Electronic Supporting Information

for

Bifurcated μ_2-I···(N,O) Halogen Bonding: The Case of (Nitrosoguanidinate)Ni^{II} Co-crystals with Iodine(I)-based σ-Hole Donors

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Crystal data and structure refinement

Table S1. Crystal data and structure refinement for **1**·2(1,2-FIB), **1**·C_2I_4, **2**·2(1,2-FIB), and **2**·2(1,4-FIB).

	1·2(1,2-FIB)	**1**·C_2I_4	**2**·2(1,2-FIB)	**2**·2(1,4-FIB)
CCDC No.	2036670	2036671	2036672	2036673
Empirical formula	$C_{18}H_{14}F_8I_4N_8NiO_2$	$C_8H_{14}I_4N_8NiO_2$	$C_{28}H_{18}F_8I_4N_8NiO_2$	$C_{28}H_{18}F_8I_4N_8NiO_2$
M_W/g	1092.68	820.58	1216.81	1216.81
T/K	100(2)	100(2)	100(2)	100(2)
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.7107)
Crystal color, shape	red, prism	red, prism	red, prism	red, prism
Crystal size/mm^3	0.30 × 0.22 × 0.16	0.28 × 0.16 × 0.12	0.25 × 0.20 × 0.18	0.26 × 0.18 × 0.14
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	P-1	P-1	$P2_1/c$	P-1
a/Å	5.4904(5)	8.3289(3)	23.1438(4)	5.6497(4)
b/Å	10.4468(7)	8.9118(3)	7.99700(10)	12.4400(13)
c/Å	12.5239(7)	13.3421(5)	18.8981(3)	13.0921(4)
α/°	103.887(5)	87.145(3)	90	76.487(5)
β/°	91.850(6)	84.833(3)	93.464(2)	84.740(4)
γ/°	92.587(7)	84.478(3)	90	80.803(8)
V/Å^3	695.94(9)	980.88(6)	3491.29(9)	881.75(12)
Z	1	2	4	1
ρ_c/g·cm^{-3}	2.607	2.778	2.315	2.292
μ/mm^{-1}	5.222	7.302	4.177	4.135
F(000)	506.0	748.0	2280.0	570.0
2*Θ* range/°	5.828 to 54.998	5.42 to 62.238	6.196 to 56.998	6.412 to 52
Reflections collected	10641	17909	46994	7577
Independent reflections	3198 [R_{int} = 0.0514, R_{sigma} = 0.0437]	5640 [R_{int} = 0.0320, R_{sigma} = 0.0358]	8840 [R_{int} = 0.0393, R_{sigma} = 0.0289]	3446 [R_{int} = 0.0424, R_{sigma} = 0.0527]
Data/restraints/parameters	3198/0/189	5640/0/212	8840/0/462	3446/0/233
Goodness-of-fit on F^2	1.089	1.037	1.061	1.090
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0414, wR_2 = 0.1031	R_1 = 0.0252, wR_2 = 0.0465	R_1 = 0.0249, wR_2 = 0.0494	R_1 = 0.0439, wR_2 = 0.1067
Final *R* indexes [all data]	R_1 = 0.0494, wR_2 = 0.1111	R_1 = 0.0341, wR_2 = 0.0498	R_1 = 0.0328, wR_2 = 0.0527	R_1 = 0.0532, wR_2 = 0.1183
Largest diff. peak/hole/ *e*·Å^{-3}	1.67/-1.94	1.36/-1.33	0.61/-0.57	2.38/-1.64

Table S2. Crystal data and structure refinement for **2**·2C_2I_4, **3**·2(1,2-FIB), and **3**·2(1,3,5-FIB).

	2·2C_2I_4	**3**·2(1,2-FIB)	**3**·2(1,3,5-FIB)
CCDC No.	2036674	2036675	2036676
Empirical formula	$C_{20}H_{18}I_8N_8NiO_2$	$C_{24}H_{22}F_8I_4N_8NiO_2$	$C_{24}H_{22}F_6I_6N_8NiO_2$
M_W/g	1476.33	1172.80	1388.60
T/K	100(2)	100(2)	100(2)
Radiation	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.71073)
Crystal color, shape	red, prism	red, prism	red, prism
Crystal size/mm^3	0.26 × 0.20 × 0.16	0.18 × 0.12 × 0.10	0.24 × 0.20 × 0.18
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	8.3457(4)	8.4755(4)	9.270(3)
b/Å	9.9691(3)	9.0877(6)	9.7991(19)
c/Å	10.7301(5)	11.8801(8)	10.790(7)
α/°	90.952(3)	86.501(5)	81.20(4)
β/°	106.299(4)	75.723(5)	71.84(5)
γ/°	90.632(3)	66.104(5)	72.97(2)
V/$Å^3$	856.62(7)	809.98(9)	888.4(7)
Z	1	1	1
ρ_c/g·cm^{-3}	2.862	2.404	2.595
μ/mm^{-1}	7.807	4.496	5.827
F(000)	662.0	550.0	638.0
2*Θ* range/°	5.498 to 61.646	5.42 to 61.912	5.572 to 62.118
Reflections collected	15285	7986	8478
Independent reflections	4890 [R_{int} = 0.0367, R_{sigma} = 0.0398]	4466 [R_{int} = 0.0328, R_{sigma} = 0.0591]	4894 [R_{int} = 0.0329, R_{sigma} = 0.0517]
Data/restraints/parameters	4890/0/179	4466/0/214	4894/0/214
Goodness-of-fit on F^2	1.064	1.014	0.940
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0251, wR_2 = 0.0467	R_1 = 0.0381, wR_2 = 0.0754	R_1 = 0.0243, wR_2 = 0.0404
Final *R* indexes [all data]	R_1 = 0.0330, wR_2 = 0.0497	R_1 = 0.0557, wR_2 = 0.0831	R_1 = 0.0344, wR_2 = 0.0430
Largest diff. peak/hole/ *e*·$Å^{-3}$	0.88/-1.08	1.86/-0.94	1.28/-1.23

View of the molecular structure of adducts with HSA

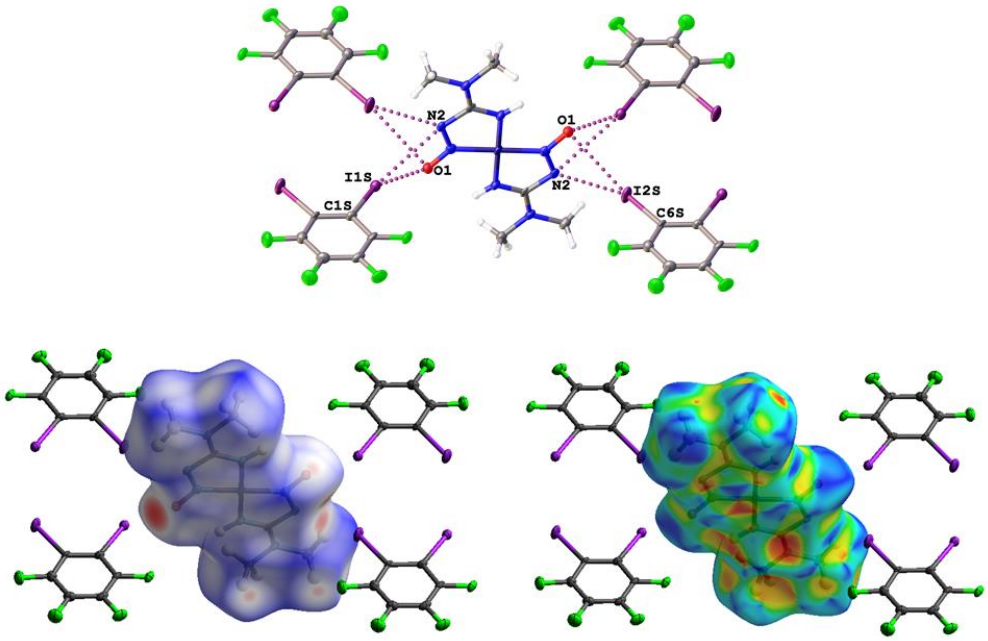

Figure S1. View of the molecular structure of **1**·2(1,2-FIB) with bifurcated XB (dotted lines) between I atom of 1,2-FIB and N and O atoms of the nitrosoguanidinate ligand. Here and later thermal ellipsoids are shown at the 50% probability level (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **1** in the XRD structure of **1**·2(1,2-FIB) (bottom).

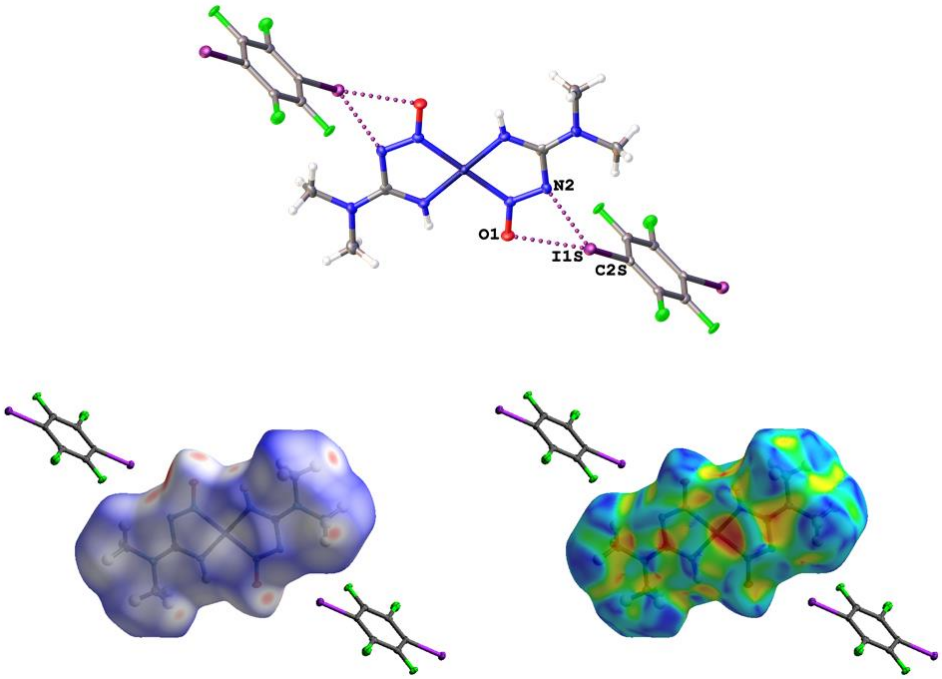

Figure S2. View of the molecular structure of **1**·(1,4-FIB) with bifurcated XB (dotted lines) between I atom of 1,4-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **1** in the XRD structure of **1**·(1,4-FIB) (bottom).

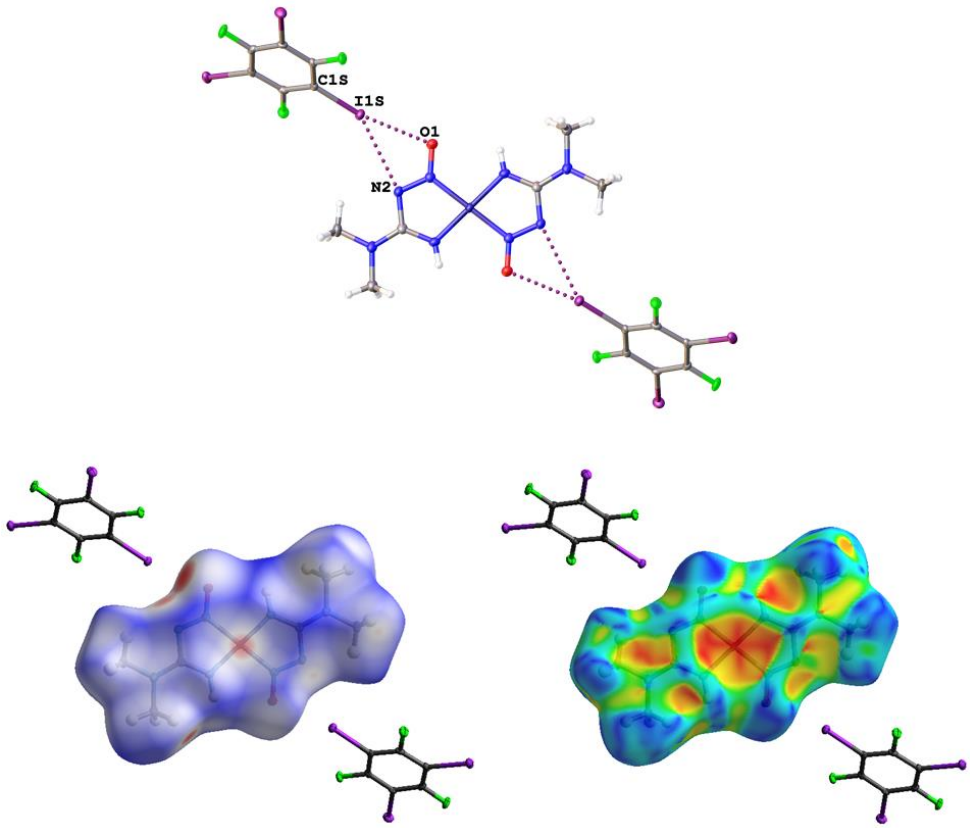

Figure S3. View of the molecular structure of **1**·2(1,3,5-FIB) with bifurcated XB (dotted lines) between I atom of 1,3,5-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **1** in the XRD structure of **1**·2(1,3,5-FIB) (bottom).

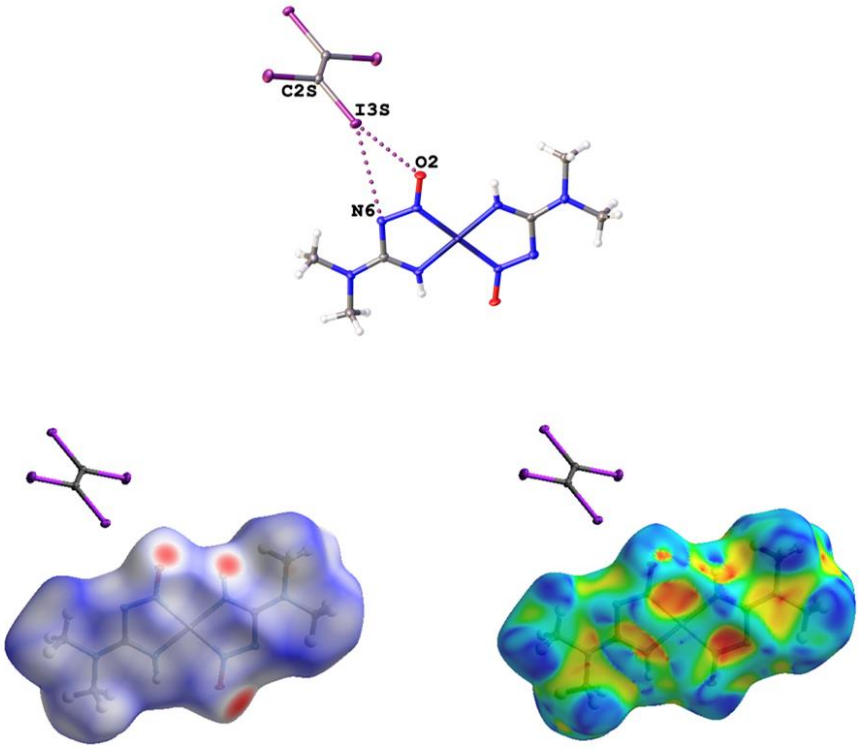

Figure S4. View of the molecular structure of **1**·C_2I_4 with bifurcated XB (dotted lines) between I atom of C_2I_4 and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **1** in the XRD structure of **1**·C_2I_4 (bottom).

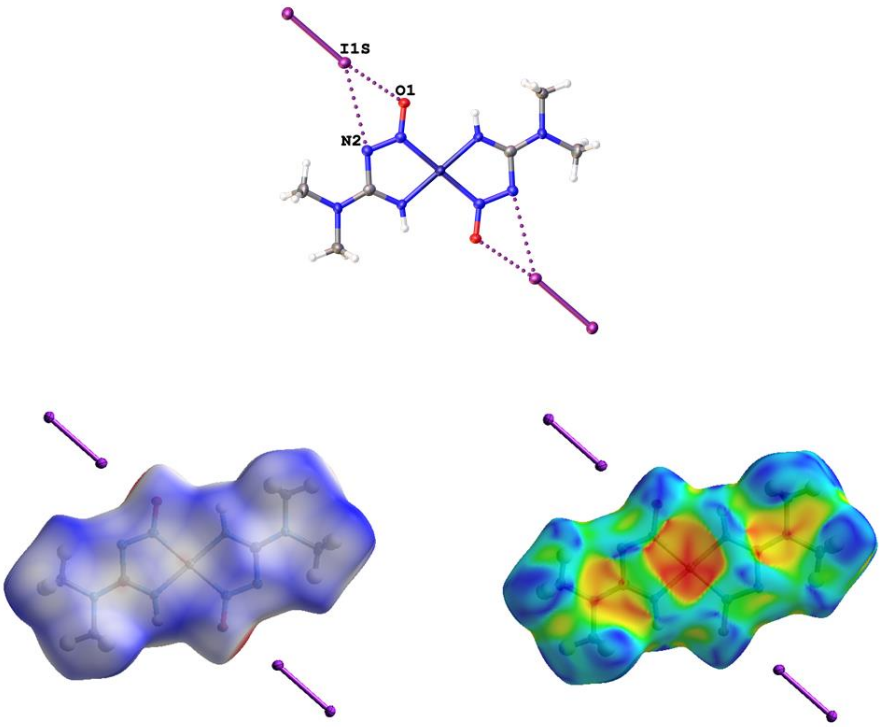

Figure S5. View of the molecular structure of **1**·2I_2 with bifurcated XB (dotted lines) between I atom of I_2 and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **1** in the XRD structure of **1**·2I_2 (bottom).

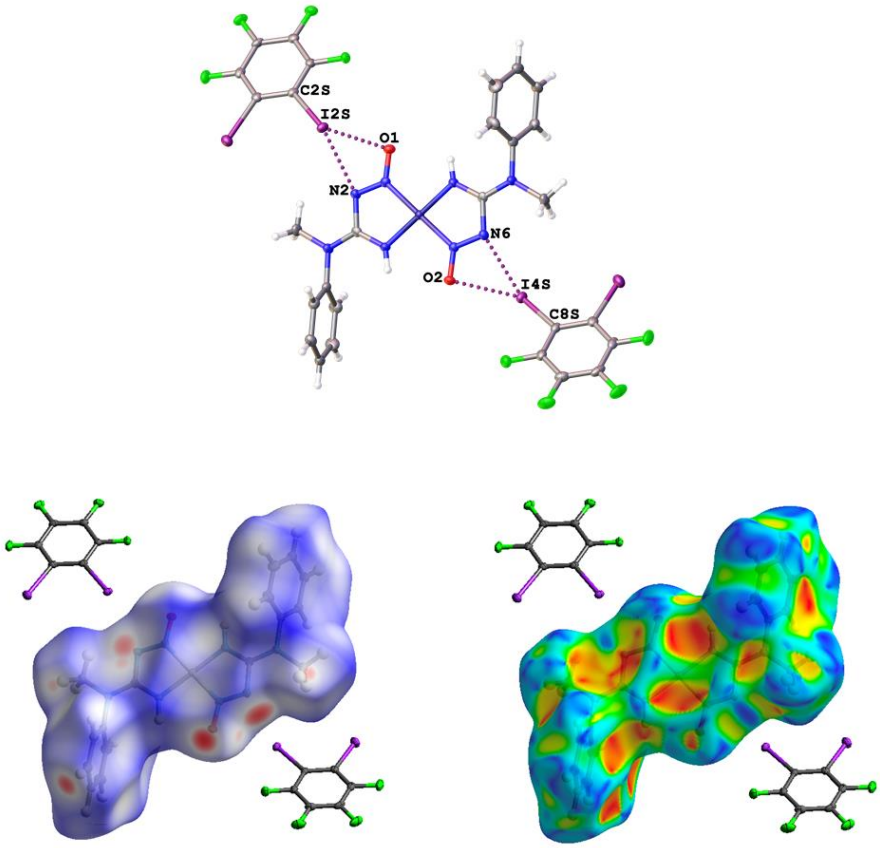

Figure S6. View of the molecular structure of **2**·2(1,2-FIB) with bifurcated XB (dotted lines) between I atom of 1,2-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **2** in the XRD structure of **2**·2(1,2-FIB) (bottom).

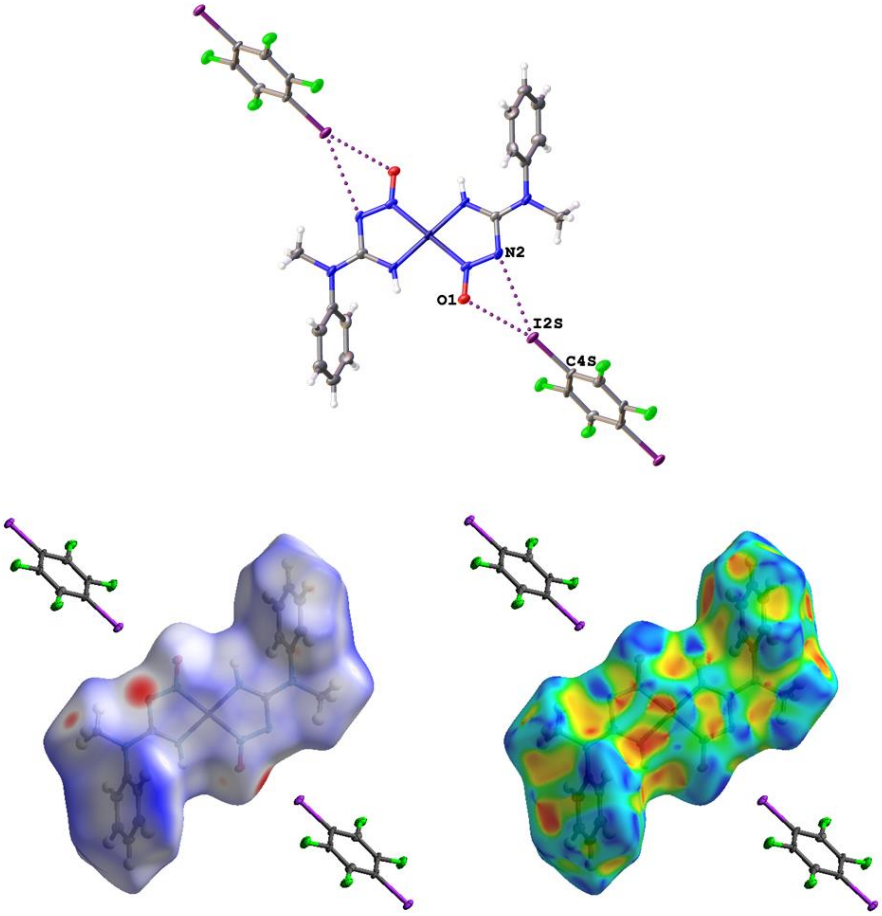

Figure S7. View of the molecular structure of **2**·2(1,4-FIB) with bifurcated XB (dotted lines) between I atom of 1,4-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **2** in the XRD structure of **2**·2(1,4-FIB) (bottom).

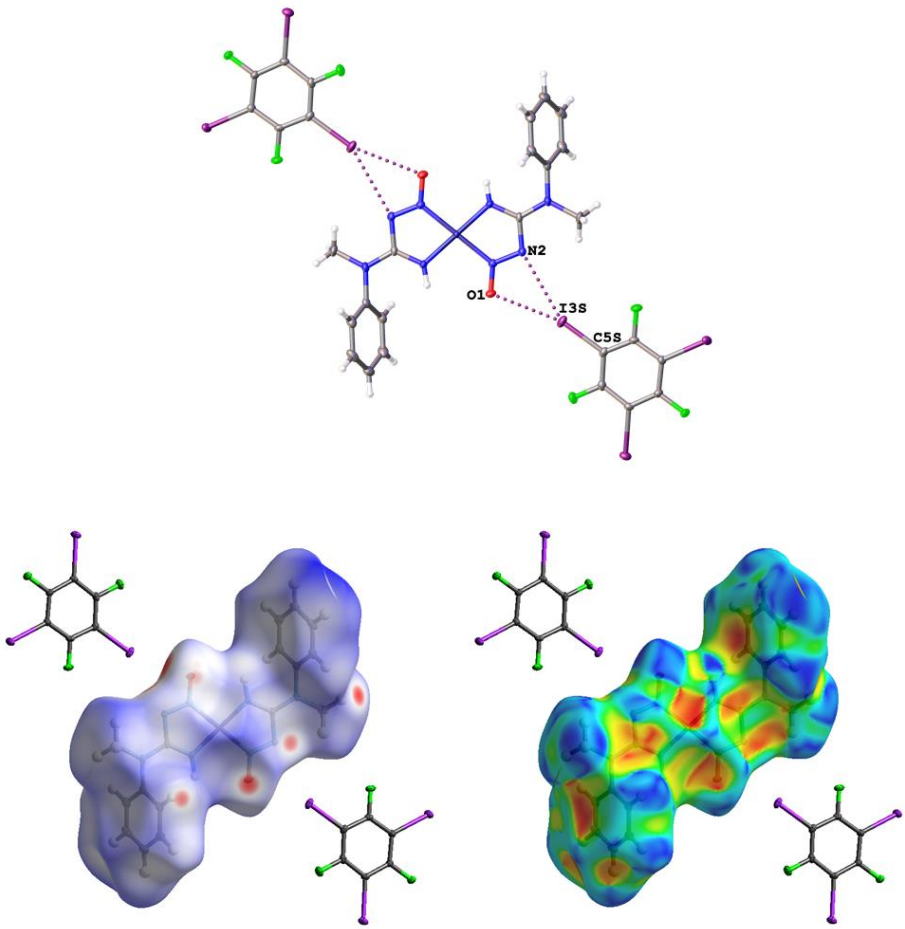

Figure S8. View of the molecular structure of **2**·2(1,3,5-FIB) with bifurcated XB (dotted lines) between I atom of 1,3,5-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **2** in the XRD structure of **2**·2(1,3,5-FIB) (bottom).

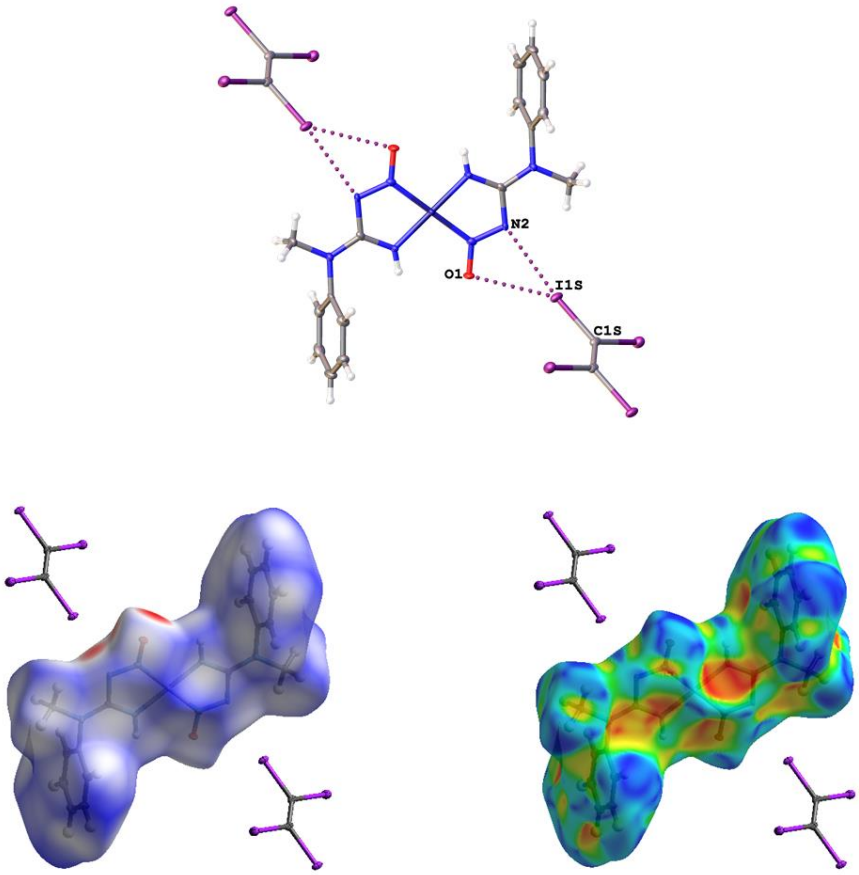

Figure S9. View of the molecular structure of **2**·2C_2I_4 with bifurcated XB (dotted lines) between I atom of C_2I_4 and N and O atoms of the nitrosoguanidinate ligand. (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **2** in the XRD structure of **2**·2C_2I_4 (bottom).

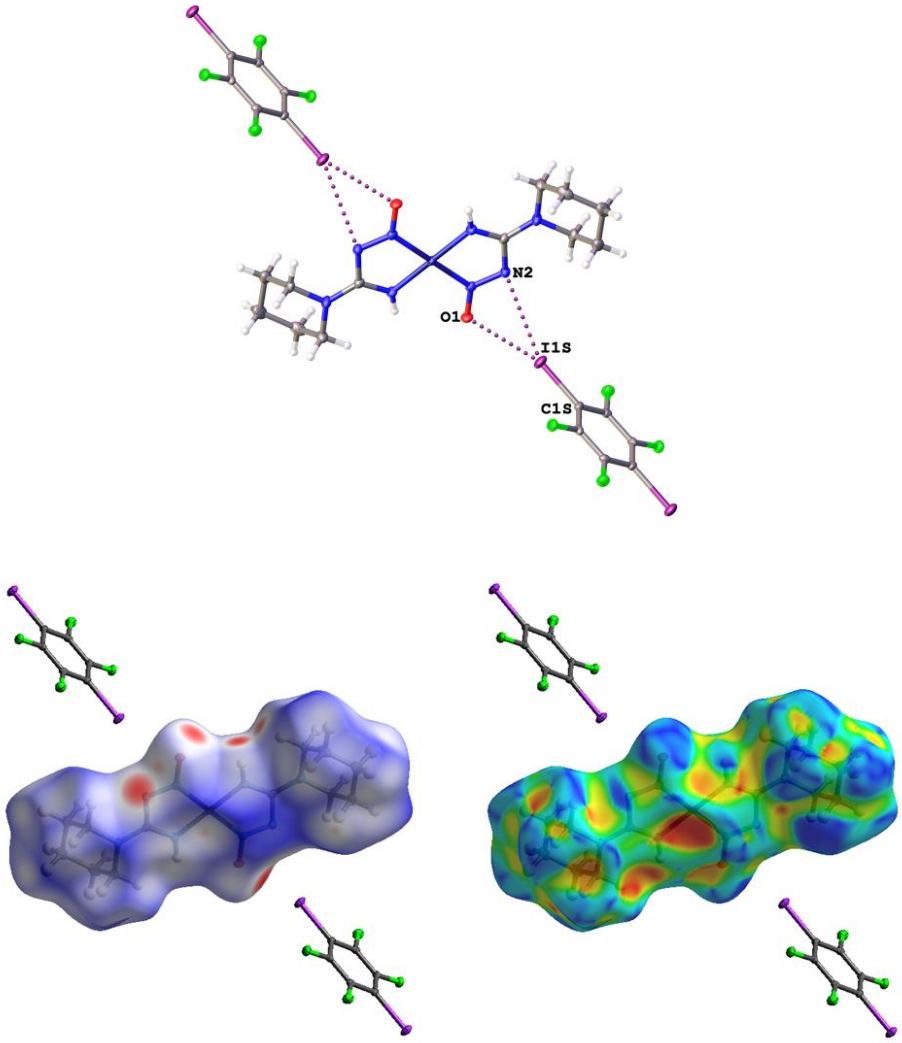

Figure S10. View of the molecular structure of **3**·2(1,4-FIB) with bifurcated XB (dotted lines) between I atom of 1,4-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **3** in the XRD structure of **3**·2(1,4-FIB) (bottom).

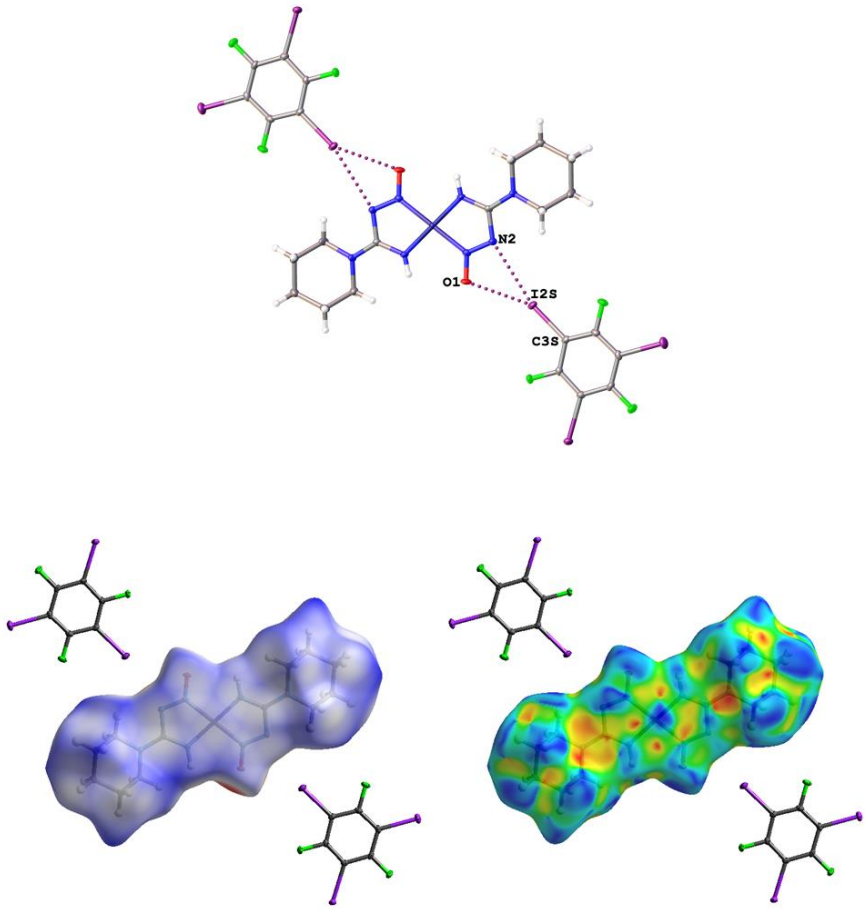

Figure S11. View of the molecular structure of **3**·2(1,3,5-FIB) with bifurcated XB (dotted lines) between I atom of 1,3,5-FIB and N and O atoms of the nitrosoguanidinate ligand (top). HSA mapped with d_{norm} over the range –0.2744 (red) to 1.1474 (blue) and shape index S, mapped from –1.0 (concave hollows; red) –1→ 0.0 (minimal saddle; green) → +1.0 (convex bumps; blue) for **3** in the XRD structure of **3**·2(1,3,5-FIB) (bottom).

Results of the Hirshfeld surface analysis

Table S3. Results of the Hirshfeld surface analysis for **1**, **2**, and **3** in X-ray structures of the co-crystals.

X-ray structure	Contributions of various intermolecular contacts to the molecular Hirshfeld surface of **1**, **2**, and **3**
1·2(1,2-FIB)	H–F 35.2%, H–N/N–H 16.4%, H–O/O–H 7.2%, H–I 7.1%, H–H 5.9%, O–I 5.7%, H–C/C–H 5.2%, N–I 3.5%, H–Ni/Ni–H 2.6%, N–Ni/Ni–N 2.6%, C–N/N–C 2.2%, O–C 2.1%, N–N 2.0%
1·(1,4-FIB)	H–F 22.5%, H–N/N–H 19.4%, H–O/O–H 14.3%, H–H 10.5%, H–I 9.0%, H–C/C–H 5.7%, H–Ni/Ni–H 4.2%, N–N 3.6%, O–I 2.0%, O–C 1.8%, C–N/N–C 1.7%, O–F 1.4%
1·2(1,3,5-FIB)	H–F 26.1%, H–N/N–H 15.8%, H–H 15.6%, H–I 10.9%, O–I 7.0%, N–I 6.3%, H–C/C–H 5.0%, H–O/O–H 4.8%, O–C 3.1%, Ni–I 2.6%, N–F 1.4%
1·C_2I_4	H–N/N–H 23.2%, H–I 21.9%, H–O/O–H 20.6%, H–H 17.2%, H–Ni/Ni–H 4.2%, H–C/C–H 3.2%, %, N–I 2.1%, C–N/N–C 2.0%, O–I 1.8%, N–Ni/Ni–N 1.2%, N–N 1.2%
1·2I_2	H–I 26.3%, H–H 23.6%, H–N/N–H 16.6%, H–O/O–H 16.2%, N–I 7.3%, O–I 4.8%, C–I 2.8%, Ni–I 2.6%
2·2(1,2-FIB)	H–F 28.1%, H–N/N–H 21.3%, H–H 16.7%, H–I 9.0%, H–O/O–H 7.8%, C–H/H–C 7.0%, N–I 5.0%, C–F 3.8%, O–F 3.4%, H–Ni/Ni–H 3.1%, C–I 2.3%, C–C 2.4%, N–F 1.3%
2·2(1,4-FIB)	H–H 27.0%, H–F 19.5%, C–H/H–C 12.8%, H–I 7.1%, H–O/O–H 6.0%, H–N/N–H 4.8%, O–I 3.9%, N–I 3.7%, H–Ni/Ni–H 3.4%, C–F 2.9%, N–N 2.9%, C–N/N–C 2.2%, C–O/O–C 1.8%
2·2(1,3,5-FIB)	H–H 19.2%, H–F 18.8%, H–I 13.8%, C–H/H–C 11.6%, H–N/N–H 10.6%, H–O/O–H 9.1%, C–I 4.2%, O–I 1.9%, c–F 1.3%, H–Ni/Ni–H 1.2%, Ni–F 1.1%
2·2(C_2I_4)	H–H 27.1%, H–I 21.9%, C–H/H–C 17.8%, H–O/O–H 7.7%, N–J 7.1%, H–N/N–H 6.2%, O–I 5.0%, C–I 3.2%, H–Ni/Ni–H 1.7%
3·2(1,2-FIB)	H–F 28.9%, H–H 18.2%, H–N/N–H 11.9%, H–O/O–H 11.7%, H–I 6.8%, C–H/H–C 6.2%, H–Ni/Ni–H 4.1%, N–I 3.3%, N–F 2.9%, O–F 2.2%, O–I 1.7%, C–F 1.1%
3·2(1,4-FIB)	H–H 25.7%, H–F 22.7%, H–N/N–H 14.2%, H–I 9.5%, H–O/O–H 5.1%, C–H/H–C 5.0%, H–Ni/Ni–H 4.6%, N–I 4.2%, O–I 3.7%, O–C 2.8%
3·2(1,3,5-FIB)	H–H 22.0%, H–F 21.4%, H–I 20.3%, H–C 7.3%, O–I 6.3%, N–C 5.5%, N–I 5.1%, O–F 3.0%, Ni–C 2.0%, N–F 2.0%, C–I 1.2%

Description of hydrogen bonds and other contacts

HB. In the crystal structures of all adducts, we identified the following HBs: N–H···F HB in **1**·2(1,2-FIB), **1**·(1,4-FIB), **3**·2(1,2-FIB), and **3**·2(1,4-FIB), C–H···F in **1**·2(1,2-FIB), **1**·(1,4-FIB), **1**·2(1,3,5-FIB), **2**·2(1,2-FIB), **2**·2(1,4-FIB), **2**·2(1,3,5-FIB), **3**·2(1,2-FIB), and **3**·2(1,4-FIB), N–H···I in **1**·2I_2, and **3**·2(1,3,5-FIB), C–H···I in **1**·2I_2, **1**·C_2I_4, **2**·2(1,2-FIB), and **3**·2(1,3,5-FIB), N–H···O= in **1**·C_2I_4, C–H···O= in **1**·C_2I_4, **2**·2(1,2-FIB), **2**·2(1,4-FIB), and **2**·2(1,3,5-FIB), and C–H···N in **1**·C_2I_4, **1**·2(1,3,5-FIB), **2**·2(1,3,5-FIB), and **3**·2(1,2-FIB) (**Table S4**). As is follows from **Table S4**, HB with F are characteristic for adducts with perfluorinated arenes, while for adducts of I_2 and C_2I_4 HB with I are predominant. The strongest HB were found in adducts **1**·2(1,3,5-FIB) (C2–H2C···F2S 2.373 Å), **1**·C_2I_4 (N3–H3···O2 2.394 Å), and **2**·2(1,2-FIB) (C16–H16···F5S 2.374 and C15–H15···O2 2.384 Å).

Table S4. Parameters of HB in the studied co-crystals.

Co-crystals	**Contact A–H•••B**	**A•••B, Å**	**∠(A–H•••B),°**
1·2(1,2-FIB)	N3–H3···F1S	3.272(5)	149.7
	C2–H2A···F2S	3.362(6)	142.7
	C3–H3C···F3S	3.387(7)	144.7
1·(1,4-FIB)	N3–H3···F2S	3.424(4)	163.8
	C2–H2B···F1S	3.393(4)	153.1
	C2–H2C···I1S	4.066(4)	178.2
1·2(1,3,5-FIB)	C2–H2A···F1S	3.392(5)	139.1
	C2–H2C···F2S	3.270(7)	151.9
	C3–H3C···N2	3.467(8)	138.5
1·C_2I_4			
	N3–H3···O2	3.054(4)	133.9
	C3–H3C···O1	3.213(4)	127.4
	C3–H3A···I3S	3.836(3)	136.3
	C6–H6B···I3S	4.080(4)	160.6
	C6–H6A···N2	3.507(4)	144.9
	N8–H8···O1	3.236(4)	124.6
	C6–H6A···O1	3.642(4)	162.4
1·2I_2	N3–H3···I2S–I1S	3.926(3)	174.5
	C2–H2B···I2S–I1S	3.951(4)	165
2·2(1,2–FIB)	C7–H7A···O1	3.328(4)	153.9
	C15–H15···O2	3.269(3)	158.8
	C8–H8···F1S	3.172(3)	117.9
	C16–H16···F5S	3.190(3)	146.2
	C2–H2A···F1S	3.450(3)	152
	C10–H10A···F6S	3.295(3)	136.1
	C2–H2C···I2S	3.972(3)	164.2

2·2(1,4-FIB)	C8–H8···O1 C2–H2A···F1S C7–H7···F3S C6–H6···F2S	3.286(10) 3.219(6) 3.292(9) 3.336(8)	130.2 142.2 132.2 131.7
2·2(1,3,5-FIB)	C2–H2B···O1 C4–H4A···N2 C5–H5···F2S	3.389(3) 3.441(3) 3.210(3)	161.9 151 118.3
3·2(1,2-FIB)	N3–H3···F2S C6–H6B···F2S C5–H5B···F3S C4–H4A···N1	3.131(5) 3.448(6) 3.648(4) 3.506(6)	123.4 142.6 130.2 137
3·2(1,4-FIB)	N3–H3···F2S C2–H2B···F1S	3.248(3) 3.405(3)	168 171.7
3·2(1,3,5-FIB)	N3–H3···I1S C6–H6A···I1S	3.959(4) 4.027(3)	160.7 147.4

¶

R is interatomic distance to vdW sum ratio, the sum of Bondi vdW radii $R_{vdW}(H) + R_{vdW}(O) = 2.72$, $R_{vdW}(H) + R_{vdW}(N) = 2.75$, $R_{vdW}(H) + R_{vdW}(F) = 2.67$, and $R_{vdW}(H) + R_{vdW}(I) = 3.18$ Å.

Table S5. Parameters of lone pair–π interactions in the studied co-crystals.

Co-crystals	**Contact C···X–R**	**C···X, Å**	**R¶**	**∠(C···X–R),°**	**Comments**
1·(1,4-FIB)	C3S···O1–N1	3.067(4)	0.95	164.4(2)	lp(O)-πh(Ar_F) reported, Ref.[2]
1·2(1,3,5-FIB)	C6S···I3S–C3S	3.598(5)	0.98	73.73(16)	lp(I)-πh(Ar_F) reported, Ref.[1]
1·C_2I_4	C1S···I4S–C2S	3.639(3)	0.99	138.30(11)	lp(I)-πh(C_2I_4)
1·2I_2	C1···I1S–I2S	3.598(5)	0.98	82.13(6)	lp(I)-πh(C_{NG}) reported, Ref.[1]
2·2(1,2–FIB)	C1···I1S–C1S C9···I3S–C7S C11S···I4S–C8S C5S···I2S–C2S C10S···O2–N5 C11S···O2–N5	3.609(3) 3.648(3) 3.682(3) 3.664(3) 3.012(4) 3.099(4)	0.98 0.99 1.00 1.00 0.94 0.96	130.11(8) 123.47(8) 84.47(8) 81.08(8) 145.33(16) 157.46(16)	lp(I)-πh(C_{NG}) lp(I)-πh(C_{NG}) lp(I)-πh(Ar_F) lp(I)-πh(Ar_F) lp(O)-πh(Ar_F) lp(O)-πh(Ar_F)
2·2(1,3,5-FIB)	C4S···O1–N1 C3S···O1–N1	3.132(3) 3.186(3)	0.97 0.99	86.30(13) 111.50(14)	lp(O)-πh(Ar_F) reported, Ref.[2]
3·2(1,4-FIB)	C3S···O1–N1 C4S···F1S–C2S	2.903(3) 3.076(3)	0.90 0.96	159.06(16) 109.07(14)	lp(O)-πh(Ar_F) reported, Ref.[2] lp(I)-πh(Ar_F)

¶R is interatomic distance to vdW sum ratio, the sum of Bondi vdW radii $R_{vdW}(C) + R_{vdW}(O) = 3.22$, $R_{vdW}(C) + R_{vdW}(I) = 3.68$, and $R_{vdW}(C) + R_{vdW}(F) = 3.17$ Å.

Table S6. Parameters of Type II halogen–halogen interactions in the structures of **1**·C_2I_4 and **1**·2(1,3,5-FIB).

Co-crystals	**Contact C–I···I–C**	**I···I, Å**	**R¶**	**∠(C–I···I),°**	**∠(I···I–C),°**
1·C_2I_4	C1S–I2S···I3S–C2S	3.7449(4)	0.95	166.14(9)	84.20(9)
1·2(1,3,5-FIB)	C3S–I2S···I13–C1S	3.8234(6)	0.97	171.88(12)	111.50(14)

¶R is interatomic distance to vdW sum ratio, the sum of Bondi vdW radii $2R_{vdW}(I) = 3.96$ Å.

MEP surfaces of the XB donors

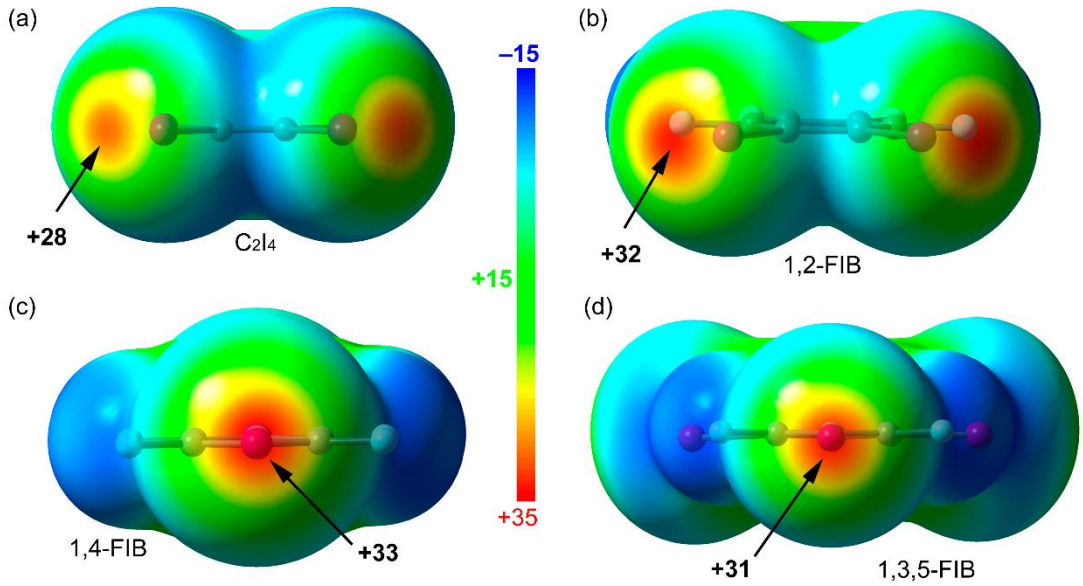

Figure S12. MEP surfaces (isosurface 0.001 a.u.) of the XB donors. The energies at selected points of the surfaces are given in kcal/mol.