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Supporting information for article:

Competition between chalcogen and halogen bonding assessed through isostructural species

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S1. Synthesis and characterization

S1.1. Synthesis of 2-iodo-5-(4-iodophenyl)-1,3,4-thiadiazole (T1)

Orange solid. Yield 52%. MP:180-190 º C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H).

S1.2. Synthesis of 2-bromo-5-(4-bromophenyl)-1,3,4-selenadiazole (T2)

Orange solid. Yield 80%. MP: 140-155˚C. 1H NMR (400 MHz, DMSO-d6) δ 7.90 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H).

S1.3. Synthesis of 2-bromo-5-(4-iodophenyl)-1,3,4-selenadiazole (T3)

Yellow solid. Yield 78%. MP: 147-158 º C. 1H NMR (400 MHz, DMSO-d6) δ 7.91 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H).

S1.4. Synthesis of 2-bromo-5-(4-iodophenyl)-1,3,4-thiadiazole (T4)

Yellow solid. Yield 78%. MP: 143-148 º C. 1H NMR (400 MHz, DMSO-d6) δ 7.95 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H).

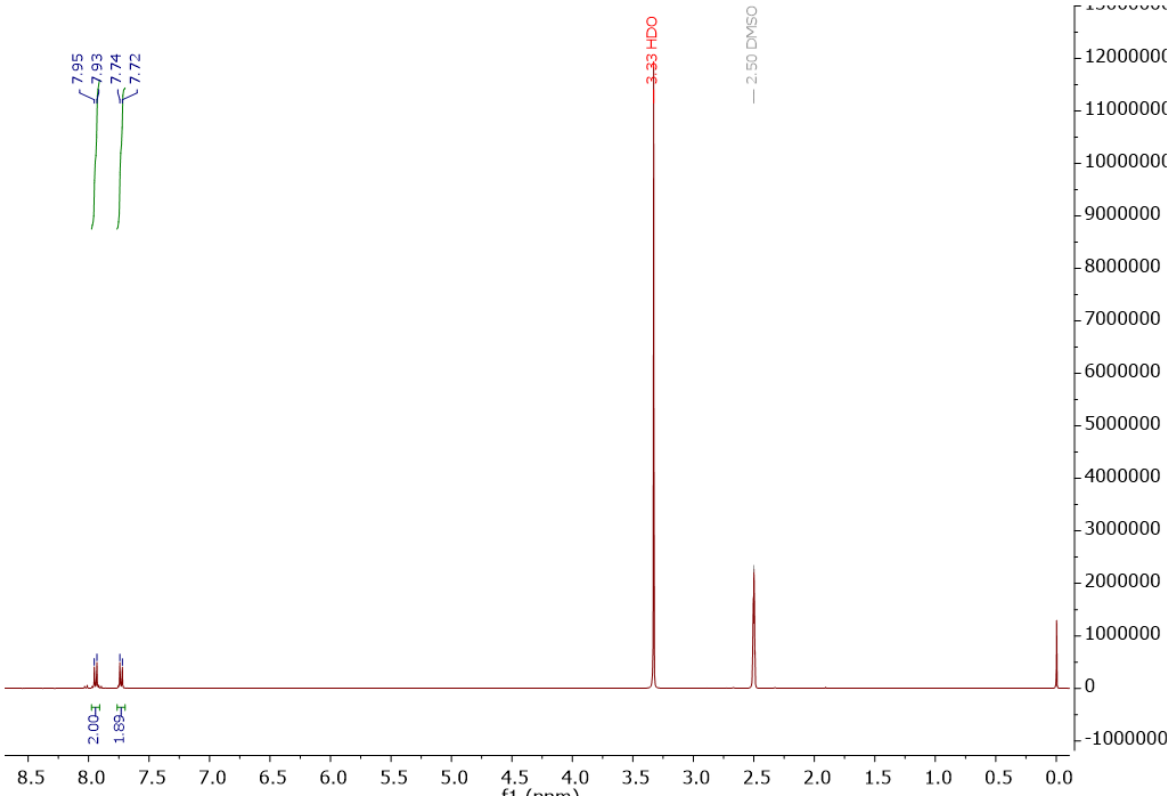

Figure S1 NMR Spectrum of **T1**

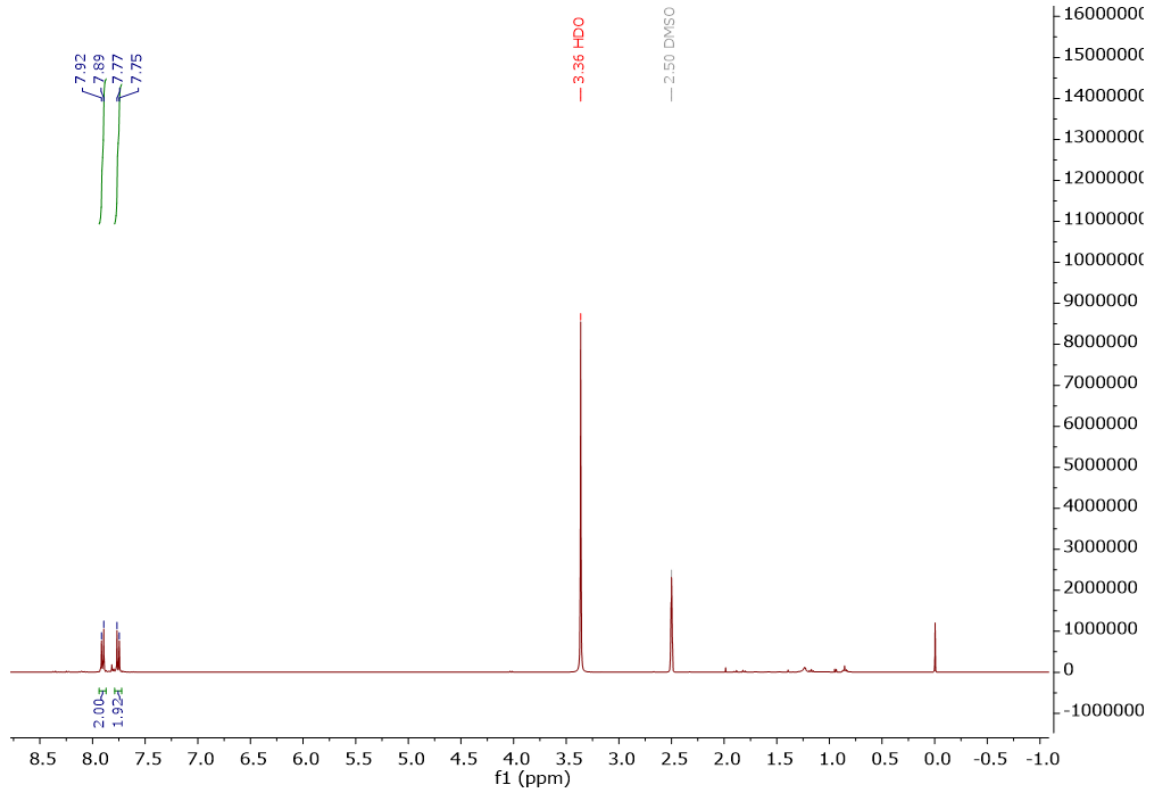

Figure S2 NMR Spectrum of **T2**

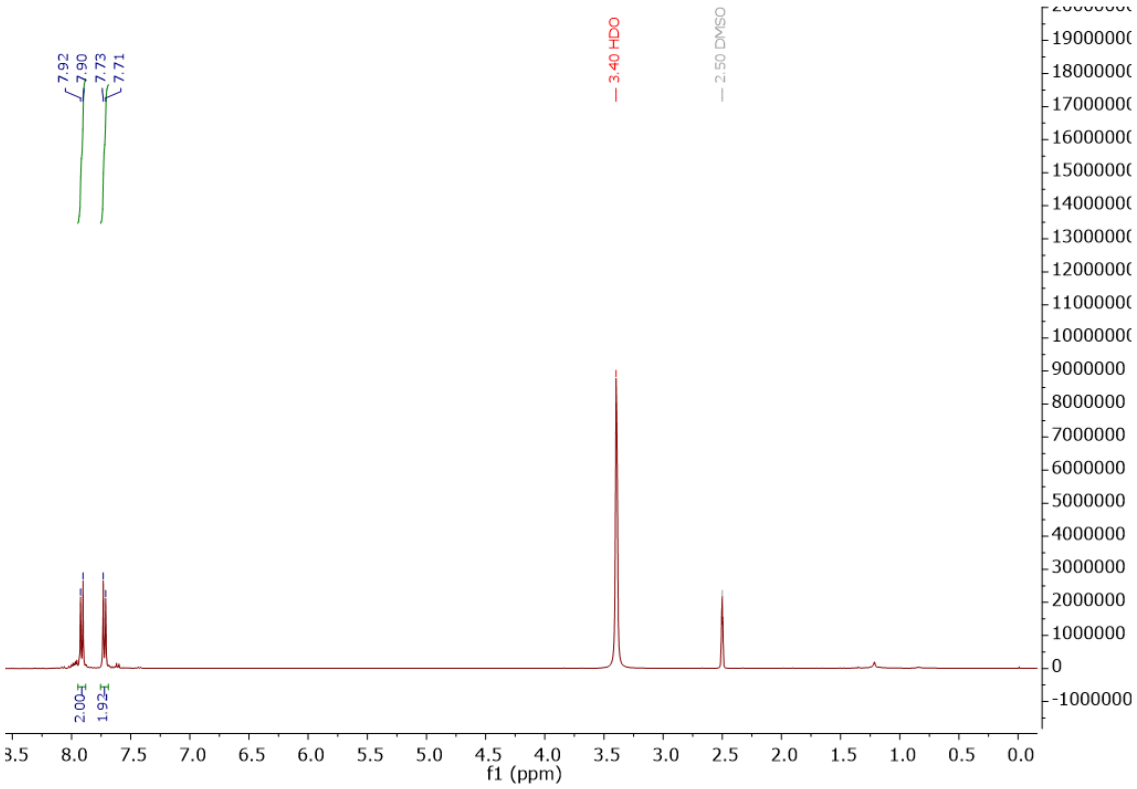

Figure S3 NMR Spectrum of **T3**

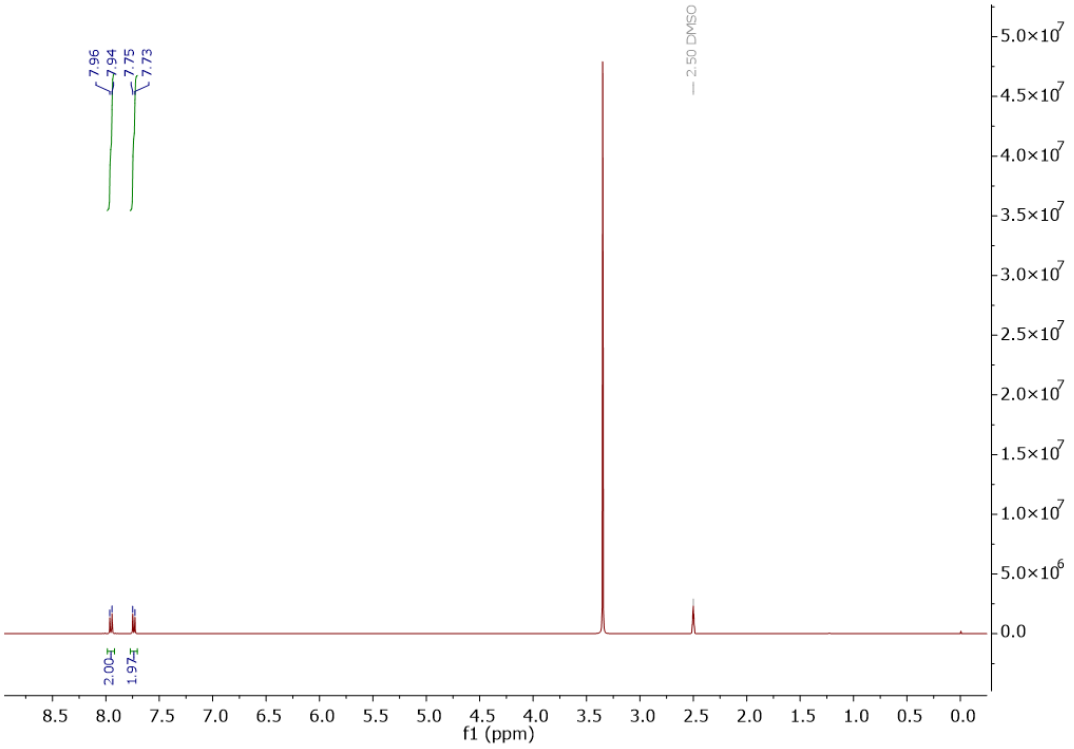

Figure S4 NMR Spectrum of **T4**

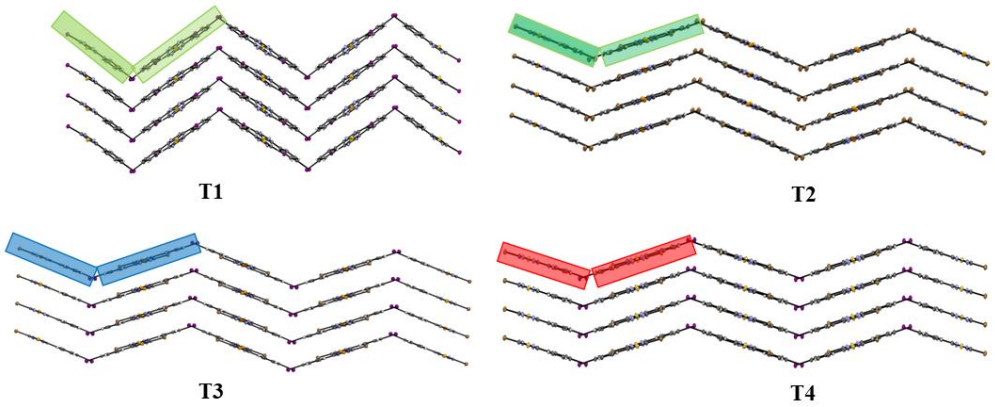

Figure S5 Crystal packing of **T1-T4**

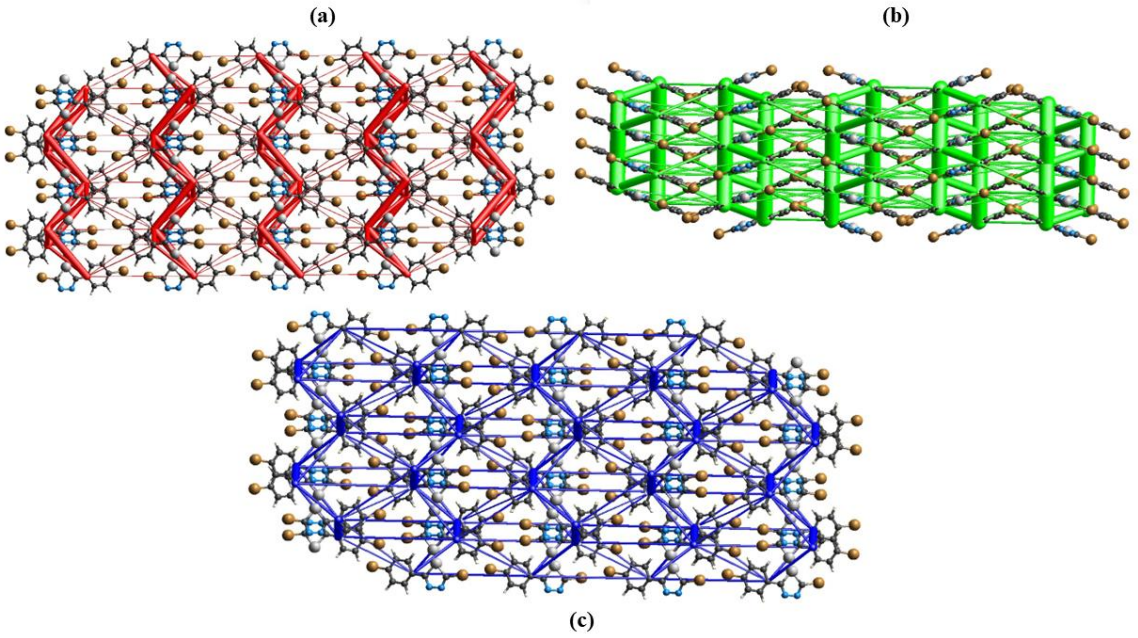

Figure S6 (a) Coulombic interactions (b)dispersion interactions, (c) total interaction energies of **T2**

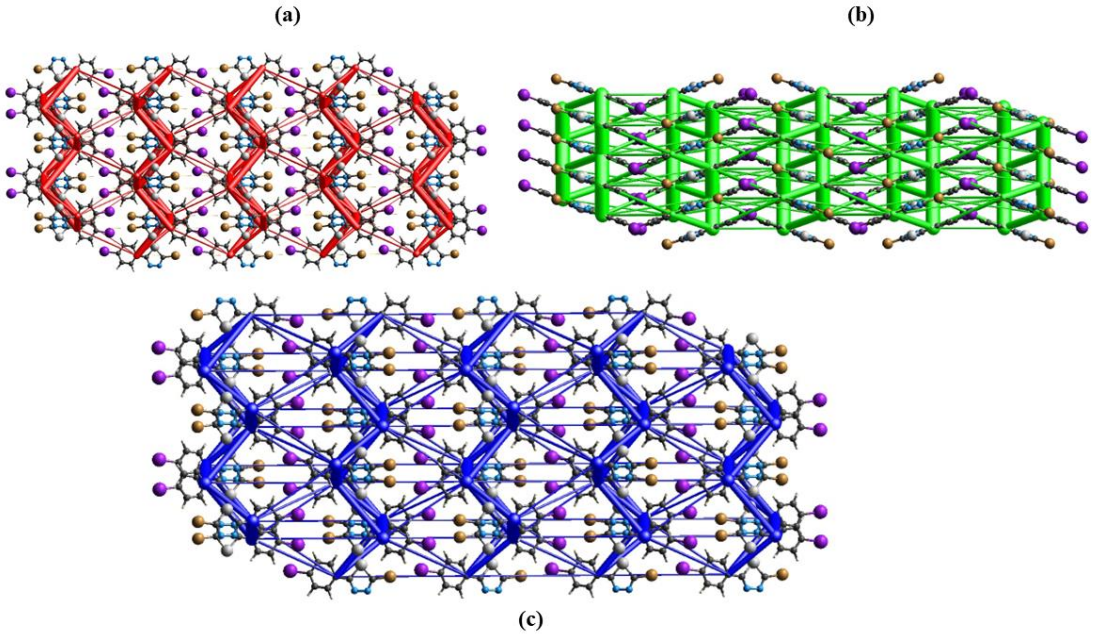

Figure S7 (a) Coulombic interactions(b)dispersion interactions, (c)total interaction energies of **T3**

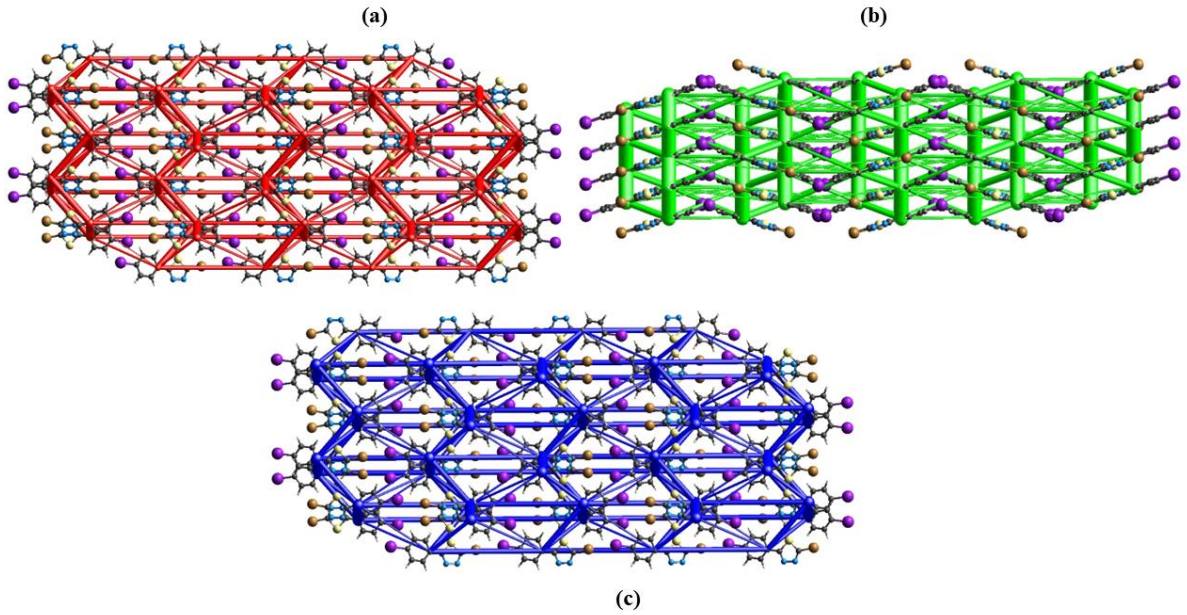

Figure S8 (a)Coulombic interactions (b)dispersion interactions, (c)total interaction energies of **T4**

Table S1 Crystallographic data for **T1-T4**

Code	**T1**	**T2**	**T3**	**T4**
Formula moiety	$C_8H_4I_2N_2S$	$C_8H_4Br_2N_2Se$	$C_8H_4IBrN_2Se$	$C_8H_4IBrN_2S$
Empirical formula	$C_8H_4I_2N_2S$	$C_8H_4Br_2N_2Se$	$C_8H_4IBrN_2Se$	$C_8H_4IBrN_2S$
Deposition Number	2202927	2202928	2202931	2202932
Molecular weight	413.99	366.91	413.90	367.00
Color, Habit	Colorless, Block	Orange, irregular	Clear light yellow, plate	Colorless, plate
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group, *Z*	Pbca, 8	Pbca, 8	Pbca, 8	Pbca, 8
a, Å	11.0392(2)	11.1945(5)	11.1735(4)	10.9919(2)
b, Å	8.1756(2)	7.1006(3)	7.1222(2)	6.99450(10)
c, Å	23.3673(4)	25.4725(9)	26.1875(8)	26.4076(4)
α, °	90	90	90	90

β, º	90	90	90	90
γ, º	90	90	90	90
Volume, Å^3	2108.95(7)	2024.74(15)	2084.00(11)	2030.29(6)
Density, g/cm^3	2.608	2.407	2.638	2.401
T, ºK	293(2)	100.00(10)	100.00(10)	293(2)
Crystal size, min x mid x max	0.027×0.054×0.065	0.02×0.02×0.02	0.06×0.1×0.3	0.012×0.039×0.048
X-ray wavelength, Å	1.54184	1.54184	0.71073	1.54184
μ, mm^{-1}	48.342	13.895	10.355	30.946
Trans min / max	0.209/ 0.522	0.68222/1.00000	0.33758/1.00000	0.37294/1.00000
θ_{min}, º	3.783	3.470	2.396	3.347
θ_{max}, º	69.060	74.839	26.019	70.701
Reflections				
collected	8336	6457	12091	7258
independent	1942	1965	2055	1920
observed	1753	1709	1815	1802
R_{int}	0.0243	0.0368	0.0351	0.0246
Threshold expression	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)
No. parameters	118	118	118	118
No. restraints	0	0	0	0
R_1 (observed)	0.0262	0.0442	0.0296	0.0210
wR_2 (all)	0.0709	0.1088	0.0697	0.0517
Goodness of fit (all)	1.088	1.048	1.082	1.069
ρ_{max}, ρ_{min}, e Å^{-3}	1.328, -1.221	1.950, -1.464	2.003, -1.013	0.566, -0.670
Completeness to 2θ limit	0.991	0.945	1.000	0.984