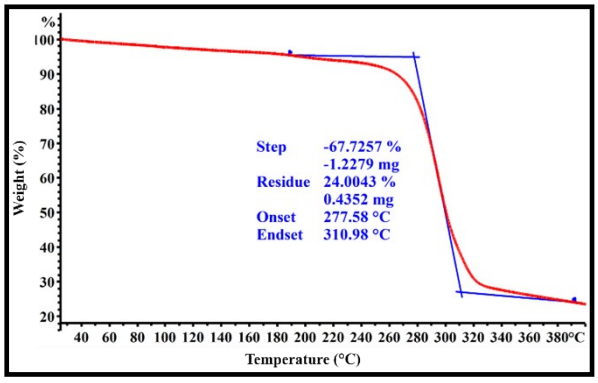
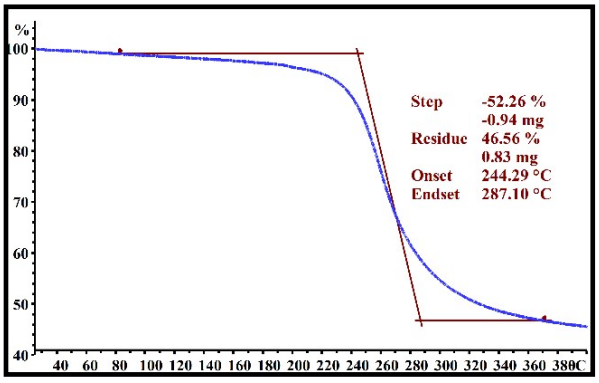


(e)



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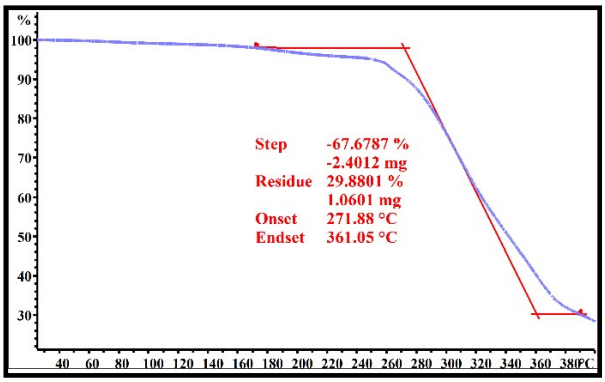


(g)

Fig. S7 The TGA thermogram of (a) **CBHBz** shows thermally stable upto 210°C followed by sublimation and then decomposition, (b) **NBB** shows thermally stable up to 260°C, (c) **NMBB** shows thermally stable upto 280°C, (d) **FBB** shows thermally stable upto 300 °C, (e) **EIBHB** shows thermally stable upto 260°C, (f) **FNBHB** shows thermal stability upto 240°C, and (g) **DIBHG** shows thermally stable upto 250°C followed by decomposition of compounds respectively.

7. Parameters of torsional angle and the dihedral angle

Table S12 Presence of torsional and dihedral angles in the crystal structure of different polymorphs.

Compound	Polymorph of compound	Angle between the average plane of phenyl ring	Torsion angle	Packing index (%)
FBB	FBB-I	20.95	124.3(1),133.6(1),-79.9(2)	67.1
	FBB-II	16.15	120.4(3),-128.5(2),79.8(3)	65.5
CBHBz	CBHBz-I	75.3	176.8(2),-114.9(2),82.4(2)	66.3
	CBHBz-II	79.35	172.2(2),-116.7(2),82.0(2)	66.6
	CBHBz-III	80.22	170.1(2),152.5(2),-84.7(2)	64.6
NBB	NBB-I	88.53	-154.4(2),176.7(2),88.7(2)	66.0
	NBB-II	78.71	-154.0(1),173.0(1),89.9(2)	65.6
NMBB	NMBB-I	83.28	-119.3(4),171.1(4),94.2(4)	66.5
	NMBB-II	2.67	-137.2(3), 79.7(3)	66.2
	NMBB-III	11.26	-132.1(2),143.2(1),69.4(2)	64.4
DIBHG	DIBHG-I	77.50	175.4(2)	67.9
	DIBHG-II	75.17	169.9(6)	65.3

EIBHB	Torsional angle of unit having terminal N,N-diethyl substituted phenyl rings	Torsional angle of unit having terminal iodosubstituted phenyl rings	Average angle between the plane of terminal N,N diethyl substituted phenyl rings	Average angle between the plane of terminal iodo substituted phenyl rings	Packing index (%)
EIBHB-I	140.1(4)	-137.1(4)	65.77	66.06	64.6
EIBHB-II	-197.7(4)	167.3(4)	66.14	71.46	63.3
EIBHB-III	-136.6(4)	-177.0(4)	62.94	72.47	64

Polymorph of FNBHB	Torsional angle of –CH=N-N=CH- unit at the side of fluorenone moieties	Torsional angle of –CH=N-N=CH- unit at the side of NO_2 substituted phenyl ring	Packing index (%)
FNBHB-I	129.2(1)	-122.8(2)	67.7
FNBHB-II	152.9 (2)	-177.7(2)	69.7

8. Parameters of interactions

The parameters of interactions present in the crystal structure of polymorphs of a compounds are given below.

Table S13 The interactions present in the crystal structure of different polymorphs.

Compound	**D–H···A**	**D–H (Å)**	**H···A (Å)**	**D–A (Å)**	**∠ D–H···A**
FBB-I	C(19)–H(16)···Cg	0.930	2.817	3.583(2)	140.5
	C(23)–H(23)···C(17)	0.930	2.880	3.583	156.7
FBB-II	C(18)–H(18)···Centroid od C26,C27	0.930	2.735	3.640	164.65
	C(33)–H(33)···C(39)	0.930	2.892	3.559(5)	129.7
CBHBz-I	C(31)–H(31)···C(27)	0.930	2.843	3.609(4)	140.5
	C(30)–H(30)···Cg	0.930	2.958	3.781	148.35
	C(16)–H(16)···C(14)	0.930	2.787	3.558(4)	140.9
CBHBz-II	C(20)–H(20)···Cg	0.930	2.91	3.642(3)	137
	C(12)–H(12)···C(30)	0.930	2.813	3.481(3)	129.7
CBHBz-III	C(7)–H(7)···Cg	0.930	2.902	3.510	124.19
NBB-I	C(23)–H(23)···O(2)	0.930	2.452	3.320(3)	155.3
	C(24)–H(24)···C(9)	0.930	2.876	3.611(3)	136.8
	C(19)–H(19)···C(2)	0.930	2.882	3.599(4)	134.9
	C(18)–H(18)···C(10)	0.930	2.855	3.730(4)	157.2
NBB-II	C(4)–H(4)···C(18)	0.930	2.895	3.805(2)	166.2
	C(38)–H(38B)···Cg	0.960	2.824	3.579	136.13
	C(12)–H(12)···O(1)	0.930	2.687	3.605(2)	169.21
NMBB-I	C(28)–H(28B)···Cg	0.960	2.706	3.587(6)	152.97
	C(33)–H(33)···C(8)	0.930	2.859	3.542(8)	131.3
	C(1)–H(1A)···O(1)	0.960	2.711	3.333(9)	123.0
NMBB-II	C(28)–H(28B)···C(32)	0.960	2.800	3.421(6)	123.2
	C(1)–H(1A)···O(1)	0.960	2.711	3.333(9)	123.0

	C(17)–H(17B)···C(12)	0.930	2.893	3.558(7)	129.6
NMBB-III	C(40)–H(40B)···N(2)	0.960	2.711	3.472(3)	136.6
	C(18)–H(18)···C(31)	0.930	2.999	3.645(3)	127.9
	C(36)–H(36)···O(2)	0.930	2.532	3.435(3)	164.0
EIBHB-I	C(20)–H(20)···C(7)	0.950	2.865	3.694(7)	146.4
	C(9)–H(9)···N(3)	0.950	2.722	3.462(6)	135.3
	C(26)–H(26C)···I(2)	0.98	3.0742	3.95(1)	150
EIBHB-II	C(17)–H(17B)···C(23)	0.9560	2.811	3.662(9)	148.2
EIBHB-III	C(37)–H(37B)···C(13)	0.96	2.878	3.661(1)	133.8
	C(5)–H(5)···N(3)	0.930	2.740	3.353(7)	124.3
	C(12)–H(12)···C(30)	0.930	2.897	3.824(7)	175.1
	C(12)–H(12)···C(31)	0.930	2.845	3.673(8)	149.0
FNBHB-I	C(20)–H(20)···O(2)	0.930	2.520	3.360(3))	150.4
	C(4)–H(4)···C(10)	0.930	2.894	3.803(3)	165.9
	C(10)–H(10)···C(4)	0.930	2.842	3.619(3)	141.8
FNBHB-II	C(18)–H(18)···C(14)	0.98(2)	2.88(2)	3.849(3)	172(1)
	C(9)–H(9)···O(2)	0.930	2.624	3.419(3)	143.8
DIBHG-II	C(14)–H(1)···I(1)	0.93(3)	3.02(2)	3.838(2)	149(2)

9. Lattice Energy Calculation table

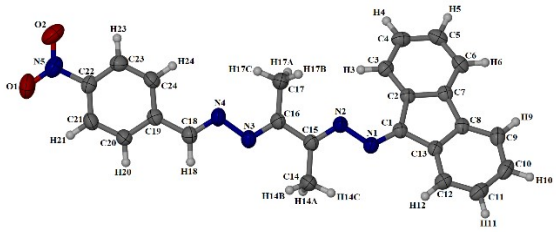
The lattice energy calculations of compounds **1-7** polymorphs were calculated using Crystal Explorer 21.5.[8] The crystal lattice energy calculations were carried out by constructing clusters using radius of 20Å for each polymorph.

Table S14 The lattice energy and density of different polymorphs.

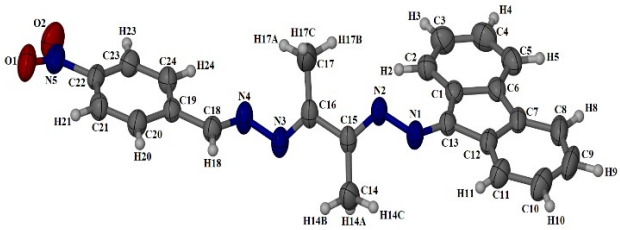
Polymorphs	**Lattice energy (kJ mol-^{1})**	**Method**	**Density (g/cm^{3}) (from SCXRD data)**
FNBHB-I	-199.3	B3LYP/6-31G(d,p)	1.356
FNBHB-II	-182.8	B3LYP/6-31G(d,p)	1.317
EIBHB-I	-307.75	HF/3-21G	1.494
EIBHB-II	-326	HF/3-21G	1.492
EIBHB-III	-272.95	HF/3-21G	1.485
DIBHG-I	-328.1	HF/3-21G	2.097
DIBHG-II	-145.6	HF/3-21G	2.176
FBB-I	-201.2	B3LYP/6-31G(d,p)	1.277
FBB-II	-191.7	B3LYP/6-31G(d,p)	1.248
NBB-I	-260.8	B3LYP/6-31G(d,p)	1.246

NBB-II	-273.95	B3LYP/6-31G(d,p)	1.241
NMBB-I	-264.85	B3LYP/6-31G(d,p)	1.278
NMBB-II	-248.9	B3LYP/6-31G(d,p)	1.224
NMBB-III	-255.1	B3LYP/6-31G(d,p)	1.198
CBHBz-I	-204.2	B3LYP/6-31G(d,p)	1.210
CBHBz-II	-205.8	B3LYP/6-31G(d,p)	1.213
CBHBz-III	-217.2	B3LYP/6-31G(d,p)	1.181

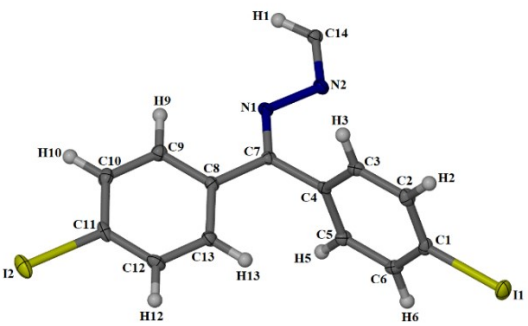
10. **Thermal ellipsoid plot of asymmetric unit**



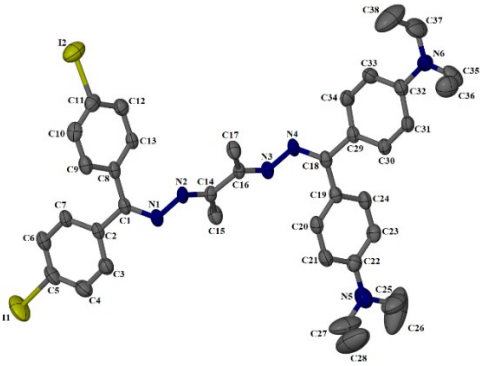
(a)



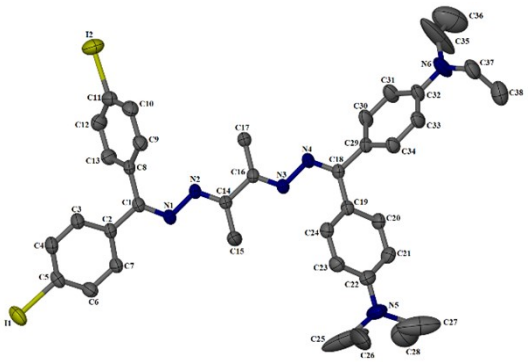
(b)



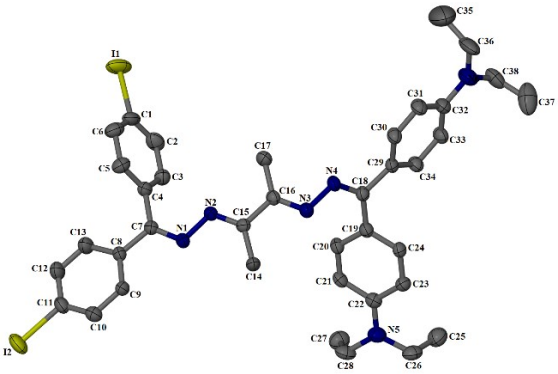
(c)



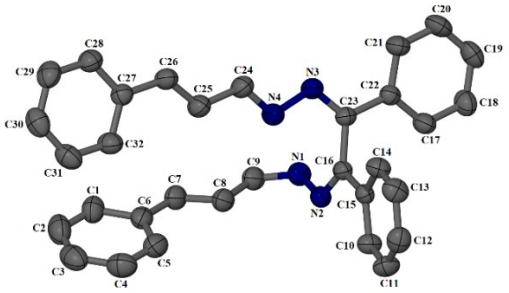
(d)



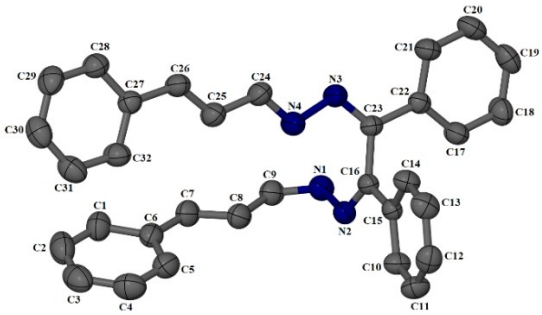
(e)



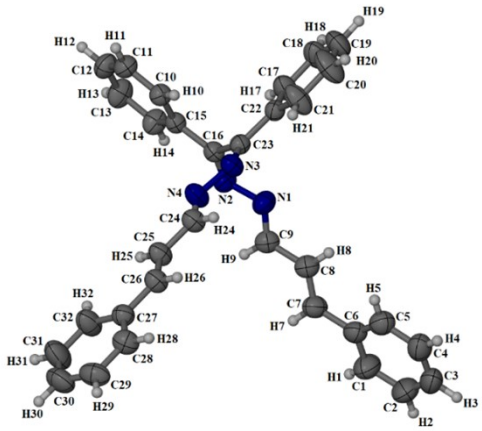
(f)



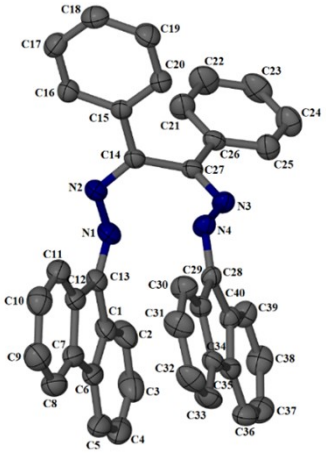
(g)



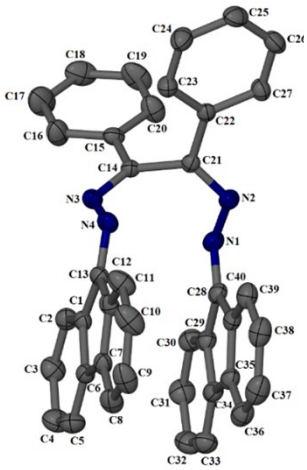
(h)



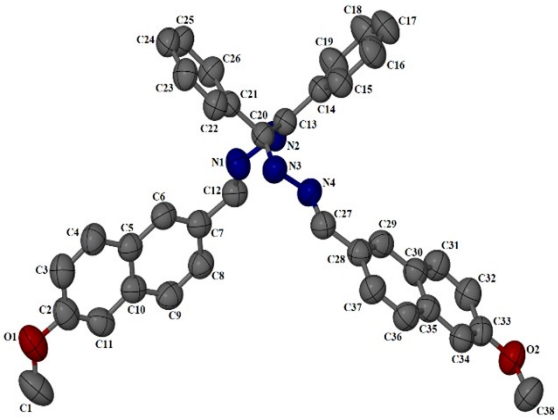
(i)



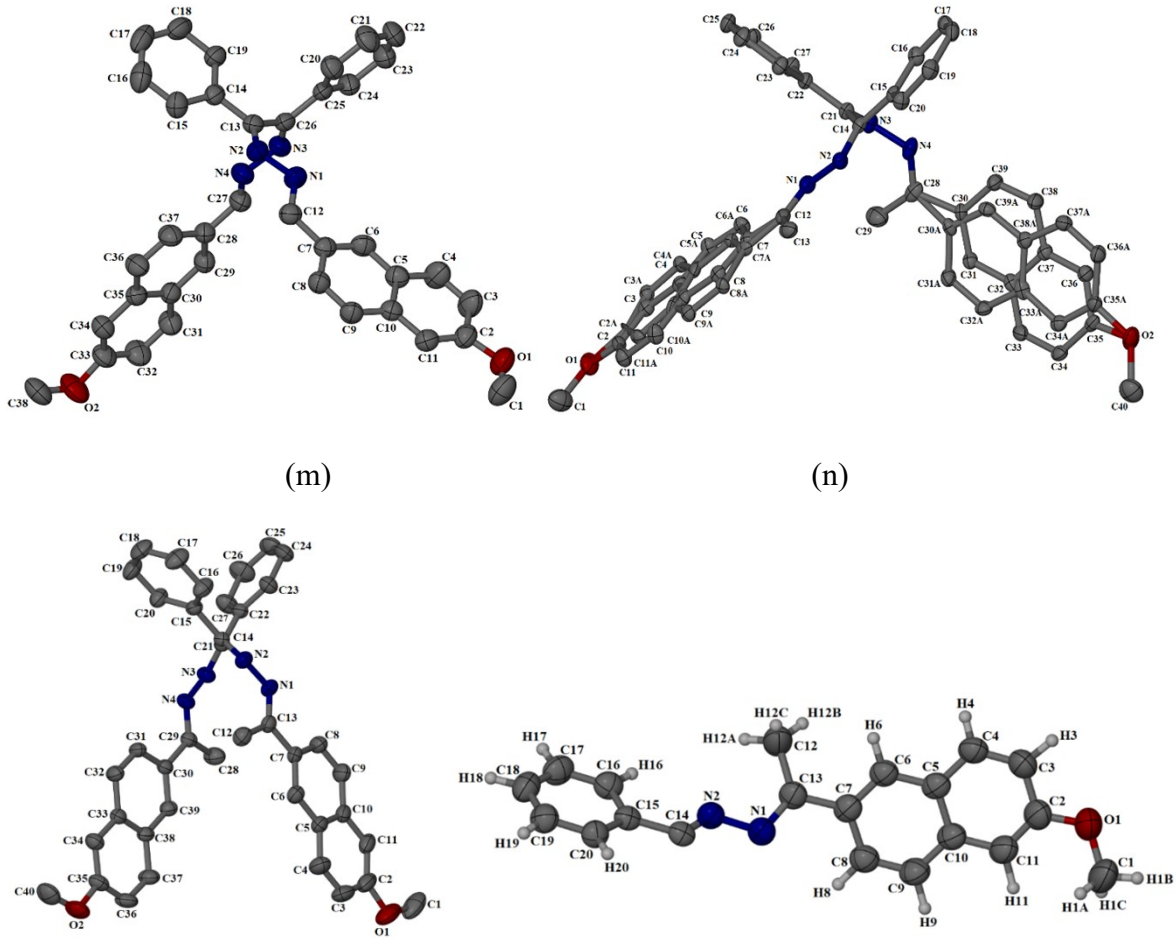
(j)



(k)



(l)

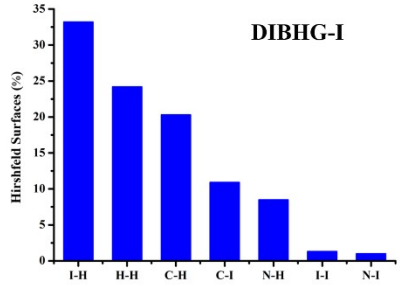


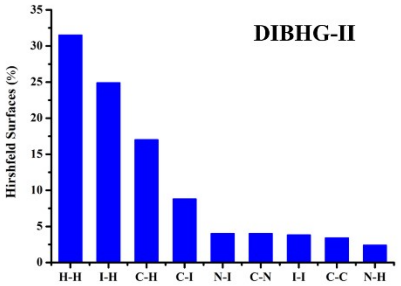
(m) (n)

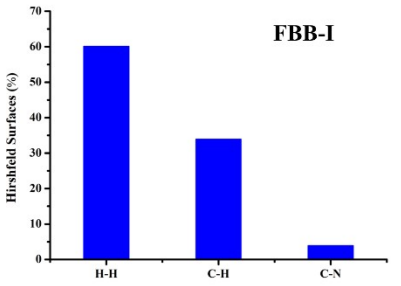
(o) (p)

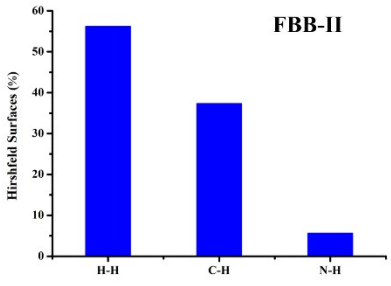
Fig. S8 The thermal ellipsoid plot of (a) **FNBHB-I**, (b) **FNBHB-II,** (c) **DIBHG-II**, (d) **EIBHB-I,** (e) **EIBHB-II**, (f) **EIBHB-III,** (g) **CBHBz-I**, (h) **CBHBz-II**, (i) **CBHBz-III,** (j) **FBB-I,** (k) **FBB-II,** (l)**NBB-I**, (m) **NBB-II,** (n)**NMBB-I,** (o) **NMBB-III** and (p) **NMBB-II** respectively. In case of (d), (e), (f), (g), (h), (j) and (n) to (p), the H-atoms are not shown here for the clarity of the picture. In case of **EIBHB-I**, **EIBHB-II** and **EIBHB-III** atoms are calculated with 40% probability while in others atoms are calculated with 50% probability.

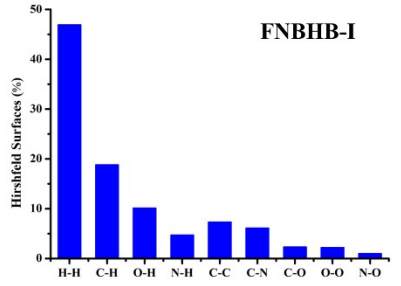
11. **Hirshfeld surface analysis**

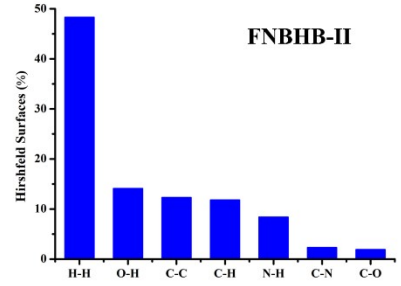

DIBHG-I
Hirshfeld Surfaces (%)
I-H
H-H
C-H
C-I
N-H
I-I
N-I

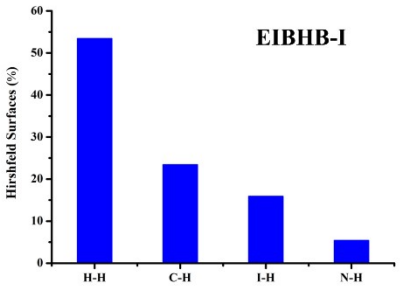

DIBHG-II
Hirshfeld Surfaces (%)
H-H
I-H
C-H
C-I
N-I
C-N
I-I
C-C
N-H

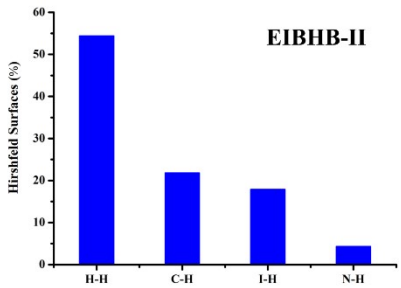

FBB-I
Hirshfeld Surfaces (%)
H-H
C-H
C-N

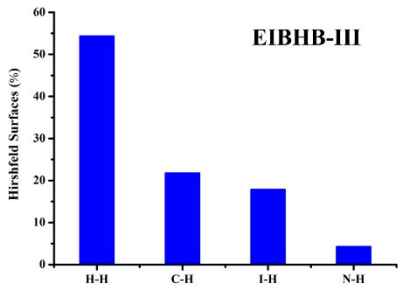

FBB-II
Hirshfeld Surfaces (%)
H-H
C-H
N-H

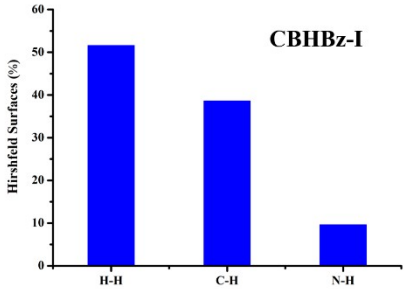

FNBHB-I
Hirshfeld Surfaces (%)
H-H
C-H
O-H
N-H
C-C
C-N
C-O
O-O
N-O

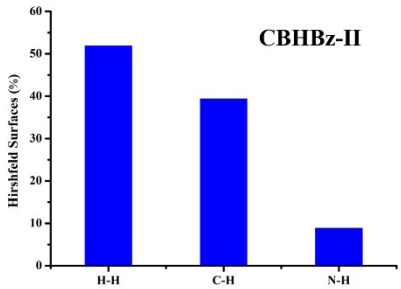

FNBHB-II
Hirshfeld Surfaces (%)
H-H
O-H
C-C
C-H
N-H
C-N
C-O

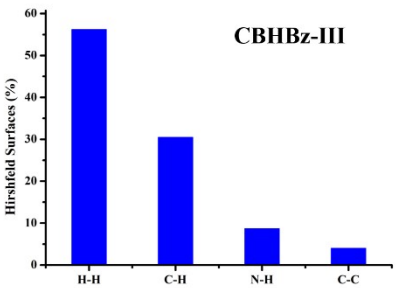

EIBHB-I
Hirshfeld Surfaces (%)
H-H
C-H
I-H
N-H


EIBHB-II
Hirshfeld Surfaces (%)
H-H
C-H
I-H
N-H


EIBHB-III
Hirshfeld Surfaces (%)
H-H
C-H
I-H
N-H


CBHBz-I
Hirshfeld Surfaces (%)
H-H
C-H
N-H


CBHBz-II
Hirshfeld Surfaces (%)
H-H
C-H
N-H


CBHBz-III
Hirshfeld Surfaces (%)
H-H
C-H
N-H
C-C

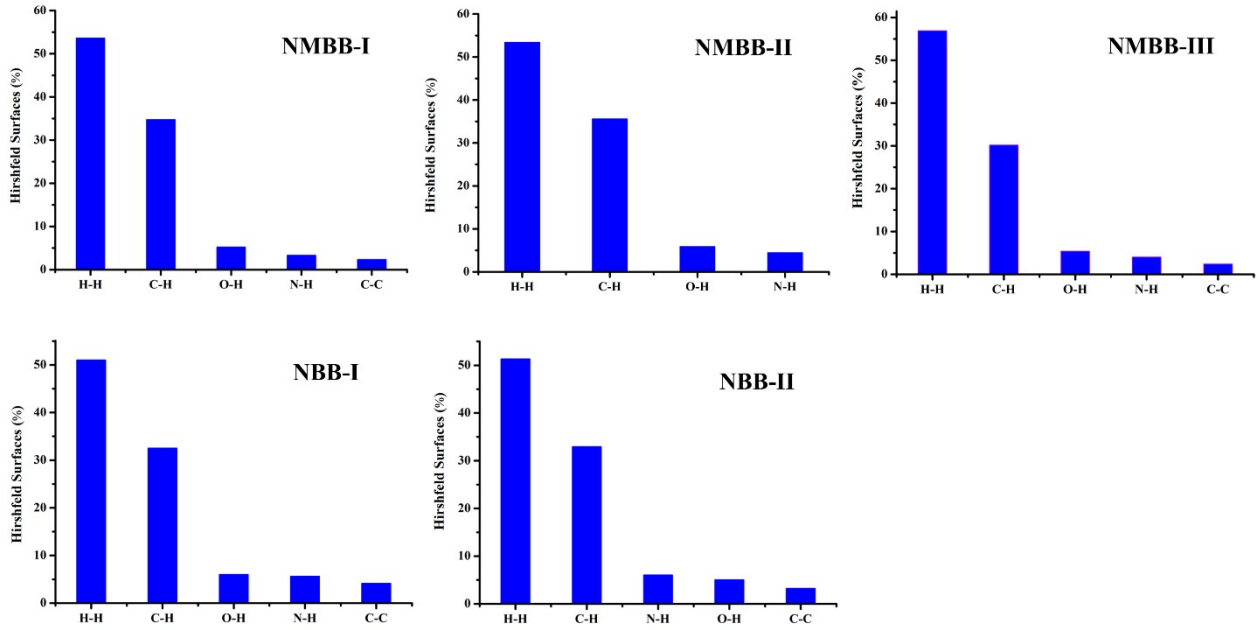
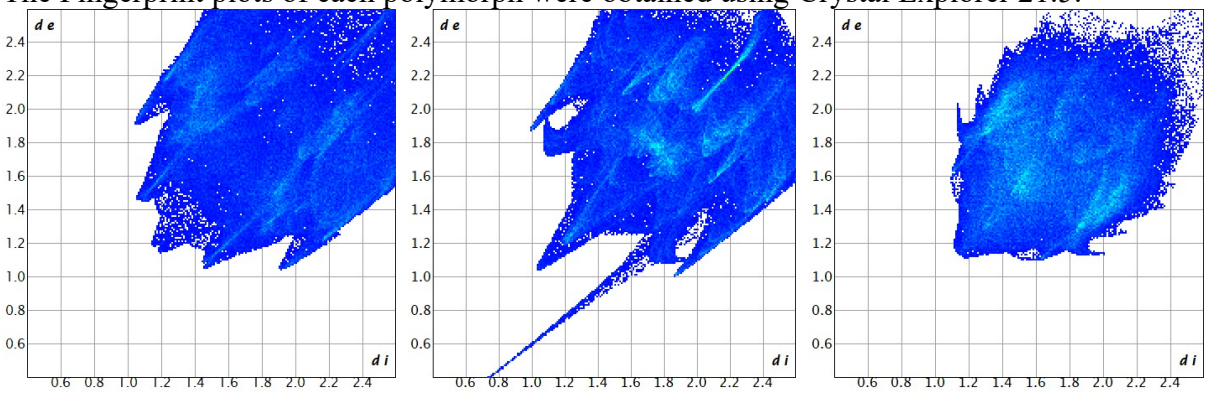


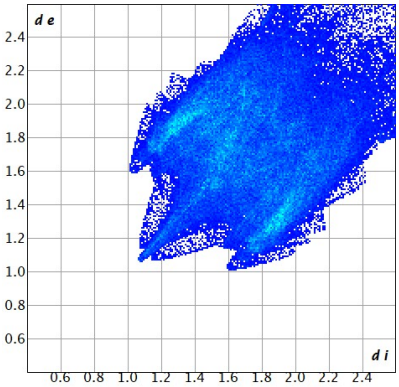
Fig. S9 Graphical representation of relative contributions of various intermolecular interactions

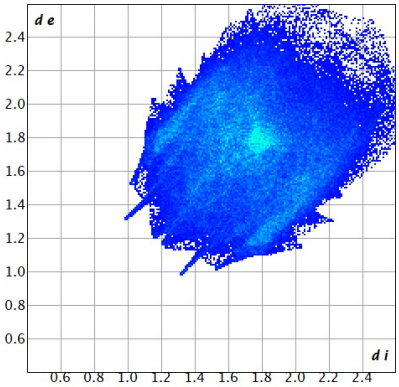
12. **Fingerprint plots**

The Fingerprint plots of each polymorph were obtained using Crystal Explorer 21.5.[8]

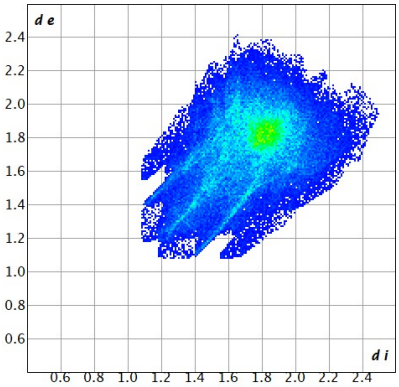


DIBHG-I **DIBHG-II** **FBB-I**

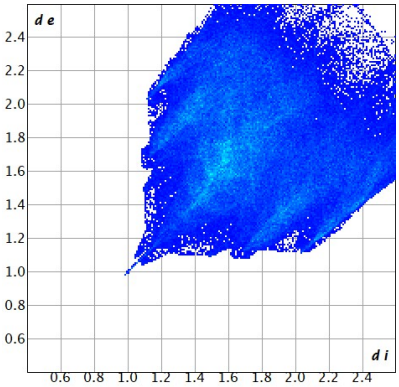




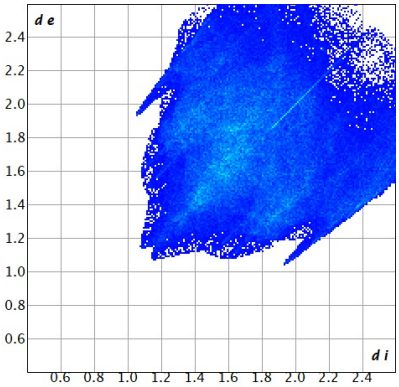
FBB-II

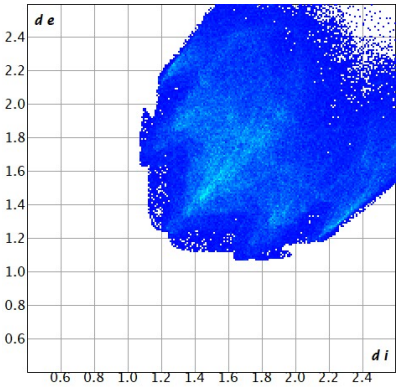


FNBHB-I



FNBHB-II

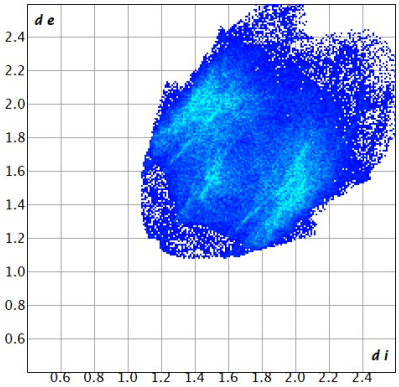


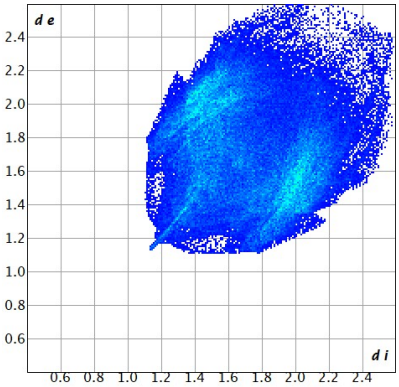


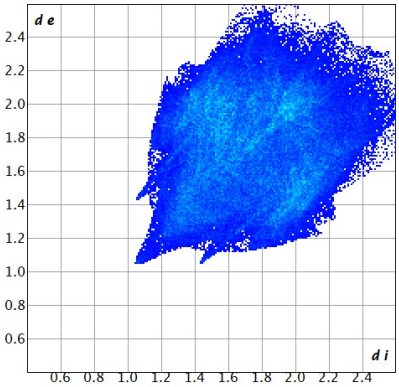
EIBHB-I

EIBHB-II

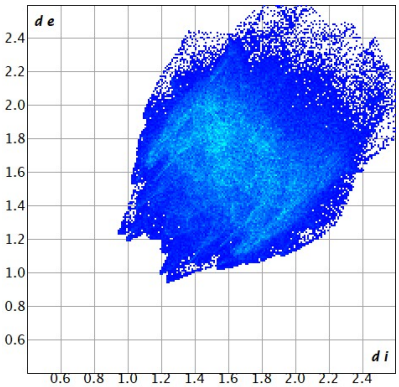
EIBHB-III

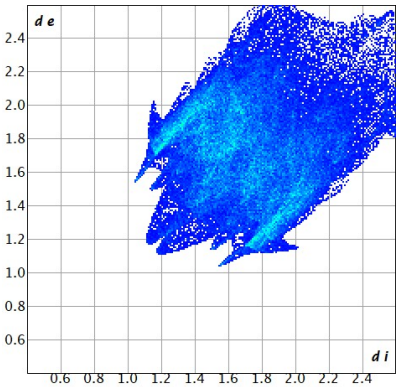


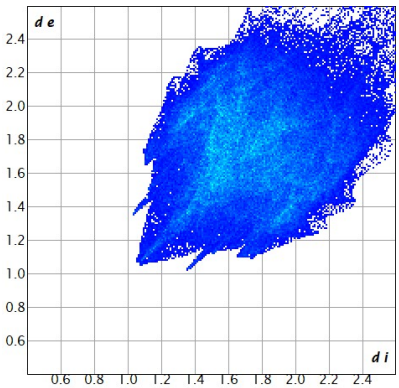




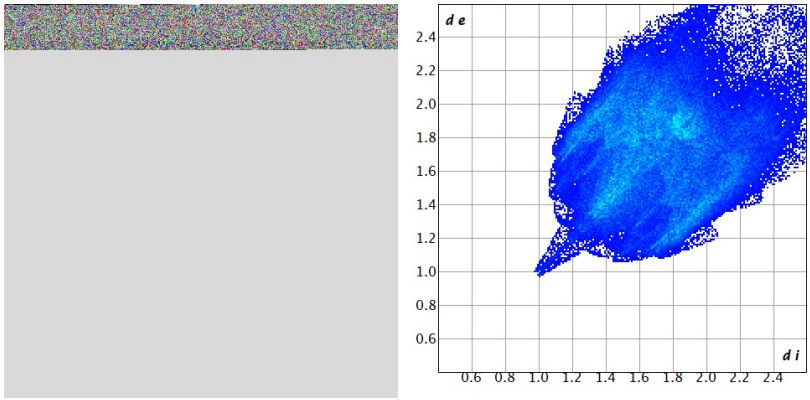
CBHBz-I **CBHBz-II** **CBHBz-III**







NMBB-I **NMBB-II** **NMBB-III**



NBB-I **NBB-II**

13. **References**

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