Supporting Information

Novel applications of functionalized 2,1,3-benzothiadiazoles for coordination chemistry and crystal engineering

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Table S1. Crystallographic data of compounds **1-4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_6H_5N_3S$	$C_{12}H_{10}Cl_2N_6S_2Zn$	$C_6H_3N_3O_2S$	$C_{12}H_8N_6O_2S_2$
Formula weight	151.19	438.65	181.17	332.36
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	*Pccn*	*C*2/*c*	$P2_1/c$	*P*-1
Unit cell dimensions *a* [Å]	12.9346(4)	27.5548(8)	4.6171(2)	7.4742(2)
b [Å]	21.7846(8)	4.6491(2)	9.9885(4)	8.3487(3)
c [Å]	4.7923(2)	12.4548(4)	14.8728(6)	11.8518(4)
α [°]	90	90	90	82.880(2)
β [°]	90	102.699(1)	98.403(1)	79.480(2)
γ [°]	90	90	90	69.068(1)
Volume [Å ^{3}]	1350.35(9)	1556.49(9)	678.54(5)	677.74(4)
Z	8	4	4	2
Density (calcd.) [g cm^{-3}]	1.487	1.872	1.773	1.629
F(000)	624	880	368	340
Abs. coefficient [mm^{-1}]	0.393	2.195	0.428	0.410
Crystal size [mm^3]	0.40x0.25x0.15	0.30x0.22x0.18	0.38x0.12x0.08	0.35x0.15x0.04
$2\theta_{max}$ [°]	55.02	65.18	65.60	52.74
Index range	-16<=h<=12 28<=k<=28 6<=l<=4	-41<=h<=24 7<=k<=6 18<=l<=18	-6<=h<=6 9<=k<=15 14<=l<=22	-9<=h<=9 10<=k<=10 14<=l<=14
Reflections collected	9160	7745	6440	5604
Independent reflections	1546 [R(int) = 0.0288]	2818 [R(int) = 0.0319]	2465 [R(int) = 0.0159]	2754 [R(int) = 0.0304]
Completness to θ [%]	99.6 %	99.7 %	99.8 %	99.4 %
Reflections, $I \geq 2\sigma(I)$	1411	2470	2142	2144
Parameters	91	113	109	200
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0352, wR2 = 0.1017	R1 = 0.0250, wR2 = 0.0622	R1 = 0.0302, wR2 = 0.0806	R1 = 0.0360, wR2 = 0.0879
R indices (all data)	R1 = 0.0381, wR2 = 0.1043	R1 = 0.0306, wR2 = 0.0644	R1 = 0.0368, wR2 = 0.0839	R1 = 0.0509, wR2 = 0.0925
GoF	1.082	1.077	1.062	1.032
Residual electron density (min / max, e/Å^3)	-0.412 / 0.437	-0.409 / 0.422	-0.173 / 0.599	-0.253 / 0.230

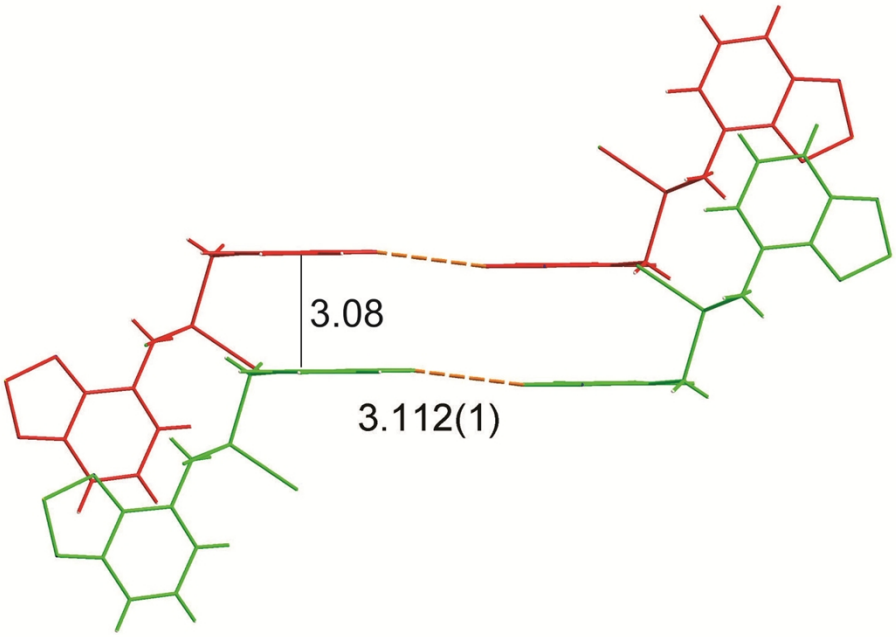
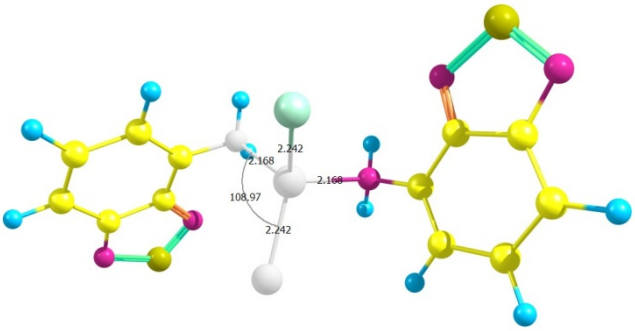


Fig. S1. Packing diagram of **2** showing relative arrangement of stacks.

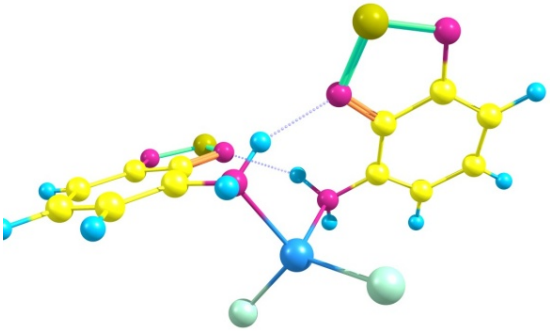


A

G_{rel} = 0 kcal·mol^{-1}

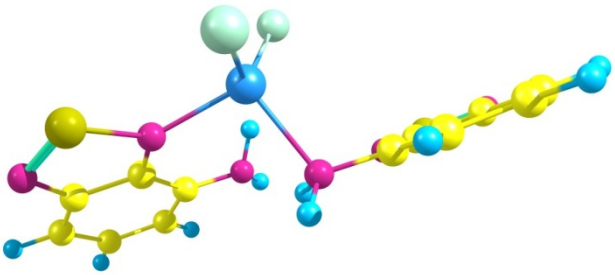
$Zn(THF)_2Cl_2 + 2\ \mathbf{1} = Zn(\mathbf{1})_2Cl_2 + 2$ THF

ΔG^0= 2.4 kcal·mol^{-1}



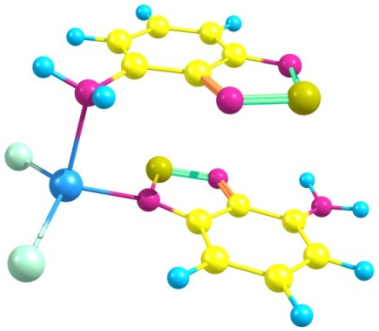
B

G_{rel} = –5.9 kcal·mol^{-1}



C

G_{rel} = –4.4 kcal·mol^{-1}



D

G_{rel} = –11.6 kcal·mol^{-1}

Fig. S2. Selected structures of complex **2** optimized at the B97-D3/def2-TZVP level of theory in THF solution with different types of coordination: both ligands are coordinated by N atoms of NH_2 groups (A and B), and one ligand is coordinated by N atom of NH_2 group and another by N atom of heterocycle (C and D).

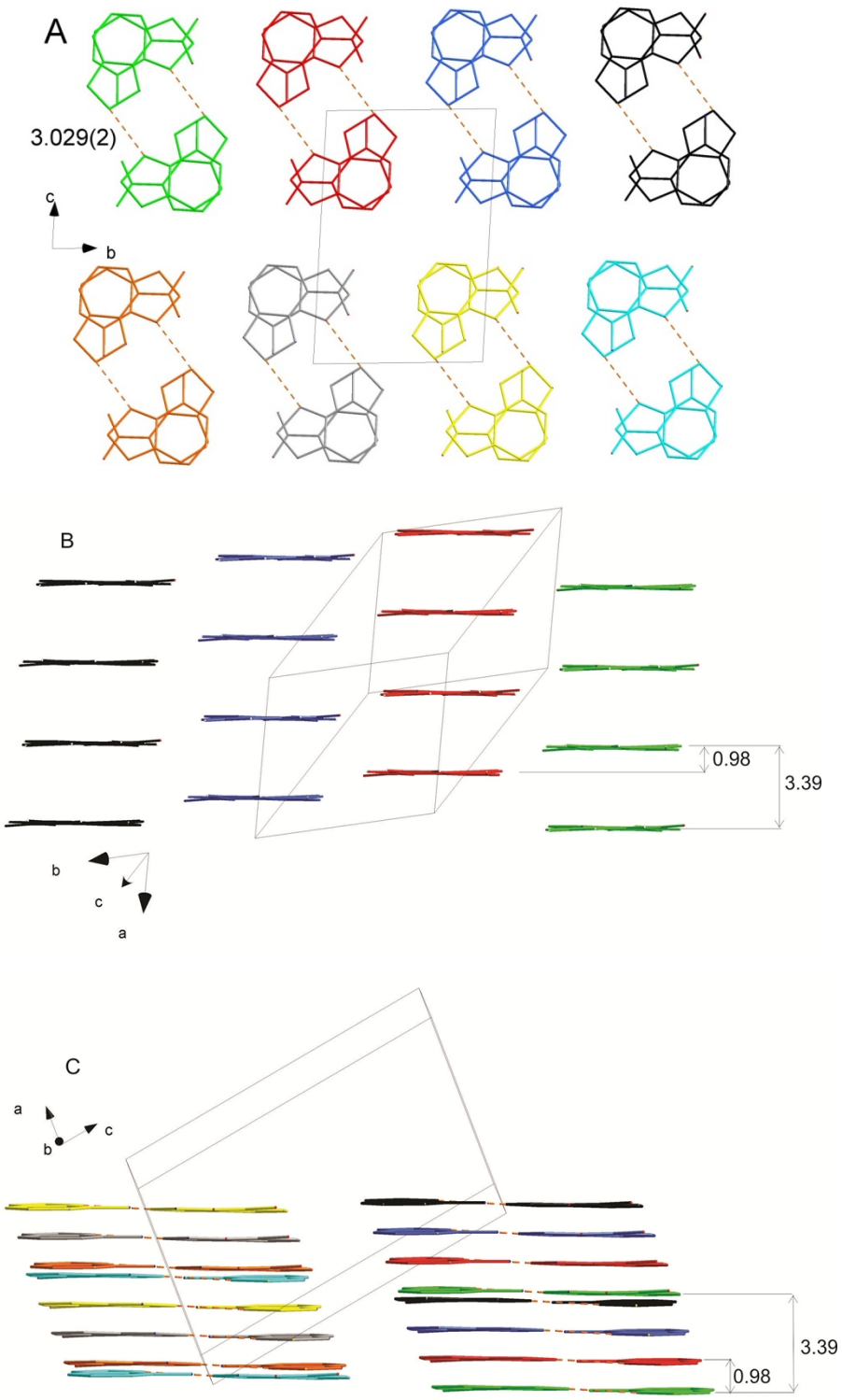


Fig. S3. Packing diagram of complex **4** viewed along *a* axis (A) and those showing relative arrangement of stacks (B and C).

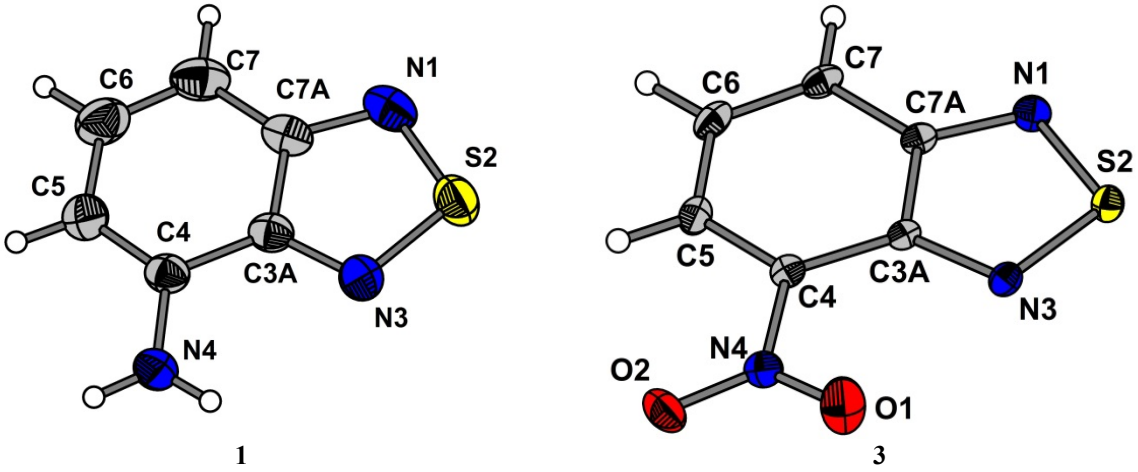
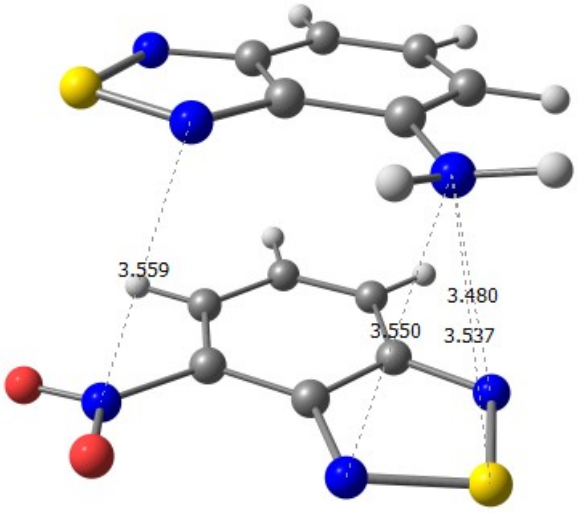
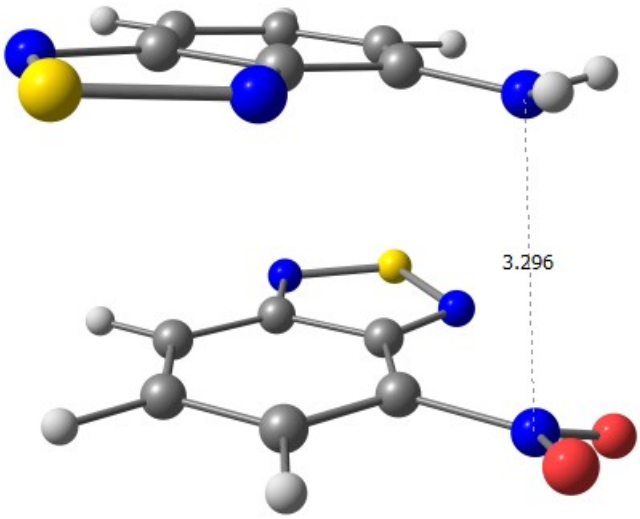


Fig. S4. ORTEP plots of **1** and **3** showing 50% probability ellipsoids (H atoms are shown as circles).



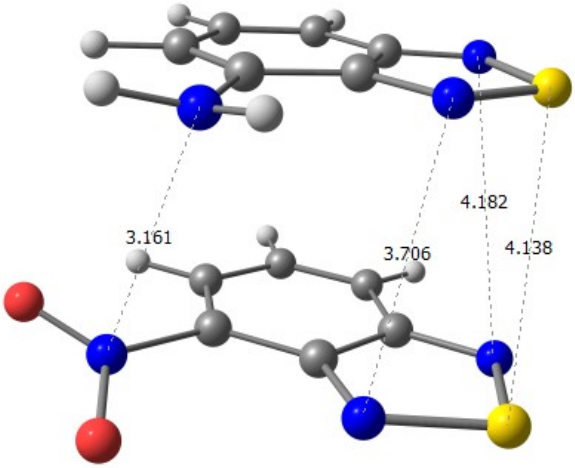
4a, $\Delta H^0 = -8.5$ kcal·mol^{-1}, $\Delta G^0 = 4.1$ kcal·mol^{-1}

$\Delta Q = 0.022e$, $\lambda_{max}(CT) = 552$ nm, f =0.009



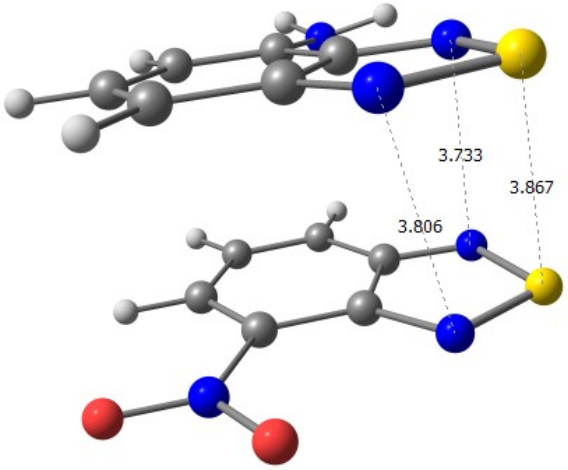
4b, $\Delta H^0 = -9.5$ kcal·mol^{-1}, $\Delta G^0 = 3.1$ kcal·mol^{-1}

$\Delta Q = 0.016e$, $\lambda_{max}(CT) = 598$ nm, f = 0,001



4c, $\Delta H^0 = -9.5$ kcal·mol^{-1}, $\Delta G^0 = 3.1$ kcal·mol^{-1}

$\Delta Q = 0.041e$, $\lambda_{max}(CT) = 580$ nm, f = 0.005



4d, $\Delta H^0 = -8.5$ kcal·mol^{-1}, $\Delta G^0 = 4.2$ kcal·mol^{-1}

$\Delta Q = 0.052e$, $\lambda_{max}(CT) = 582$ nm, f = 0.02

Figure S5. Structures of 1 : 1 complexes between **1** and **3** (complex **4** with different relative arrangement of the units**, 4a**–**4d**) optimized at the B97-D3/def2-TZVP level and thermodynamics of complex formation (ΔH^0, ΔG^0) in THF solution (thermodynamics in CH_2Cl_2 solution coincides within 0.1 kcal·mol^{-1}).