Supplementary data for article:

Chongboriboon, N.; Samakun, K.; Inprasit, T.; Kielar, F.; Dungkaew, W.; Wong, L. W.-Y.; Sung, H. H.-Y.; Ninković, D. B.; Zarić, S. D.; Chainok, K. Two-Dimensional Halogen-Bonded Organic Frameworks Based on the Tetrabromobenzene-1,4-Dicarboxylic Acid Building Molecule. *CrystEngComm* **2019**, *22* (1), 24–34.
https://doi.org/10.1039/c9ce01140d

Supporting Information

Two-dimensional halogen-bonded organic frameworks based on the tetrabromobenzene-1,4-dicarboxylic acid building molecule

Nucharee Chongboriboon,[a] Kodchakorn Samakun,[a] Thitirat Inprasit,[a] Filip Kielar,[b] Winya Dungkaew,[c] Lawrence W.-Y. Wong,[d] Herman H.-Y. Sung,[d] Dragan B. Ninković,[e] Snežana D. Zaric[f,g] and Kittipong Chainok[a]*

[a]*Materials and Textile Technology, Faculty of Science and Technology, Thammasat University, Pathum Thani 12121, Thailand, E-mail: kc@tu.ac.th; Fax: +66 2 654 4548; Tel: +66 86 339 5079*

[b]*Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand*

[c]*Department of Chemistry, Faculty of Science, Mahasarakham University, Maha Sarakham 44150, Thailand*

[d]*Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

[e]*Innovation Center, Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia*

[f]*Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, 11000, Serbia*

[g]*Science Program, Texas A&M University at Qatar, Education City, Doha, Qatar*

E-mail: kc@tu.ac.th; Fax: +66 2 654 4548; Tel: +66 86 339 5079

Table S1 Crystallographic data and refinement summary for all of the solvates at 296(2) K.

	$\mathbf{1}_{ATN}$	$\mathbf{2}_{EtOH}$
Formula	$C_{14}H_{14}Br_4O_6$	$C_{12}H_{14}Br_4O_6$
Formula weight	597.89	573.87
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pnma*
a (Å)	25.174(5)	9.1624(5)
b (Å)	9.1572(18)	23.4820(12)
c (Å)	8.9838(17)	8.9930(4)
β (°)	93.250(7)	90
V (Å^3)	2067.7(7)	1934.86(17)
D_{calc} (g cm^{-3})	1.921	1.970
Z	4	4
μ (mm^{-1})	7.809	8.340
F(000)	1144	1096
Diffractometer	Bruker D8 QUEST CMOS	Bruker D8 QUEST CMOS
λ (Å)	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)
Reflections collected	23666	32805
Unique Reflections	1973	1938
Parameters	155	136
R_1, wR_2 ($I > 2\sigma(I)$)	0.0306, 0.0598	0.0275, 0.0688
R_1, wR_2 (all data)	0.0488, 0.0655	0.0344, 0.0730
GOF on F^2, *S*	1.020	1.037
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.40	0.40, −0.65
CCDC No.	1941498	19414500
	$\mathbf{3}_{DMSO}$	$\mathbf{4}_{EG}$
Formula	$C_{12}H_{14}Br_4O_6S_2$	$C_{12}H_{14}Br_4O_8$
Formula weight	637.99	605.87
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pbca*
a (Å)	9.2133(2)	8.134(2)
b (Å)	25.7139(6)	9.964(3)
c (Å)	8.9323(2)	23.849(6)
β (°)	90	90
V (Å^3)	2116.15(8)	1933.0(9)
D_{calc} (g cm^{-3})	2.003	2.082
Z	4	4
μ (mm^{-1})	7.827	8.362
F(000)	1224.0	1160
Diffractometer	Bruker D8 QUEST CMOS	Bruker D8 QUEST CMOS
λ (Å)	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)
Reflections collected	52655	30880
Unique Reflections	2683	1962
Parameters	115	122
R_1, wR_2 ($I > 2\sigma(I)$)	0.0446, 0.1124	0.0417, 0.1021
R_1, wR_2 (all data)	0.0650, 0.1229	0.0549, 0.1116
GOF on F^2, *S*	1.098	1.042
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, −0.55	1.49, −1.14
CCDC No.	19414502	19414504

Table 2 Hydrogen bond geometry (Å, °) for all the solvates at 100(2) and 296(2) K.

Solvate	Temperature	D–H···A	D–H	H···A	D···A	D–H···A
1$_{ATN}$	100	O1–H1···O3*a*	0.83(2)	1.79(2)	2.588(3)	161(3)
	100	O1–H1···O3*b*	0.83(2)	1.77(2)	2.598(4)	172(3)
	100	C7*A*–H7*ab*···O2^{i}	0.98	2.50	3.349(4)	148
	296	O1–H1···O3*a*	0.82(2)	1.83(2)	2.610(9)	161(4)
	296	O1–H1···O3*b*	0.82(2)	1.80(2)	2.618(10)	178(4)
	296	C7*A*–H7*ab*···O2^{i}	0.96	2.61	3.452 (10)	146
2$_{EtOH}$	100	O1–H1···O3	0.82(2)	1.70(2)	2.516(2)	171(3)
	100	O3–H3···O2^{ii}	0.83(2)	1.93(2)	2.746(2)	170(3)
	296	O1–H1···O3	0.82(1)	1.74(2)	2.541 (4)	166(4)
	296	O3–H3···O2^{ii}	0.82	1.99	2.792 (4)	166
3$_{DMSO}$	100	O1–H1···O3	0.84(2)	1.66(2)	2.505(2)	175(11)
	100	C6–H6b···O2^{iii}	0.98	2.31	3.272(6)	167
	296	O1–H1···O3	0.82(1)	1.69(2)	2.506(5)	173(12)
	296	C6–H6b···O2^{iii}	0.96	2.33	3.291 (7)	176
4$_{EG}$	100	O1–H1···O3	0.84(2)	1.70 (2)	2.528(2)	167(3)
	100	O3–H3···O4^{iv}	0.84(2)	1.83 (2)	2.669(2)	176(3)
	100	O4–H4···O2^{V}	0.83(2)	2.04 (2)	2.799(2)	152(3)
	296	O1–H1···O3	0.82(1)	1.75(2)	2.550(5)	164(6)
	296	O3–H3···O4^{iv}	0.82(1)	1.89(2)	2.688(5)	166(5)
	296	O4–H4···O2^{V}	0.82(1)	2.05(2)	2.851(5)	167(8)

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2, (ii) −*x*+2, −*y*+1, −*z*+1, (iii) −*x*+1, −*y*+1, −*z*+1, (iv) −*x*+1, *y*−1/2, −*z*+1/2; (v) *x*−1/2, *y*, −*z*+1/2.

Table S3 Percentage contributions of interatomic contacts to the Hirshfeld surface of all solvates at 100(2) K.

Contact type	**1**$_{ATN}$	**2**$_{EtOH}$	**3**$_{DMSO}$	**4**$_{EG}$
H_2Br_4BDC				
Br···H/H···Br	28.5	24.6	24.2	26.5
Br···C/C···Br	25.2	25.4	25.4	23.1
O···H/H···O	22.3	20.4	22.4	23.2
Br···O/O···Br	12.7	15.4	13.8	13.0
Br···Br	4.0	6.8	8.0	6.7
H···H	7.2	7.2	5.8	5.5
C···H/H···C	0.2	0.3	0.2	1.4
solvent				
O···H/H···O	27.7	32.8	42.1	49.6
H···H	53.1	50.9	29.7	32.3

Table S4 Br/O=C and Br/O-H interaction energies (in kcal/mol) in two crystal structures.

	Br/O=C	Br/O-H
Type I	-1.71	-0.55
Type II	-1.78	-0.59

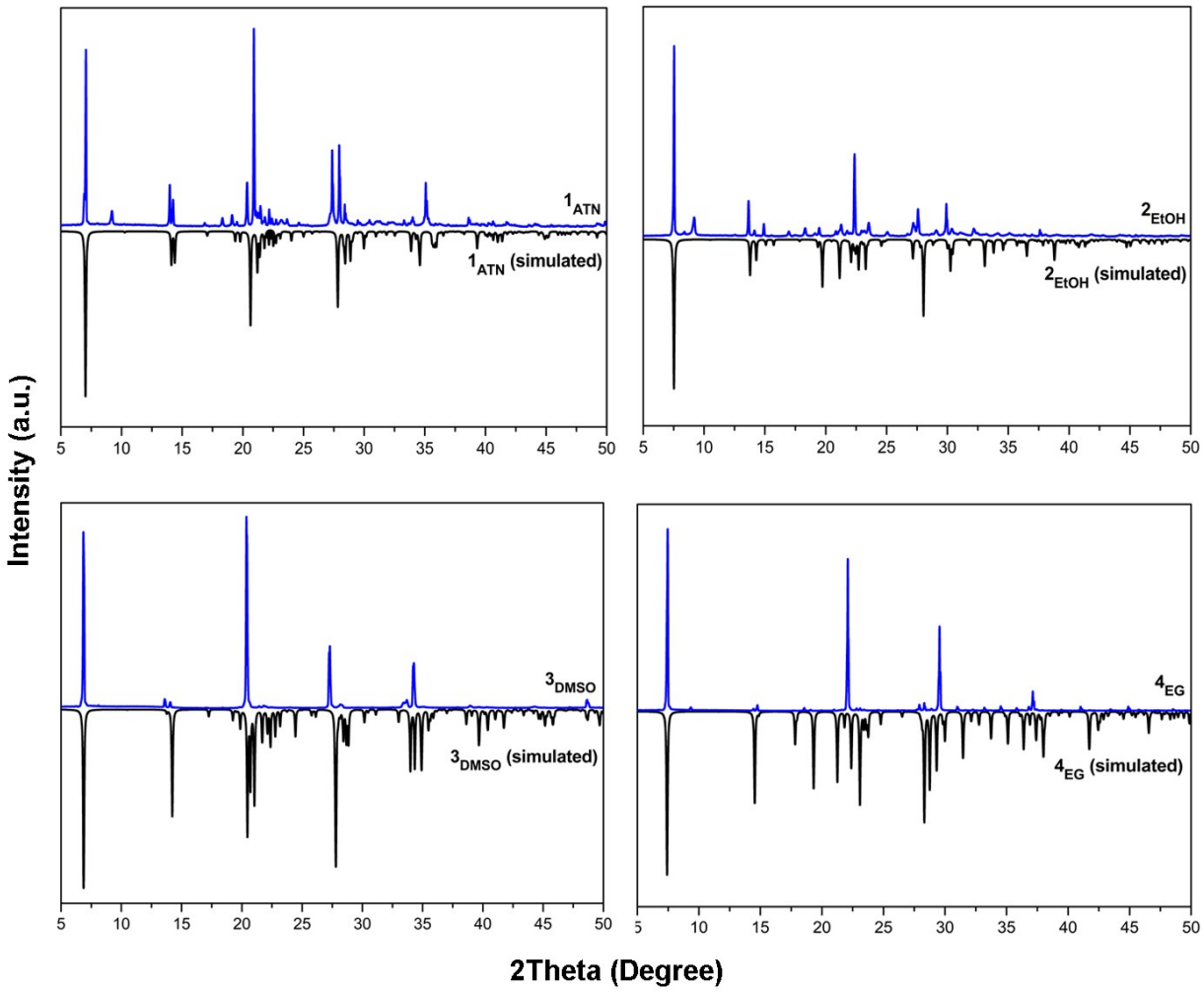


Figure S1 Comparison of the simulated and experimental powder X-ray diffraction patterns of all the solvates.

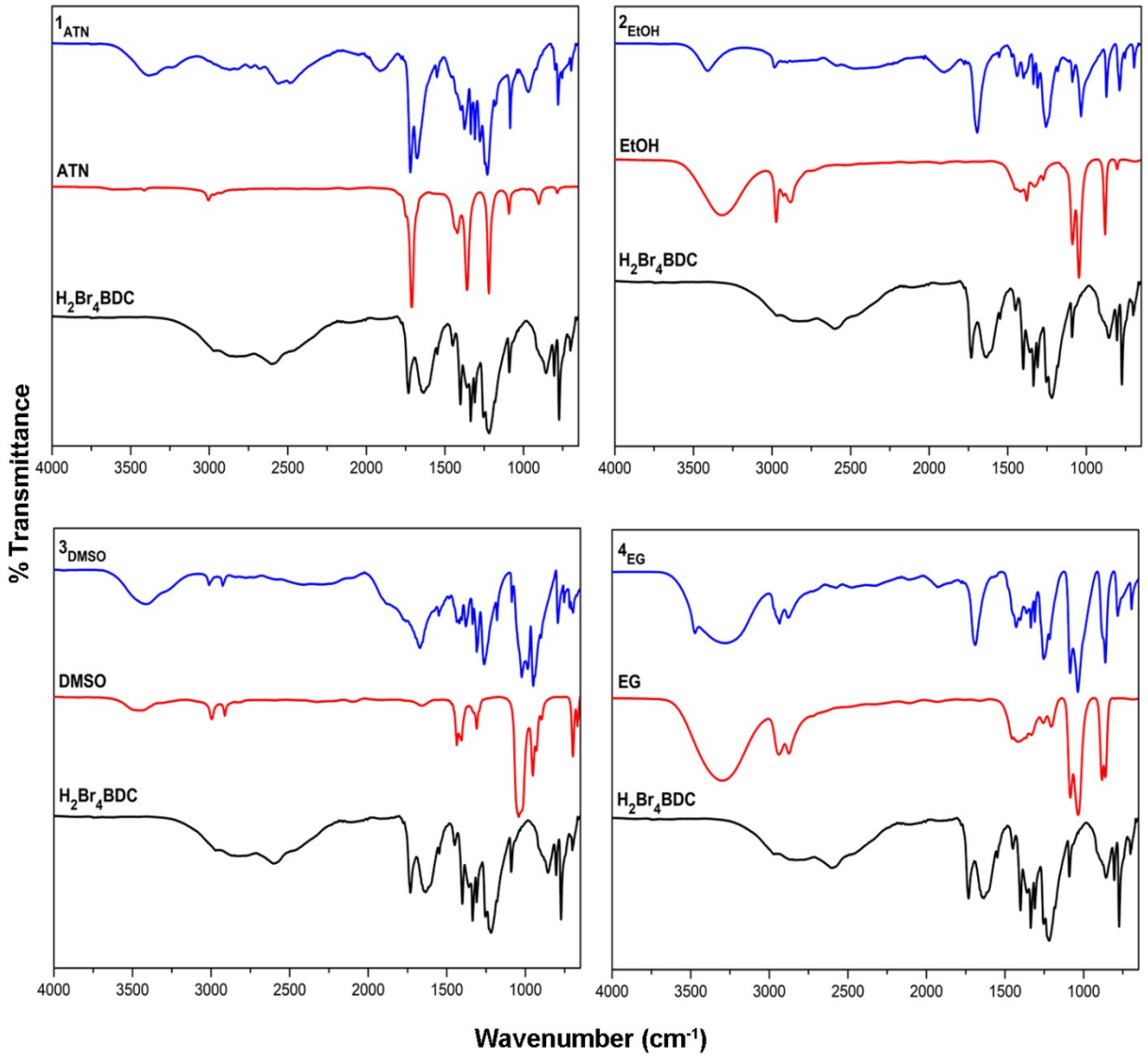
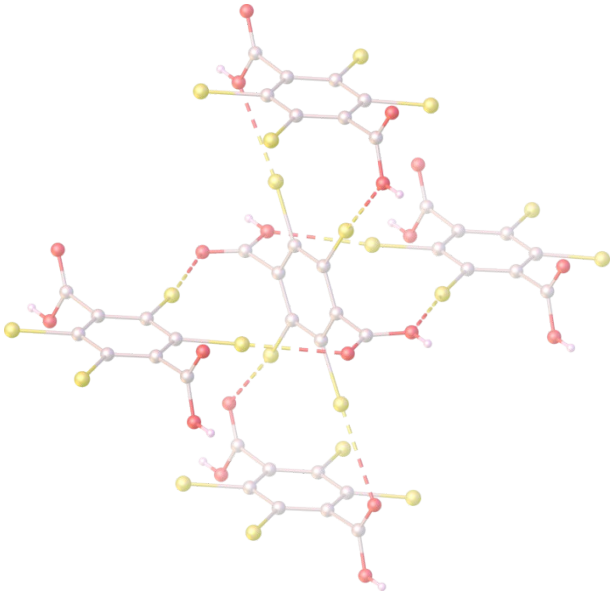
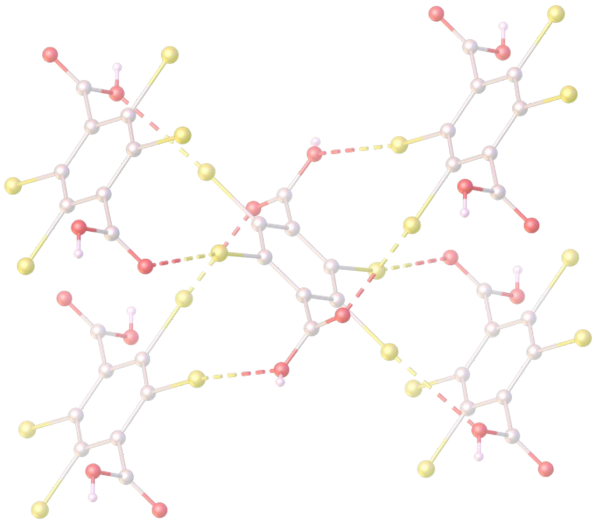


Figure S2 IR spectra for the starting materials and all the solvates.



(a)



(b)

Figure S3 Network of interactions between H_2Br_4BDC molecules in crystal structure type I (a) and type II (b).

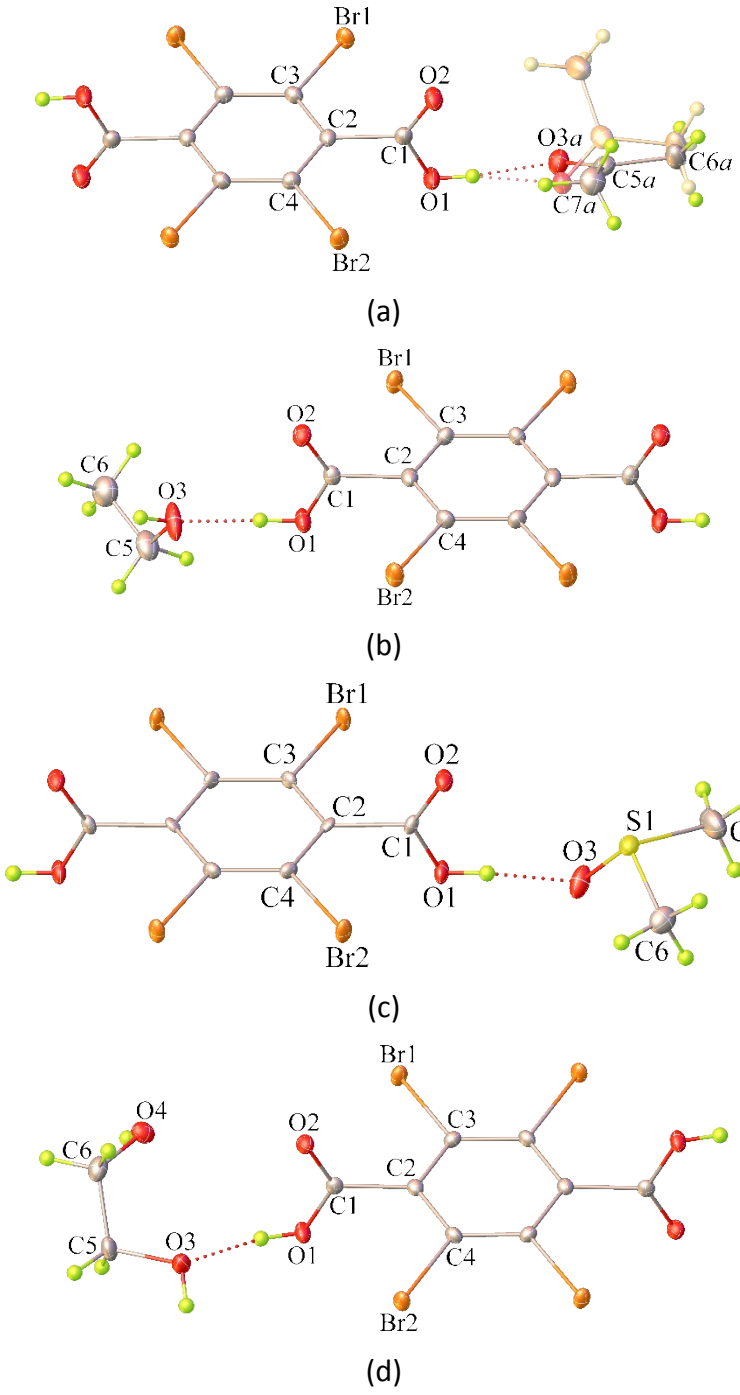


Figure S4 Views of the crystal structure and asymmetric unit numbering scheme of the solvates (a) $\mathbf{1}_{ATN}$, (b) $\mathbf{2}_{EtOH}$, (c) $\mathbf{3}_{DMSO}$, and (d) $\mathbf{4}_{EG}$. Thermal ellipsoids are given at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radii. The dashed line corresponds to the hydrogen bond within the asymmetric unit.

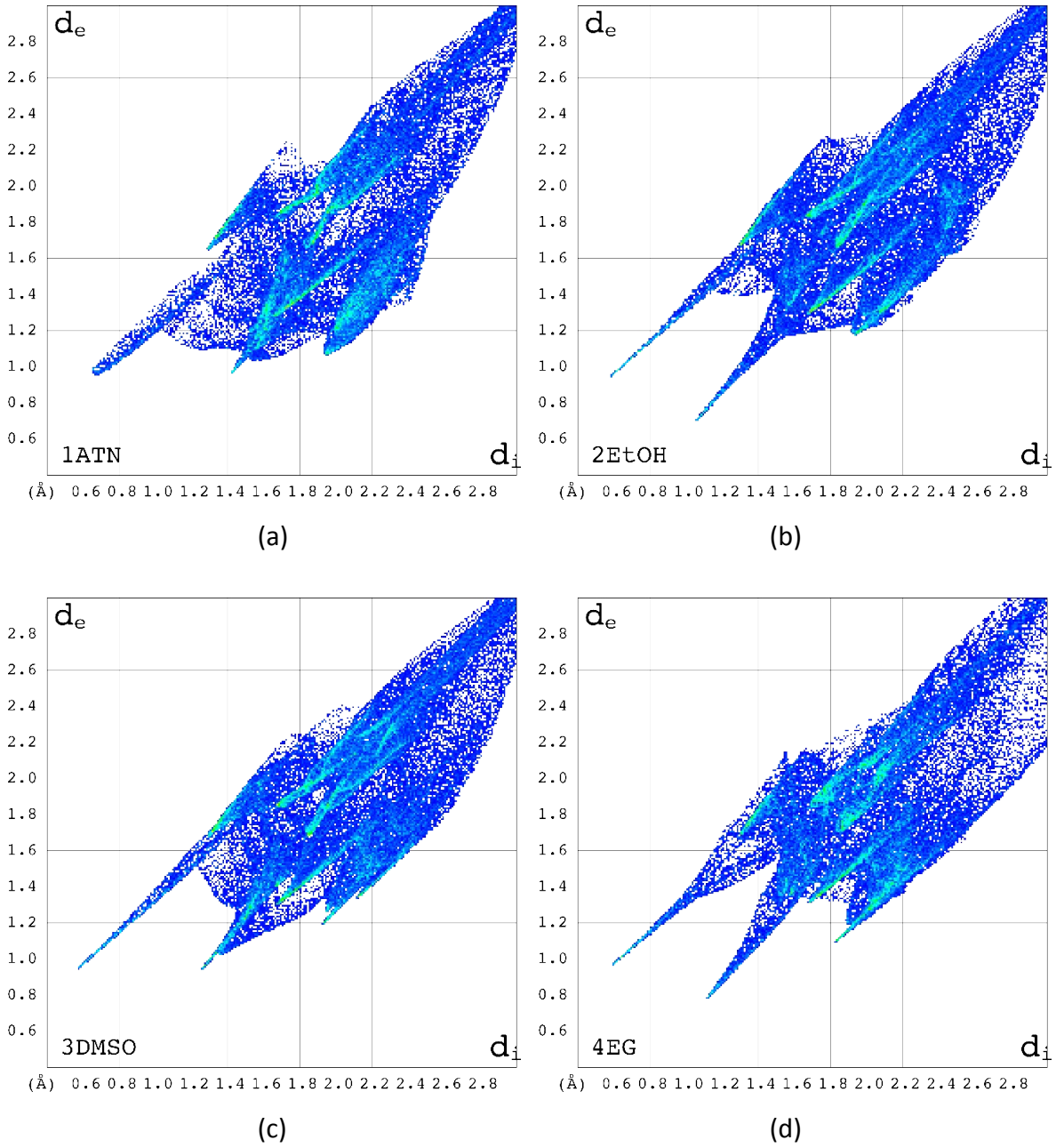


Figure S5 Fingerprint plots for the H_2Br_4BDC molecules for the solvates (a) $\mathbf{1}_{ATN}$, (b) $\mathbf{2}_{EtOH}$, (c) $\mathbf{3}_{DMSO}$, and (d) $\mathbf{4}_{EG}$.

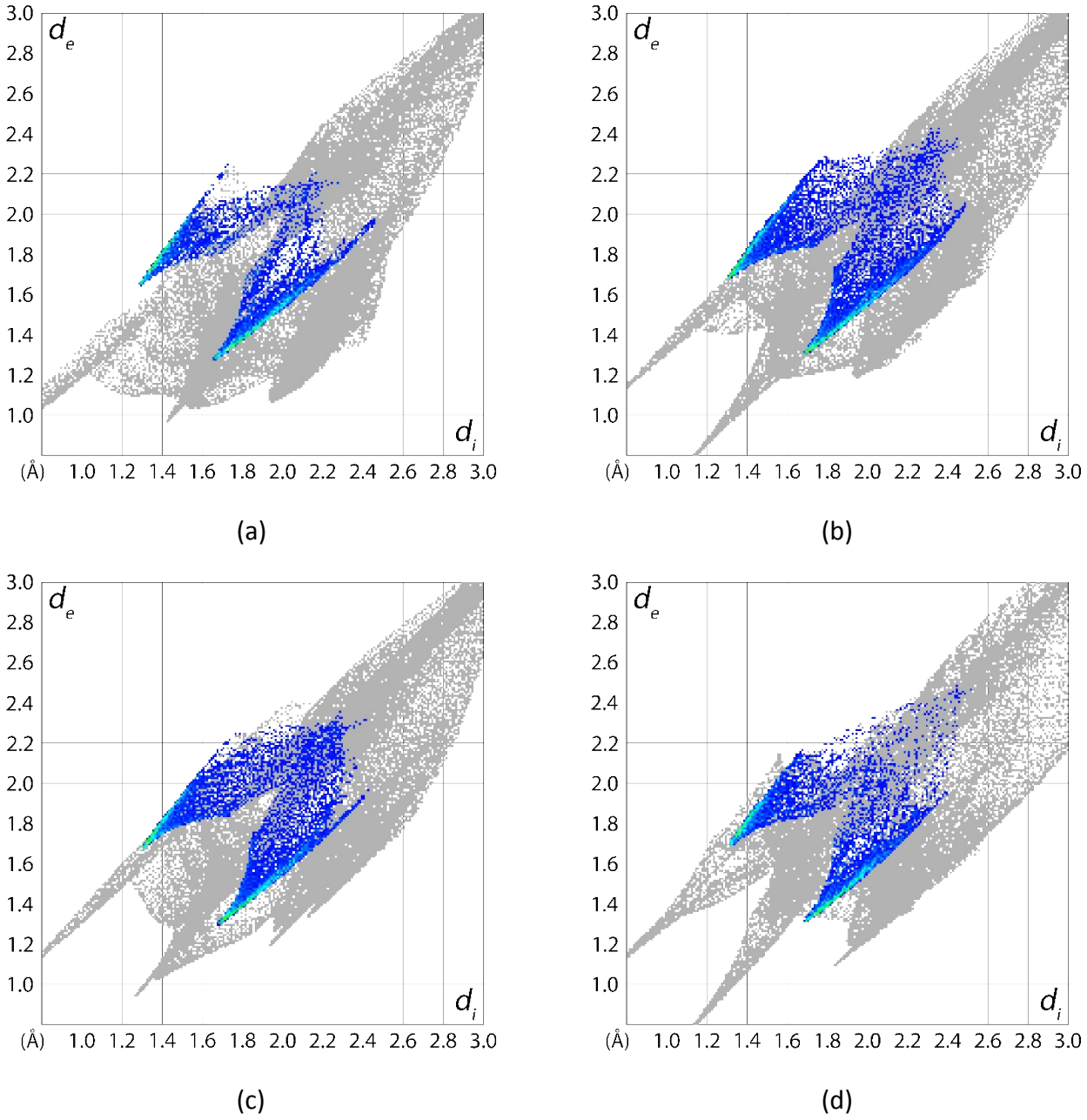


Figure S6 Fingerprint plots resolved into Br···O/O···Br contacts for the H_2Br_4BDC molecules for the solvates $\mathbf{1}_{ATN}$ (a), $\mathbf{2}_{EtOH}$ (b), $\mathbf{3}_{DMSO}$ (c) and $\mathbf{4}_{EG}$ (d).

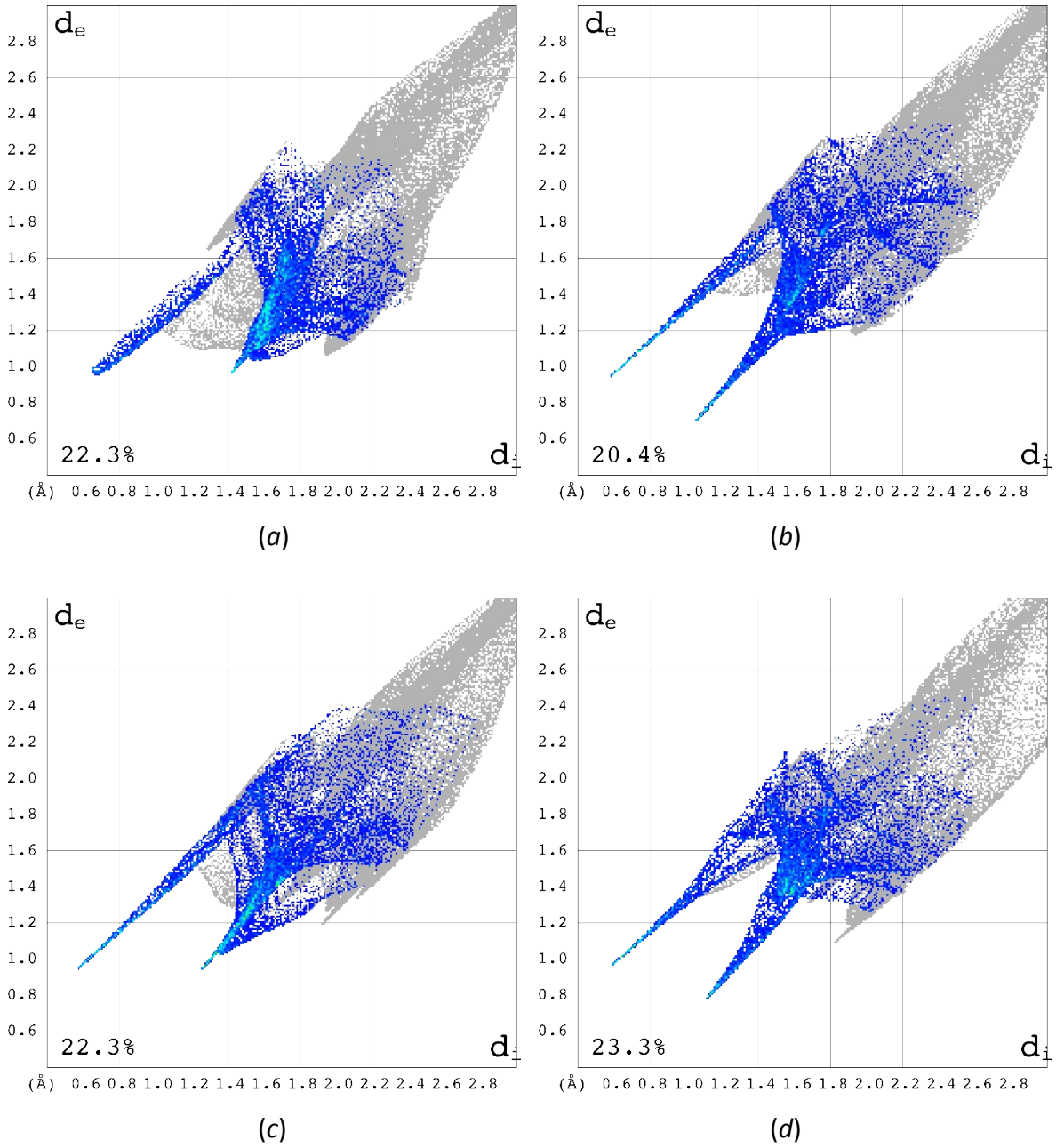


Figure S7 Fingerprint plots resolved into O···H contacts for the H_2Br_4BDC molecules for the solvates (a) $\mathbf{1}_{ATN}$, (b) $\mathbf{2}_{EtOH}$, (c) $\mathbf{3}_{DMSO}$, and (d) $\mathbf{4}_{EG}$.

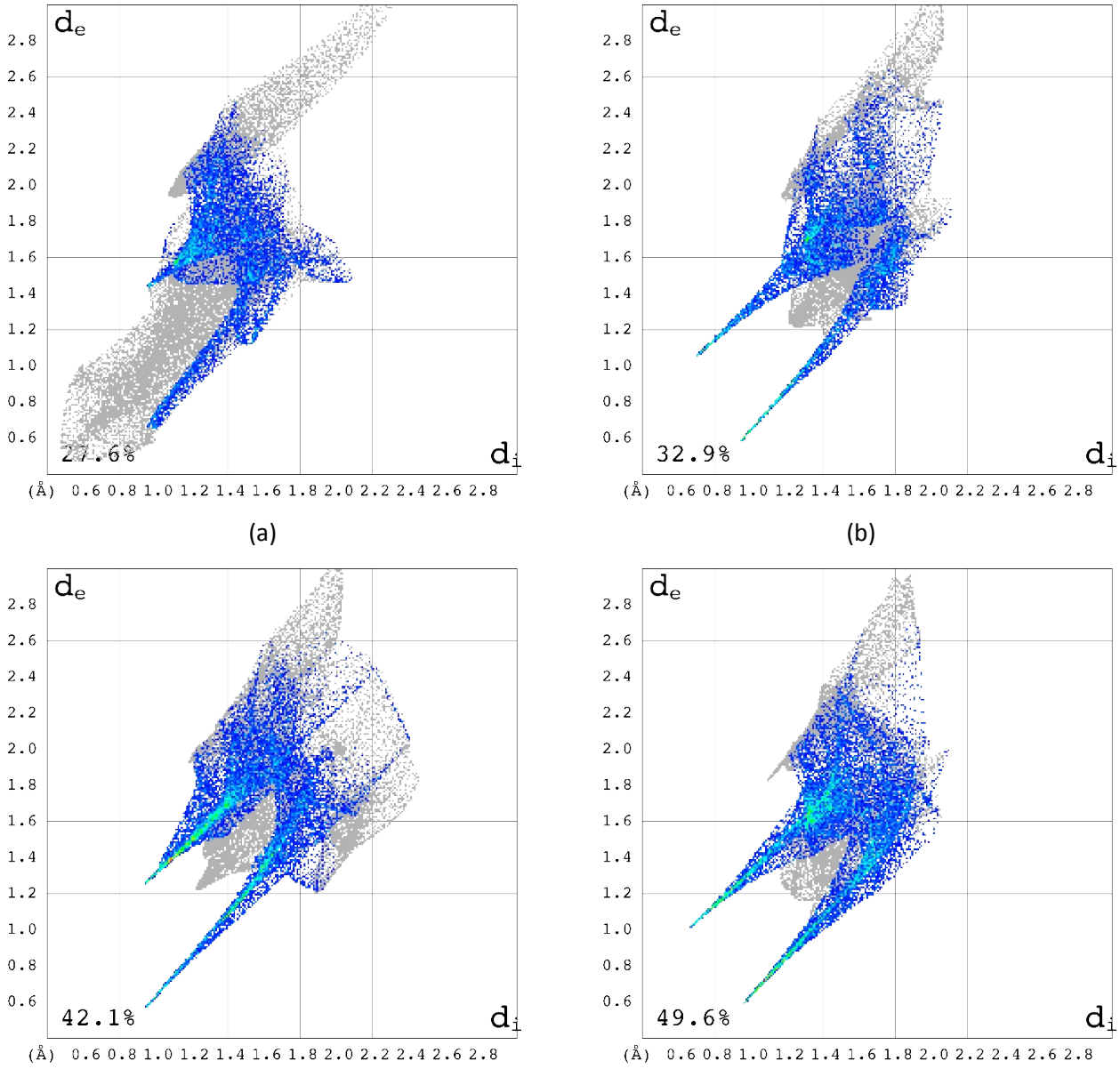


Figure S8 Fingerprint plots resolved into O···H contacts for the solvent molecules for the solvates (a) $\mathbf{1}_{ATN}$, (b) $\mathbf{2}_{EtOH}$, (c) $\mathbf{3}_{DMSO}$, and (d) $\mathbf{4}_{EG}$.

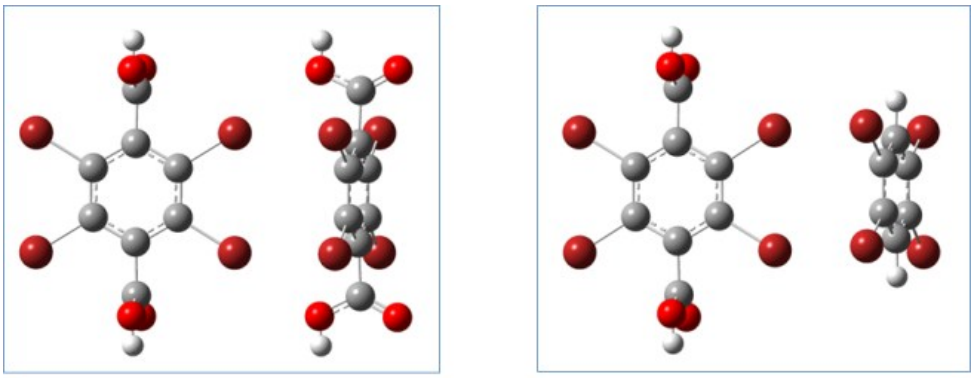


Figure S9 Model systems used to calculate Br···OH interaction energy in type-I crystal structure. Model system based on molecules from crystal structures (A), model system in which COOH groups in one molecule are replaced with hydrogen atoms (B).

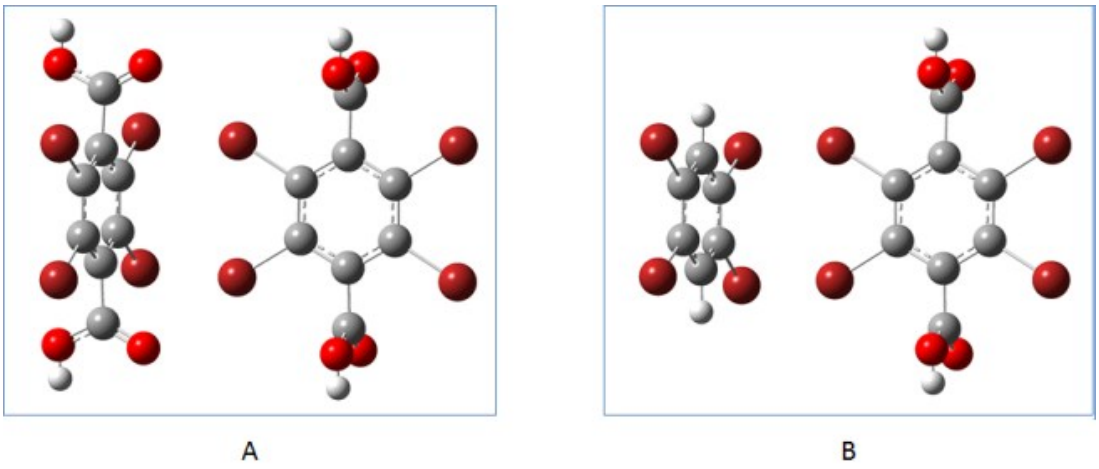


Figure S10 Model systems used to calculate Br···O=C interaction energy in type-I crystal structure. Model system based on molecules from crystal structures (A), model system in which COOH groups in one molecule are replaced with hydrogen atoms (B).

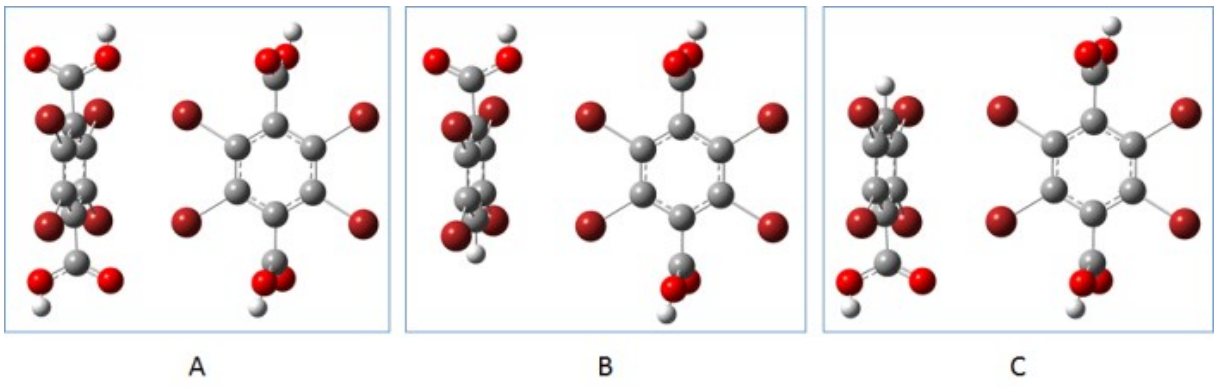


Figure S11 Model systems used to calculate Br···O=C and Br···O-H interaction energies in type-II crystal structure. Model system based on molecules from crystal structures (A), model system in which COOH group in one molecule is replaced with hydrogen atoms (B) to eliminate Br···O=C interaction and model system in which COOH group in one molecule is replaced with hydrogen atoms (C) to eliminate Br···O-H interaction.

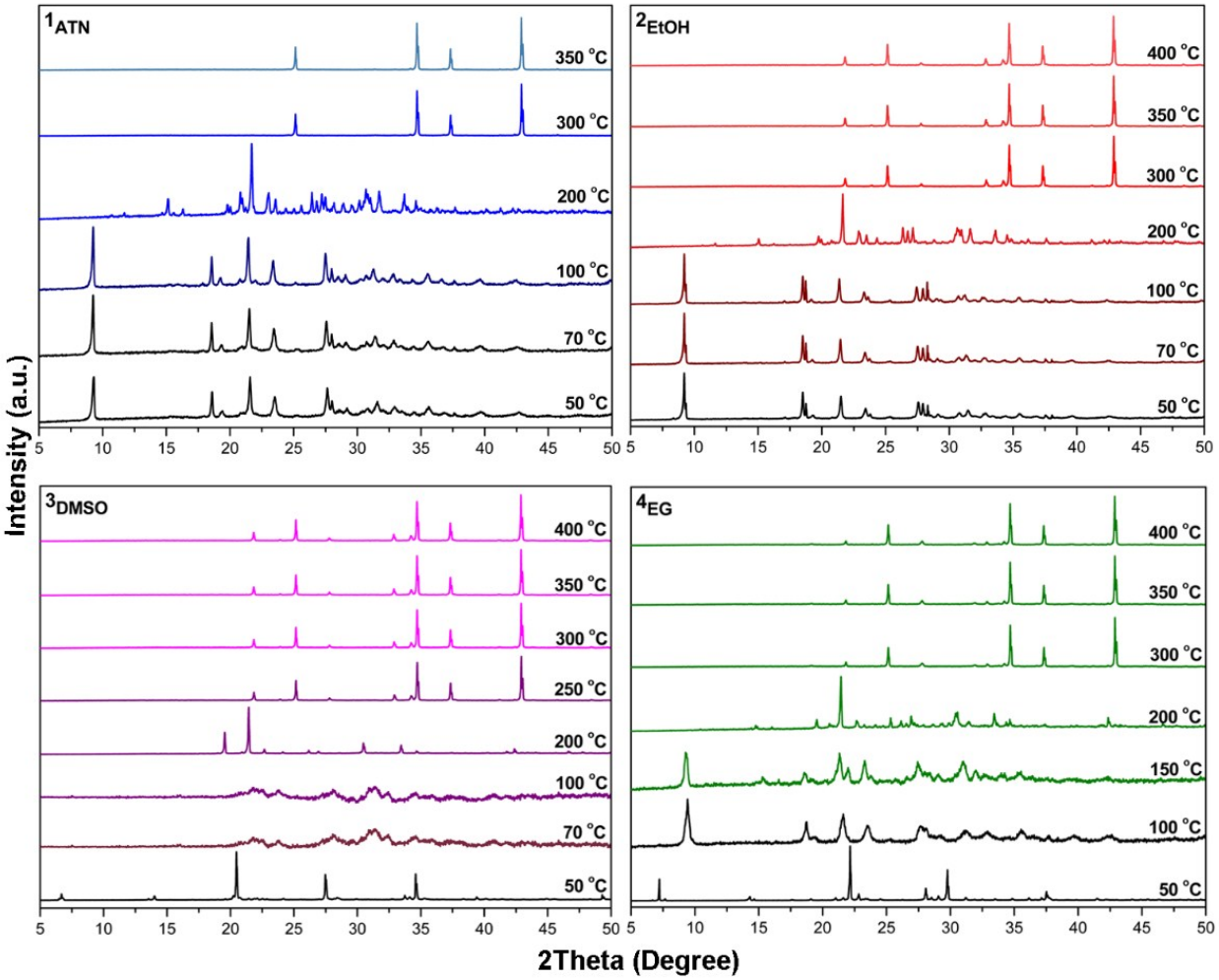
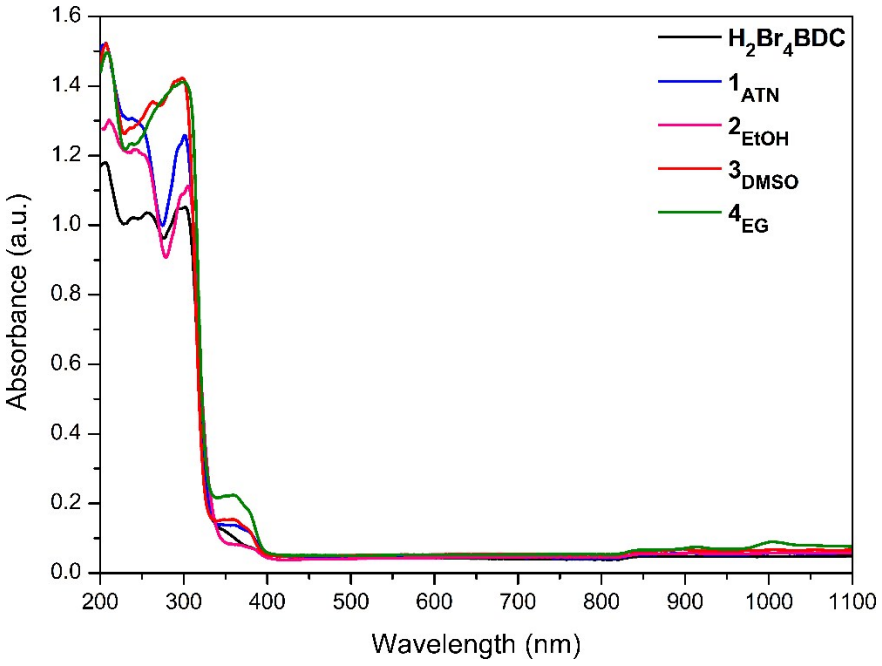
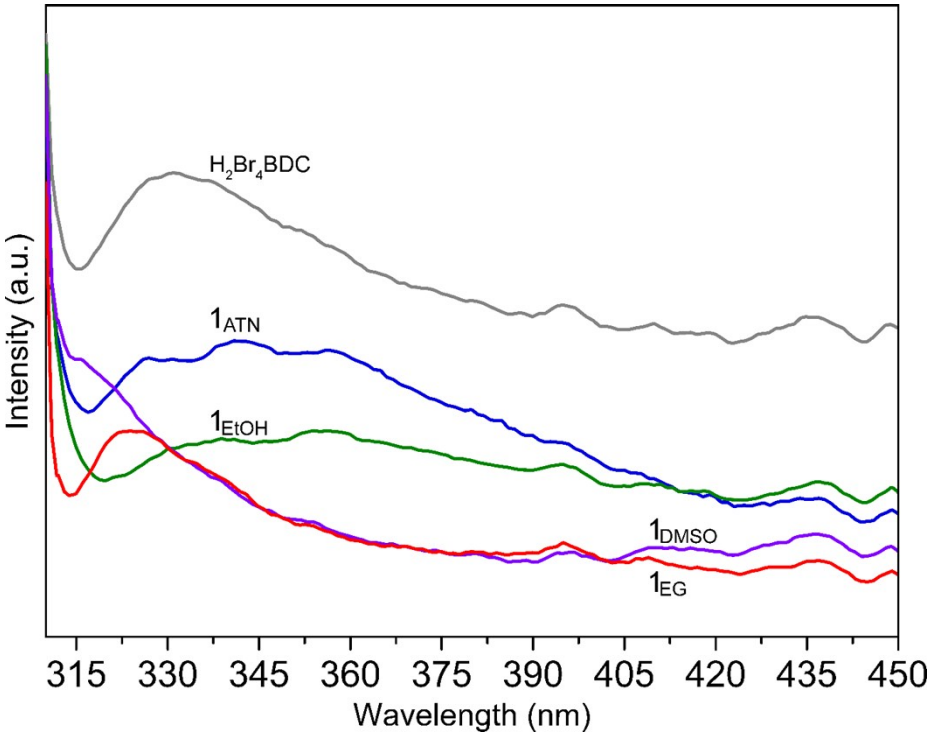


Figure S12 Variable-temperature PXRD patterns for all the solvates.



(a)



(b)

Figure S13 Solid-state UV-Vis (a) and photoluminescence (PL) (b) spectra of H_2Br_4BDC and all the solvates at temperature.