Electronic Supporting Information

Hybrid 2D Supramolecular Organic Frameworks (SOFs) Assembled by the Cooperative Action of Hydrogen and Halogen Bonding and π⋯π Stacking Interactions

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S1. X-ray diffraction data

Table S1. Crystal data and structure refinement parameters for cocrystals *cis*-**A**·½(1,2-DCE) and *cis*-**A**·½(1,2-**DBE**).
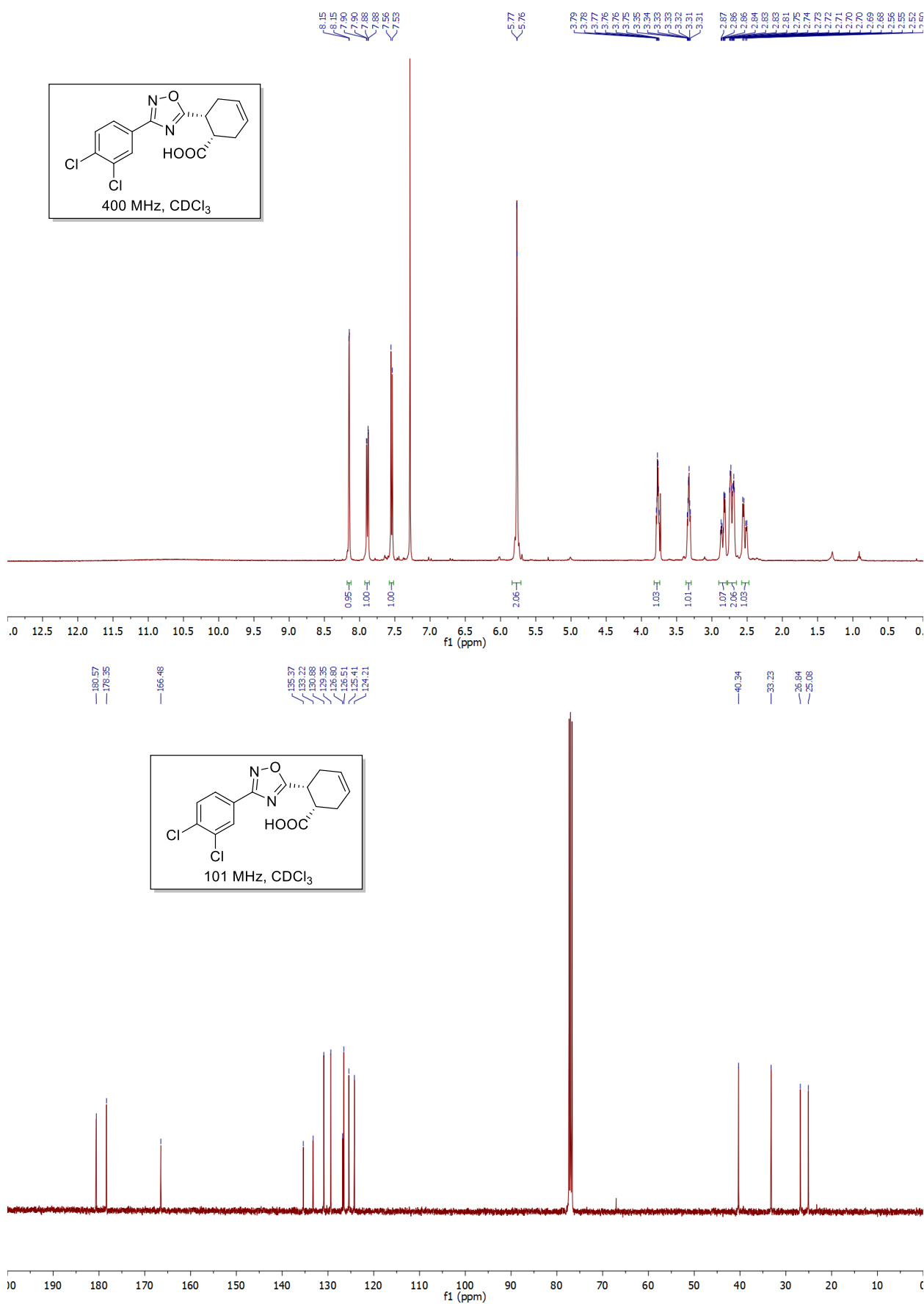
Structure	*cis*-**A**·½(1,2-DCE)	*cis*-**A**·½(1,2-**DBE**)
Identification code	BSC-231	BSC-240
CCDC number	2314868	2314869
Empirical formula	$C_{16}H_{14}Cl_3N_2O_3$	$C_{16}H_{14}BrCl_2N_2O_3$
Formula weight	388.64	433.10
Temperature, K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a, Å	6.9888(3)	7.0698(5)
b, Å	11.6332(6)	11.6573(7)
c, Å	12.0134(6)	11.9914(7)
α, °	66.054(5)	65.626(5)
β, °	75.188(4)	75.012(5)
γ, °	76.989(4)	76.789(5)
Volume, Å^3	854.80(8)	861.19(10)
Z	2	2
ρ_{calc}g, cm^3	1.510	1.670
μ, mm^{-1}	0.553	6.267
F(000)	398.0	434.0
Crystal size, mm^3	$0.22 \times 0.17 \times 0.15$	$0.21 \times 0.18 \times 0.16$
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection, °	6.088 to 64.674	8.238 to 152.13
Index ranges	–10 ≤ h ≤ 10, –17 ≤ k ≤ 17, –17 ≤ l ≤ 17	–8 ≤ h ≤ 6, –14 ≤ k ≤ 14, –14 ≤ l ≤ 14
Reflections collected	18152	6270
Independent reflections	5484 [R_{int} = 0.0269, R_{sigma} = 0.0316]	3492 [R_{int} = 0.0329, R_{sigma} = 0.0318]
Data/restraints/parameters	5484/0/218	3492/0/218
Goodness–of–fit on F^2	1.048	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1130	R_1 = 0.0436, wR_2 = 0.1202
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1181	R_1 = 0.0455, wR_2 = 0.1222
Largest diff. peak/hole/ eÅ^{-3}	0.53/–0.99	1.04/–1.01

Table S2. Crystal data and structure refinement parameters for cocrystal *cis*-**A**·½C$_6$H$_{14}$ and compound *trans*-**A**.

Structure	*cis*-**A**·½C$_6$H$_{14}$	*trans*-**A**
Identification code	BSC-242	BSC-221
CCDC number	2314870	2314867
Empirical formula	C$_{18}$H$_{17}$Cl$_2$N$_2$O$_3$	C$_{15}$H$_{12}$Cl$_2$N$_2$O$_3$
Formula weight	380.23	339.17
Temperature, K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a, Å	7.0450(3)	10.2007(3)
b, Å	11.5316(3)	11.1248(3)
c, Å	12.0752(4)	14.0504(4)
α, °	67.014(3)	73.976(2)
β, °	74.958(4)	76.447(2)
γ, °	76.945(3)	77.314(2)
Volume, Å^3	863.56(6)	1469.21(8)
Z	2	4
ρ$_{calc}$g, cm^3	1.462	1.533
μ, mm^{-1}	3.559	4.110
F(000)	394.0	696.0
Crystal size, mm^3	0.19 × 0.18 × 0.15	0.12 × 0.11 × 0.1
Radiation	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection, °	8.412 to 141.232	6.66 to 142.128
Index ranges	–8 ≤ h ≤ 8, –11 ≤ k ≤ 14, –14 ≤ l ≤ 14	–11 ≤ h ≤ 12, –12 ≤ k ≤ 13, –17 ≤ l ≤ 17
Reflections collected	9185	15780
Independent reflections	3278 [R$_{int}$ = 0.0340, R$_{sigma}$ = 0.0379]	5601 [R$_{int}$ = 0.0390, R$_{sigma}$ = 0.0459]
Data/restraints/parameters	3278/0/227	5601/0/399
Goodness–of–fit on F^2	1.058	1.071
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0496, wR$_2$ = 0.1359	R$_1$ = 0.0400, wR$_2$ = 0.1019
Final R indexes [all data]	R$_1$ = 0.0556, wR$_2$ = 0.1415	R$_1$ = 0.0469, wR$_2$ = 0.1065
Largest diff. peak/hole/ eÅ^{-3}	0.61/–0.58	0.90/–0.39

S2. Copies of the NMR spectra of *cis*-**A** and *trans*-**A**
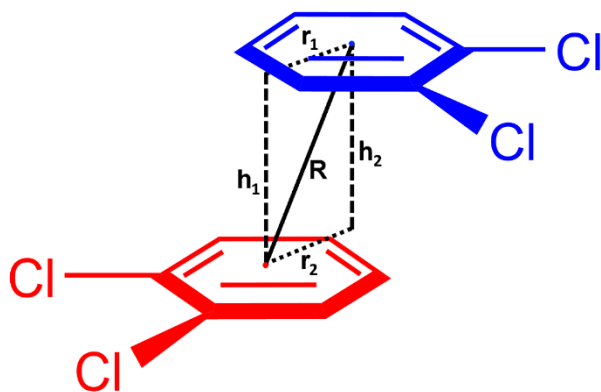
^{1}H and ^{13}C spectra of *cis*-**A**
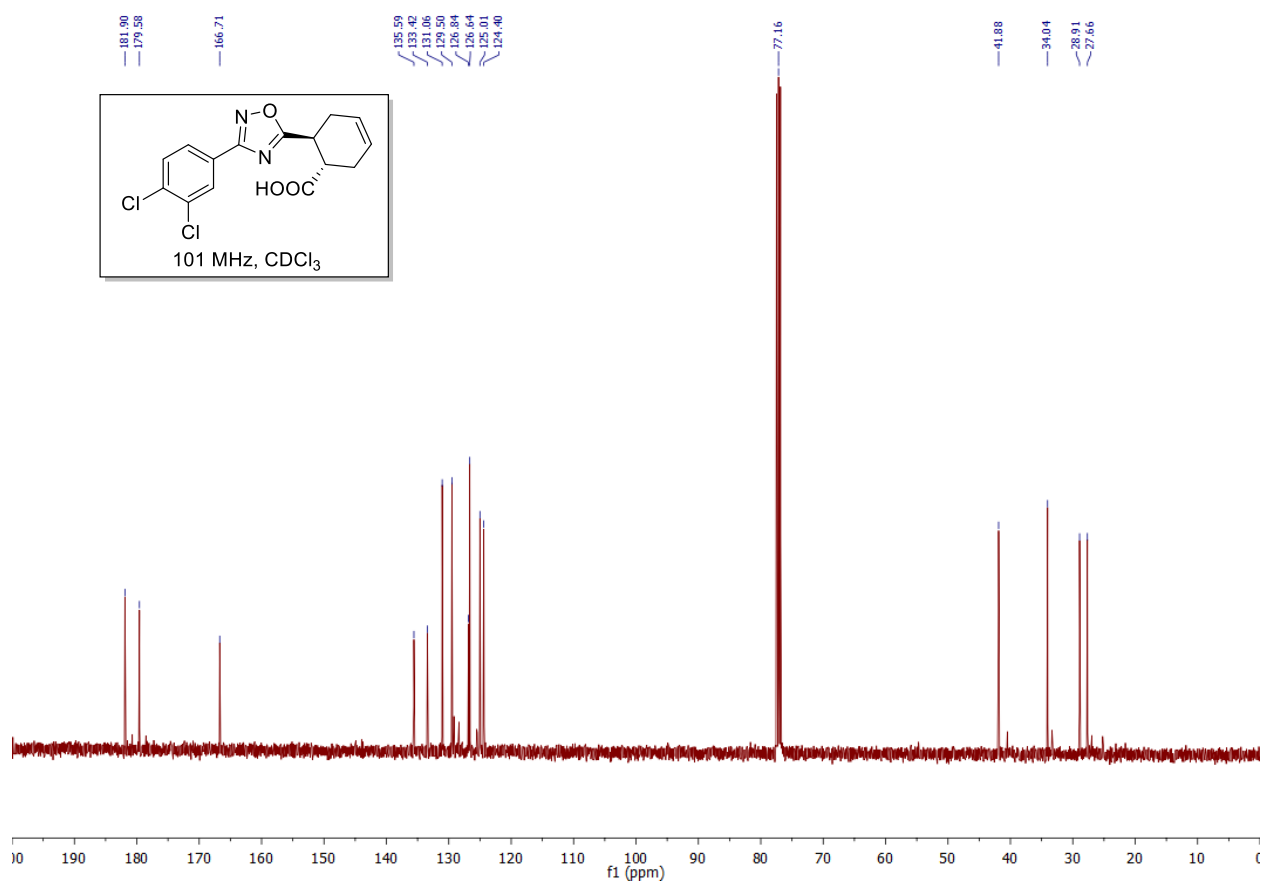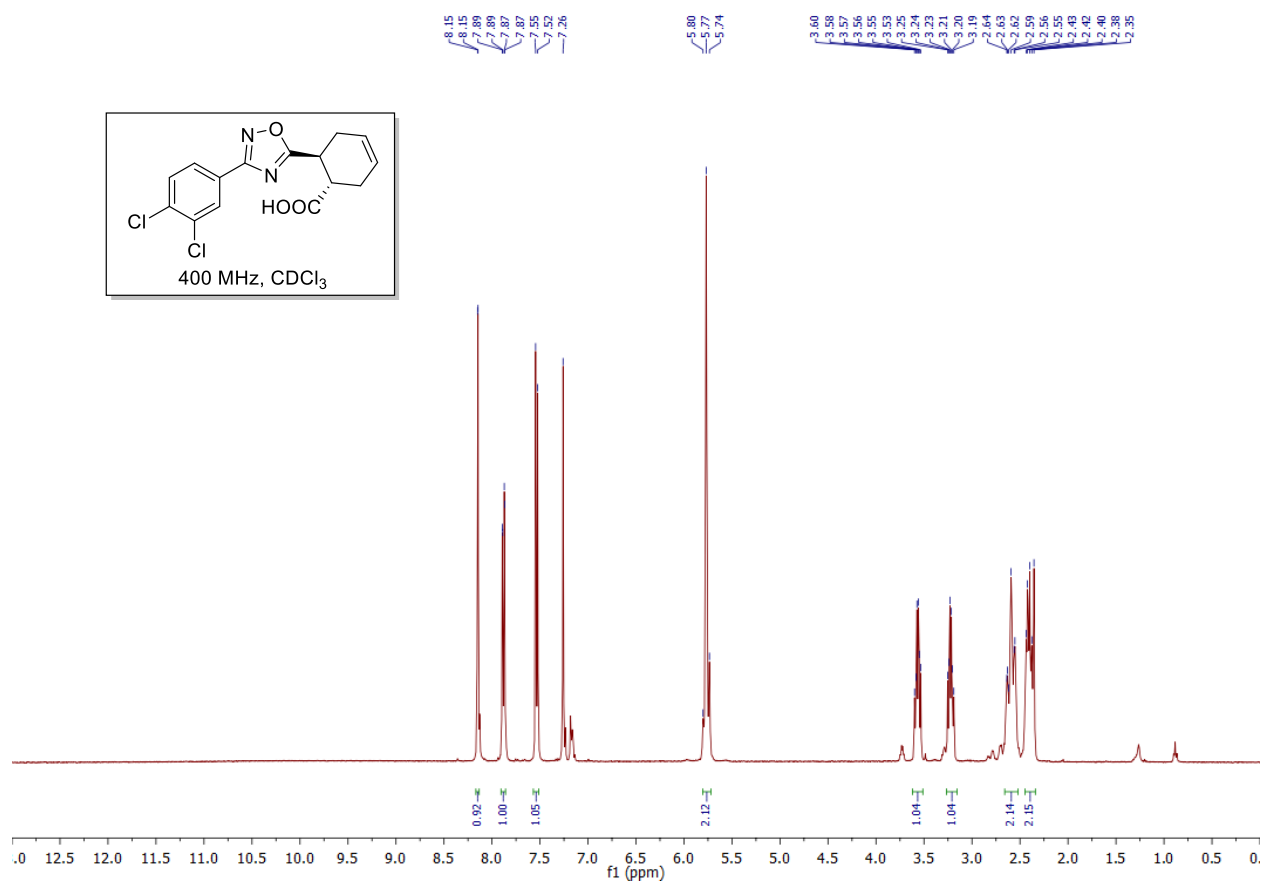
S3. Noncovalent interactions in the structure of *trans*-**A**

Table S3. Geometrical parameters of hydrogen bonds in the structure of *trans*-**A**.

Contact	d(H···O), Å	d(O···O), Å	∠(O–H···O), °	R[a]
O1–H1···O2	1.8123(13)	2.6512(18)	176.51(11)	0.67
O1A–H1A···O2A	1.8174(15)	2.656(2)	176.73(13)	0.67

[a] R is interatomic distance to Bondi (*J. Phys. Chem., 1964, 68, 441–451*) Σ_{vdW} ratio, Σ_{vdW} H + O = 2.72 Å.

Table S4. Geometrical parameters of π···π stacking interactions in the structures of *cis*-**A**·½(1,2-DCE), *cis*-**A**·½(1,2-DBE), and *cis*-**A**·½C$_6$H$_{14}$.

Structure	R, Å[a]	h, Å[b]	r, Å[c]	φ, °[d]	θ, °[e]
cis-**A**·½(1,2-DCE)	3.5964(13)	3.4358(15)	1.063(3)	0.000(7)	0.00(1)
cis-**A**·½(1,2-DBE)	3.602(4)	3.394(4)	1.204(7)	0.00(2)	0.000(18)
cis-**A**·½C6H14	3.6364(16)	3.4134(18	1.254(3)	0.0(1)	0.00(7)

[a] R, distance between the centroid of one ring and the centroid of a π···π stacked ring;
[b] h_1 and h_2, distance between the centroid of one ring and the plane of a π···π stacked ring;
[c] r_1 and r_2, distance between the centroid of one ring and the projection of the centroid of a π···π stacked ring to the first plane (rings offset);
[d] φ, twist angle is defined as the angle between the plane of the anchoring ring and the plane containing six atoms of aromatic ring;
[e] θ, angle between planes of adjacent π···π stacked ring.

Table S5. Geometrical parameters of π···π stacking interactions in the structure of *trans*-**A**.

Plane[a]	R, Å[b]	h$_1$, Å[c]	h$_2$, Å[c]	r$_1$, Å[d]	r$_2$, Å[d]	φ, °[e]	θ, °[f]
Cg[f]1···Cg1	3.6239(17)	3.365(2)	-3.365(2)	1.345(3)	1.345(3)	0.0(3)	0.00
Cg2···Cg2	3.9102(16)	3.468(2)	-3.468(2)	1.807(3)	1.807(3)	180.0(3)	180.0(2)
Cg1···Cg2	3.6313(12)	3.5891(12)	-3.5435(13)	0.552(3)	0.794(3)	120.6(4)	168.81(7)

[a] Cg are planes of the 3,4-dichlorophenyl moieties (**Figure 5**).
[b] R, distance between the centroid of one ring and the centroid of a π···π stacked ring;
[c] h_1 and h_2, distance between the centroid of one ring and the plane of a π···π stacked ring;
[d] r_1 and r_2, distance between the centroid of one ring and the projection of the centroid of a π···π stacked ring to the first plane (rings offset);
[e] φ, twist angle is defined as the angle between the plane of the anchoring ring and the plane containing six atoms of aromatic ring;
[f] θ, angle between planes of adjacent π···π stacked ring.

S4. Void channels in structures of *cis*-**A**·½(1,2-DBE) and *cis*-**A**·½C₆H₁₄
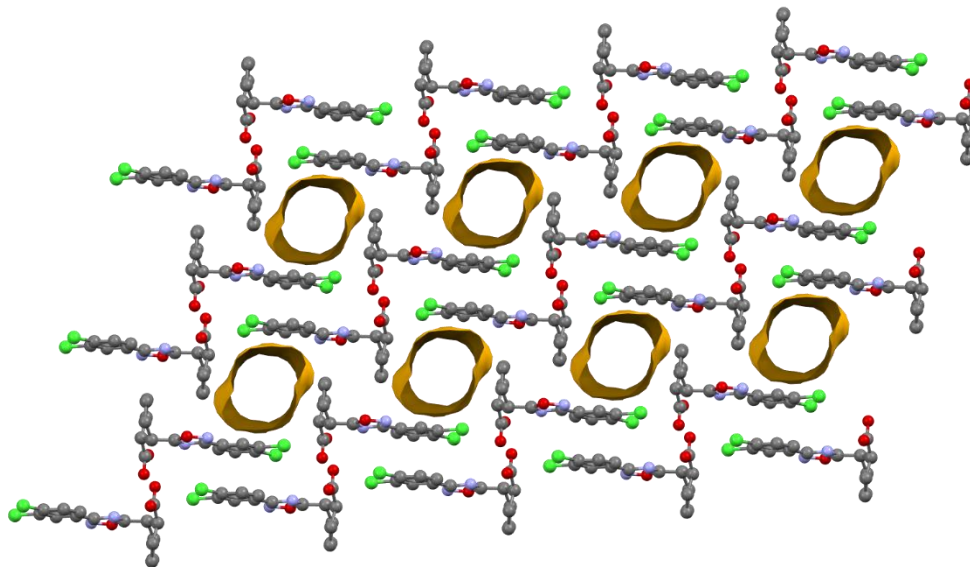
Figure S1. Partial representation (Mercury 4.3.1, ball and stick) of the crystal packing of *cis*-**A**·½(1,2-DBE) after orientations evidencing the cylindrical shape and the parallel arrangement of the channels (contact surfaces in ocher). A probe radius of 1.2 Å and an approximate grid spacing of 0.7 Å were used to generate channels. Solvent molecules in the voids and H-atoms are omitted for the sake of clarity. Color coding: grey, carbon; red, oxygen; blue, nitrogen; green, chlorine.
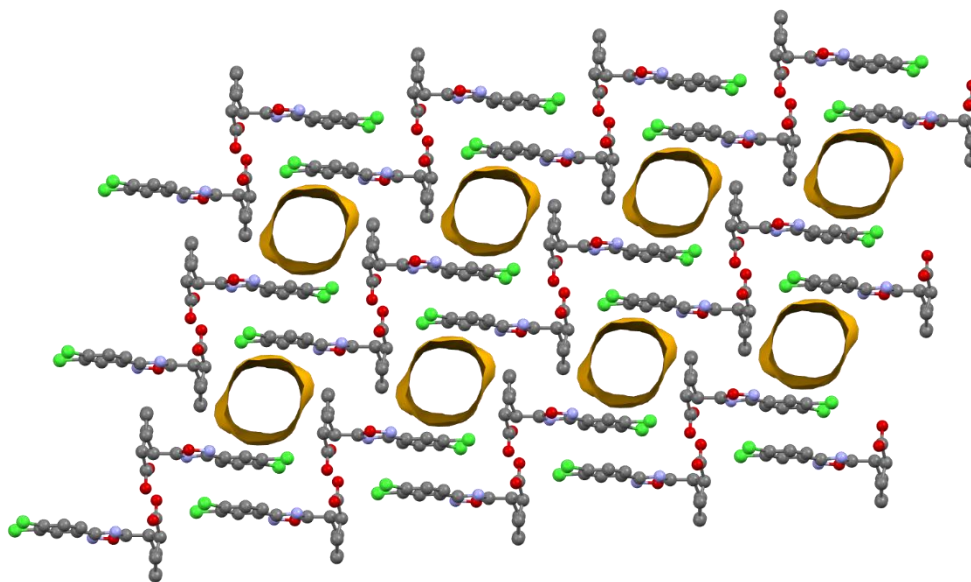
Figure S2. Partial representation (Mercury 4.3.1, ball and stick) of the crystal packing of *cis*-**A**·½C₆H₁₄ after orientations evidencing the cylindrical shape and the parallel arrangement of the channels (contact surfaces in ocher). A probe radius of 1.2 Å and an approximate grid spacing of 0.7 Å were used to generate channels. Solvent molecules in the voids and H-atoms are omitted for the sake of clarity. Color coding: grey, carbon; red, oxygen; blue, nitrogen; green, chlorine.