Electronic Supplementary Information

Ligand Steric Hindrances Switch Bridging (μ_2-I)···O,O to Two-center I···O Halogen Bonding Mode in the Assembly of Diketonate Copper(II) Species

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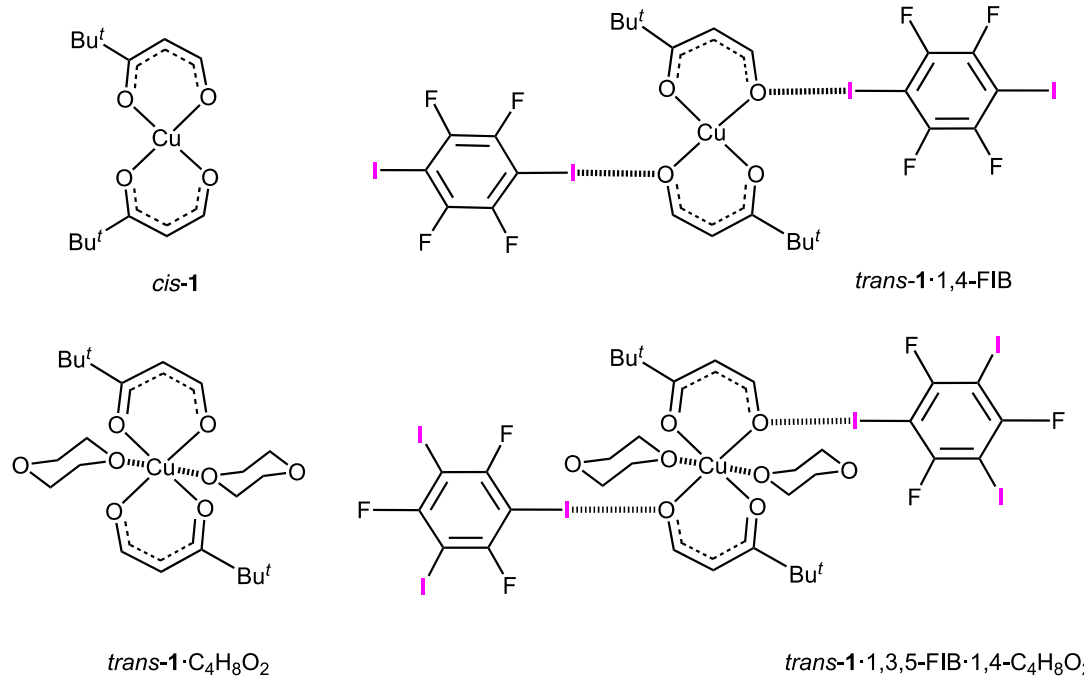
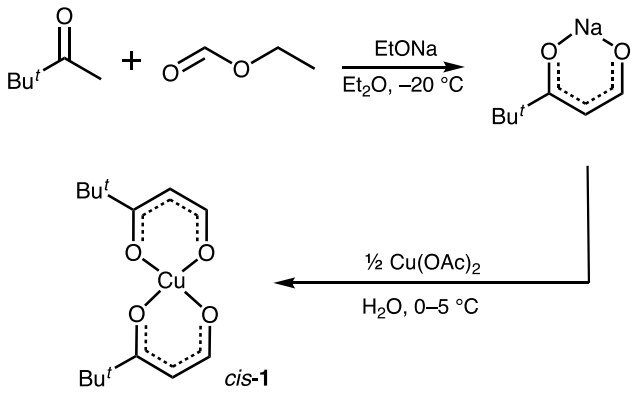
Table S1. Crystallography data and refinement details for crystals *cis*-**1**, *trans*-**1**·1,3,5-FIB·$C_4H_8O_2$, *trans*-**1**·$C_4H_8O_2$, and *trans*-**1**·1,4-FIB.

Compound	*cis*-**1**					*trans*-**1**·1,3,5-FIB·$C_4H_8O_2$	*trans*-**1**·$C_4H_8O_2$	*trans*-**1**·1,4-FIB				
Formula	$C_{14}H_{22}CuO_4$					$C_{24}H_{30}CuF_3I_3O_6$	$C_{18}H_{30}CuO_6$	$C_{20}H_{22}CuF_4I_2O_4$				
Mass	317.85					915.72	405.96	719.71				
Crystal system	monoclinic					monoclinic	Triclinic	triclinic				
Space group	$P2_1/c$					$P2_1/c$	P-1	P-1				
T, K	100	150	200	250	300	100	100	100	150	200	250	300
Z (Z')	4 (1)	4 (1)	4 (1)	4 (1)	4 (1)	4	2 (0.5)	2 (1.5)	2 (1.5)	2 (1.5)	2 (1.5)	2 (0.5)
a, Å	9.36110(10)	9.3903(3)	9.42360(10)	9.4593(2)	9.50516(18)	7.1664(3)	6.9762(3)	5.8660(4)	5.8998(4)	5.9405(3)	5.9945(3)	6.0903(17)
b, Å	12.4194(2)	12.4545(5)	12.5017(2)	12.5537(2)	12.6220(3)	15.7523(5)	8.2841(4)	12.3881(9)	12.4312(8)	12.4752(6)	12.5260(7)	10.041(3)
c, Å	12.5216(2)	12.5555(4)	12.5961(2)	12.6410(2)	12.6986(3)	26.3818(8)	8.9187(4)	24.8709(18)	24.8874(17)	24.8995(13)	24.9016(13)	10.540(3)
α, °	90	90	90	90	90	90	74.484(4)	101.8640(10)	101.9100(10)	101.9480(10)	101.9500(10)	75.308(6)
β, °	92.6120(10)	92.778(3)	92.9760(10)	93.223(2)	93.5048(18)	93.604(4)	74.683(4)	95.9280(10)	95.7890(10)	95.6090(10)	95.3650(10)	81.046(6)
γ, °	90	90	90	90	90	90	88.906(4)	95.0310(10)	95.3360(10)	95.6960(10)	96.1490(10)	88.879(6)
V, $Å^3$	1454.24(4)	1466.66(9)	1481.96(4)	1498.73(5)	1520.66(5)	2972.28(18)	478.26(4)	1748.2(2)	1764.7(2)	1783.07(16)	1805.84(17)	615.8(3)
d_{calc}, gЧcm^{-3}	1.452	1.439	1.425	1.409	1.388	2.046	1.409	2.051	2.032	2.011	1.985	1.941
F(000)	668	668	668	668	668	1748	215	1035	1035	1035	1035	345
$2\theta_{max}$, °	154	154	154	154	156	58	135	56	58	58	58	58
Reflections measured	11575	11076	15554	14325	13399	7845	7411	19301	21331	22091	22662	7723
Independent reflections	3034	3034	3077	3106	3136	7845	1822	8443	9337	9452	9591	3281
Reflections with I>2σ(I)	2839	2802	2846	2839	2809	7051	1720	7243	7540	7566	6923	2463
Number of parameters	178	178	178	178	178	341	115	430	430	430	430	158
R_1	0.0291	0.0320	0.0289	0.0301	0.0304	0.0430	0.0306	0.0349	0.0355	0.0307	0.0324	0.0316
wR_2	0.0801	0.0939	0.0893	0.0942	0.1027	0.0859	0.0804	0.0762	0.0739	0.0664	0.0714	0.1052
GOF	1.080	1.025	1.001	1.040	1.094	1.144	1.077	1.097	1.029	1.020	0.982	0.940
Residual electron density, eЧ$Å^{-3}$(d_{min}/d_{max})	0.385/-0.460	0.339/-0.443	0.307/-0.430	0.273/-0.372	0.246/-0.368	1.225/-1.300	0.245/-0.456	1.193/-2.110	1.236/-1.503	0.875/-0.775	0.845/-0.392	0.625/-0.467



Scheme S1. Schematic representation of the studied structures; stacking interactions and semicoordination bonding are given by dashed lines.



Scheme S2. Synthesis of complex *cis*-**1**.

The condensation of 3,3-dimethylbutan-2-one with ethyl formate in the presence of sodium ethanolate (Et_2O, 5 h) gives the sodium salt of the diketone. Its reaction with copper(II)acetate in water furnishes *cis*-**1**.

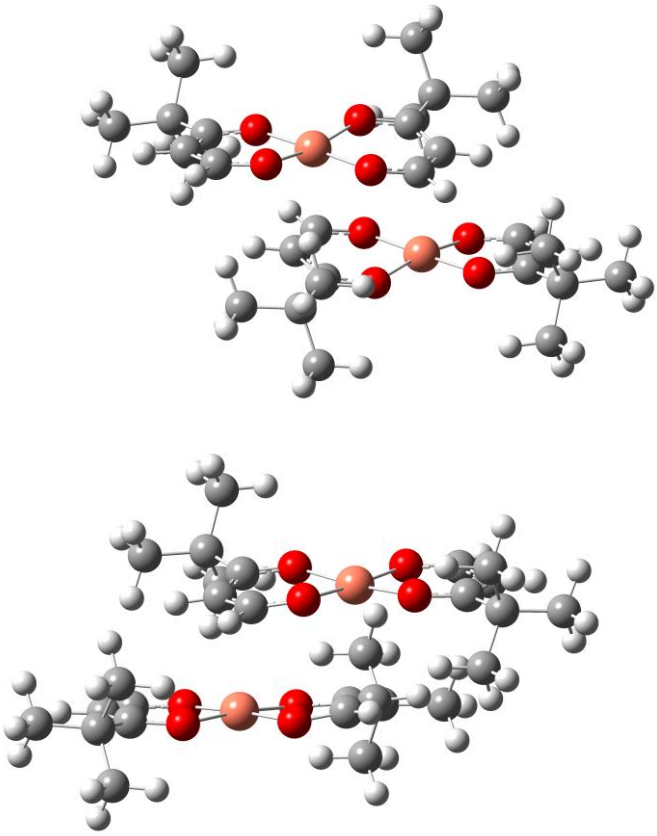


Figure S1. The model supramolecular dimers of *cis* (left panel) and *trans* (right panel) isomers of **1**.

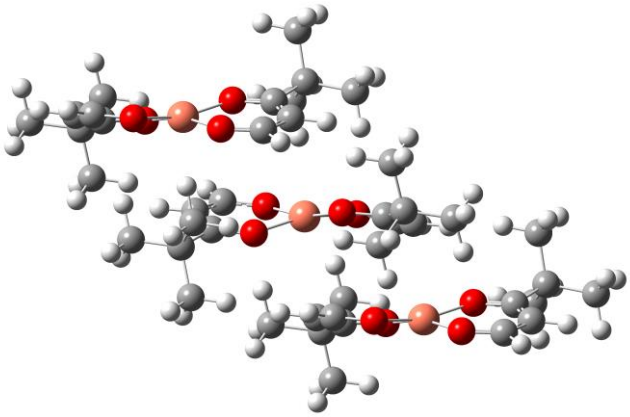


Figure S2. The model supramolecular trimer of *cis*-**1**.

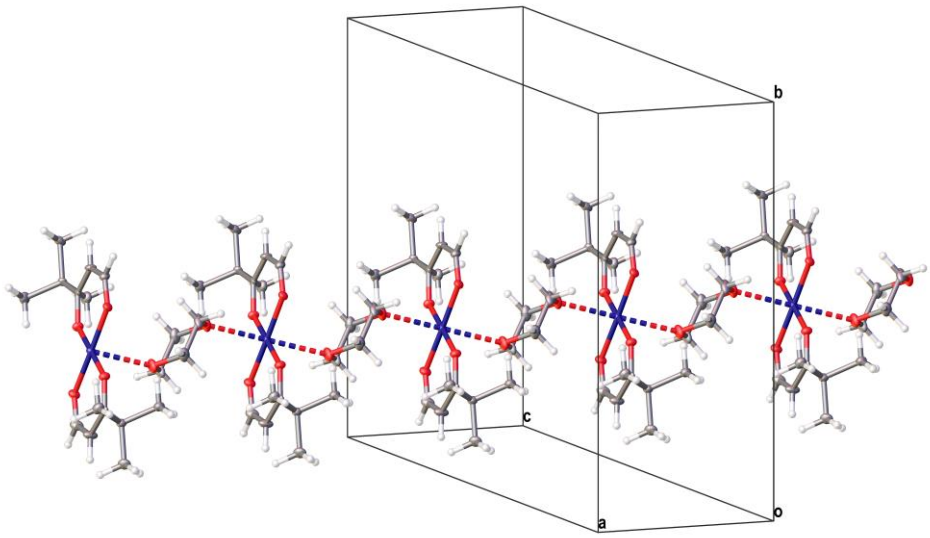


Figure S3. A fragment of 1D-coordination polymer in co-crystal *trans*-**1**·1,3,5-FIB·$C_4H_8O_2$. The semicoordination bonds Cu···O(dioxane) are given by dashed lines. Non-hydrogen atoms are given as probability ellipsoids of atomic displacements (p = 0.5).

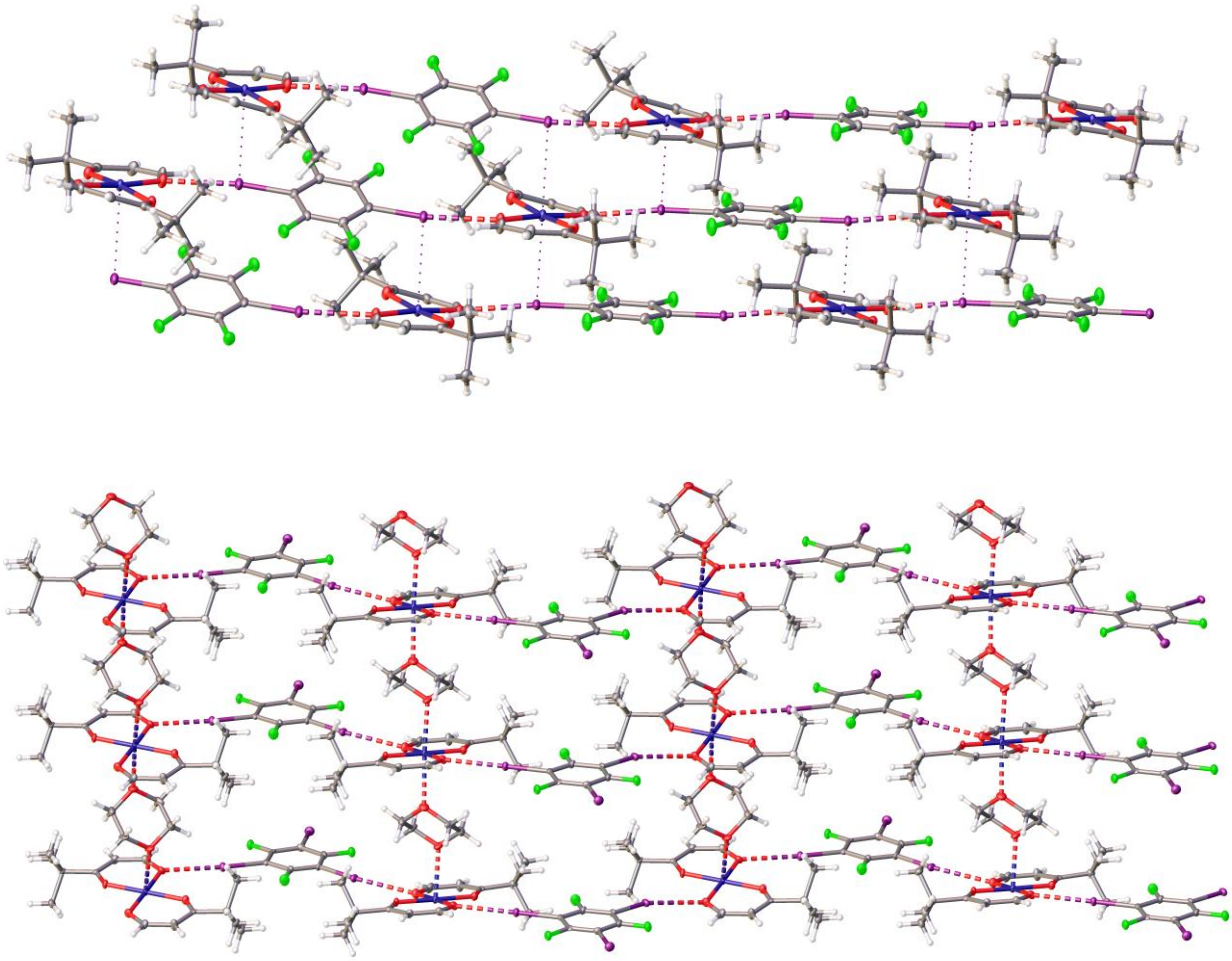


Figure S4. Fragments of layers in the crystal packing of *trans*-**1**·1,4-FIB (top panel) and *trans*-**1**·1,3,5-FIB·$C_4H_8O_2$ (bottom panel). The Cu···I semicoordination contacts are denoted by small balls, while HaBs and semicoordination Cu···$O_{dioxane}$ bonds are given by dashed lines.

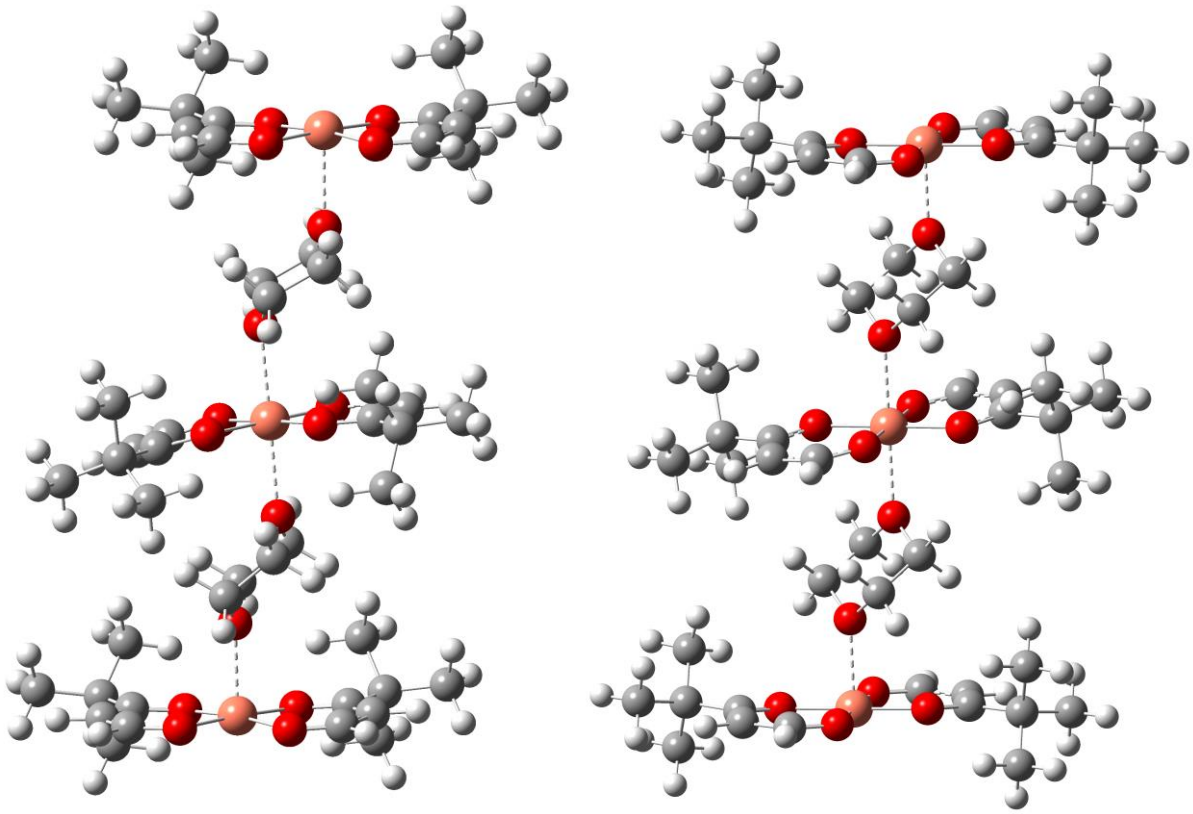


Figure S5. Model supramolecular complexes *cis*-**1**···$C_4H_8O_2$···*cis*-**1**···$C_4H_8O_2$···*cis*-**1** (left panel) and *trans*-**1**···$C_4H_8O_2$···*trans*-**1**···$C_4H_8O_2$···*trans*-**1** (right panel) partially optimized in the isolated state.

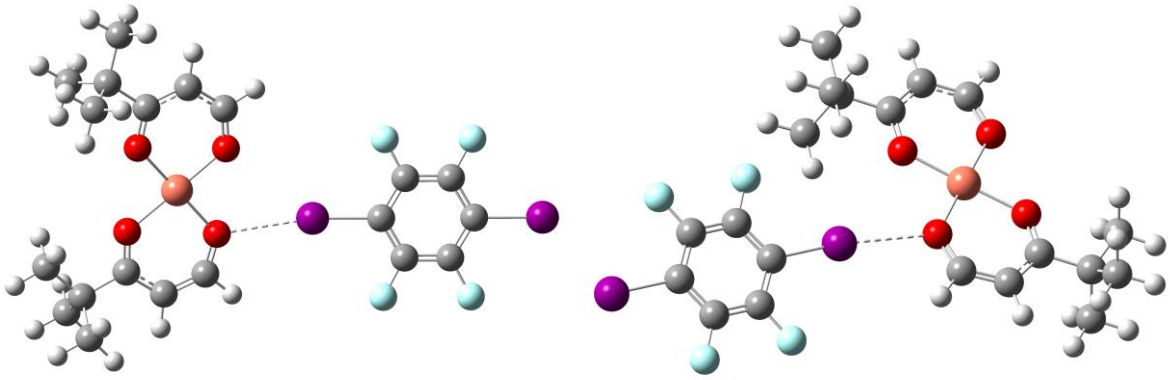


Figure S6. Model supramolecular complexes *cis*-**1**···1,4-FIB (left panel) and *trans*-**1**···1,4-FIB (right panel) optimized in the isolated state.

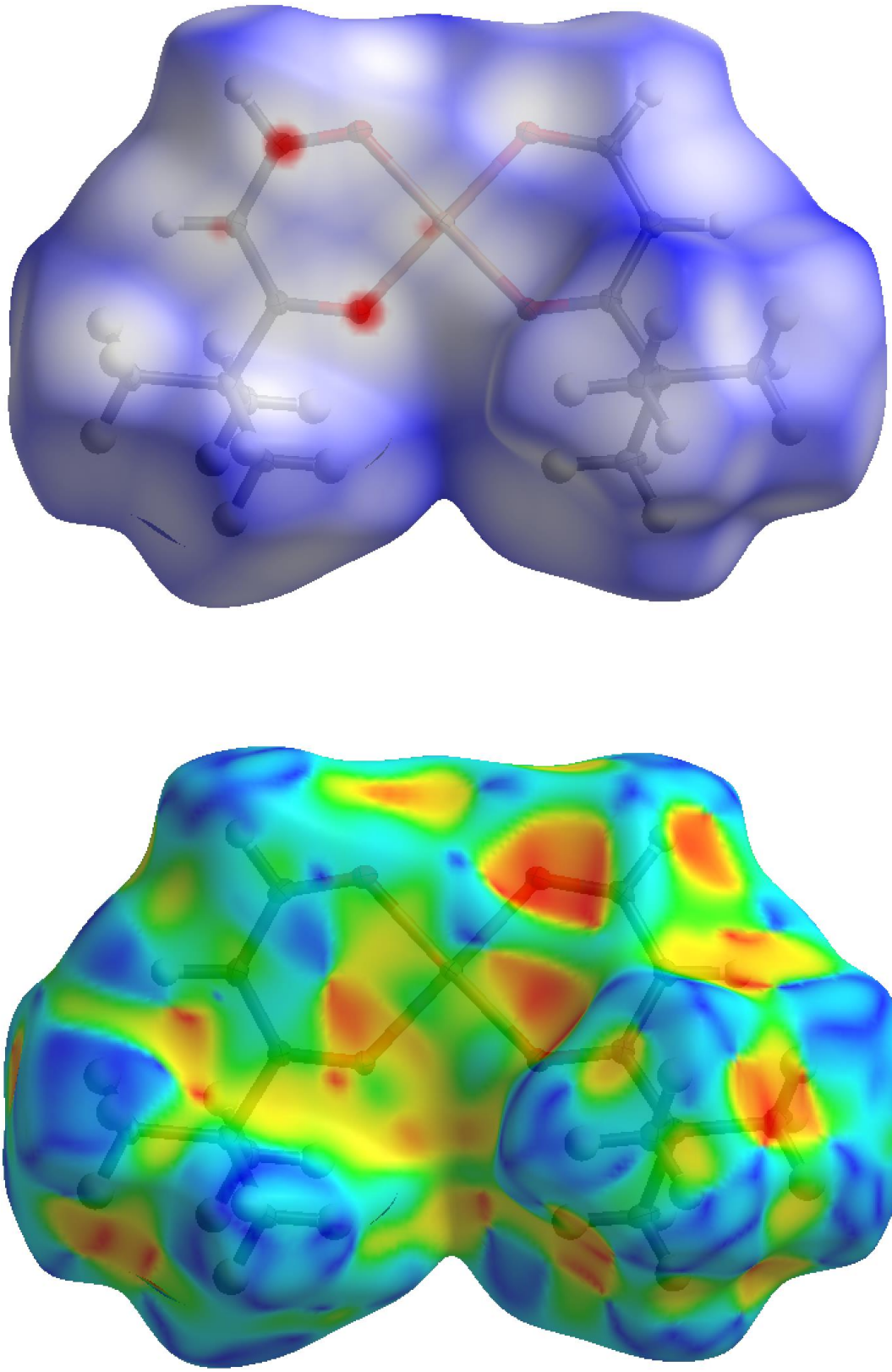


Figure S7. Hirshfeld surfaces for *cis*-**1** in the XRD structure of *cis*-**1**. Intermolecular contacts closer than the sum of Bondi vdW radii (Σ_{vdW})[125] highlighted in red, longer contacts are shown in blue, and contacts with a value of approximately Σ_{vdW} are shown in white.

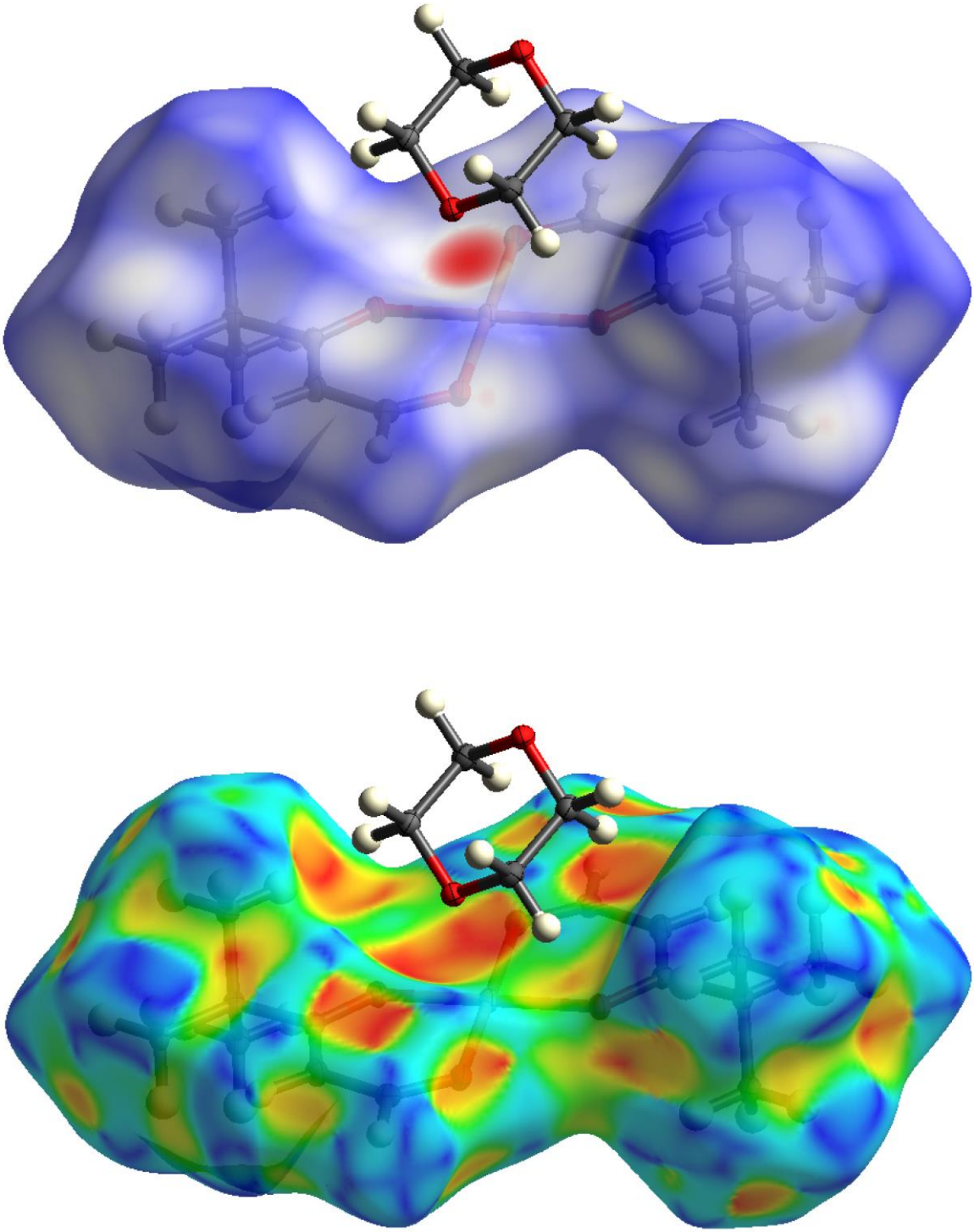


Figure S8. Hirshfeld surfaces for *trans*-**1** in the XRD structure of *trans*-**1**·dioxane. Intermolecular contacts closer than the sum of Bondi vdW radii (Σ_{vdW})[125] highlighted in red, longer contacts are shown in blue, and contacts with a value of approximately Σ_{vdW} are shown in white.

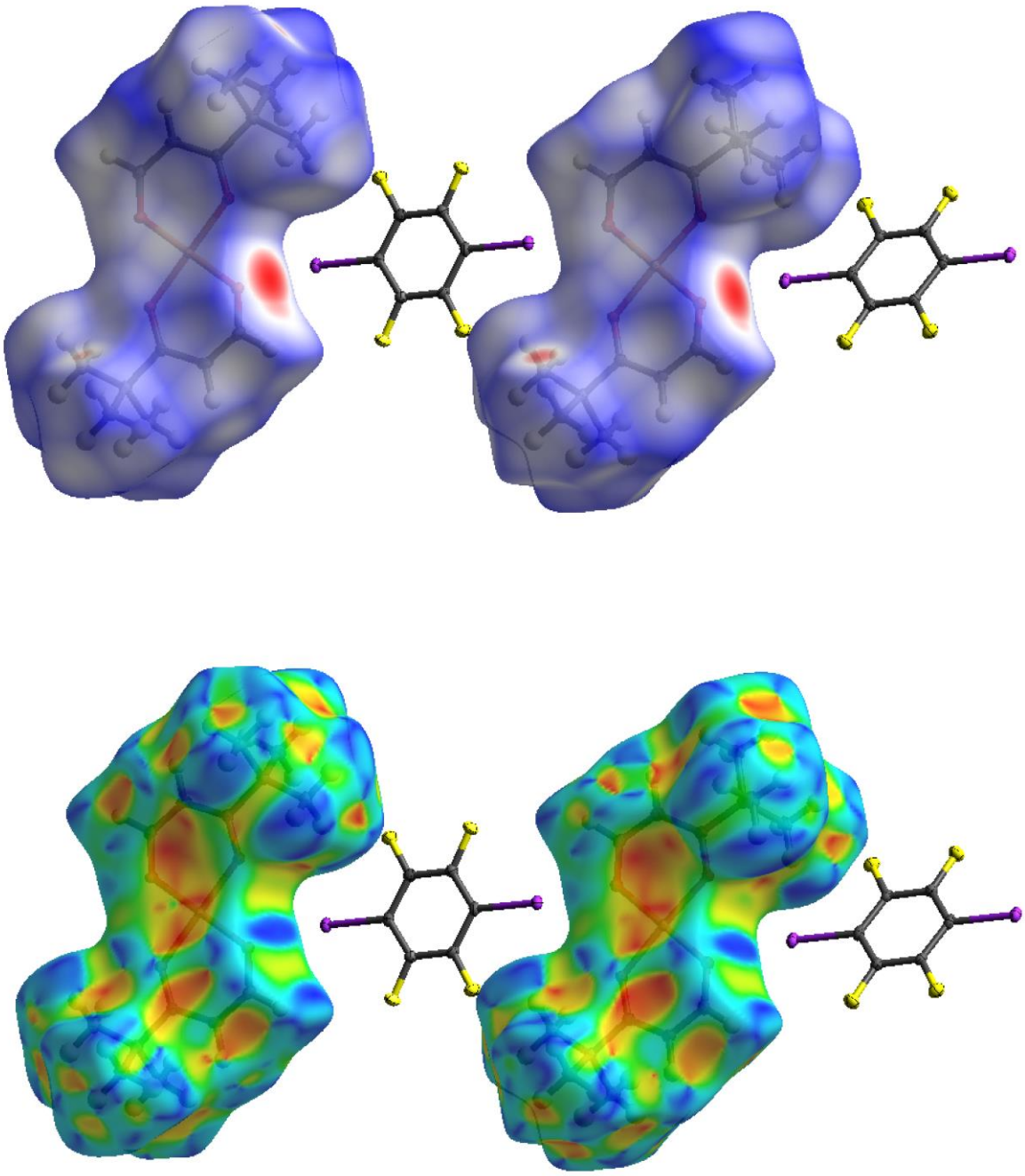


Figure S9. Hirshfeld surfaces for *trans*-**1** (two nonequivalent molecules) in the XRD structure of *trans*-**1**·1,4-FIB. Intermolecular contacts closer than the sum of Bondi vdW radii (Σ_{vdW})[125] highlighted in red, longer contacts are shown in blue, and contacts with a value of approximately Σ_{vdW} are shown in white.

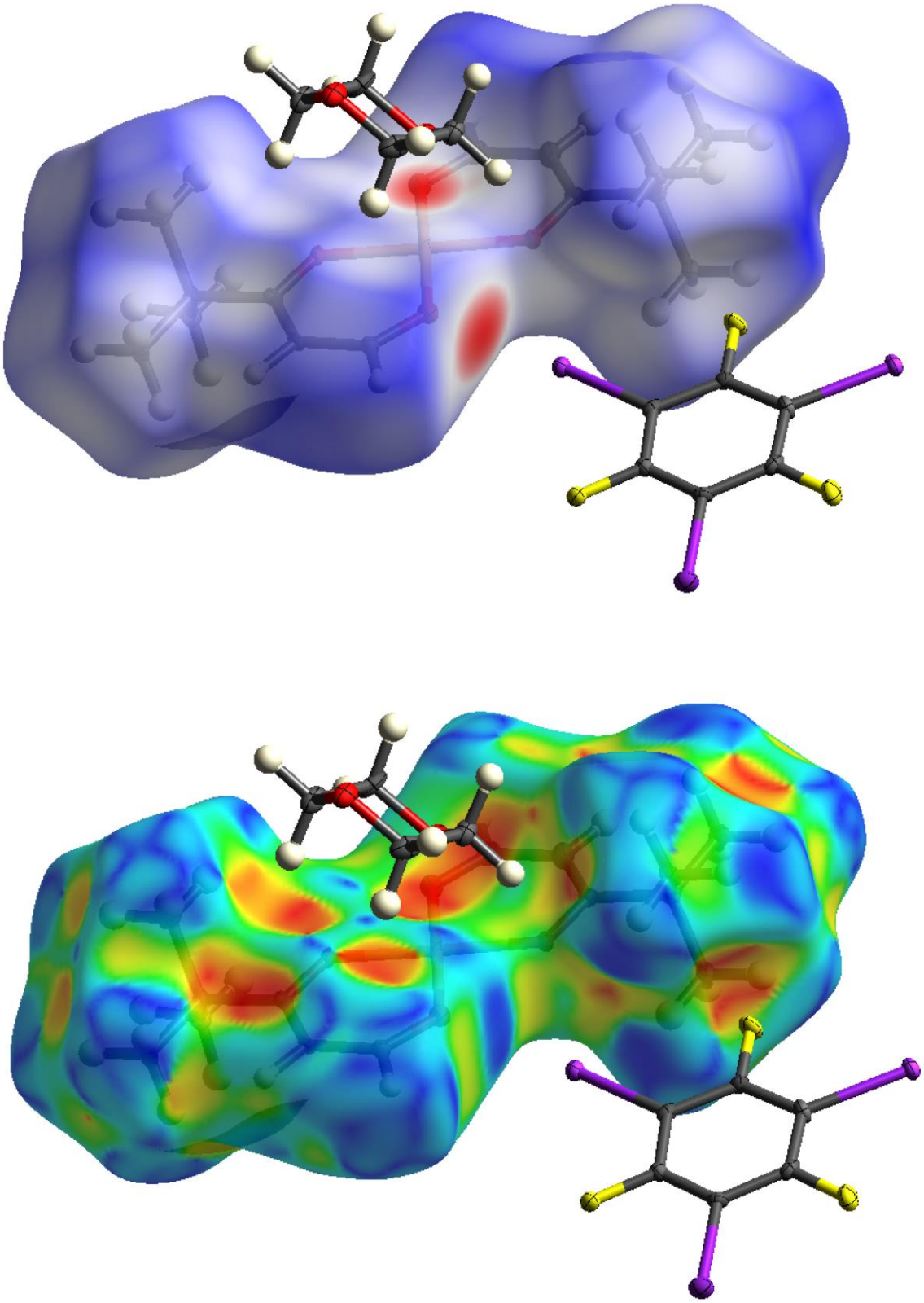


Figure S10. Hirshfeld surfaces for *trans*-**1** in the XRD structure of *trans*-**1**·dioxane·1,3,5-FIB. Intermolecular contacts closer than the sum of Bondi vdW radii (Σ_{vdW})[125] highlighted in red, longer contacts are shown in blue, and contacts with a value of approximately Σ_{vdW} are shown in white.

Table S2. Results of Hirshfeld surface analysis for the XRD structures of the cocrystals.

XRD structure	**Contributions of different intermolecular contacts to the molecular Hirshfeld surface***
cis-**1**	H–H 67.9%, H–O 19.1%, C–O 4.2%, H–C 4.1%, C–Cu 2.4%, H–Cu 1.9%
trans-**1**·$C_4H_8O_2$	H–H 72.0%, H–O 15.6%, H–C 8.2%, Cu–O 2.2%, O–O 1.6%
trans-**1**·1,4-FIB	H–H 48.7%, H–F 19.6%, H–C 8.4%, O–I 6.6%, H–I 4.4%, H–O 3.4%, C–O 2.6%, Cu–I 2.1%, C–F 1.6%, O–F 1.1%
trans-**1**·1,3,5-FIB·$C_4H_8O_2$	H–H 61.5%, H–I 9.5%, H–O 8.7%, H–C 7.0%, H–F 5.9%, O–I 2.5%, Cu–O 2.2%, O–O 1.9%

*The contributions of all other intermolecular contacts do not exceed 1%.

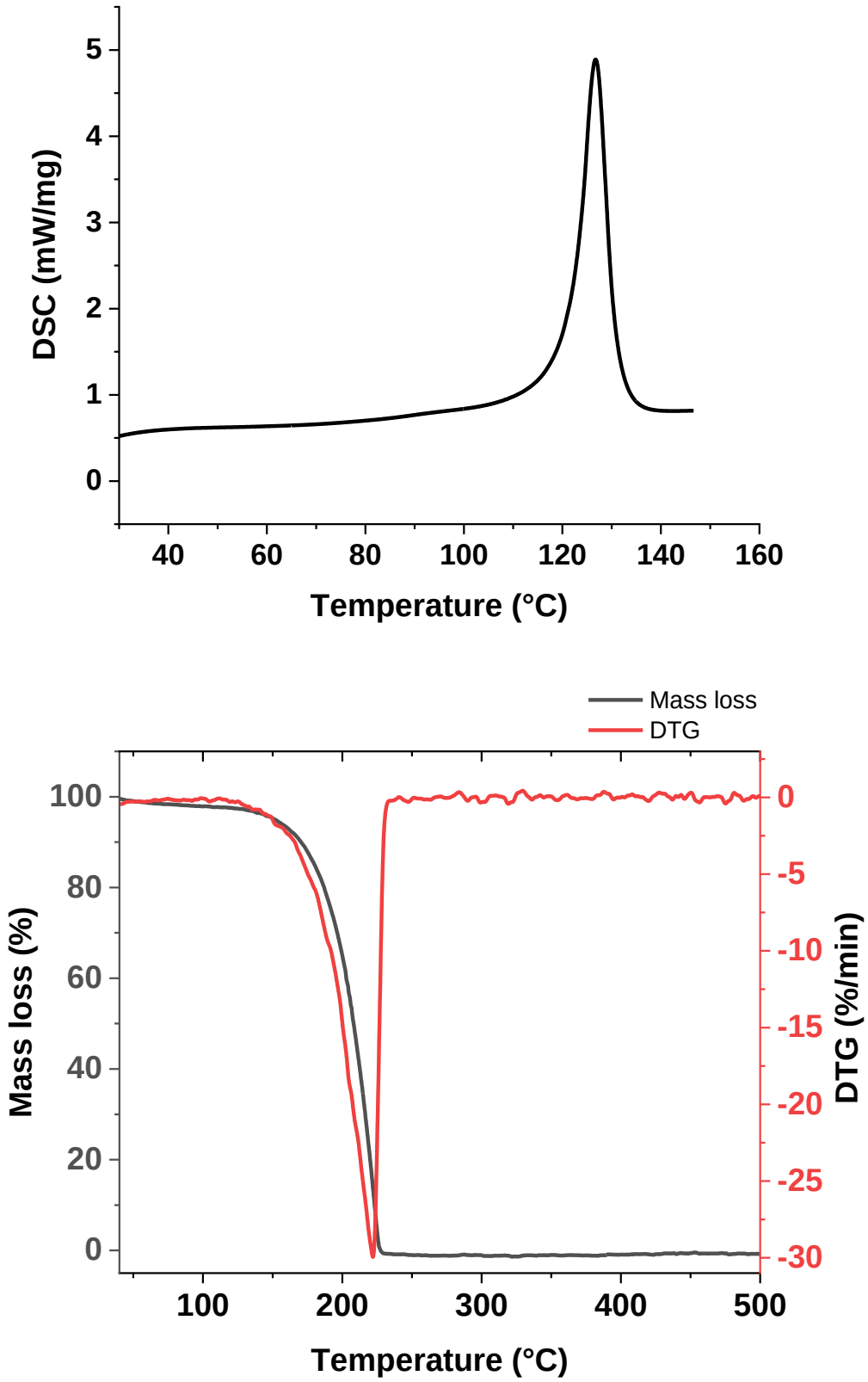
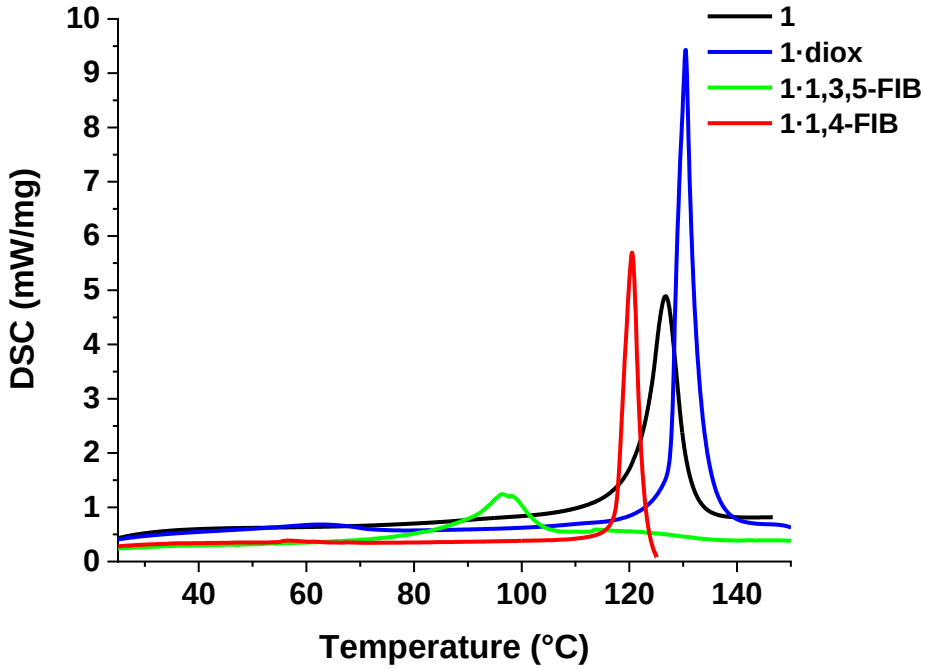


Figure S11. DSC (top panel) and TGA (bottom panel) data for *cis*-**1**.



Compound	m.p., °C
1	128
1·diox	131
1·1,3,5-FIB	97
1·1,4-FIB	120

Figure S12. DSC data and detected melting points.

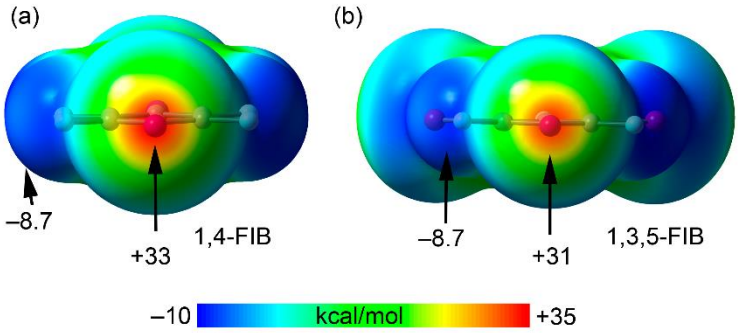


Figure S13. MEP surfaces of 1,4-FIB (a) and 1,3,5-FIB (b) at the PBE0-D3/def2-TZVP level of theory. Isosurface = 0.001 a.u. The values at selected points of the surfaces are indicated in kcal/mol.