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Electronic Supplementary Information

On the importance of π-hole spodium bonding in tricoordinated Hg^{II} complexes

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Experimental

Materials and physical measurements

All reagents were provided from commercial companies and used without further purification. Microanalyses were performed using a LECO-elemental analyzer.

Synthesis of HL^{I} and HL^{II}

A mixture of 2-aminothiophenol or isonicotinohydrazide (1 mmol; 0.125 and 0.137 g, respectively) and 3-(2-nitrophenyl)acrylaldehyde or 3-nitrobenzaldehyde (1 mmol; 0.177 and 0.151 g, respectively) in ethanol (50 mL) was refluxed for 12 h under nitrogen atmosphere. After cooling to room temperature, the resulting yellow or white precipitate was filtered off, washed with ethanol and dried in air.

HL^{I}: Yield: 0.230 g (81%). Anal. Calc. for $C_{15}H_{12}N_2O_2S$ (284.33): C 63.36, H 4.25 and N 9.85%; found: C 63.71, H 4.01 and N 10.11%.

HL^{II}: Yield: 0.192 g (71%). Anal. Calcd. for $C_{13}H_{10}N_4O_3$ (270.25): C 57.78, H 3.73 and N 20.73%; found: C 57.91, H 3.69, N 20.67%.

Synthesis of 1 and 2

The synthesis was carried out using a branched tube method.[1] A mixture of HgI_2 (1 mmol, 0.454 g) and **HL^{I}** or **HL^{II}** (1 mmol; 0.284 or 0.270 g, respectively) was placed in the main arm of the branched tube, and methanol (25 mL) was carefully added to fill the arms. The tube was sealed and immersed in an oil bath at 60 °C, while the branched arm was kept at ambient temperature. After few days, needle- or rod-like X-ray suitable crystals were formed in the cooler arm. Crystals were isolated by filtration and dried in air.

1: Yield: 0.373 g (61%). Anal. Calc. for $C_{15}H_{11}HgIN_2O_2S$ (610.82): C 29.50, H 1.82 and N 4.59%; found: C 29.68, H 1.76 and N 4.48%.

2: Yield: 0.493 g (68%). Anal. Calcd. for $C_{13}H_{10}HgI_2N_4O_3$ (724.65): C 21.55, H 1.39 and N 7.73%; found: C 21.48, H 1.51, N 7.71%.

Single-crystal X-ray diffraction of 1 and 2

Diffraction data for **1** were collected on a Bruker Apex-II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at T = 173(2) K. LP corrections were performed with the APEX SUITE software[2] and a numerical absorption correction was applied using SADABS.[3]. Structure solution and refinement were performed with SHELXS/L-97.[4]

Diffraction data for **2** were collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at T = 130(1) K. Cell refinement, indexing, and scaling of the data sets were performed using the CrysAlisPro program.[5] A numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied to the data set.[6] The structure was solved by direct methods with SHELXT.[4] Non hydrogen atoms were refined by full-matrix least-squares on F^2 with anisotropic displacement parameters using the program SHELXL-2014/7.[4] The contribution of H-atoms at calculated positions was included in the final cycles of refinements.

1: $C_{15}H_{11}HgIN_2O_2S$, M_r = 610.81 g mol^{-1}, monoclinic, space group *Cc*, a = 27.761(3), b = 3.9611(5), c = 15.6659(16) Å, β = 111.098(4)°, V = 1607.2(3) Å^3, Z = 4, ρ = 2.524 g cm^{-3}, μ(Mo-Kα) = 11.634 mm^{-1}, reflections: 7427 collected, 3945 unique, R_{int} = 0.054, R_1(all) = 0.0889, wR_2(all) = 0.0886, S = 0.915.

2: $C_{13}H_{10}HgI_2N_4O_3$, M_r = 724.64 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 4.5942(1), b = 28.1575(9), c = 13.2262(3) Å, β = 93.104(2)°, V = 1708.45(8) Å^3, Z = 4, ρ = 2.817 g cm^{-3}, μ(Mo-Kα) = 12.641 mm^{-1}, reflections: 17349 collected, 6625 unique, R_{int} = 0.058, R_1(all) = 0.0574, wR_2(all) = 0.1120, S = 0.885.

Theoretical methods

The non-covalent interactions were analyzed energetically using Gaussian-16[7] at the PBE0-D3/def2-TZVP level of theory. The binding energies have been corrected using the Boys and Bernardi counterpoise method.[8] The Grimme's D3 dispersion correction has also been used in the calculations.[9] To evaluate interactions in the solid state, the crystallographic coordinates were used and only the position of the hydrogen bonds has been optimized. This methodology and level of theory have previously been used to analyze non-covalent interactions in the solid state.[10,11] The interaction energies were estimated by calculating the difference between the energies of the isolated monomers and the ones of their assembly. The QTAIM analysis[12] and NCIplot index[13] have been computed at the same level of theory by means of the AIMAll program.[14]

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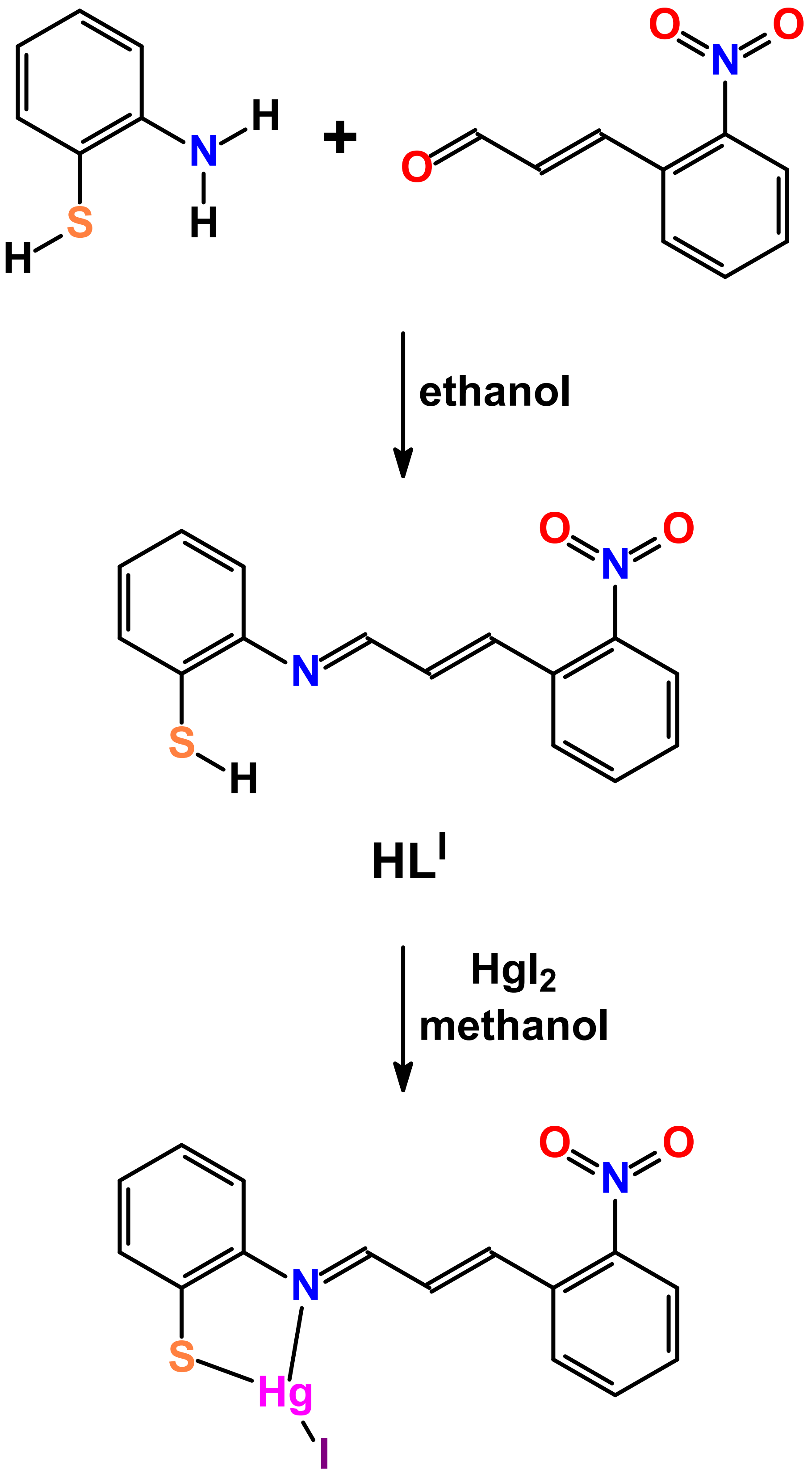
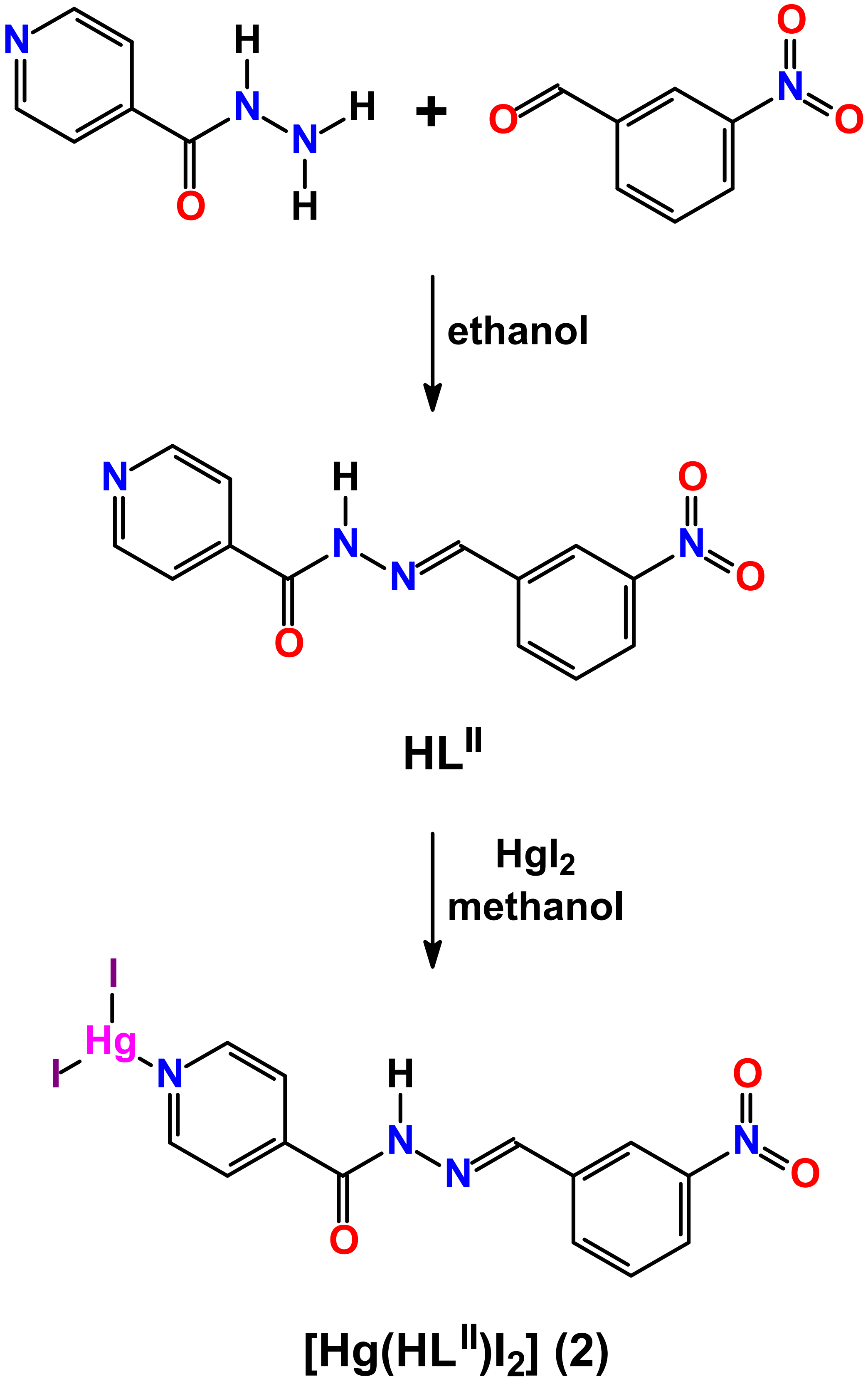


HL^I

$[Hg(L^I)I]_n$ (1)

Scheme S1. Synthesis of **1**.



Scheme S2. Synthesis of **2**.

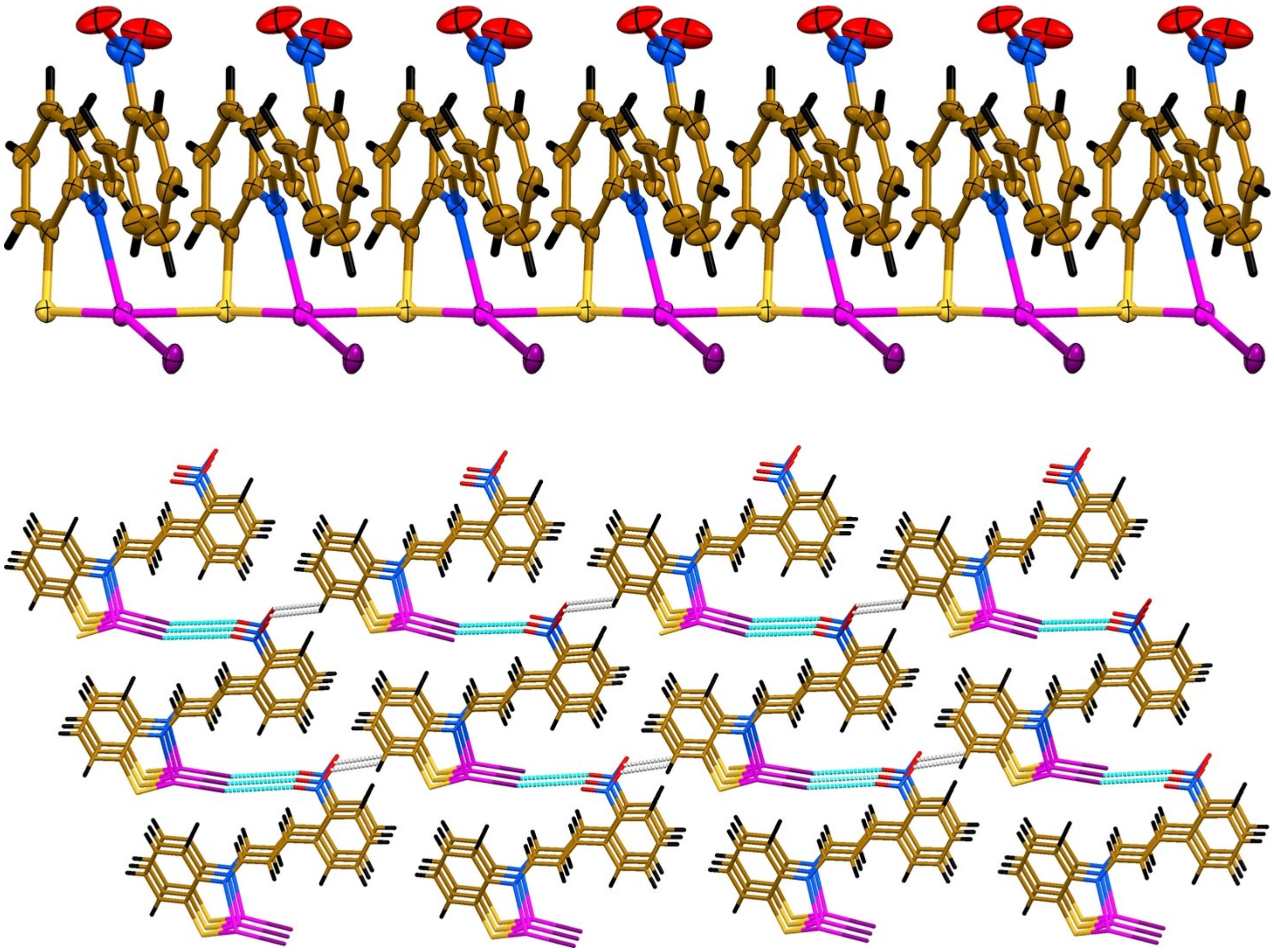


Fig. S1. (top) A 1D polymeric chain in the crystal structure of **1**. (bottom) A 3D supramolecular framework in the crystal structure of **1**, built by the N=O···I halogen bonds and C–H···O interactions. Color codes: H = black, C = gold, N = blue, O = red, S = yellow, I = purple, Hg = magenta; cyan dashed line = N=O···I halogen bond, grey dashed line = C–H···O interaction.

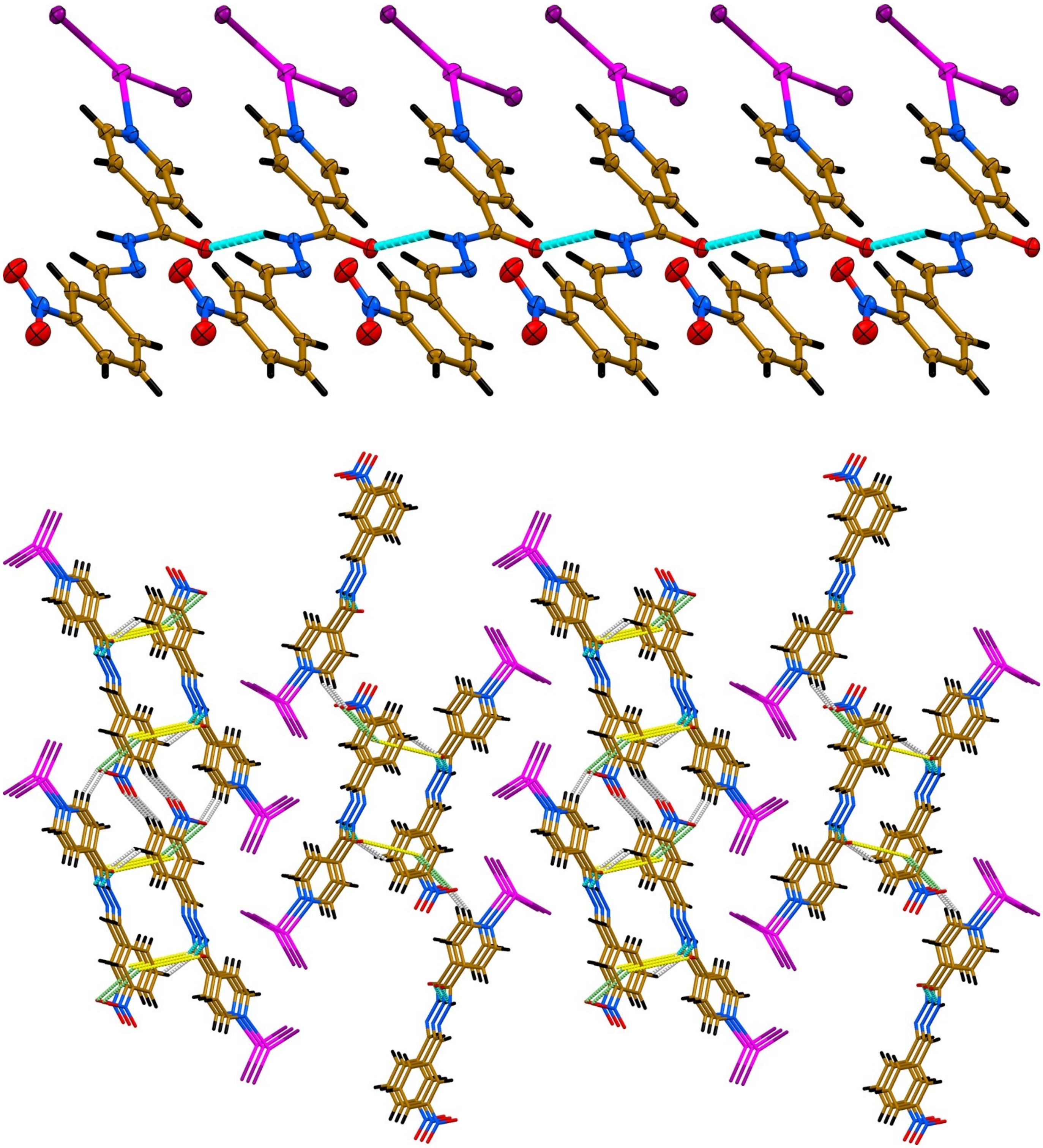


Fig. S2. (top) A 1D supramolecular polymeric chain in the crystal structure of **2**, built by the N–H···O hydrogen bonds. (bottom) A supramolecular framework in the crystal structure of **2**, built by the N–H···O hydrogen bonds, C–H···O, C=O···$C_6H_4(NO_2)$ and N=O···$C_6H_4(NO_2)$ interactions. Color codes: H = black, C = gold, N = blue, O = red, I = purple, Hg = magenta; cyan dashed line = N–H···O hydrogen bond, grey dashed line = C–H···O interaction, yellow dashed line = C=O···$C_6H_4(NO_2)$ interaction, green dashed line = N=O···$C_6H_4(NO_2)$ interaction.

Table S1 Selected bond lengths (Å) and bond and torsion angles (°) in the crystal structure of **1**.

Bond lengths[a]			
Hg–N1	2.452(13)	C1–S1	1.788(17)
Hg–S1	2.428(4)	N1–C6	1.41(2)
Hg–S1_b$^{\#1}$	2.803(4)	N1–C7	1.29(2)
Hg–I1	2.6274(17)	N2–C15	1.47(2)
Hg···Hg_a$^{\#2}$	3.9611(9)	N2–O1	1.19(3)
Hg···Hg_b$^{\#1}$	3.9611(9)	N2–O2	1.20(2)
Bond angles[a]			
N1–Hg–S1	78.1(3)	Hg–N1–C6	112.0(10)
N1–Hg–S1_b$^{\#1}$	99.2(3)	Hg–N1–C7	126.6(12)
N1–Hg–I1	118.9(3)	Hg–S1–C1	99.6(6)
I1–Hg–S1	153.41(11)	Hg–S1–Hg_a$^{\#2}$	98.19(14)
I1–Hg–S1_b$^{\#1}$	98.84(9)	C1–S1–Hg_a$^{\#2}$	101.3(6)
S1–Hg–S1_b$^{\#1}$	98.19(14)		
Dihedral angles			
C1–C6–N1–C7	–146.5(17)	C8–C9–C10–C11	–23(3)
C5–C6–N1–C7	37(2)	C8–C9–C10–C15	159(2)
C_6H_4(S)···$C_6H_4(NO_2)$[b]	16.4(9)		

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*, 1 + *y*, *z*; #2 *x*, –1 + *y*, *z*.

[b] Dihedral angle between the least-square planes, formed by the benzene rings of the same ligand **L**$^{\text{I}}$.

Table S2 π···π interaction lengths (Å) and angles (°) for **1**.[a,b]

Cg(*I*)···Cg(*J*)	*d*[Cg(*I*)···Cg(*J*)]	α	β	γ	slippage
$C_6H_4(S)\cdots C_6H_4(S)^{\#1}$	3.961(11)	0	27.2	27.2	1.812
$C_6H_4(S)\cdots C_6H_4(S)^{\#2}$	3.961(11)	0	27.2	27.2	1.812
$C_6H_4(NO_2)\cdots C_6H_4(NO_2)^{\#1}$	3.961(12)	0	20.7	20.7	1.398
$C_6H_4(NO_2)\cdots C_6H_4(NO_2)^{\#2}$	3.961(12)	0	20.7	20.7	1.398

[a] Cg(*I*)···Cg(*J*): distance between ring centroids; α: dihedral angle between planes Cg(*I*) and Cg(*J*); β: angle Cg(*I*) → Cg(*J*) vector and normal to plane *I*; γ: angle Cg(*I*) → Cg(*J*) vector and normal to plane *J*; slippage: distance between Cg(*I*) and perpendicular projection of Cg(*J*) on ring *I*.

[b] Symmetry transformations used to generate equivalent atoms: #1 x, $-1 + y$, z; #2 x, $1 + y$, z.

Table S3 Non-covalent bond lengths (Å) and angles (°) for **1** and **2**.

Complex	D–X···A	*d*(D–X)	*d*(X···A)	*d*(D···A)	∠(DXA)
1[a]	C2–H2···O2[#1]	0.95	2.52	3.19(2)	127
	N2=O1···I1[#2]	1.19(3)	3.346(18)	4.50(2)	164.3(14)
2[b]	N2–H2A···O1[#1]	0.84(6)	2.02(5)	2.752(5)	146(5)
	C5–H5···O2[#2]	0.93	2.39	3.228(7)	150
	C11–H11···O3[#3]	0.93	2.42	3.231(7)	146
	C12–H12···O1[#4]	0.93	2.48	3.275(7)	143
	C6=O1···$C_6H_4(NO_2)$[#5]	1.225(6)	3.907(5)	3.987(5)	84.8(3)
	N4=O2···$C_6H_4(NO_2)$[#1]	1.230(7)	3.567(5)	3.801(5)	91.4(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 1/2 + *x*, 1/2 – *y*, 1/2 + *z*; #2 *x*, 2 – *y*, –1/2 + *z*.

[b] Symmetry transformations used to generate equivalent atoms: #1 1 + *x*, *y*, *z*; #2 –1 + *x*, *y*, 1 + *z*; #3 1 – *x*, 1 – *y*, –*z*; #4 –*x*, 1 – *y*, 1 – *z*; #5 1 – *x*, 1 – *y*, 1 – *z*.

Table S4 Selected bond lengths (Å) and bond and torsion angles (°) in the crystal structure of **2**.

Bond lengths[a]			
Hg1–N1	2.412(4)	N2–N3	1.362(6)
Hg1–I1	2.6217(5)	N2–C6	1.350(6)
Hg1–I2	2.6430(6)	N3–C7	1.282(7)
Hg1···Hg1_a[#1]	4.5942(4)	N4–C10	1.471(7)
Hg1···Hg1_b[#2]	4.5942(4)	N4–O2	1.230(7)
C6–O1	1.225(6)	N4–O3	1.215(6)
Bond angles			
N1–Hg1–I1	104.81(10)	Hg1–N1–C1	121.3(4)
N1–Hg1–I2	101.41(10)	Hg1–N1–C5	120.1(3)
I1–Hg1–I2	153.62(2)		
Dihedral angles			
C2–C3–C6–N2	28.3(7)	C9–C8–C7–N3	157.7(5)
C2–C3–C6–O1	–150.3(5)	C13–C8–C7–N3	–21.1(8)
C4–C3–C6–N2	–155.4(5)	Py···$C_6H_4(NO_2)$[b]	2.3(2)
C4–C3–C6–O1	26.0(7)		

[a] Symmetry transformations used to generate equivalent atoms: #1 –1 + *x*, *y*, *z*; #2 1 + *x*, *y*, *z*.

[b] Dihedral angle between the least-square planes, formed by the benzene rings of the same ligand **HL^{II}**.