Electronic Supplementary Information (ESI)

Selective inclusion of *p*-xylene by bis-hydrazone compounds

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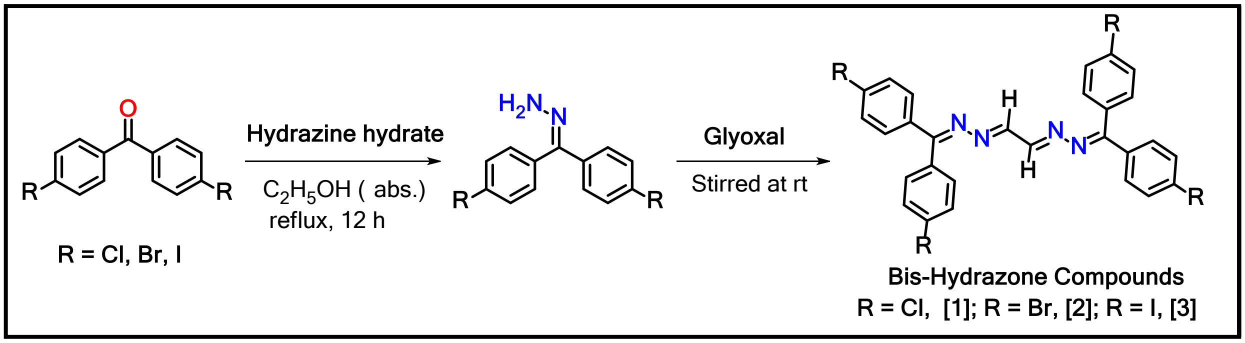
Table of content

1. **Experimental section:** Synthesis and characterization of compounds **1, 2** and **3**.
   - **Fig. S1** ^{1}H NMR spectra of compounds **1**
   - **Fig. S2** MASS spectrometry of compounds **1**
   - **Fig. S3** FT-IR spectra of compounds **1**
   - **Fig. S4** ^{1}H NMR spectra of compounds **2**
   - **Fig. S5** MASS spectrometry of compounds **2**
   - **Fig. S6** FT-IR spectra of compounds **2**
   - **Fig. S7** ^{1}H NMR spectra of compounds **3**
   - **Fig. S8** MASS spectrometry of compounds **3**
   - **Fig. S9** FT-IR spectra of compounds **3**
2. **Powder X-ray Diffraction**
   - **Fig. S10** PXRD pattern of compounds **1**
   - **Fig. S11** PXRD pattern of compounds **2**
   - **Fig. S12** PXRD pattern of compounds **3**
3. **Single Crystal X-ray Diffraction Study**
   - **Table S1** Crystal data and structure refinement parameters.
4. **Shape of Channels:**
   - **Fig. S13** Shape of channels in the crystal structures of (a) 1.*p*-XY (b) 2.*p*-XY (c) 3.*p*-XY.
5. **Photomicrographs of crystals**
   - **Fig. S14** Pictures of unsolvated crystal of (a) α form of 1 (b) α form of 2 and (c) α form of 3.
   - **Fig. S15** Pictures of solvated crystal of (a) 1.*p*-XY (b) 2.*p*-XY (c) 3.*p*-XY.
   - **Fig. S16** Pictures of desolvated crystal of (a) 1.*p*-XY (b) 2.*p*-XY (c) 3.*p*-XY.
6. **Thermal Ellipsoid plot of the asymmetric unit for the compound 1, 2 and 3**
   - **Fig. S17** Thermal ellipsoid plots of 1.*p*-XY
   - **Fig. S18** Thermal ellipsoid plots of 2.*p*-XY
   - **Fig. S19** Thermal ellipsoid plots of 3.*p*-XY
7. **Hirshfeld surface analysis**
   - **Fig. S20** 2D fingerprint plot of the crystal structure of α form of 1
   - **Fig. S21** 2D fingerprint plot of the crystal structure of α form of 2
   - **Fig. S22** 2D fingerprint plot of the crystal structure of α form of 3
   - **Fig. S23** 2D fingerprint plot of the crystal structure of 1•*p*-XY
   - **Fig. S24** 2D fingerprint plot of the crystal structure of 2•*p*-XY
   - **Fig. S25** 2D fingerprint plot of the crystal structure of 3•*p*-XY
   - **Fig. S26** Hirshfeld surface mapped with d_{norm} of *p*-xylene in crystal structure of 1•*p*-XY
   - **Fig. S27** Hirshfeld surface mapped with d_{norm} of *p*-xylene in crystal structure of 2•*p*-XY
   - **Fig. S28** Hirshfeld surface mapped with d_{norm} of *p*-xylene in crystal structure of 3•*p*-XY
8. **References**

1. Experimental section:

Synthesis and characterization of compounds 1, 2 and 3

All the chemicals and solvents were of reagent grade that used for the synthesis and crystallization of hydrazone compounds **1, 2** and **3** were received from commercial source such as Sigma –Aldrich and Alfa Aesar. ^{1}H NMR (500MHz) spectra were recorded by Bruker spectrometer in $CDCl_3$. Chemical shift for the protons are reported in ppm relative to the solvent peak using TMS as a standard. Spin multiplicity are given as singlet (s), doublet (d), and triplet (t) with the coupling constant (*J*) in Hz or multiplet (m). The compounds **1, 2** and **3** were prepared *via* slight modification in the previously reported methods.[1] The structure and purity of these compounds were confirmed by characterization techniques such as NMR, MASS, IR and SCXRD.



Scheme S1

NMR, MS and IR data for compound **1**

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 2H), 7.60 (d, $J = 8.5$ Hz, 4H), 7.42 (d, $J = 8.5$ Hz, 4H), 7.37 (d, $J = 8.2$ Hz, 4H), 7.19 (d, $J = 8.2$ Hz, 4H).

TOF-MS (m/z):553.0334 (100.0%), 551.0364 (78.2%), 555.0305 (47.9%).

FTIR (cm^{-1}): 3051, 1592, 1530, 1488, 1397.

Melting Point (^{o}C): 185-188 ^{o}C

NMR, MS and IR data for compound **2**

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.13 (s, 2H), 7.57 (d, J = 8.2 Hz, 4H), 7.53 (s, 8H), 7.12 (d, J = 8.2 Hz, 4H).

TOF-MS (m/z):731.8381 (100.0%), 729.8401 (68.5%), 733.8360 (64.9%).

FTIR (cm^{-1}):3087, 3059, 2975, 1579, 1529, 1481.

Melting Point (^{o}C): 192-198 ^{o}C

NMR, MS and IR data for compound **3**

^{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)

TOF-MS (m/z): 917.7710(100%),918.7744(30.3%), 919.7777(4.4%), 918.7681 (1.5%)

FTIR (cm^{-1}): 3047, 1584, 1477,1396, 991

Melting Point (^{o}C): 261-266 ^{o}C

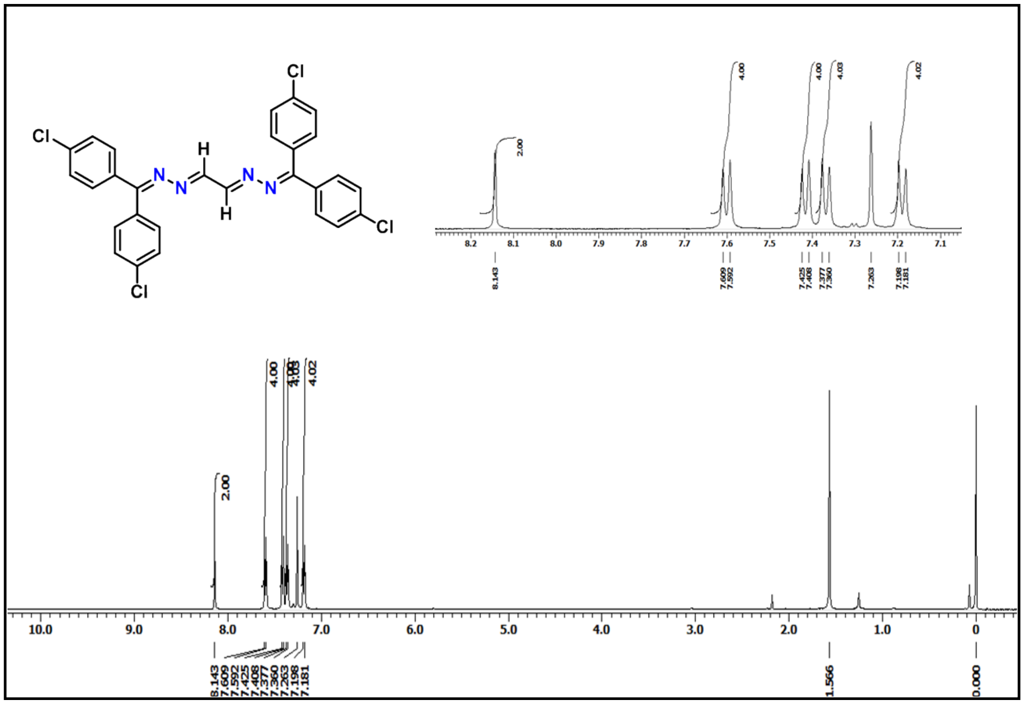


Fig. S1 500 MHz ^{1}H NMR spectrum of compound **1** in CDCl$_3$ at RT.

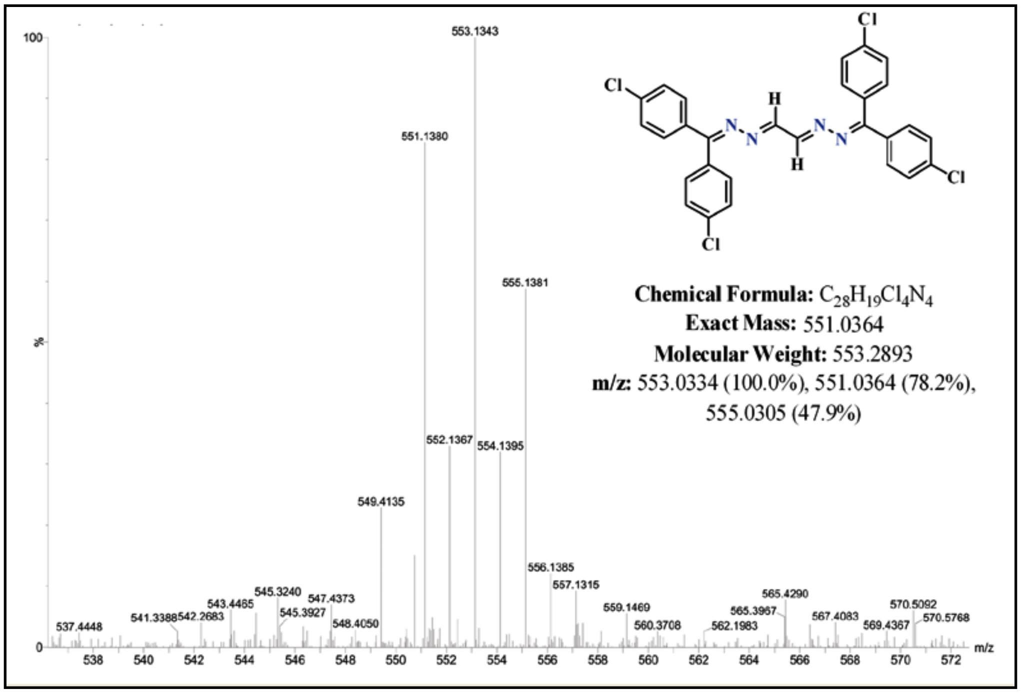


Fig. S2 TOF mass spectrum of compound **1** TOF-MS (m/z).

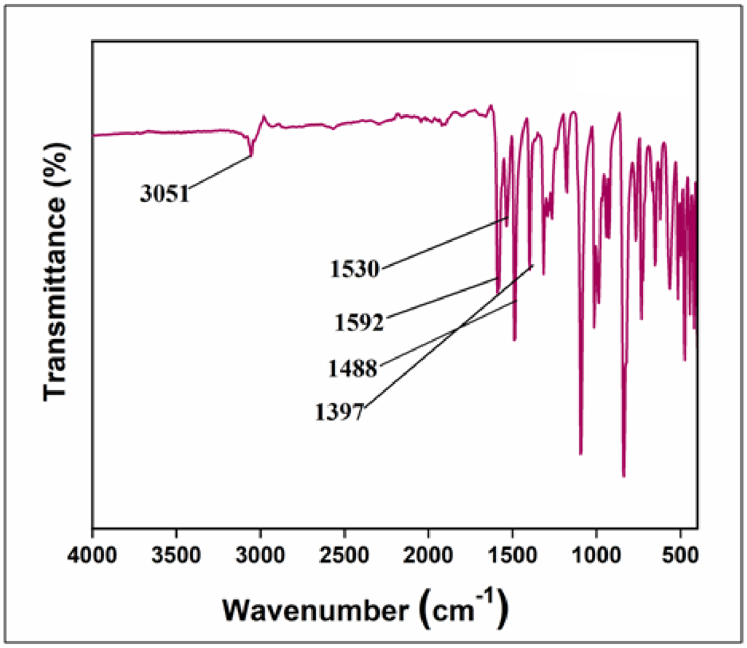


Fig. S3 FT-IR spectra of the powder of compound **1** recorded in Shimadzu (IRAffinity-1SWL).

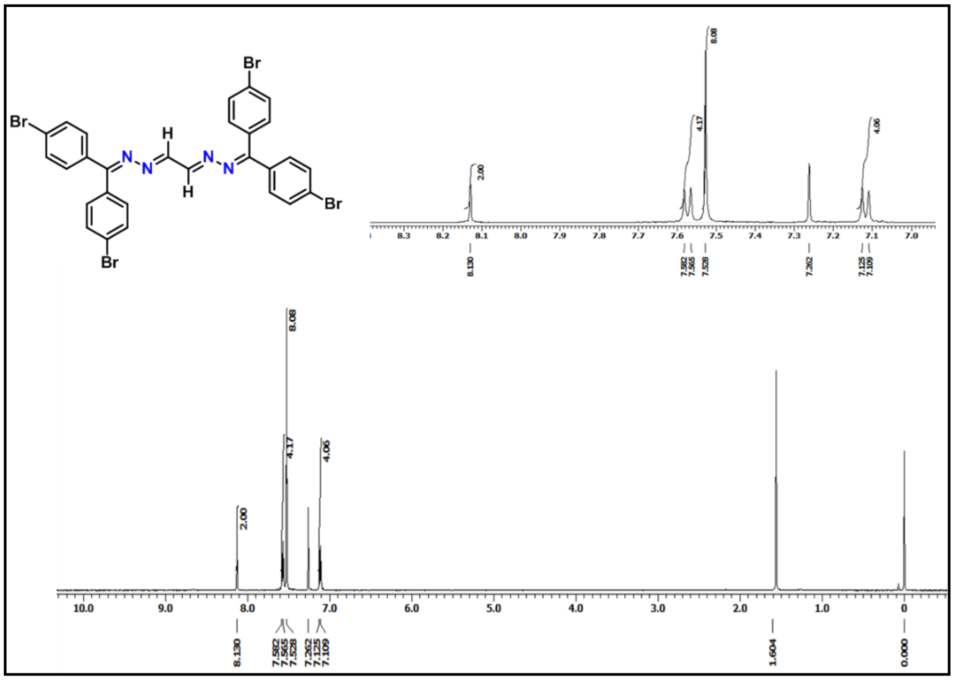


Fig. S4 500 MHz ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at RT

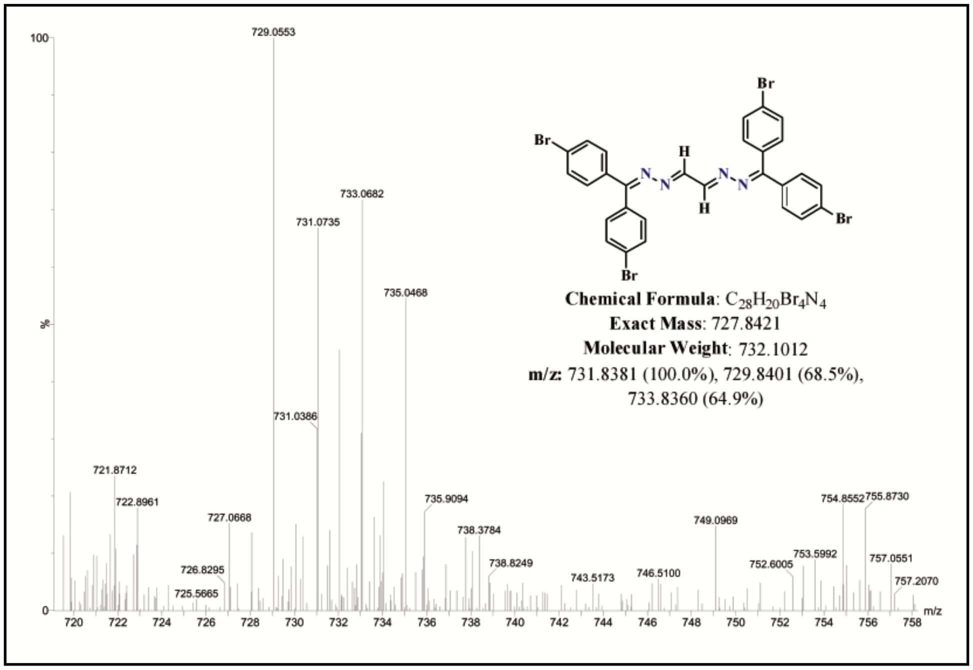


Fig. S5 TOF mass spectrum of compound **2** TOF-MS (m/z).

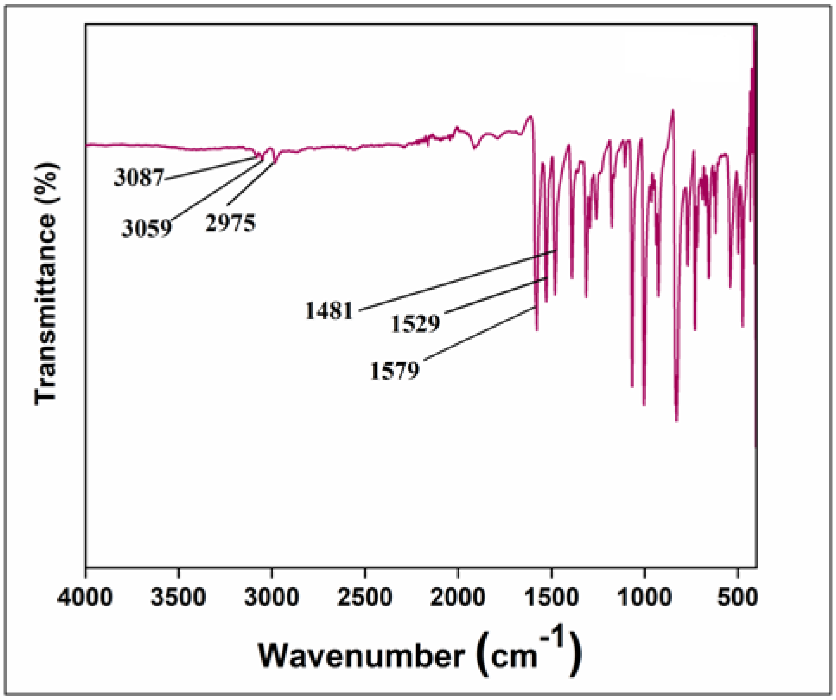


Fig. S6 FT-IR spectra of the powder of compound **2** recorded in Shimadzu (IRAffinity-1SWL)

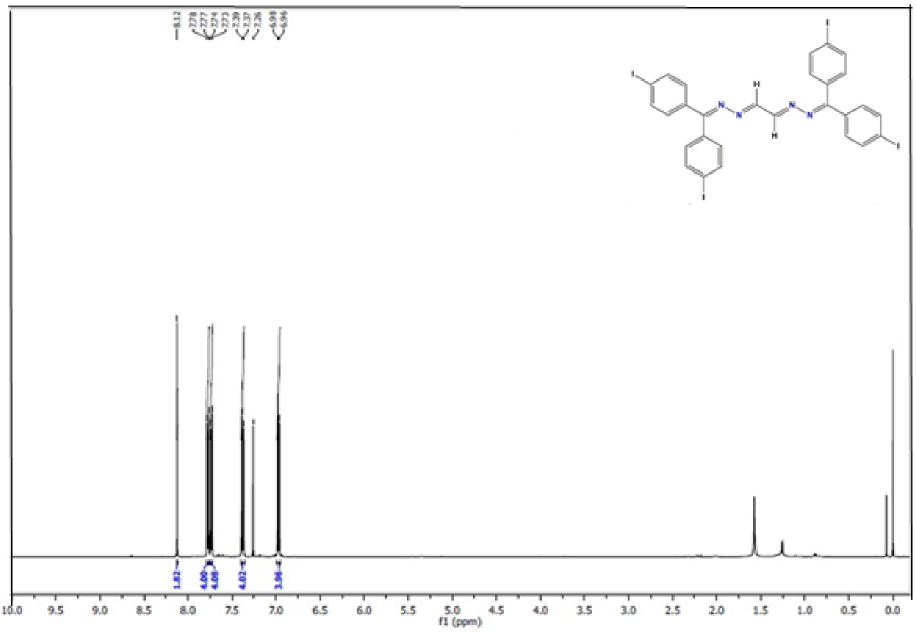


Fig. S7 500 MHz ^{1}H NMR spectrum of compound **3** in $CDCl_3$ at RT.

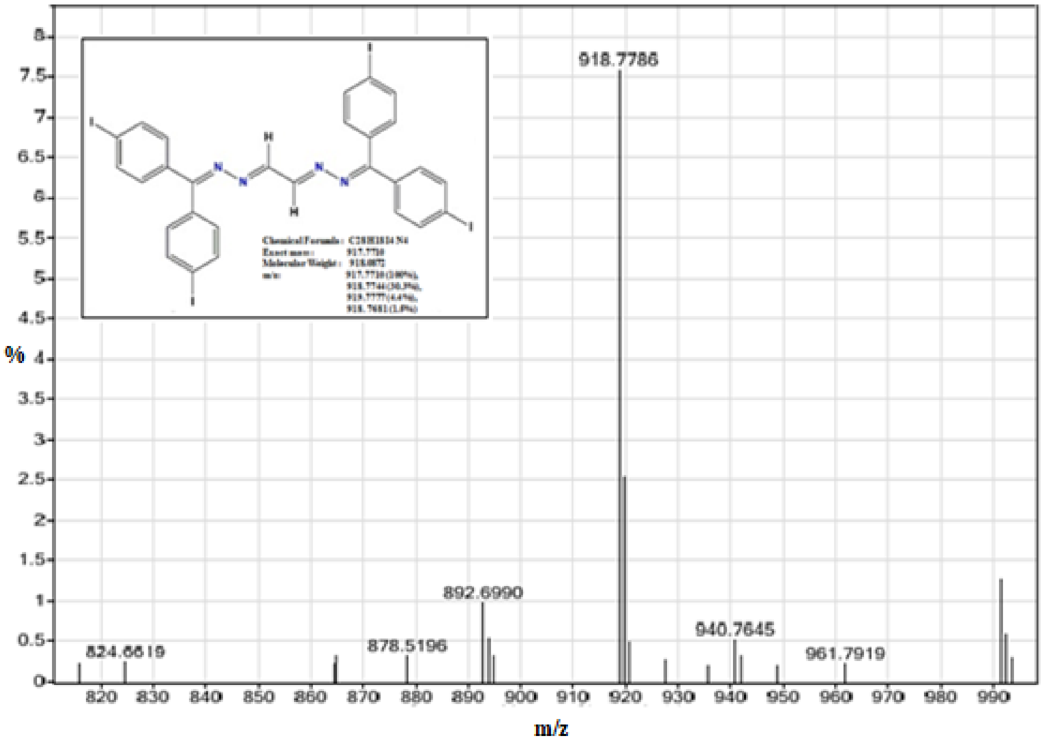


Fig. S8 TOF mass spectrum of compound **3** TOF-MS (m/z).

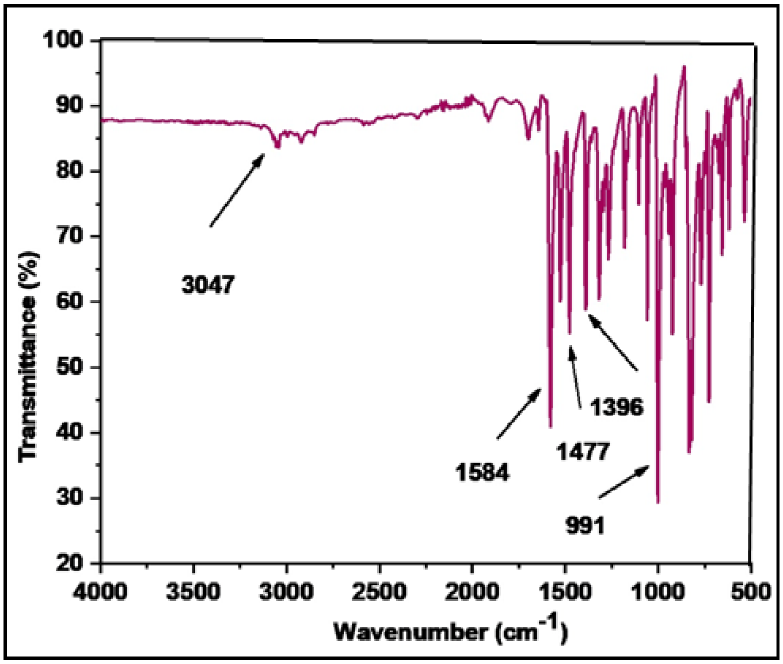


Fig. S9 FT-IR spectra of the powder of compound **3** recorded in Shimadzu (IRAffinity-1SWL)

2. Powder X-ray Diffraction

Powder X-ray diffractogram was measured on Rigaku powder X-ray diffractometer (Miniflex-600 with Cu Kα radiation, λ = 1.54059 Å) operating in Bragg−Brentano geometry. The crystals of the compounds were separated from mother liquor dried using blotting paper then crushed gently and layered on a sample holder. Data was collected at room temperature at a scan rate of 2°/min from 5° to 40° (2θ value).

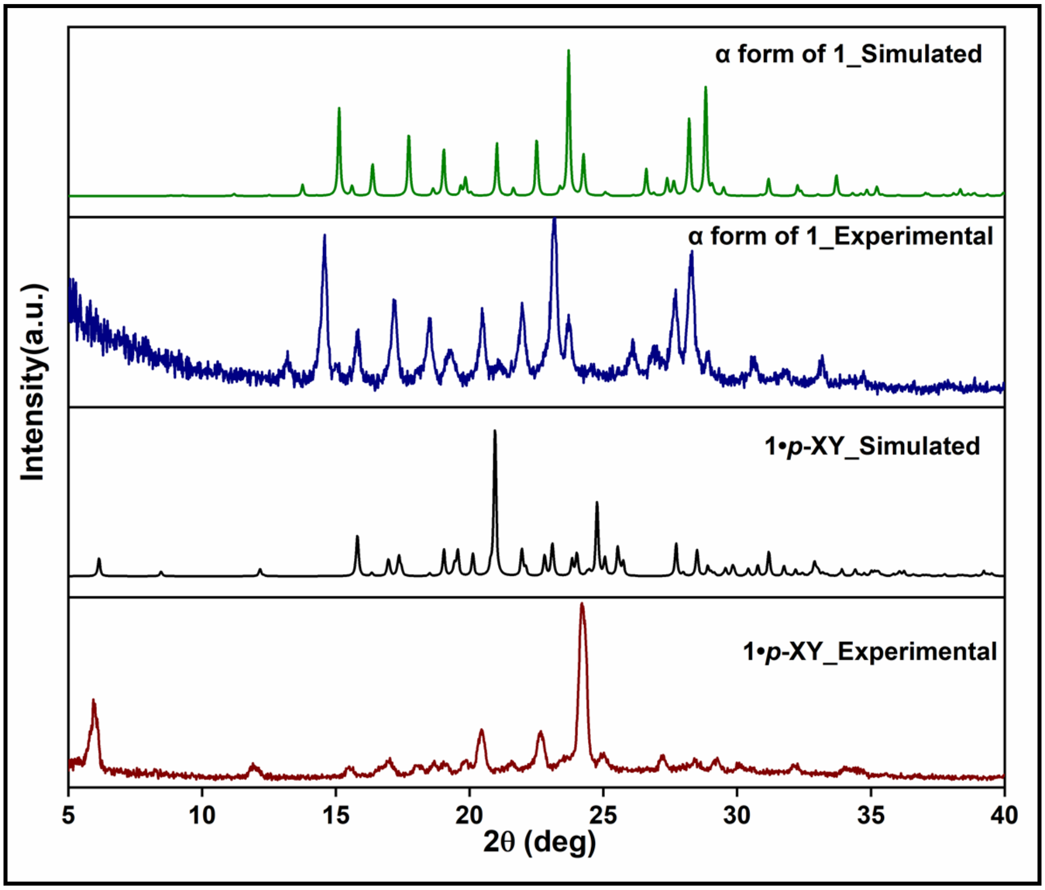


Fig. S10 PXRD pattern of inclusion compound of **1•*p*-XY** matching with bulk material and simulated PXRD of **α form of 1**.

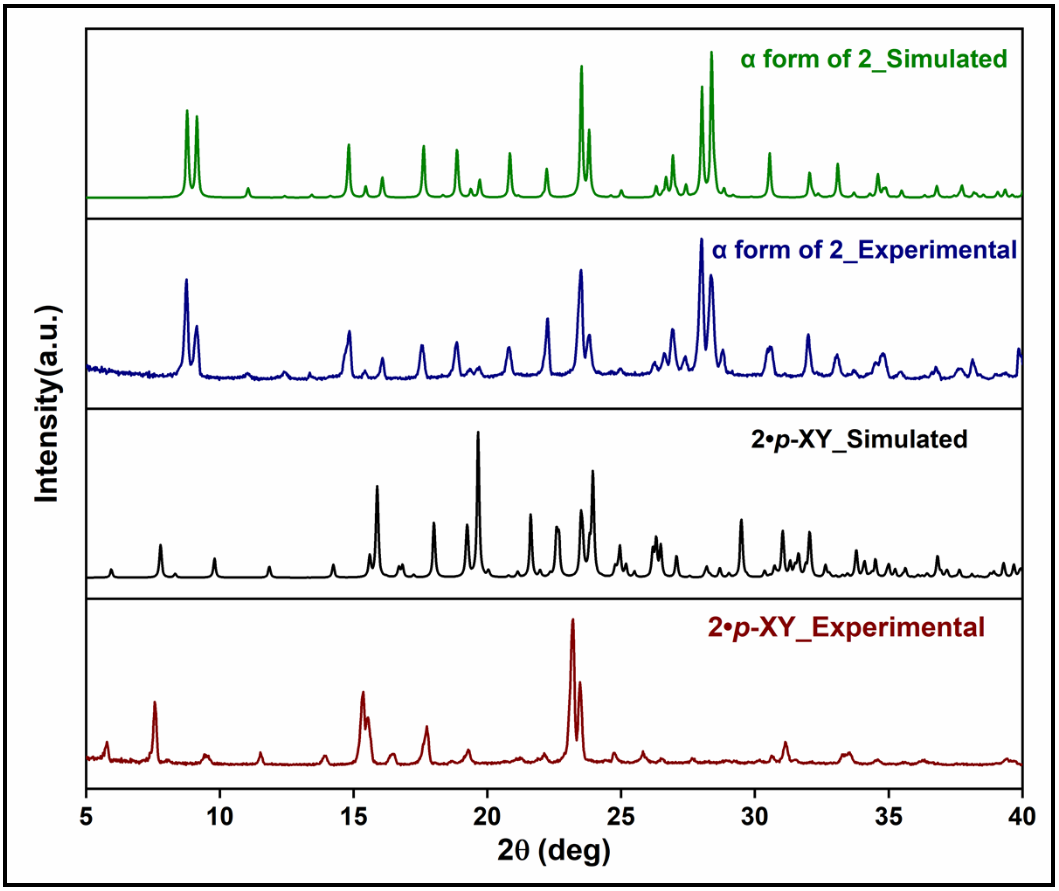


Fig. S11 PXRD pattern of inclusion compound of **2•*p*-XY** matching with bulk material and simulated PXRD of **α form of 2**.

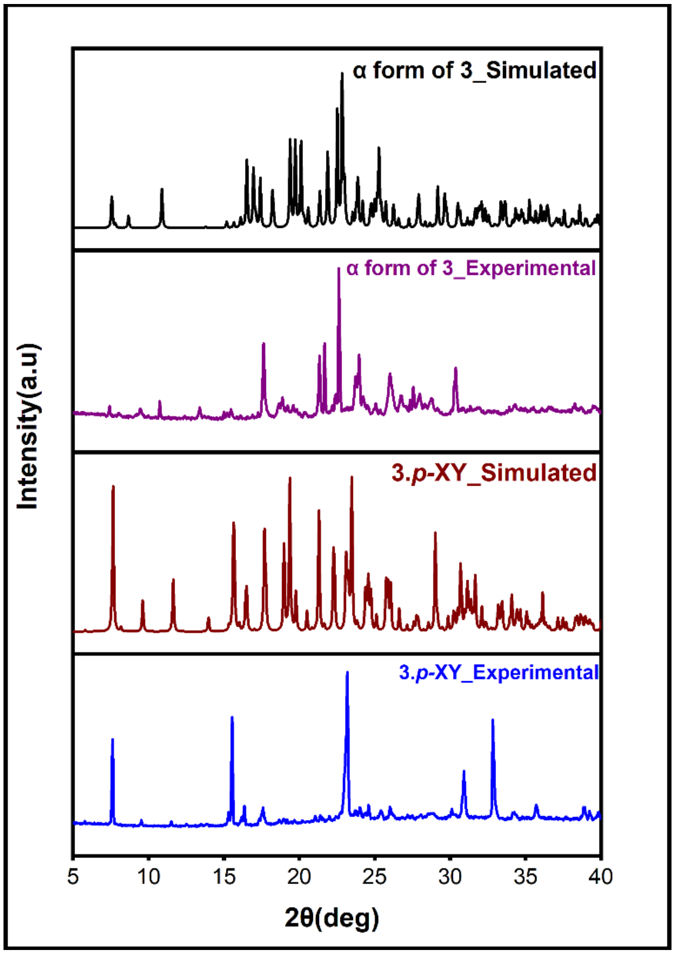


Fig. S12 PXRD Pattern of inclusion compound **3.*p*-XY** matching with the bulk material and simulated PXRD of **α form of 3.**

3. Single Crystal X ray diffraction (SCXRD) analysis

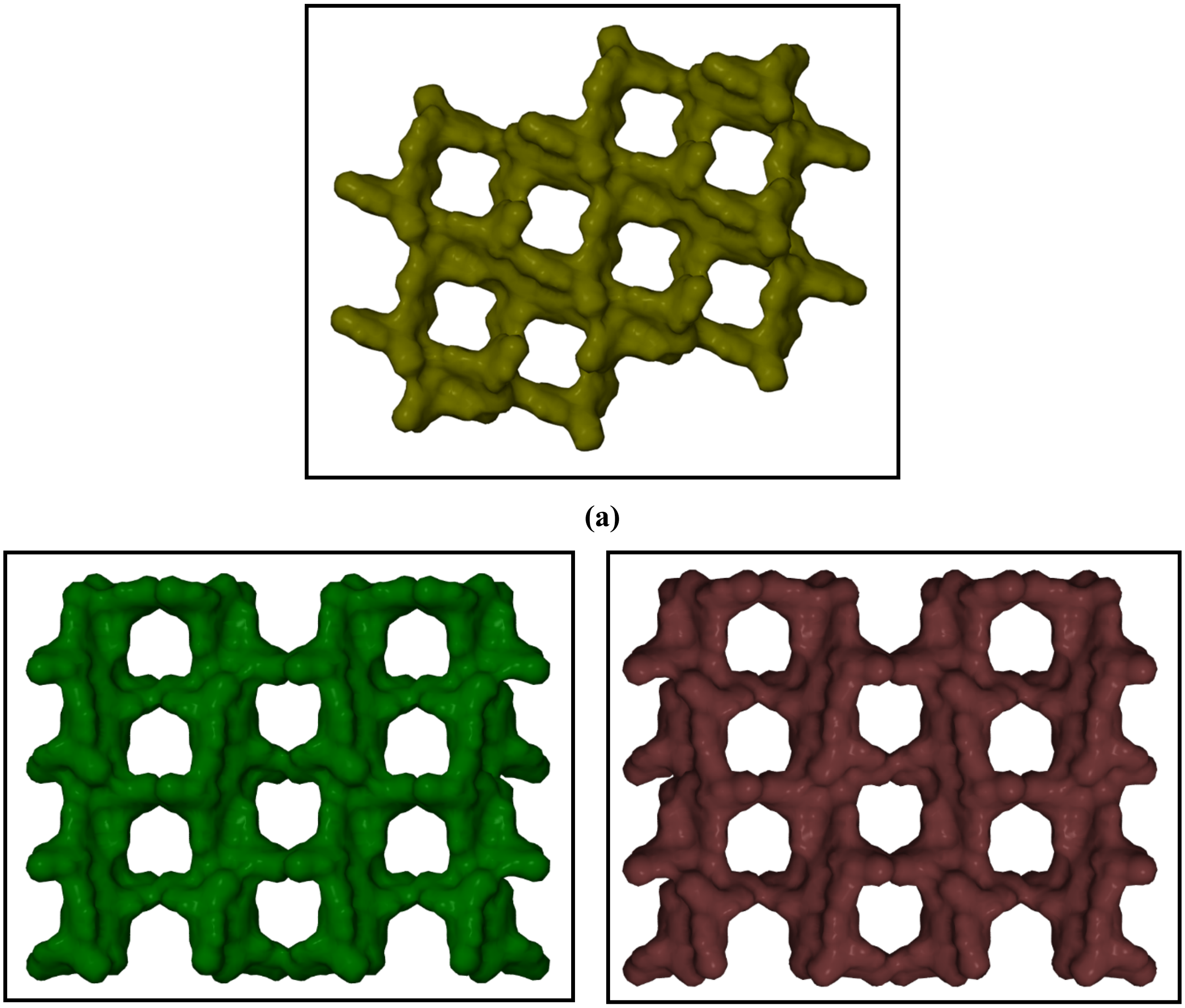
The crystal structure data of the inclusion compounds were recorded by collecting X-ray diffraction on a Bruker D8 Quest diffractometer. The chosen crystals of solvate cut and put into the paraton oil to prevent the loss of solvent. Data were collected for all the inclusion compounds at 100K using temperature-controlled device Oxford Cryosystreame 800 plus cryostat along with the CMOS detector utilizing microfocus anode (MoKα). The integration and scale up of all the data were done by Bruker suits.[2] All the crystal structure were deduced by direct method and its refinements was performed by full matrix least squares on F^2 using version SHELXL-2018.

Anisotropic refinement of all non-hydrogen atoms was done and position of hydrogen atoms were calculated by using the riding model.

Table S1 Crystal data and structure refinement parameters.

Compounds	**1•*p*-XY**	**2•*p*-XY**	**3•*p*-XY**	**α form of 1**	**α form of 2**	**α form of 3**
Moiety formula	$C_{44}H_{38}Cl_4N_4$	$C_{44}H_{38}Br_4N_4$	$C_{44}H_{38}I_4N_4$	$C_{28}H_{18}Cl_4N_4$	$C_{28}H_{18}Br_4N_4$	$C_{28}H_{18}I_4N_4$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Orthorhombic
Space group	$P2_1/n$	Pbca	Pbca	$P4_2/n$	$P4_2/n$	$Pna2_1$
Crystal size	0.510×0.220 ×0.110	0.330×0.240 ×0.110	0.340×0.210 ×0.180	0.280×0.240 ×0.120	0.269×0.219 ×0.120	0.173×0.135 ×0.121
a/Å	15.4025(9)	5.8699(2)	5.9329(3)	14.1377(5)	14.2289(6)	22.6243(16)
b/Å	5.8486(3)	22.6993(9)	23.0822(12)	14.1377(5)	14.2289(6)	5.5145(4)
c/Å	22.1487(13)	29.7060(14)	30.2786(16)	12.8642(5)	13.1662(8)	23.3125(18)
α/(°)	90	90	90	90	90	90
β/(°)	109.329(2)	90	90	90	90	90
γ/(°)	90	90	90	90	90	90
V/Å^3	1882.76(18)	3958.1(3)	4146.5(4)	2571.2(2)	2665.7(3)	2908.5(4)
Z	2	4	4	4	4	4
D_{cal}/g cm^{-3}	1.349	1.581	1.811	1.427	1.819	2.097
T/K	90(2)	100(2)	100(2)	298(2)	298(2)	293(2)
μ/mm^{-1}	0.353	4.104	3.041	0.486	6.064	4.309
F_{000}	796	1880	2168	1128	1416	1704
Reflections measured	40648	26627	55244	9246	46444	29890
Unique reflections	4645	4908	5147	3211	3332	5927
Observed reflections	3330	3362	4278	2276	2383	5495
Parameters	238	237	237	164	164	335
R_{int}	0.0875	0.0818	0.0555	0.0433	0.0417	0.0391
final R (I >2σ(I))	0.0453	0.0515	0.0274	0.0387	0.0328	0.0247
final R (all data)	0.0806	0.0944	0.0406	0.0663	0.0580	0.0317
GOF on F^2	0.988	1.040	1.126	1.013	0.936	1.078

4. Shape of Channels:

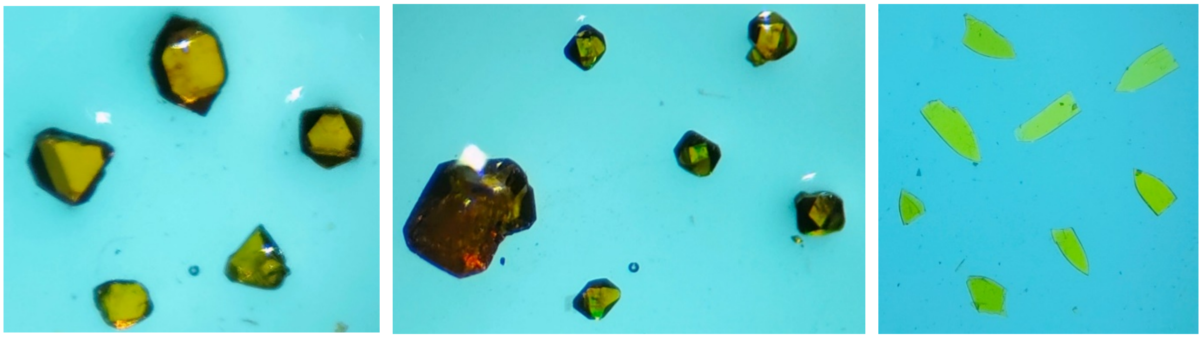

(a)

(b)

(c)

Fig. S13 Shape of channels in the crystal structures of (a) **1•*p*-XY** (b) **2•*p*-XY** (c) **3•*p*-XY**.

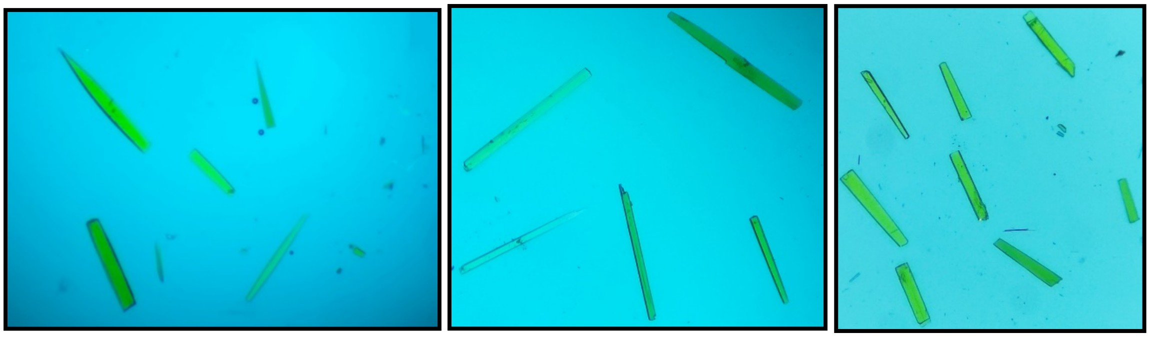
5. Photo-micrographs of crystals


(a)

(b)

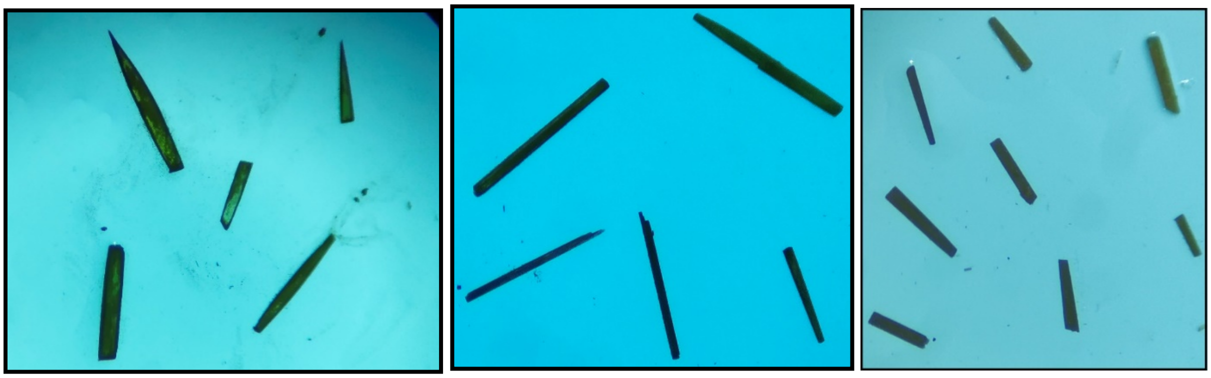
(c)

Fig. S14 Pictures of unsolvated crystal of (a) α form of 1 (b) α form of 2 and (c) α form of 3.



(a) (b) (c)

Fig. S15 Pictures of solvated crystal of (a) **1•*p*-XY** (b) **2•*p*-XY** (c) **3•*p*-XY**.



(a) (b) (c)

Fig. S16 Pictures of desolvated crystal of (a) **1•*p*-XY** (b) **2•*p*-XY** (c) **3 •*p*-XY**.

6. Thermal ellipsoid plots:

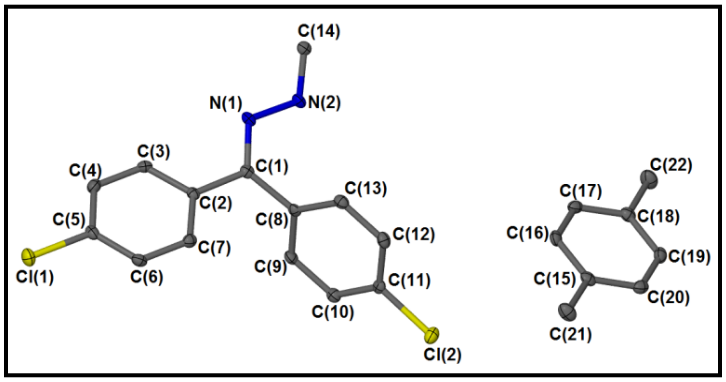


Fig. S17 Thermal ellipsoid plot of the asymmetric unit of **1•*p*-XY**. Thermal ellipsoid plots are shown in 50 % probability.

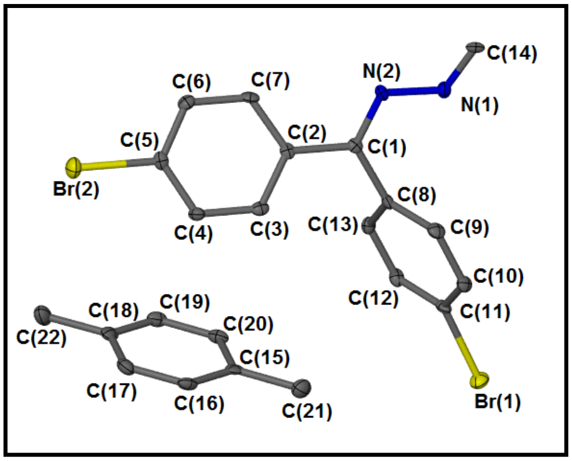


Fig. S18 Thermal ellipsoid plot of the asymmetric unit of **2•*p*-XY**. Thermal ellipsoid plots are shown in 50 % probability.

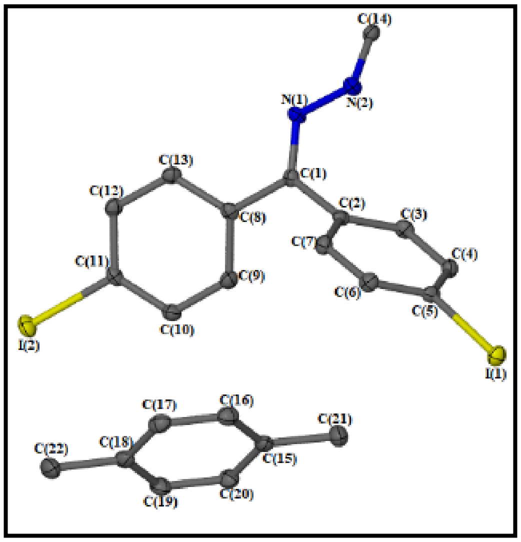


Fig. S19 Thermal ellipsoid plot of the asymmetric unit of **3•*p*-XY**. Thermal ellipsoid plots are shown in 50 % probability.

7. Hirshfeld surface analysis

Quantitative analysis of intermolecular interactions has been carried out using Crystal Explorer 3.1 program.[3] Crystallographic information file (CIF) was used as input for the analysis.

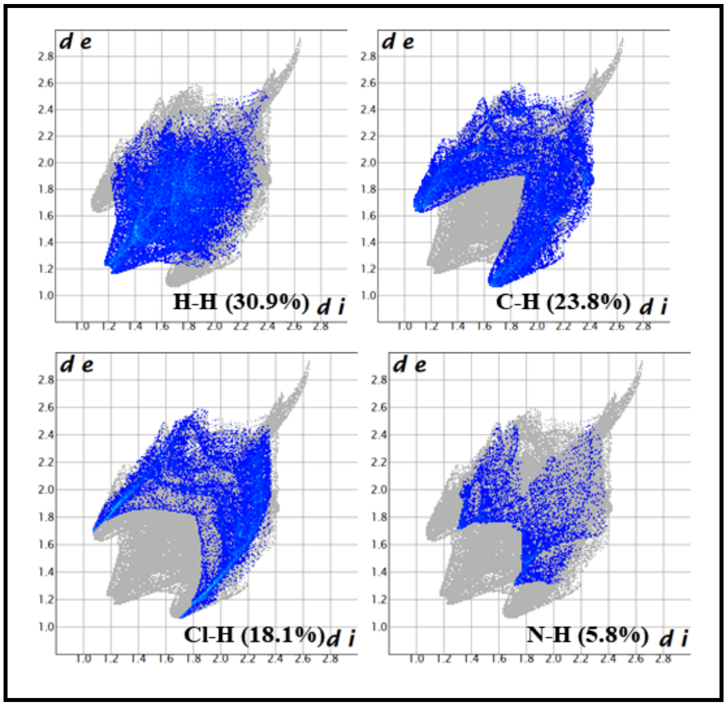


Fig. S20 2D fingerprint plot of the crystal structure of **α form of 1.**

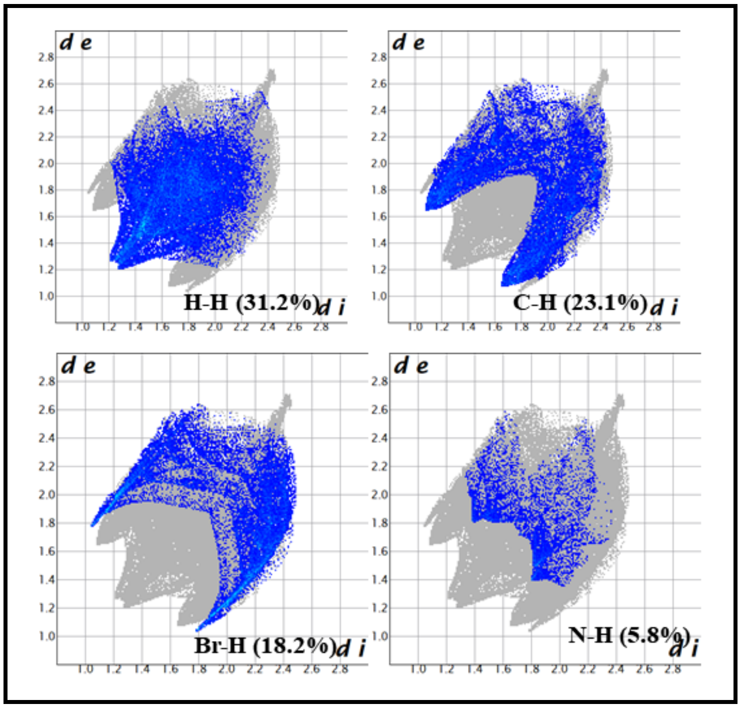


Fig. S21 2D fingerprint plot of the crystal structure of **α form of 2.**

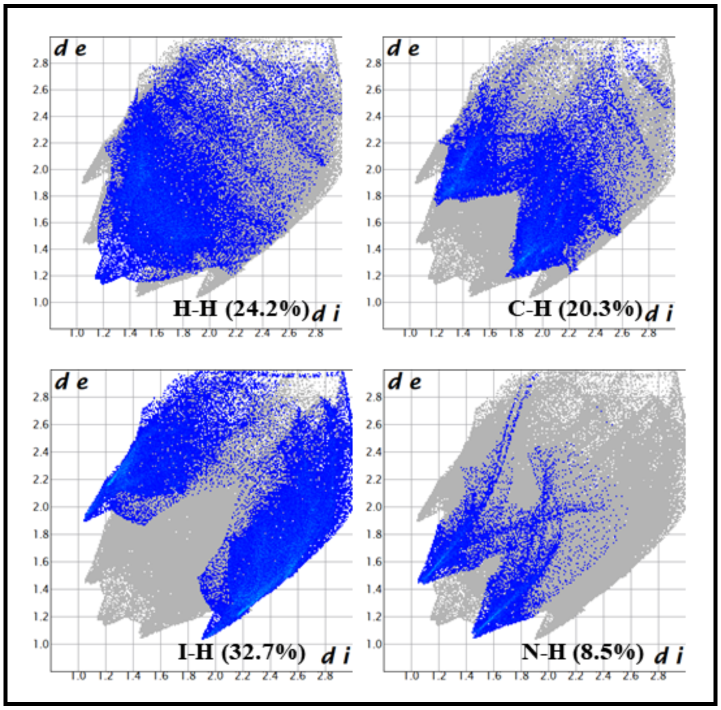


Fig. S22 2D fingerprint plot of the crystal structure of **α form of 3.**

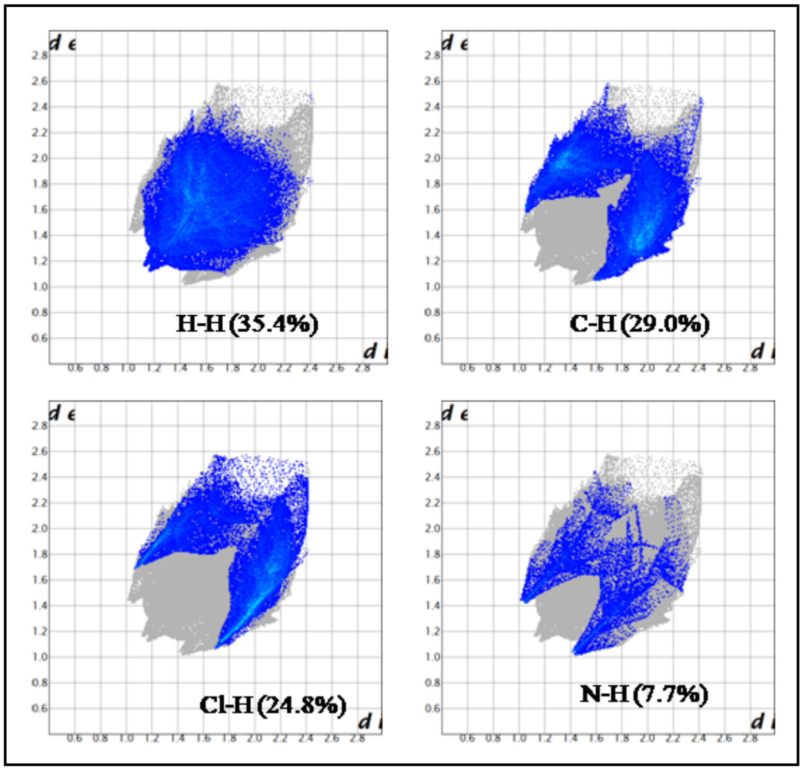


Fig. S23 2D fingerprint plot of the crystal structure of **1•*p*-XY.**

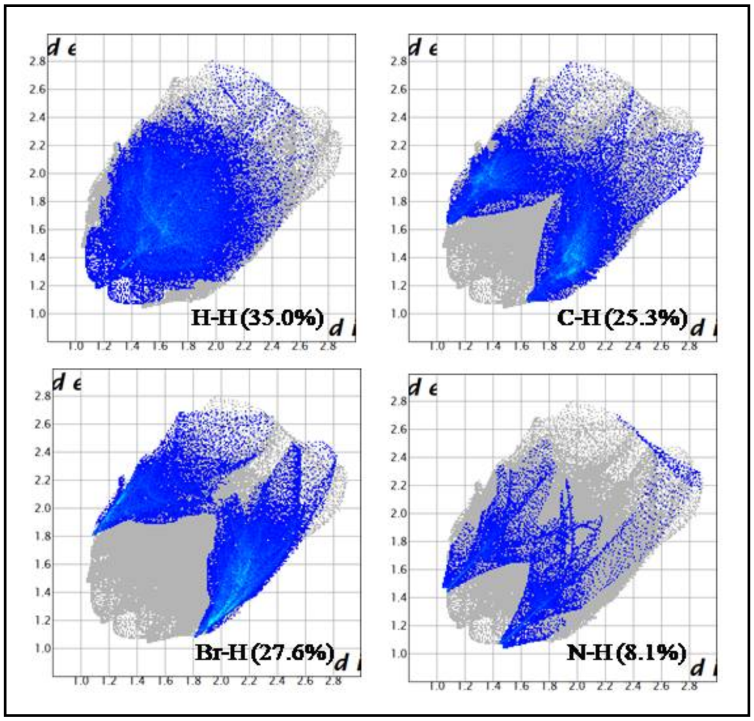


Fig. S24 2D fingerprint plot of the crystal structure of **2•*p*-XY.**

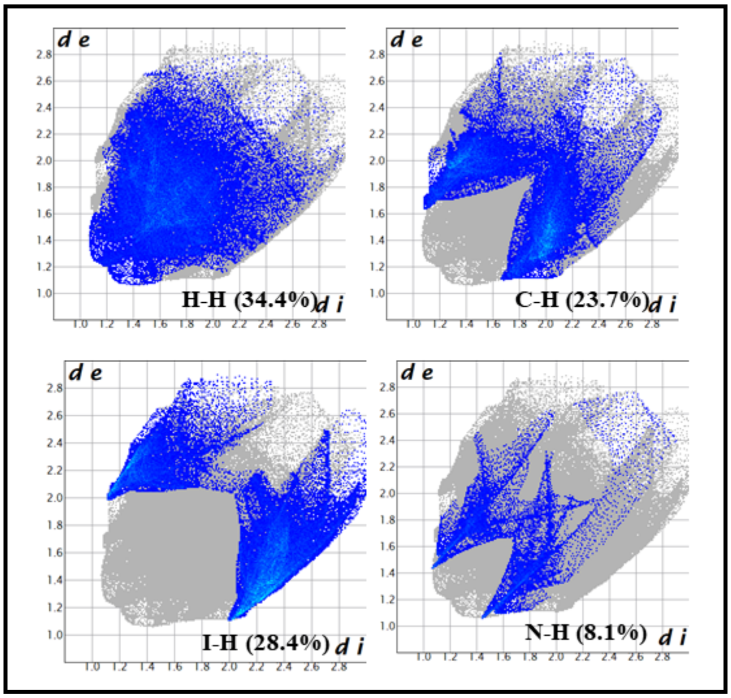
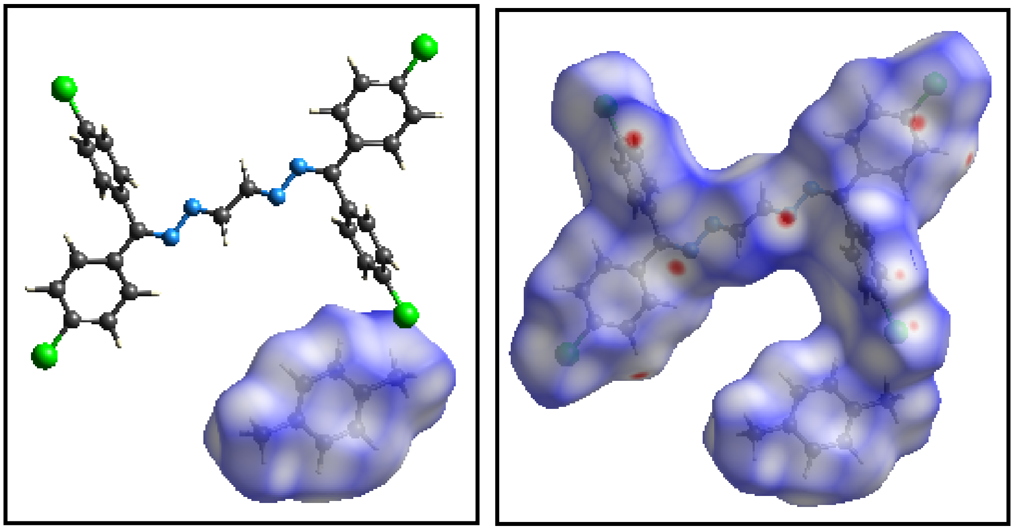
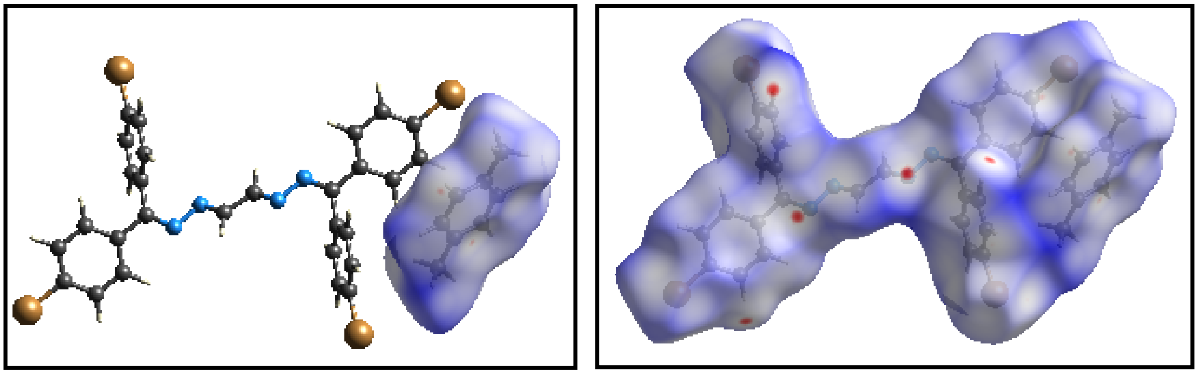


Fig. S25 2D fingerprint plot of the crystal structure of **3•*p*-XY.**



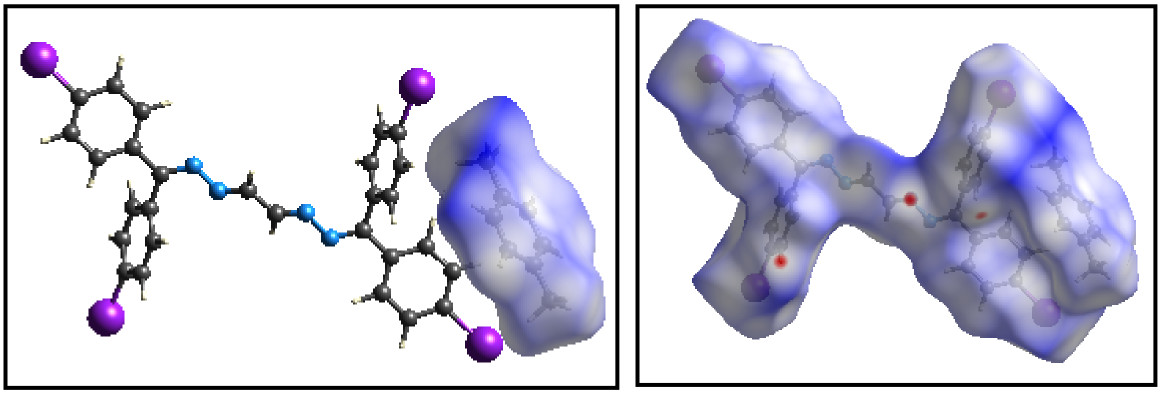
(a) (b)

Fig. S26 Hirshfeld surface mapped with d_{norm} of *p*-xylene in crystal structure of **1•*p*-XY.**



(a) (b)

Fig. S27 Hirshfeld surface mapped with d_{norm} of *p*-xylene in crystal structure of **2•*p*-XY.**



(a) (b)

Fig. S28 Hirshfeld surface mapped with d_{norm} of *p*-xylene in crystal structure of **3•*p*-XY.**

8. References:

1. R. R. Gallucci, *J. chem. Eng. Data*, 1982, **27,** 217-219.
2. SAINT; Bruker AXS Inc., Madison, Wisconsin, USA, 2013. SADABS; Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
3. S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, *Crystal Explorer*, 2012, Version 3.0. University of Western Australia, Australia.