Electronic Supplementary Material (ESI) for CrystEngComm.

Experimental and Computational Approaches to Produce and Characterise Isostructural Solvates

Doris E. Braun*, Thomas Gelbrich and Ulrich J. Griesser

*** Correspondence:** doris.braun@uibk.ac.at

Table of Contents

1. Pawley Fitting

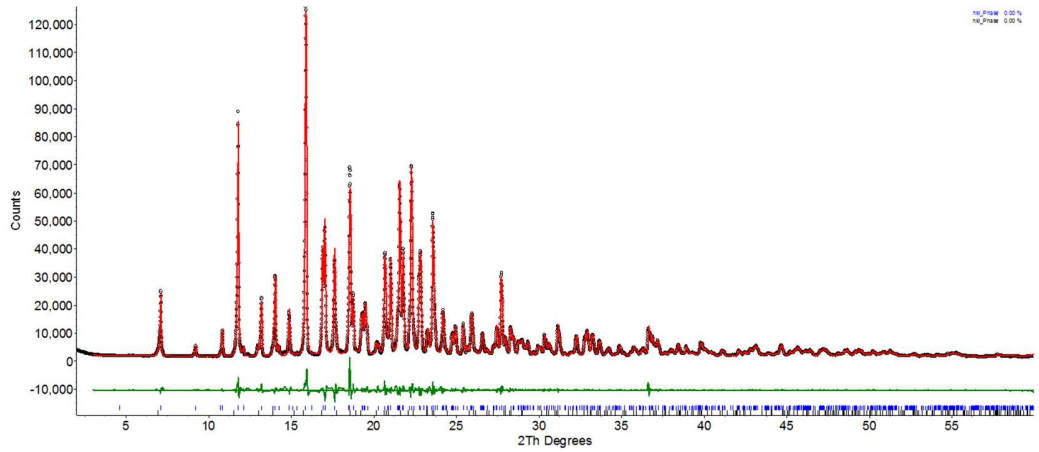

Figure S1. Pawley fit between the PXRD data of $\mathbf{S_{0.5ACN}}$ with a model consisting of the cell parameters derived from indexing the PXRD pattern (note that form **III** impurities are present). Black dots indicate the raw data, while the red line indicates the calculated model. Tick marks (blue – solvate and black – form **III**) are the 2θ positions for the *hkl* reflections. The difference pattern is shown in green.

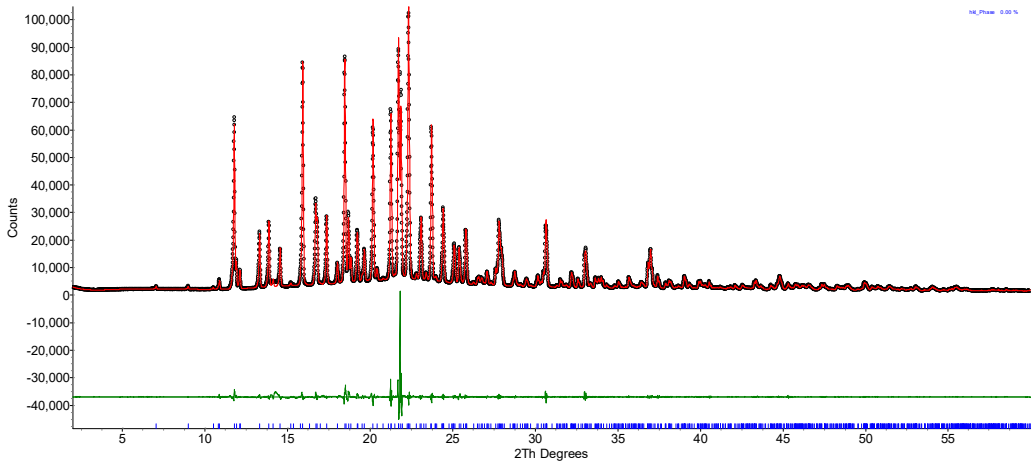

Figure S2. Pawley fit between the PXRD data of $\mathbf{S_{0.5NM}}$ with a model consisting of the cell parameters derived from indexing the PXRD pattern. Black dots indicate the raw data, while the red line indicates the calculated model. Tick marks are the 2θ positions for the *hkl* reflections. The difference pattern is shown in green.

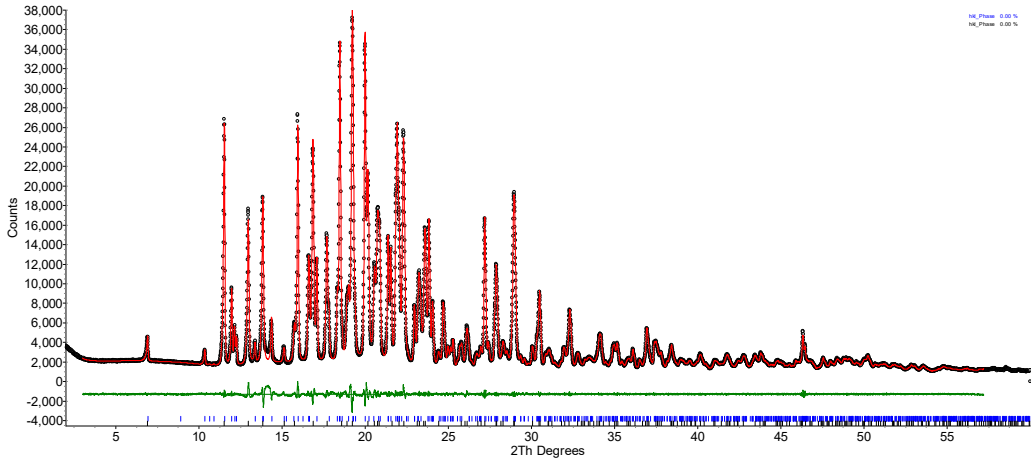

Figure S3. Pawley fit between the PXRD data of **$S_{0.5DCM}$** with a model consisting of the cell parameters derived from indexing the PXRD pattern (note that form **III** impurities are present). Black dots indicate the raw data, while the red line indicates the calculated model. Tick marks (blue – solvate and black – form **III**) are the 2θ positions for the *hkl* reflections. The difference pattern is shown in green.

Table S1. Unit cell parameters and space group symmetry derived from indexation of DDS hemisolvates and Form **III** PXRD patterns recorded at room temperature.

Solid Form	SG	a / Å	b / Å	c / Å	β / °	Volume / Å^3	R_{exp}	R_{wp}	R_p
Anhydrate									
Form **III**	$P2_12_12_1$	5.7501(<1)	8.0472(<1)	25.4957(3)	90	1179.73(2)	*3.65*	*3.95*	*3.04*
Hemi-Solvates									
$S_{0.5ACN}$	$P2_1/c$	8.5352(2)	16.3078(4)	22.2536(7)	120.500(1)	2668.87(14)	1.49	6.04	3.69
$S_{0.5NM}$	$P2_1/c$	8.4638(3)	16.2489(7)	22.8563(9)	120.578(<1)	2705.71(19)	1.50	3.21	4.26
$S_{0.5DCM}$	$P2_1/c$	8.3560(2)	16.6089(4)	20.5183(7)	104.250(1)	2759.99(15)	1.65	3.10	1.91

2. Single Crystal X-ray Diffraction

Table S2. Crystallographic data.

Compound	**$S_{0.5ACN}$**	**$S_{0.5NM}$**
Chemical formula	$C_{26}H_{27}N_5O_4S_2$	$C_{25}H_{27}N_5O_6S_2$
Chemical formula	$2(C_{12}H_{12}N_2O_2S) \cdot C_2H_3N$	$2(C_{12}H_{12}N_2O_2S) \cdot CH_3NO_2$
Formula Mass	537.64	557.63
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, Z	4	4
a / Å	8.5132(2)	8.4167(2)
b / Å	16.1830(3)	16.3415(3)
c / Å	18.9865(4)	19.1383(4)
β / °	97.818(2)	95.832(2)
Unit cell volume / Å^3	2591.44(10)	2618.69(10)
Temperature / K	100	100
No. of reflections measured	23182	48993
No. of independent reflections	5290	4977
No. of parameters	386	395
R_{int}	0.0376	0.0866
Final $R1$ value [$I > 2\sigma(I)$]	0.0393	0.0491
Final $wR(F^2)$ value (all data)	0.1056	0.1276
CCDC no.	1915951	1915952

3. Crystal Explorer Calculations

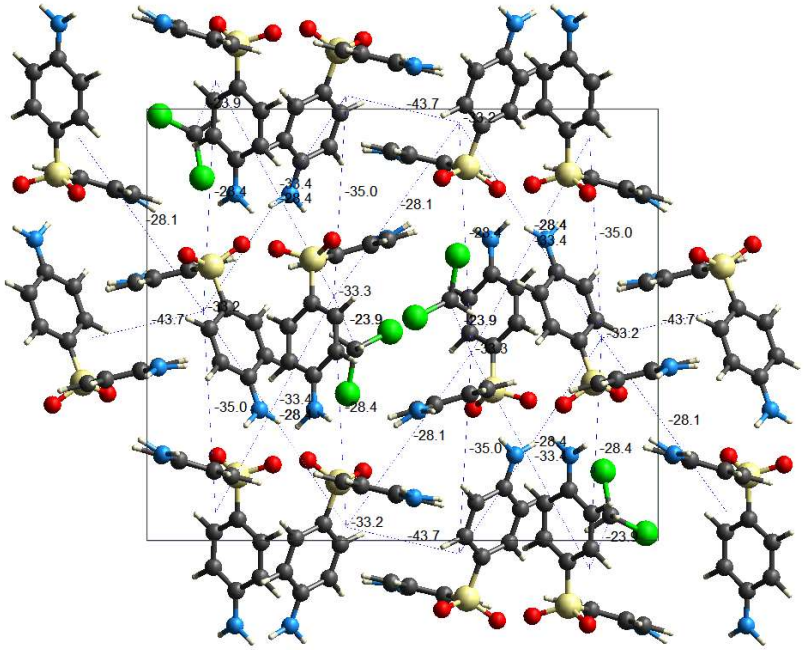

Figure S4. Energy frameworks (total energy, annotated) for **$S_{0.5DCM}$**, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

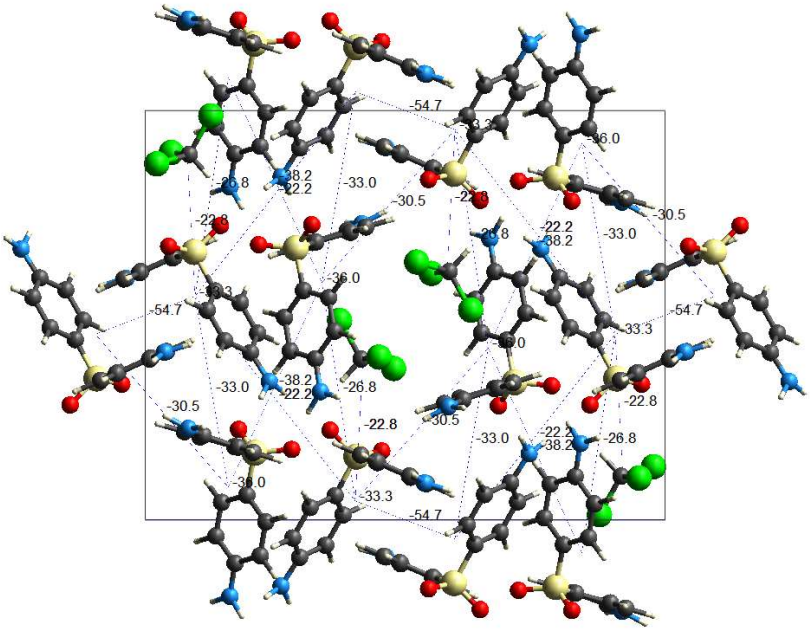

Figure S5. Energy frameworks (total energy, annotated) for $S_{0.5CHLF}$, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

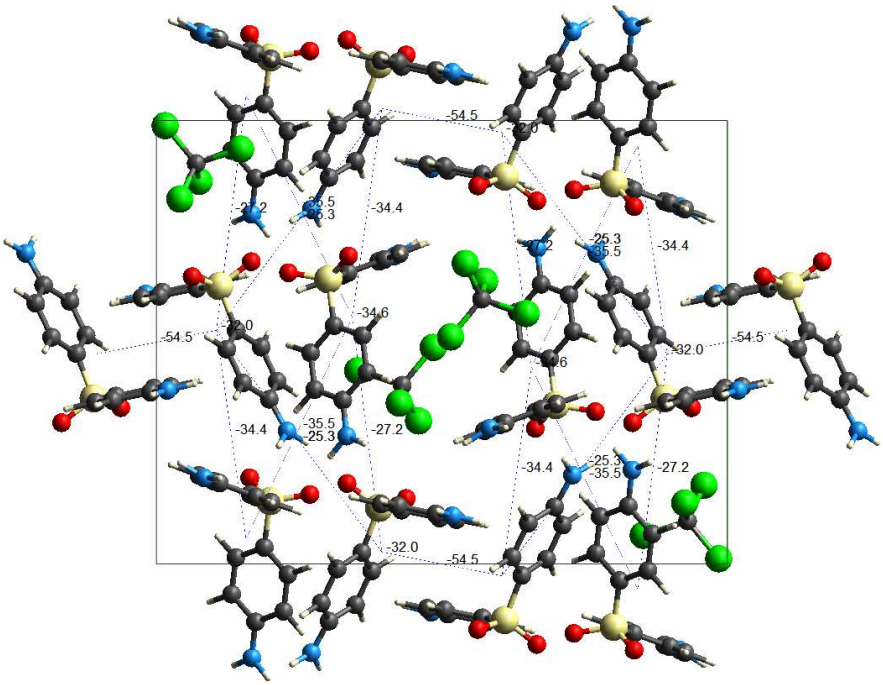

Figure S6. Energy frameworks (total energy, annotated) for $S_{0.5CTC}$, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

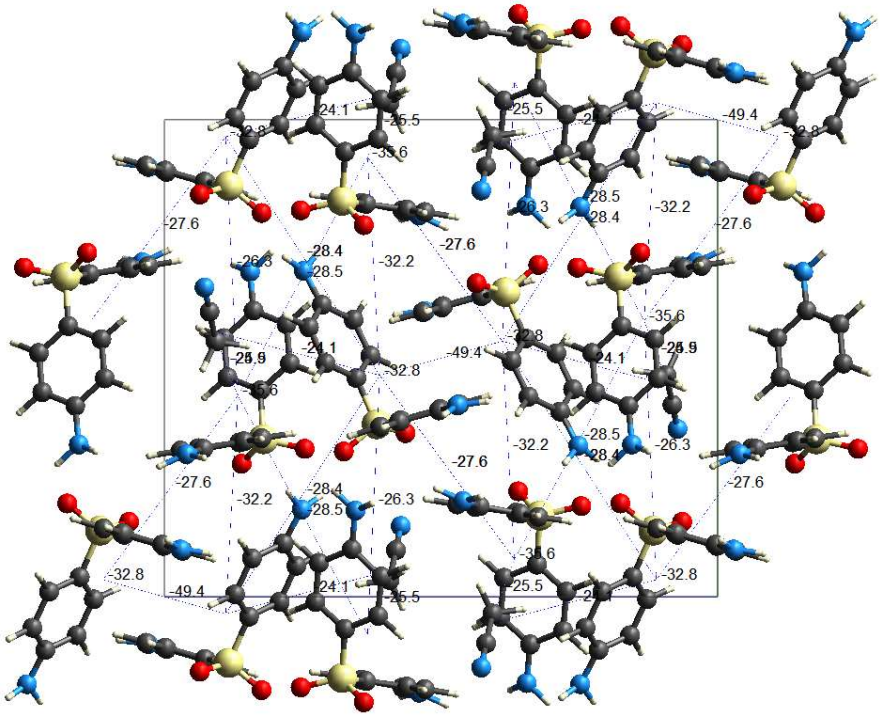

Figure S7. Energy frameworks (total energy, annotated) for $\mathbf{S_{0.5ACN}}$, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

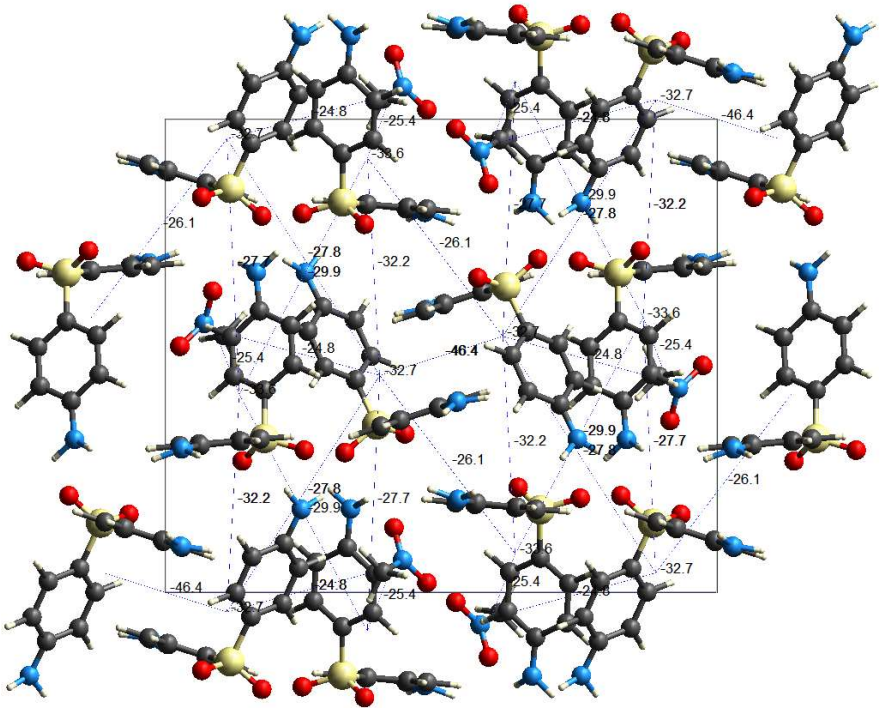

Figure S8. Energy frameworks (total energy, annotated) for **$S_{0.5NM}$**, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

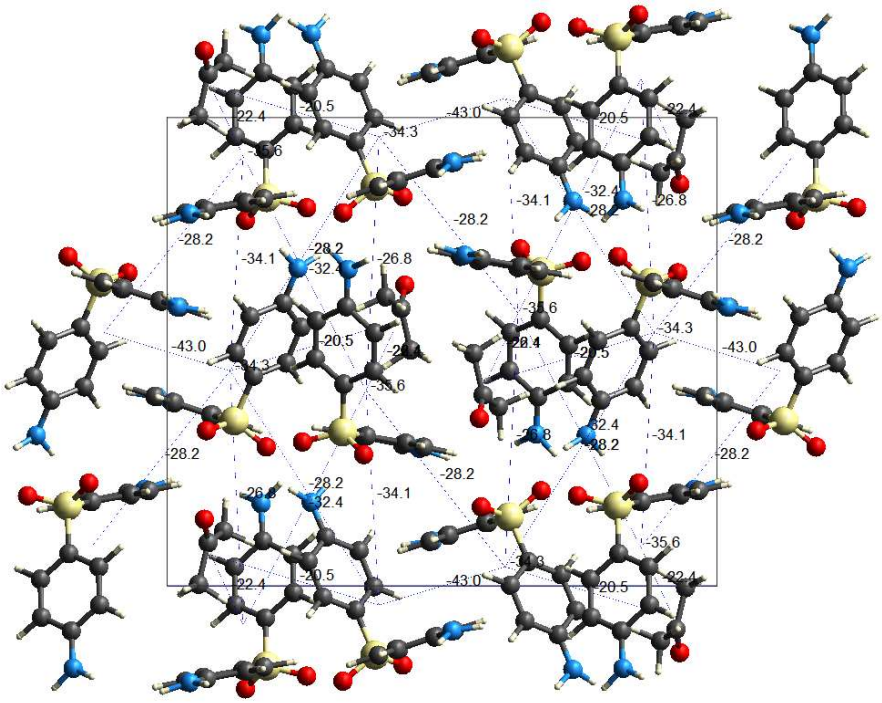

Figure S9. Energy frameworks (total energy, annotated) for $S_{0.5ACO}$, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

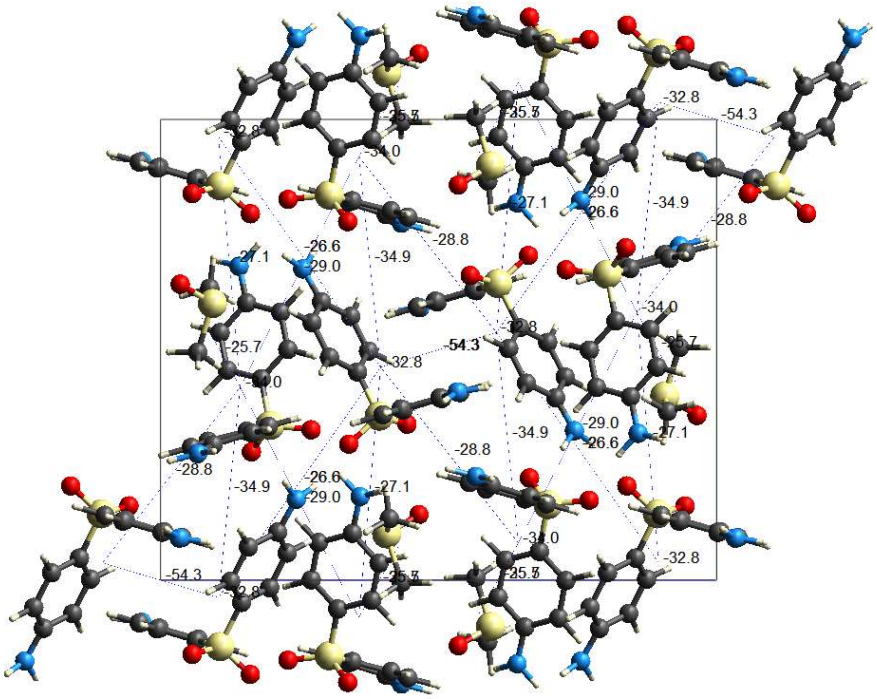

Figure S10. Energy frameworks (total energy, annotated) for **$S_{0.5DMSO}$**, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

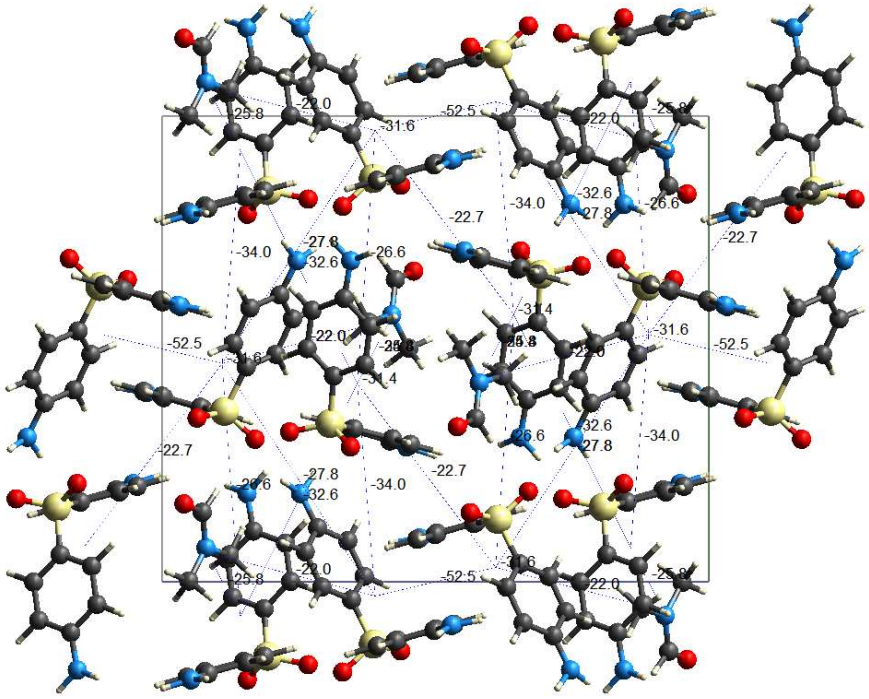

Figure S11. Energy frameworks (total energy, annotated) for $S_{0.5DMF}$, viewed along the crystallographic *a* axis. Pair-wise interaction energies with magnitudes smaller than 20 kJ mol^{-1} have been omitted.

Table S3. Pair-wise intermolecular interaction energies[a] of **DDS $S_{0.5DCM}$** (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5DCM, $E_{cluster}$ = –184.9 kJ mol^{-1}							
1 (1)	DDS···DDS	6.53	-15.5	-5.9	-48.9	31.8	-43.7
2 (2)	DDS···DDS	9.53	-38.5	-9.4	-9.9	34.3	-35
3 (2)	DDS···DDS	9.36	-33.4	-8.7	-9.2	26.5	-33.4
4 (2)	DDS···DDS	8.28	-29.5	-8.8	-17.7	32.2	-33.3
5 (2)	DDS···DDS	8.28	-28	-8.5	-18.3	30.1	-33.2
6 (2)	DDS···DDS	10.36	-21.1	-4.9	-8.7	8.2	-28.4
7 (2)	DDS···DDS	9.93	-27.4	-6.7	-6.9	18.6	-28.4
8 (2)	DDS···DDS	10.29	-23.1	-5.3	-6.5	9.5	-28.1
9 (2)	DDS···S	3.8	-9.8	-2.8	-29.8	23.4	-23.9
10 (1)	DDS···DDS	6.24	-7.2	-2	-25.6	18.9	-19.7
11 (2)	DDS···DDS	6.33	1.4	-6.3	-27.8	21.4	-14.3
12 (2)	DDS···S	6.89	-8.5	-1.3	-11	10.5	-13.1
13 (2)	DDS···DDS	6.29	7.2	-5.4	-30.4	18.5	-11.4
14 (2)	DDS···S	6.91	-6	-0.7	-7.8	4.6	-10.8
15 (1)	S···S	4.93	-7.7	-0.7	-7.1	7.9	-10
16 (2)	DDS···DDS	7.95	3.7	-4.1	-22.6	14.4	-9.9
17 (2)	DDS···S	4.32	-6.9	-0.7	-19.8	24.6	-9.9
18 (1)	DDS···DDS	9.48	-3.2	-0.3	-2.2	0	-5.5
19 (2)	DDS···DDS	9.53	-2.9	-0.5	-2.4	0.1	-5.4
20 (1)	DDS···DDS	6.47	9.5	-2.3	-18.4	5.3	-4.3
21 (2)	DDS···S	8.51	-1.7	-0.3	-2.9	0.5	-4.1
22 (2)	DDS···DDS	8.29	4.2	-2.3	-13.3	7.8	-4
23 (2)	DDS···S	6.08	2.4	-1.3	-10.1	9.7	-1.3
24 (1)	S···S	6.56	0.2	0	-0.9	0.1	-0.5
25 (2)	DDS···DDS	9.23	4.2	-1.1	-5.5	1.2	-0.4
26 (2)	DDS···DDS	9.11	0.2	0	-0.4	0	-0.1
27 (2)	DDS···DDS	9.56	0.6	0	-0.3	0	0.4

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S4. Pair-wise intermolecular interaction energies[a] of DDS $S_{0.5CHLF}$ (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5CHLF, $E_{cluster}$ = –189.4 kJ mol^{-1}							
1 (1)	DDS···DDS	6.30	-27.2	-9	-65.6	61.2	-54.7
2 (2)	DDS···DDS	8.67	-37	-10.5	-16.2	36.9	-38.2
3 (2)	DDS···DDS	8.43	-34.6	-9.6	-19.4	39.9	-36
4 (2)	DDS···DDS	8.43	-29.1	-8.6	-17.8	31.4	-33.3
5 (2)	DDS···DDS	9.63	-31.7	-7.7	-7.7	21	-33
6 (2)	DDS···DDS	10.01	-26.6	-6.6	-7.8	15.2	-30.5
7 (2)	DDS···DDS	10.32	-20.8	-5.2	-9	11.2	-26.8
8 (2)	DDS···S	5.52	-13.4	-4.5	-17.7	16.3	-22.8
9 (2)	DDS···DDS	10.24	-17	-4.1	-5.6	5.9	-22.2
10 (1)	DDS···DDS	6.05	-8.1	-2.4	-29.7	27.1	-19.5
11 (2)	DDS···DDS	6.22	-4.9	-7.5	-30.1	31.6	-17.4
12 (2)	DDS···S	4.06	-7	-1	-28.8	34.4	-12
13 (2)	DDS···DDS	6.4	6.9	-5	-33.7	25.2	-10.1
14 (2)	DDS···DDS	8.1	0.7	-3.2	-19.8	14.8	-9.8
15 (2)	DDS···DDS	7.71	0.3	-4.3	-26.3	26	-9.7
16 (2)	DDS···DDS	8.98	-4.7	-0.8	-3.4	0.2	-8.4
17 (2)	DDS···S	4.98	-4.3	-0.3	-15.7	17.3	-7.8
18 (2)	DDS···S	7.96	-4.8	-0.7	-1.2	0	-6.6
19 (2)	DDS···S	7.52	-4.1	-1	-11.3	15.3	-5.5
20 (2)	DDS···S	7.65	0.2	-1.2	-11.1	9	-4.8
21 (2)	DDS···S	8.86	-6.1	-0.4	-6	12.4	-4.3
22 (1)	DDS···DDS	10.80	-2.3	-0.2	-1.1	0	-3.6
23 (1)	S···S	4.81	-0.3	-0.1	-5.6	3.5	-3.1
24 (1)	S···S	6.77	0.2	0	-1	0	-0.6
25 (2)	DDS···DDS	8.91	4.7	-1.2	-5.4	1.1	0.1
26 (1)	DDS···DDS	7.70	6.6	-0.6	-5.3	0.1	2

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S5. Pair-wise intermolecular interaction energies[a] of DDS $S_{0.5CTC}$ (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5CTC, $E_{cluster}$ = –170.9 kJ mol^{-1}							
1 (1)	DDS···DDS	6.32	-23.6	-8.2	-56.7	41.9	-54.5
2 (2)	DDS···DDS	8.82	-33.3	-9.9	-14.4	31.7	-35.5
3 (2)	DDS···DDS	8.72	-34	-9	-14.9	33.9	-34.6
4 (2)	DDS···DDS	9.7	-36	-8.9	-9.2	29.5	-34.4
5 (2)	DDS···DDS	8.72	-29	-7.9	-13.6	26.5	-32
6 (2)	DDS···DDS	10.36	-19.7	-4.7	-8.5	7.3	-27.2
7 (2)	DDS···DDS	10.08	-20.9	-5.1	-6.1	9.5	-25.3
8 (2)	DDS···DDS	10.96	-11.5	-1.8	-2.9	0.3	-15.8
9 (2)	DDS···DDS	6.35	-0.9	-7.4	-24.8	19.9	-15.6
10 (2)	DDS···S	4.14	-4.7	-0.8	-28.6	27.3	-13.5
11 (1)	DDS···DDS	6.48	-0.2	-1.8	-17	6.2	-12.5
12 (2)	DDS···DDS	6.45	7.3	-5.9	-28.7	17.1	-11.1
13 (2)	DDS···S	5.68	-8.4	-2.3	-18.3	25.6	-10.8
14 (2)	DDS···S	4.98	-5.3	-0.3	-20.6	21.4	-10.6
15 (2)	DDS···DDS	8.18	0.5	-2.9	-20.2	15	-10
16 (2)	DDS···DDS	8.31	1.2	-2.8	-18.6	12.9	-9.1
17 (2)	DDS···S	7.3	-6	-1.1	-14.1	19.6	-7.4
18 (2)	DDS···S	7.4	-8.5	-1	-12.9	23.1	-6.7
19 (2)	DDS···DDS	9.28	-2.6	-0.5	-1.2	0	-4.2
20 (1)	DDS···DDS	10.38	-2.6	-0.2	-1.2	0	-4
21 (1)	S···S	6.95	0	0	-1.4	0	-1.2
22 (1)	S···S	5.33	-8.2	-0.1	-10.2	26.7	-1.1
23 (2)	DDS···DDS	8.41	0.4	-0.5	-1	0	-0.9
24 (2)	DDS···S	9.2	0.8	-0.5	-5.5	6.3	-0.4
25 (2)	DDS···S	10.83	0.5	-0.1	-0.8	0	-0.3
26 (1)	DDS···DDS	7.45	5.7	-0.6	-6	0.1	0.5

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S6. Pair-wise intermolecular interaction energies[a] of **DDS $S_{0.5ACN}$** (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5ACN, $E_{cluster}$ = –194.8 kJ mol^{-1}							
1 (1)	DDS···DDS	6.38	-19.7	-7	-55.7	40.6	-49.4
2 (2)	DDS···DDS	8.51	-33.2	-9.2	-16.7	33.8	-35.6
3 (2)	DDS···DDS	8.51	-28	-7.8	-15.6	26.2	-32.8
4 (2)	DDS···DDS	9.35	-29	-8	-11.4	23.4	-32.2
5 (2)	DDS···DDS	9.16	-23	-7.3	-10.2	16.3	-28.5
6 (2)	DDS···DDS	9.69	-28.9	-7.8	-8.8	25.1	-28.4
7 (2)	DDS···DDS	10.17	-22.9	-5.4	-6.9	10.7	-27.6
8 (2)	DDS···DDS	10.4	-18.8	-4.4	-8.2	6.4	-26.3
9 (2)	DDS···S	4.07	-13.1	-3.1	-26.2	21.8	-25.5
10 (2)	DDS···S	6.97	-22.3	-4	-8.9	15	-24.9
11 (2)	DDS···S	6.47	-15.7	-2.4	-12.8	8.8	-24.1
12 (1)	DDS···DDS	6.26	-4.8	-2	-24.1	16.1	-17.6
13 (2)	DDS···DDS	6.39	1.8	-5.9	-27.9	18.1	-15.6
14 (2)	DDS···DDS	6.19	5.3	-6.2	-31.8	23.7	-12.2
15 (2)	DDS···DDS	7.44	3.2	-5	-28	20.2	-12.2
16 (2)	DDS···S	8.72	-9.5	-1.9	-4	5.4	-11.7
17 (1)	DDS···DDS	6.48	6	-3.7	-26	14.4	-10.2
18 (2)	DDS···S	4.36	-1	-2.1	-14	9.8	-8.8
19 (1)	DDS···DDS	9.46	-2.4	-0.5	-3.9	0.3	-6.2
20 (2)	DDS···DDS	8.03	3.2	-2	-11.8	4.2	-5.8
21 (2)	DDS···DDS	9.2	-2.1	-0.6	-3.4	0.3	-5.4
22 (2)	DDS···S	10.68	-3.3	-0.2	-0.3	0	-3.9
23 (1)	S···S	5.40	2.2	-0.8	-3.7	1.5	-0.5
24 (1)	S···S	13.69	0.7	-0.2	-0.7	0	0
25 (2)	DDS···DDS	9.24	4.4	-0.8	-4.5	0.8	0.6
26 (2)	DDS···S	5.7	17.1	-3.1	-6.9	5.4	13.2

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S7. Pair-wise intermolecular interaction energies[a] of **DDS $S_{0.5NM}$** (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5NM, $E_{cluster}$ = –194.0 kJ mol^{-1}							
1 (1)	DDS···DDS	6.38	-19.6	-6.9	-54	42.7	-46.4
2 (2)	DDS···DDS	8.42	-26.8	-7.8	-17.2	25	-33.6
3 (2)	DDS···DDS	8.42	-27.2	-7.9	-16.3	26.1	-32.7
4 (2)	DDS···DDS	9.26	-31.1	-8.5	-12	28.3	-32.2
5 (2)	DDS···DDS	9.17	-27.2	-8.2	-10.6	23	-29.9
6 (2)	DDS···DDS	9.74	-25.9	-6.9	-8.2	19.2	-27.8
7 (2)	DDS···DDS	10.27	-21.2	-5	-9.1	10.2	-27.7
8 (2)	DDS···DDS	10.37	-20.7	-4.6	-6.3	7.5	-26.1
9 (2)	DDS···S	4.03	-11.6	-4.3	-28.5	24	-25.4
10 (2)	DDS···S	6.57	-16.4	-2.6	-14.5	11.5	-24.8
11 (2)	DDS···S	6.64	-14.3	-2	-10	9.7	-19.3
12 (1)	DDS···DDS	6.46	-5	-1.8	-19.5	9.5	-17.6
13 (1)	S···S	4.65	-13	-1.9	-6.5	6.6	-16.7
14 (2)	DDS···DDS	6.33	2.3	-5.8	-29.4	20.4	-14.8
15 (2)	DDS···DDS	7.36	3.8	-5.1	-28.8	19.5	-12.9
16 (2)	DDS···DDS	6.2	5.2	-5.5	-32.1	22.7	-12.5
17 (2)	DDS···S	4.2	-2.9	-2.9	-18.4	17.1	-10.8
18 (1)	DDS···DDS	6.80	4.4	-3	-20	8.9	-9.5
19 (2)	DDS···DDS	9.36	-2.6	-0.5	-3.1	0.2	-5.7
20 (1)	DDS···DDS	9.08	-1.9	-0.5	-3.9	0.2	-5.7
21 (2)	DDS···S	8.96	-2.9	-0.6	-1.7	0.2	-4.9
22 (2)	DDS···S	8.49	-3.5	-0.5	-0.6	0	-4.6
23 (2)	DDS···DDS	8.2	3.3	-1.7	-9.7	2.9	-4.4
24 (2)	DDS···DDS	9.32	4	-0.7	-4	0.5	0.5
25 (1)	S···S	6.41	3.2	-0.2	-0.4	0	2.9
26 (2)	DDS···S	6.05	12	-1.7	-5.3	2.3	8.2

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S8. Pair-wise intermolecular interaction energies[a] of DDS $S_{0.5ACO}$ (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5ACO, $E_{cluster}$ = –197.9 kJ mol^{-1}							
1 (1)	DDS···DDS	6.55	-18.9	-6.1	-49.5	39.8	-43
2 (2)	DDS···DDS	8.37	-35.3	-10.6	-18.4	41.4	-35.6
3 (2)	DDS···DDS	8.37	-32.2	-9.1	-18.7	36.8	-34.3
4 (2)	DDS···DDS	9.42	-33.6	-8.8	-10.3	27.3	-34.1
5 (2)	DDS···DDS	9.19	-30.5	-8.8	-11	25.7	-32.4
6 (2)	DDS···DDS	10.15	-24.6	-5.9	-7.1	13.6	-28.2
7 (2)	DDS···DDS	9.74	-30.2	-7.6	-8.1	26.6	-28.2
8 (2)	DDS···DDS	10.42	-19.5	-4.6	-8.6	7.6	-26.8
9 (2)	DDS···S	6.93	-23.2	-4.4	-14.8	23.6	-26.1
10 (2)	DDS···S	4.18	-14.2	-2.1	-33.8	38.1	-22.4
11 (2)	DDS···S	6.67	-12	-2.1	-16.5	13.2	-20.5
12 (1)	DDS···DDS	6.49	-5.6	-1.8	-19.6	10.5	-17.9
13 (2)	DDS···DDS	6.27	0.5	-6.6	-30.6	23	-16.8
14 (2)	DDS···DDS	6.11	4.6	-6.1	-35.7	29.4	-12.6
15 (2)	DDS···DDS	7.56	0.7	-4.8	-27.6	23.1	-12.5
16 (2)	DDS···S	8.55	-9.2	-2.1	-4.9	5.7	-12.1
17 (2)	DDS···S	4.44	-1.3	-1.3	-23.3	18.4	-11.2
18 (1)	DDS···DDS	9.67	-3.1	-0.4	-2.6	0	-5.8
19 (2)	DDS···DDS	9.43	-2.9	-0.5	-2.7	0.1	-5.7
20 (1)	S···S	6.48	-2.4	-0.2	-1.5	0.2	-4
21 (2)	DDS···DDS	8.09	4.6	-2.3	-13.6	8.3	-3.6
22 (2)	DDS···S	8.26	-1.8	-0.8	-1.1	0	-3.5
23 (1)	S···S	5.31	1.1	-0.8	-8.1	7	-2.3
24 (1)	DDS···DDS	6.80	12.1	-2.3	-15.4	3.3	-0.3
25 (2)	DDS···DDS	9.24	4.4	-0.9	-4.3	0.6	0.5
26 (2)	DDS···S	5.71	13.6	-3.2	-11.6	8	6.9

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S9. Pair-wise intermolecular interaction energies[a] of **DDS $S_{0.5DMSO}$** (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5DMSO, $E_{cluster}$ = –184.9 kJ mol^{-1}							
1 (1)	DDS···DDS	6.19	-27.2	-8.9	-68.6	65.9	-54.3
2 (2)	DDS···S	6.89	-30.8	-6.6	-18.1	28.7	-35.5
3 (2)	DDS···DDS	9.4	-36.2	-9.3	-9.6	30.2	-34.9
4 (2)	DDS···DDS	8.4	-33.1	-10.7	-17.6	39.1	-34
5 (2)	DDS···DDS	8.4	-29.3	-8.5	-18.8	33.5	-32.8
6 (2)	DDS···DDS	8.96	-20.3	-6.5	-11.2	11.4	-29
7 (2)	DDS···DDS	10.14	-25	-5.9	-7.3	13.4	-28.8
8 (2)	DDS···DDS	10.38	-19.7	-4.9	-9.6	9.3	-27.1
9 (2)	DDS···DDS	9.88	-24.7	-6.2	-6.8	16.2	-26.6
10 (2)	DDS···S	4.3	-18.6	-3.1	-37	46.1	-25.7
11 (1)	DDS···DDS	6.22	-4.7	-2	-24.5	17.2	-17.2
12 (2)	DDS···S	8.48	-14.2	-3.9	-5.2	8.6	-17.2
13 (2)	DDS···DDS	6.39	-0.4	-6.5	-26.8	19.8	-16.4
14 (2)	DDS···S	4.66	-6.6	-4.7	-24.8	27.4	-15.2
15 (2)	DDS···S	6.87	-11.9	-1.9	-14.6	18.7	-15.1
16 (2)	DDS···DDS	7.53	-2.8	-4.7	-29.1	28.5	-14.2
17 (2)	DDS···DDS	6.16	6.6	-6.2	-35.7	30.6	-9.8
18 (1)	S···S	6.32	-6.3	-0.7	-1.5	0	-8.5
19 (2)	DDS···DDS	7.97	2.3	-2.7	-18.2	13.3	-7.2
20 (2)	DDS···S	8.24	-4.8	-0.9	-1.2	0	-6.8
21 (2)	DDS···DDS	9.1	-2.7	-0.6	-3.3	0.2	-6
22 (1)	DDS···DDS	9.92	-2.7	-0.5	-3.1	0.1	-5.8
23 (1)	S···S	5.60	0.4	-0.9	-7.6	5	-3.7
24 (2)	DDS···DDS	9.11	5	-0.9	-4.7	0.8	1
25 (1)	DDS···DDS	7.00	13	-2.4	-14.2	3	1.5
26 (2)	DDS···S	5.52	10.1	-4.9	-16.2	15.7	2.7

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S10. Pair-wise intermolecular interaction energies[a] of **DDS** $S_{0.5DMF}$ (PBE-TS structure).

Inter-action	Molecules Involved	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
S-0.5DMF, $E_{cluster}$ = –209.0 kJ mol^{-1}							
1 (1)	DDS···DDS	6.28	-26.6	-8.4	-65	62.2	-52.5
2 (2)	DDS···S	6.68	-30.8	-6.6	-20.8	34.2	-34.4
3 (2)	DDS···DDS	9.26	-36.8	-9.8	-11.4	35.8	-34
4 (2)	DDS···DDS	9.00	-27.9	-8.3	-11.6	21.3	-32.6
5 (2)	DDS···DDS	8.51	-28.1	-7.8	-14.4	26.5	-31.6
6 (2)	DDS···DDS	8.51	-25.2	-8.2	-15.3	23.7	-31.4
7 (2)	DDS···DDS	9.76	-27	-7	-8.1	21	-27.8
8 (2)	DDS···DDS	10.32	-19.7	-4.9	-9.5	9.8	-26.6
9 (2)	DDS···S	4.38	-20	-2.9	-45.1	59.5	-25.8
10 (2)	DDS···DDS	10.66	-16.8	-3.3	-5	2.9	-22.7
11 (2)	DDS···S	6.62	-12.7	-2.4	-21.5	19.2	-22
12 (2)	DDS···S	8.98	-16.3	-3.7	-5.4	8.3	-19.5
13 (2)	DDS···DDS	6.3	-1.5	-6.9	-30	24.2	-17.8
14 (1)	DDS···DDS	6.31	-4.5	-2	-21.7	12.3	-17.7
15 (2)	DDS···DDS	7.7	0.7	-4.2	-26.7	22.9	-11.5
16 (2)	DDS···DDS	6.09	5.9	-6.4	-36.4	33	-9.7
17 (2)	DDS···S	4.42	0.5	-2.8	-24.9	23.1	-9
18 (2)	DDS···DDS	9.06	-3.6	-0.7	-3.6	0.3	-7.2
19 (2)	DDS···S	8.33	-5.1	-0.9	-1.1	0	-7
20 (1)	S···S	5.29	-1.7	-0.9	-9.8	6.7	-6.8
21 (1)	S···S	6.48	-4.5	-0.5	-2	0.2	-6.8
22 (1)	DDS···DDS	9.29	-3.2	-0.5	-3.4	0.1	-6.5
23 (2)	DDS···DDS	8.19	2.6	-2.2	-14	7.6	-6.4
24 (1)	DDS···DDS	7.02	12.1	-2.6	-14.4	3.5	0.5
25 (2)	DDS···DDS	9.37	4.5	-0.8	-4.2	0.7	0.8
26 (2)	DDS···S	5.83	10.8	-4.5	-14.5	12.3	3.1

[a](1) – interaction present once, (2) – interaction present twice. [b]Electrostatic (E_E), polarization (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

4. Packing Similarity

Table S11. CrystalCMP similarity matrix.

	$S_{0.5NM}$	$S_{0.5ACN}$	$S_{0.5ACO}$	$S_{0.5CTC}$	$S_{0.5DCM}$	$S_{0.5DMF}$	$S_{0.5DMSO}$	$S_{0.5DMSO}$
$S_{0.5NM}$								
$S_{0.5ACN}$	0.3831							
$S_{0.5ACO}$	0.2535	0.3567						
$S_{0.5CTC}$	1.3776	1.4667	1.2727					
$S_{0.5DCM}$	1.6801	1.0122	1.5993	0.9824				
$S_{0.5DMF}$	0.7888	0.7011	0.7542	1.4982	1.3345			
$S_{0.5DMSO}$	0.4909	0.3476	0.5631	0.9840	0.9204	0.6795		
$S_{0.5DMSO}$	0.8164	0.5106	0.6978	0.6611	1.0431	1.0406	0.4599	
Form III	27.6893	28.0526	27.8906	27.0483	27.0544	27.1303	27.2600	27.0526

5. DMSO Hemisolvate

The .res file of the computationally generated $S_{0.5DMSO}$ is given below.

```
TITL DMSO_HemiSolvate_PBE-TS
CELL  1.54180    8.4035   16.0552   19.5606    90.000    97.567    90.000
ZERR        4    0.0000    0.0000    0.0000     0.000     0.000     0.000
LATT   1
SYMM     0.50000 - X ,    0.50000 + Y ,    0.50000 - Z
SFAC  C  H  N  O  S
C1    1  0.15112  0.04821  0.14579  11.00000   0.0500
C2    1  0.24623 -0.05913  0.22767  11.00000   0.0500
C3    1  0.26963  0.01615  0.19621  11.00000   0.0500
C4    1  0.10167 -0.10431  0.21055  11.00000   0.0500
C5    1 -0.01411 -0.07237  0.15802  11.00000   0.0500
C6    1  0.01054  0.00258  0.12609  11.00000   0.0500
C7    1  0.35141  0.13047  0.06345  11.00000   0.0500
C8    1  0.33396  0.10563 -0.00580  11.00000   0.0500
C9    1  0.46830  0.09270 -0.03825  11.00000   0.0500
C10   1  0.62397  0.10404 -0.00229  11.00000   0.0500
C11   1  0.63946  0.12823  0.06771  11.00000   0.0500
C12   1  0.50506  0.14085  0.10011  11.00000   0.0500
C13   1  0.71410  0.06246  0.31876  11.00000   0.0500
C14   1  0.65154  0.04362  0.38005  11.00000   0.0500
C15   1  0.60671 -0.03718  0.39278  11.00000   0.0500
C16   1  0.62313 -0.10180  0.34501  11.00000   0.0500
C17   1  0.68791 -0.08169  0.28386  11.00000   0.0500
C18   1  0.73319 -0.00084  0.27116  11.00000   0.0500
C19   1  0.97359  0.17650  0.34446  11.00000   0.0500
C20   1  1.10139  0.16589  0.30588  11.00000   0.0500
C21   1  1.25645  0.18043  0.33599  11.00000   0.0500
C22   1  1.28895  0.20625  0.40559  11.00000   0.0500
C23   1  1.15915  0.21181  0.44473  11.00000   0.0500
C24   1  1.00329  0.19835  0.41445  11.00000   0.0500
C25   1  0.30579  0.50540  0.06690  11.00000   0.0500
C26   1  0.48234  0.36639  0.08849  11.00000   0.0500
H1    2  0.16267 -0.20374  0.27656 11.00000 -1.20000
H2    2  0.74638  0.08203 -0.08563 11.00000 -1.20000
H3    2 -0.02086 -0.21270  0.22376 11.00000 -1.20000
H4    2  0.86671  0.11147 -0.00998 11.00000 -1.20000
H5    2  0.33834 -0.08389  0.26673 11.00000 -1.20000
H6    2  0.38143  0.05002  0.21076 11.00000 -1.20000
H7    2 -0.12392 -0.10795  0.14341 11.00000 -1.20000
H8    2 -0.07943  0.02607  0.08551 11.00000 -1.20000
H9    2  0.21410  0.09737 -0.03372 11.00000 -1.20000
H10   2  0.45551  0.07354 -0.09219 11.00000 -1.20000
H11   2  0.75840  0.13815  0.09609 11.00000 -1.20000
H12   2  0.52041  0.16003  0.15398 11.00000 -1.20000
H13   2  0.51106 -0.19278  0.39656 11.00000 -1.20000
H14   2  0.59373 -0.22789  0.32401 11.00000 -1.20000
H15   2  1.46977  0.24145  0.48388 11.00000 -1.20000
H16   2  1.53326  0.21969  0.40431 11.00000 -1.20000
H17   2  0.63926  0.09154  0.41860 11.00000 -1.20000
```

```
H18    2  0.55959 -0.05272  0.44052 11.00000 -1.20000
H19    2  0.70315 -0.13102  0.24694 11.00000 -1.20000
H20    2  0.78385  0.01381  0.22413 11.00000 -1.20000
H21    2  1.07862  0.14801  0.25185 11.00000 -1.20000
H22    2  1.35554  0.17337  0.30583 11.00000 -1.20000
H23    2  1.18304  0.22949  0.49890 11.00000 -1.20000
H24    2  0.90395  0.20589  0.44462 11.00000 -1.20000
H25    2  0.34067  0.50542  0.01474 11.00000 -1.50000
H26    2  0.39704  0.53589  0.10391 11.00000 -1.50000
H27    2  0.19061  0.53724  0.06721 11.00000 -1.50000
H28    2  0.51807  0.38324  0.03831 11.00000 -1.50000
H29    2  0.48580  0.29867  0.09555 11.00000 -1.50000
H30    2  0.56016  0.39626  0.13097 11.00000 -1.50000
N1     3  0.07285 -0.17549  0.24424  11.00000   0.0500
N2     3  0.75729  0.09145 -0.03360  11.00000   0.0500
N3     3  0.58158 -0.18134  0.35868  11.00000   0.0500
N4     3  1.44068  0.22518  0.43331  11.00000   0.0500
O1     4  0.04265  0.16136  0.05675  11.00000   0.0500
O2     4  0.22822  0.20464  0.16153  11.00000   0.0500
O3     4  0.78156  0.17354  0.22926  11.00000   0.0500
O4     4  0.67637  0.22171  0.33651  11.00000   0.0500
O5     4  0.17190  0.35768  0.03540  11.00000   0.0500
S1     5  0.18442  0.14393  0.10669  11.00000   0.0500
S2     5  0.77843  0.16401  0.30332  11.00000   0.0500
S3     5  0.27995  0.39944  0.09342  11.00000   0.0500
END
```