Supporting Information for

Metal-Binding Studies of Linear Rigid-Axle [2]Pseudorotaxanes with In-Situ Generated Anionic Metal Halide Complexes

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Details of the crystal growing experiments.

1$(ZnCl_3)_2 \cdot H_2O \cdot 0.5CH_3OH$. Dark blue crystals were obtained after two weeks from a solution of $ZnCl_2$ (0.8 mg, 0.0057 mmol) in CH_3OH (1.8 mL) layered over a solution of PyBP·$[NO_3]_2$ (5 mg, 0.011 mmol) and BN32C8 (5.5 mg, 0.010 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.8 mL).

2$(ZnCl_3)_2$. Dark blue crystals were obtained after two weeks from a solution of $ZnCl_2$ (0.8 mg, 0.0057 mmol) in CH_3OH (1.5 mL) layered over a solution of PyBP·$[NO_3]_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL).

1$(ZnBr_3)_2 \cdot H_2O$. Dark blue crystals were obtained after two weeks from a solution of $ZnBr_2$ (1.3 mg, 0.0057 mmol) in CH_3OH (1.5 mL) layered over a solution of PyBP·$[NO_3]_2$ (2.5 mg, 0.0057 mmol) and BN32C8 (2.8 mg, 0.0050 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL).

2$(ZnBr_3)_2$. Dark blue crystals were obtained after two weeks from a solution of $ZnBr_2$ (1.3 mg, 0.0057 mmol) in CH_3OH (1.8 mL) layered over a solution of PyBP·$[NO_3]_2$ (1.3 mg, 0.0028 mmol) and BN38C10 (1.6 mg, 0.0025 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (0.75 mL).

2·$[CdBr_4] \cdot 0.5CHCl_3 \cdot 1.5CH_3OH \cdot 0.5H_2O$. Brown-yellow crystals were obtained after two weeks from a solution of $CdBr_2$ (3.9 mg, 0.0114 mmol) in CH_3OH (1.5 mL) layered over a 1:1 mixture of PyBP·$[NO_3]_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL).

3·$[CdBr_4]$. Dark maroon-red crystals were obtained after two weeks from a solution of $CdBr_2$ (3.1 mg, 0.0091 mmol) in CH_3OH (1.5 mL) layered over a 1:1 mixture of PyBP·$[NO_3]_2$ (2.0 mg, 0.0046 mmol) and BPP34C10 (2.0 mg, 0.0037 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL).

3·[CdI_4]. Dark maroon-red crystals were obtained after two weeks from a solution of CdI_2 (4.2 mg, 0.0114 mmol) in CH_3OH (1.5 mL) layered over a solution of PyBP·[NO_3]$_2$ (2.5 mg, 0.0057 mmol) and BPP34C10 (2.5 mg, 0.0047 mmol) in CH_3OH (1.5 mL).

1·[Hg_2Br_6]. A solution of $HgBr_2$ (4.2 mg, 0.0115 mmol) in CH_3OH (1.5 mL) was layered over a solution of PyBP·[NO_3]$_2$ (2.5 mg, 0.0057 mmol) and BN32C8 (2.8mg, 0.0057 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL). Very small, greenish-blue crystals formed after one week (not suitable for X-ray diffraction). Upon standing, the greenish-blue crystals slowly re-dissolved, while larger (X-ray quality), dark blue/red dichroic crystals grew over the next two weeks.

2(Hg_2Br_6)$_2$·PyBP·CH_3OH. Dark violet/yellow dichroic crystals were obtained after three weeks from a solution of $HgBr_2$ (4.2 mg, 0.0114 mmol) in CH_3OH (1.5 mL) layered over a solution of PyBP·[NO_3]$_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2mg, 0.0051 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL).

1·[Hg_2I_6]. A 2:3 mixture of CH_3OH and $CHCl_3$ was layered over a solution of PyBP·[NO_3]$_2$ (2.0 mg, 0.0046 mmol) and BN32C8 (2.8 mg, 0.0057 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL), followed by a third layer of $HgBr_2$ (4.2 mg, 0.0092 mmol) in CH_3OH (1.5 mL). No crystals formed after one week in the freezer (−20 °C). Upon warming to room temperature, dark blue/yellow dichroic, X-ray quality crystals were obtained after two weeks.

2·[Hg_2I_6]·3CH_3OH. A 2:3 mixture of CH_3OH and $CHCl_3$ was layered over a solution of PyBP·[NO_3]$_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2mg, 0.0051 mmol) in a 1:1 mixture of $CH_3OH/CHCl_3$ (1.5 mL), followed by a third layer of HgI_2 (5.2 mg, 0.0114 mmol) in CH_3OH (1.5 mL). The vial was kept in the freezer at −20 °C for one week. White needles crystallized on the bottom of the vial. Upon warming to room temperature (30-40 min), the white crystalline material re-dissolved. After two weeks at room temperature, dark green/brown dichroic, X-ray quality crystals were obtained.

[PyBP][CdI_4]. Orange-red crystals were obtained after two weeks from slow diffusion of a three-layer solution setup. 0.8 mL $CH_3OH/CHCl_3$ (2:3) solvent mixture was layered over a solution of PyBP·[NO_3]$_2$ (2.0 mg, 0.0057 mmol) and BN38C10 (2.6 mg, 0.0040 mmol) in 1.5 mL $CHCl_3/CH_3OH$ (1:1), and a third layer of CdI_2 (3.6 mg, 0.0091 mmol) in CH_3OH (1.5 mL) was added on top.

[PyBP](ZnI_3)$_2$·3CH_3OH. Dark red crystals were obtained after five days from a solution of ZnI_2 (3.6 mg, 0.0113 mmol) and KI (1.9 mg, 0.0113 mmol) in CH_3OH (1.5 mL) layered over a solution of PyBP·[NO_3]$_2$ (2.5 mg, 0.0057 mmol) and BPP34C10 (3.1 mg, 0.0057 mmol) in CH_3OH (1.5 mL).

Table S1. Products of the crystal growing setups with MX_2/KX.

MX_2/KX	**[2]Pseudorotaxane**					
	$[PyBP/BPP34C10]^{2+}$		$[PyBP/BN38C10]^{2+}$		$[PyBP/BN32C8]^{2+}$	
	solution	precipitate/ crystal	solution	precipitate/ crystal	solution	precipitate/crystal
$ZnCl_2$/KCl	Colorless solution	Light yellow precipitate	Light yellow solution	Light yellow precipitate	Light yellow solution	Colorless crystals and light yellow precipitate
$ZnBr_2$/KBr	Colorless solution	Light brown crystalline solid	Colorless solution	Light yellowish-green solid	Light blue solution	Colorless crystals and light yellow precipitate
ZnI_2/KI	Light yellow solution	Red crystals	Light yellow solution	Red crystalline aggregates	Light yellow solution	Dark blue precipitate
$CdCl_2$/KCl	Colorless solution	Light yellowish-brown precipitate	Colorless solution	Light yellowish-brown solid	Colorless solution	Light yellowish brown solid
$CdBr_2$/KBr	Colorless solution	Light yellow precipitate	Colorless solution	Light yellow precipitate	Colorless solution	Light yellow precipitate
CdI_2/KI	Bright yellow solution	Yellow crystals	Bright yellow solution	Yellow crystals	Bright yellow solution	Yellow crystals
$HgCl_2$/KCl	Light yellow solution	Light golden-brown needle shaped crystals	Light yellow solution	Light golden-brown needle shaped crystals	Light yellow solution	Light golden-brown needle shaped crystals
$HgBr_2$/KBr	Colorless solution	Light yellow solid	Colorless solution	Light yellow solid	Colorless solution	Light yellow solid
HgI_2/KI	Light yellow solution	Maroon-red precipitate	Light yellow solution	Maroon-red precipitate	Light yellow solution	Three different solid aggregates, orange, red and dark-blue

Table S2. Identity of the solid crystallization products with MX_2/KX, based on ^{1}H NMR analysis

MX_2/KX	**[2]Pseudorotaxane**		
	$[PyBP/BPP34C10]^{2+}$	$[PyBP/BN38C10]^{2+}$	$[PyBP/BN32C8]^{2+}$
$ZnCl_2$/KCl	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8
$ZnBr_2$/KBr	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8
ZnI_2/KI	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8
$CdCl_2$/KCl	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8
$CdBr_2$/KBr	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN38C10	$[PyBP][NO_3]_2$ and BN32C8
CdI_2/KI	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN38C10	$[PyBP][NO_3]_2$ and BN32C8
$HgCl_2$/KCl	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8
$HgBr_2$/KBr	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8
HgI_2/KI	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$	$[PyBP][NO_3]_2$ and BN32C8

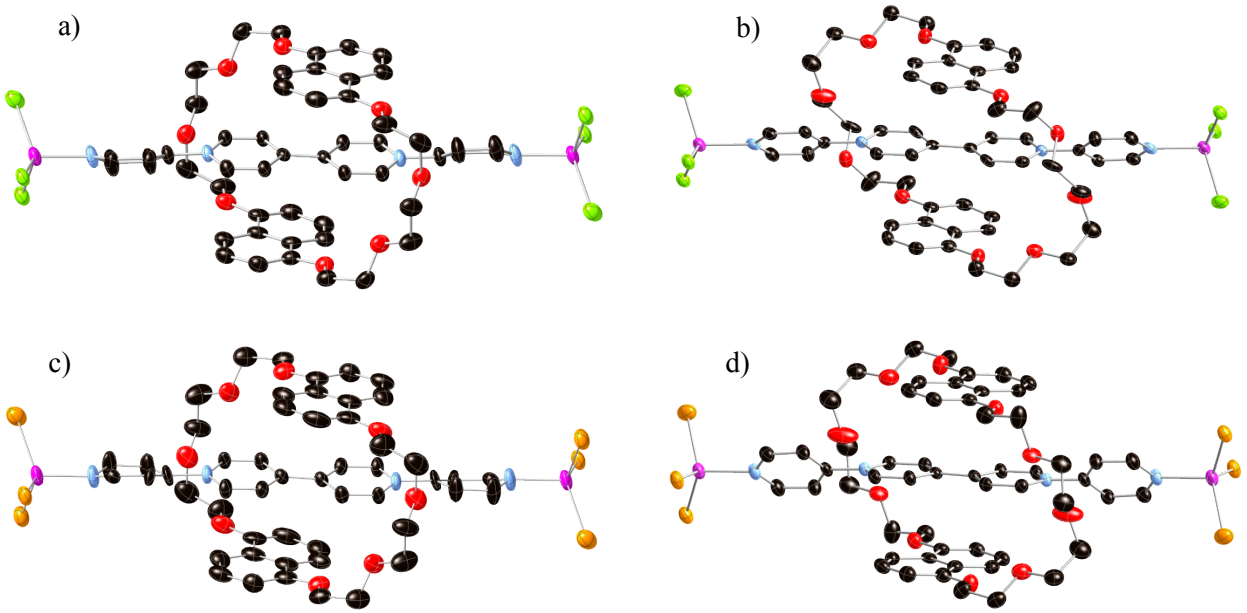

Figure S1. Thermal ellipsoid plots (50%) for a) **1**$(ZnCl_3)_2$, b) **2**$(ZnCl_3)_2$, c) **1**$(ZnBr_3)_2 \cdot CH_3OH$ and d) **2**$(ZnBr_3)_2$. H-atoms and solvent molecules are omitted for clarity. Color code: Zn−magenta; Cl−lime green; Br−orange; O−red; N−light blue; C−black.

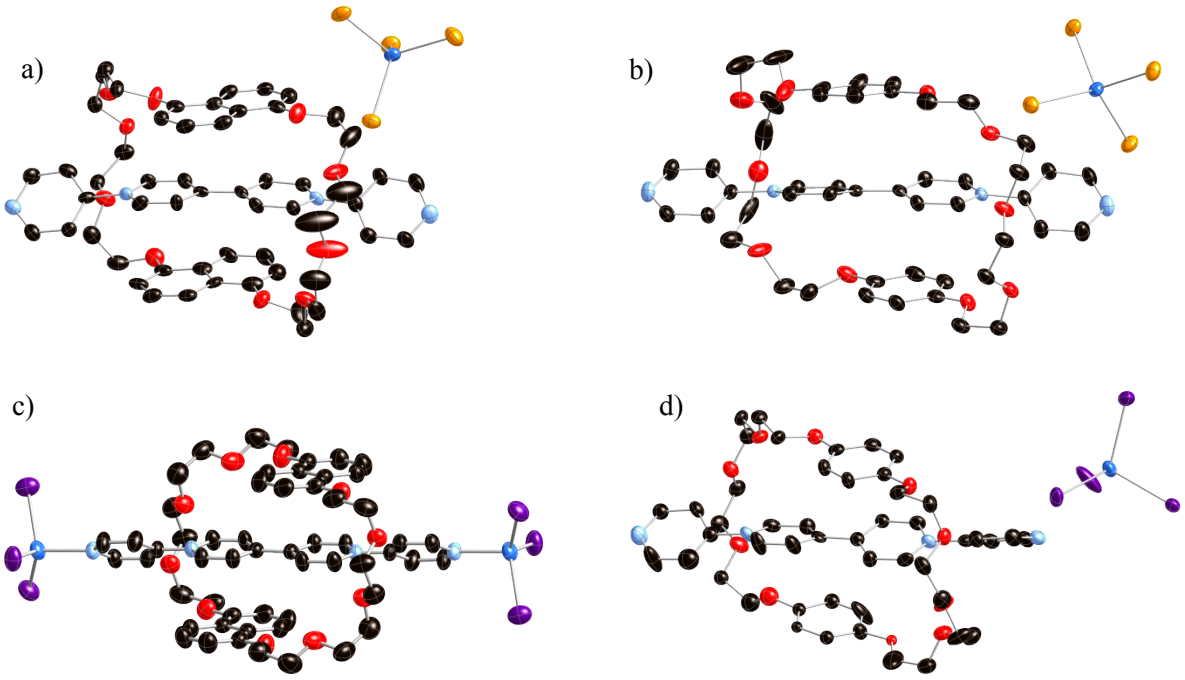

Figure S2. Thermal ellipsoid plots (50%) for **2**·[$CdBr_4$]·0.5$CHCl_3$·1.5CH_3OH·0.5H_2O, b) **3**·[$CdBr_4$], c) **2**$(CdI_3)_2$·2CH_3OH and d) **3**·[CdI_4]. H-atoms and solvent molecules are omitted for clarity. Color code: Cd−blue; Br−orange; I−violet; O−red; N−light blue; C−black.

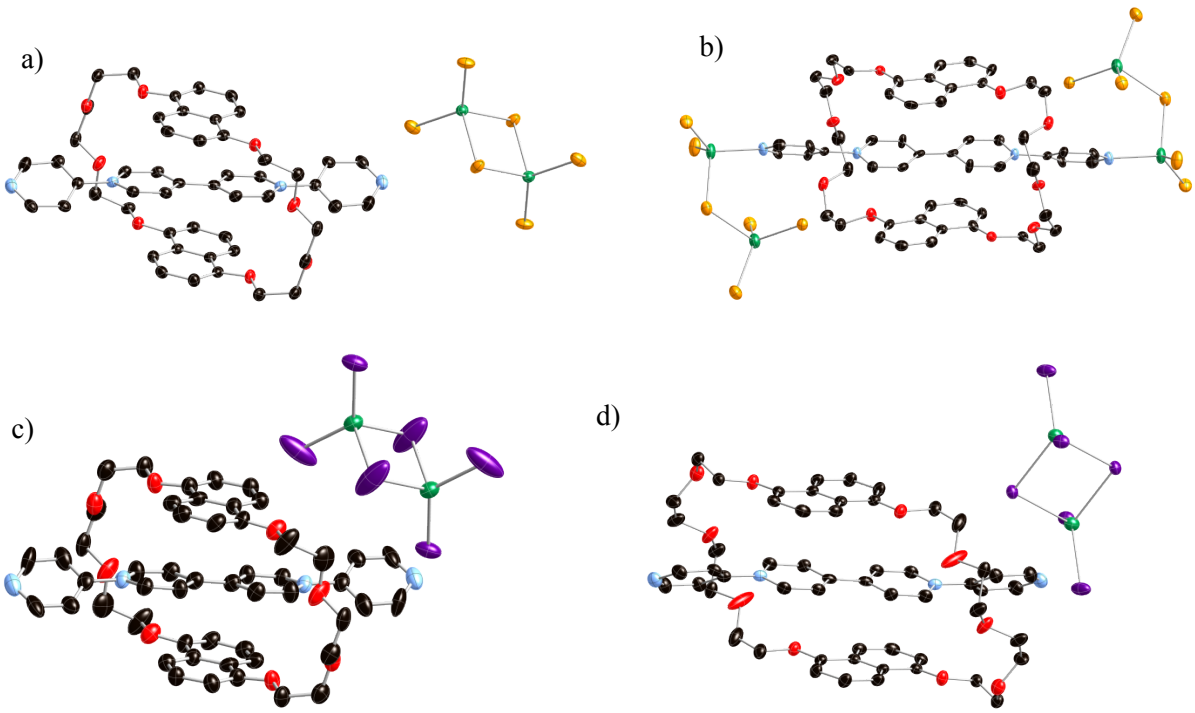

Figure S3. Thermal ellipsoid plots (50%) for a) **1**·[Hg_2Br_6], b) **2**$(Hg_2Br_6)_2$·PyBP·CH_3OH, c) **1**·[Hg_2I_6] and d) **2**·[Hg_2I_6]·3CH_3OH. H-atoms and solvent molecules are omitted for clarity. Color code: Hg−green; Br−orange; I−violet; O−red; N−light blue; C−black.

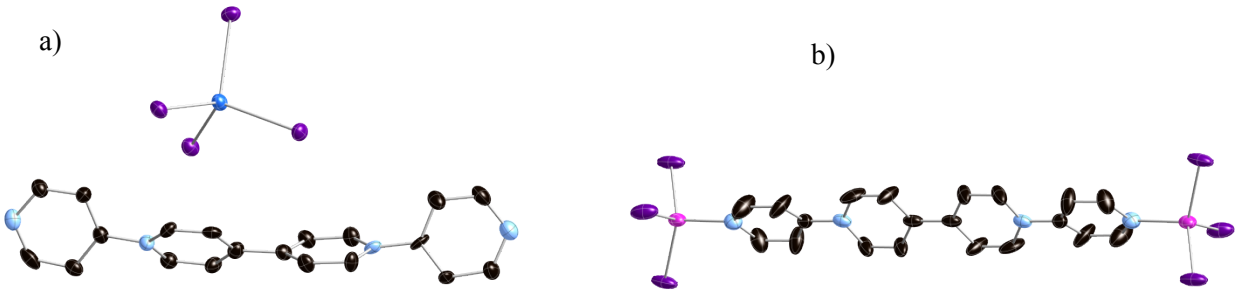

Figure S4. Thermal ellipsoid plots (50%) for a) PyBP·[CdI_4] and b) PyBP$(ZnI_3)_2$·$3CH_3OH$. H-atoms and solvent molecules are omitted for clarity. Color code: Cd−blue; Zn−magenta; I−violet; N−light blue; C−black; H−pink.

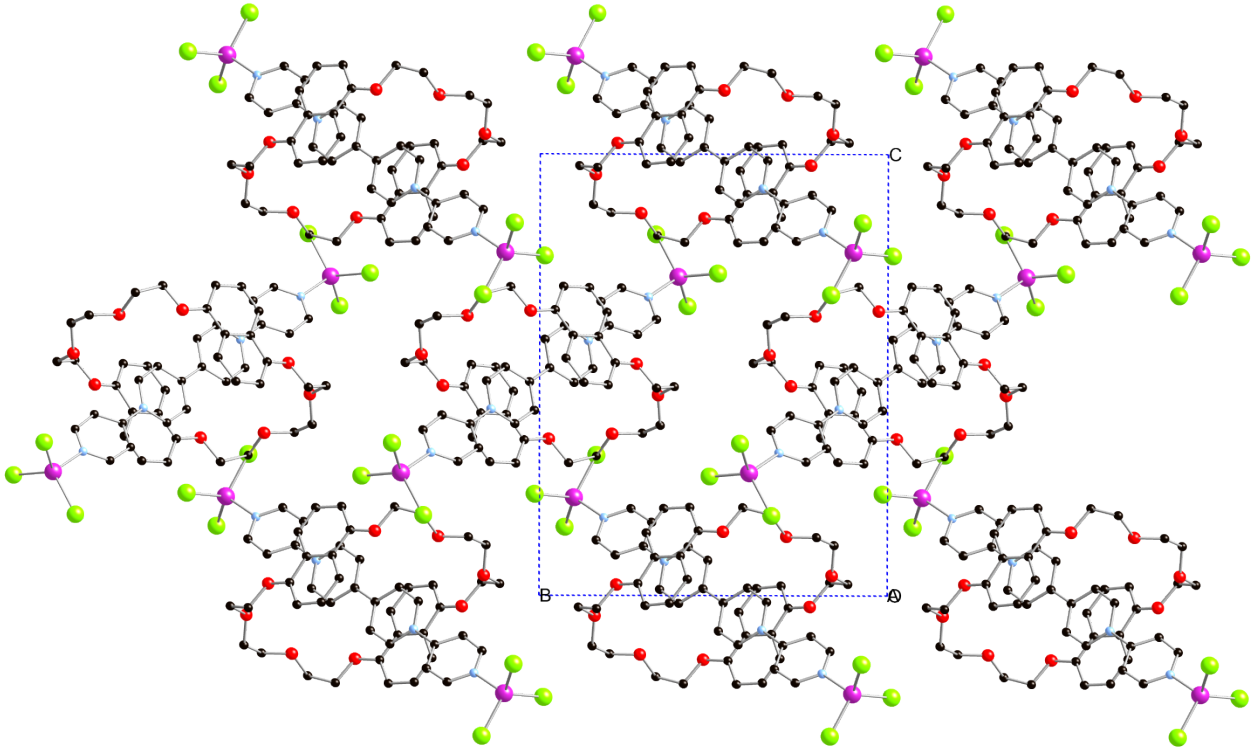

Figure S5. Packing diagram of **1**$(ZnCl_3)_2$. H-atoms are omitted for clarity. Color code: Zn−magenta; Cl−lime green; O−red; N−light blue; C−black.

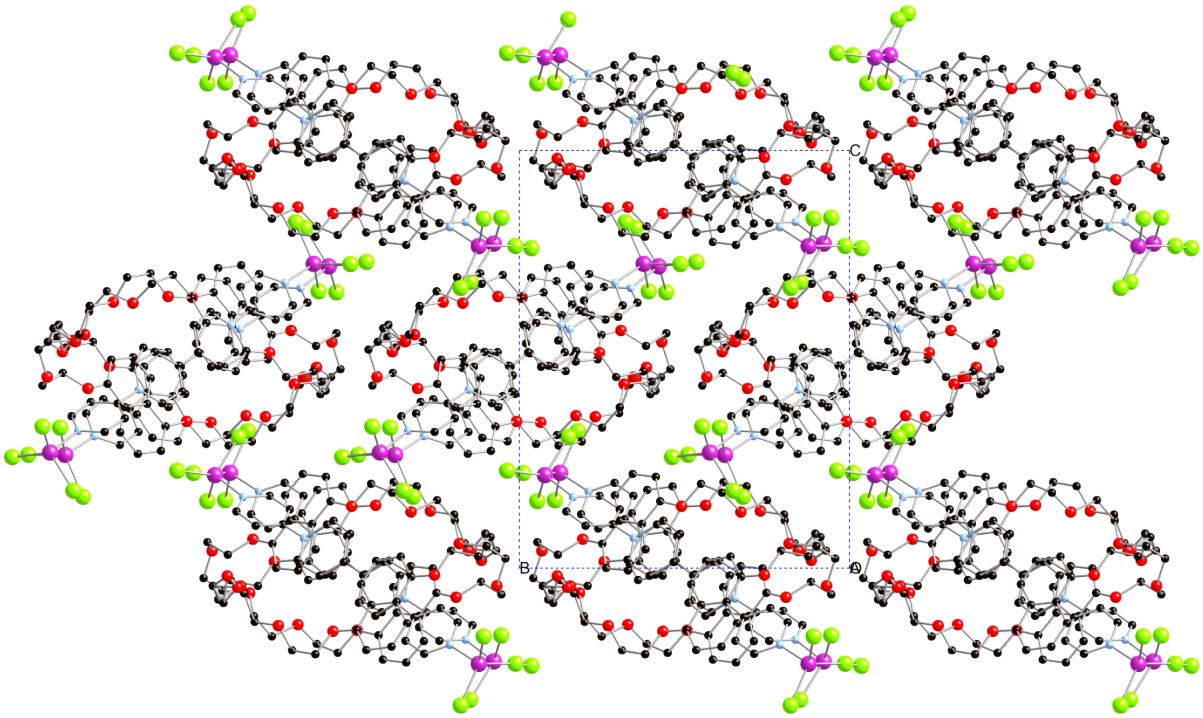

Figure S6. Packing diagram of **2**$(ZnCl_3)_2$. H-atoms are omitted for clarity. Color code: Zn−magenta; Cl−lime green; O−red; N−light blue; C−black.

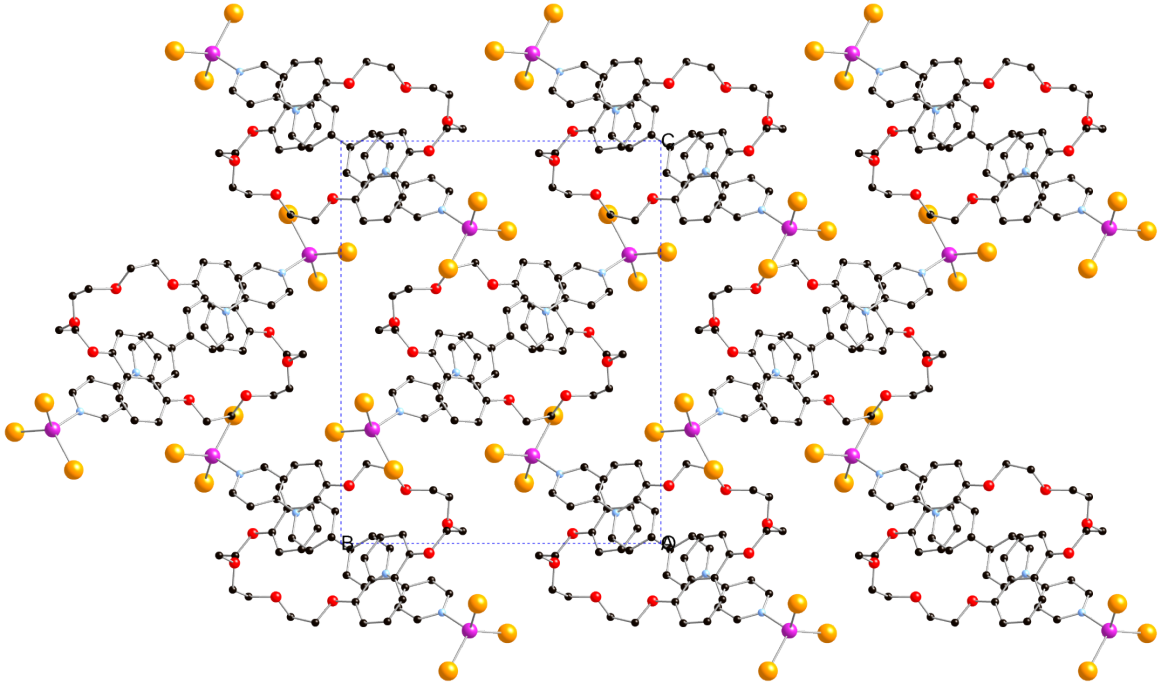

Figure S7. Packing diagram of **1**$(ZnBr_3)_2 \cdot CH_3OH$. H-atoms and solvent molecules are omitted for clarity. Color code: Zn−magenta; Br−orange; O−red; N−light blue; C−black.

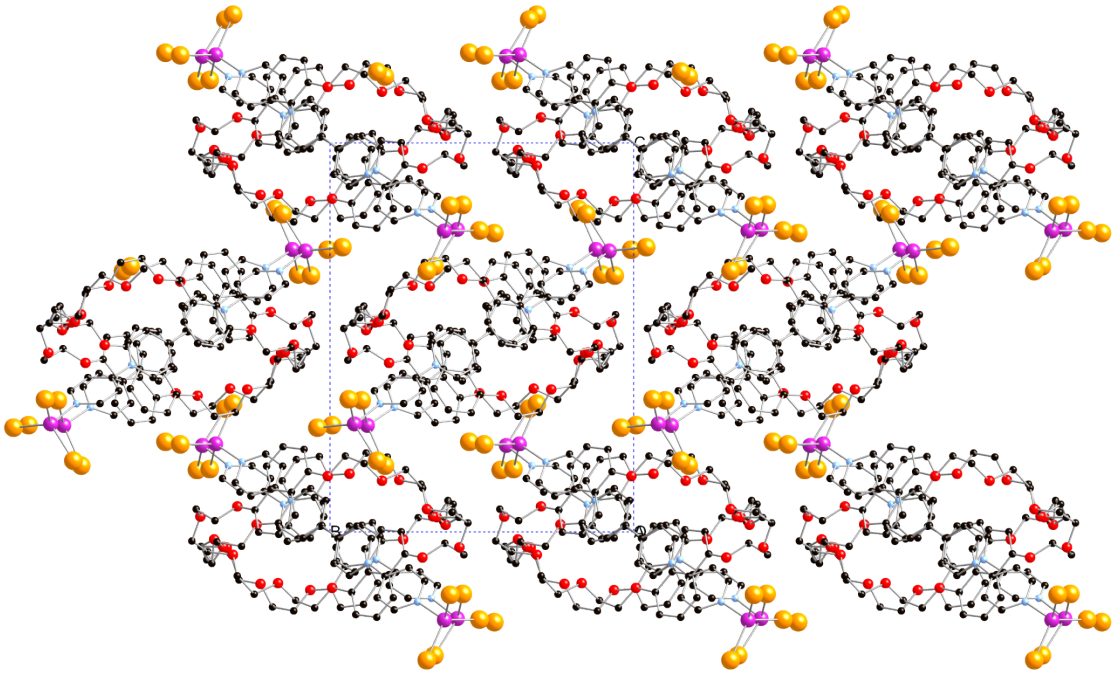

Figure S8. Packing diagram of **2**$(ZnBr_3)_2$. H-atoms are omitted for clarity. Color code: Zn−magenta; Br−orange; O−red; N−light blue; C−black.

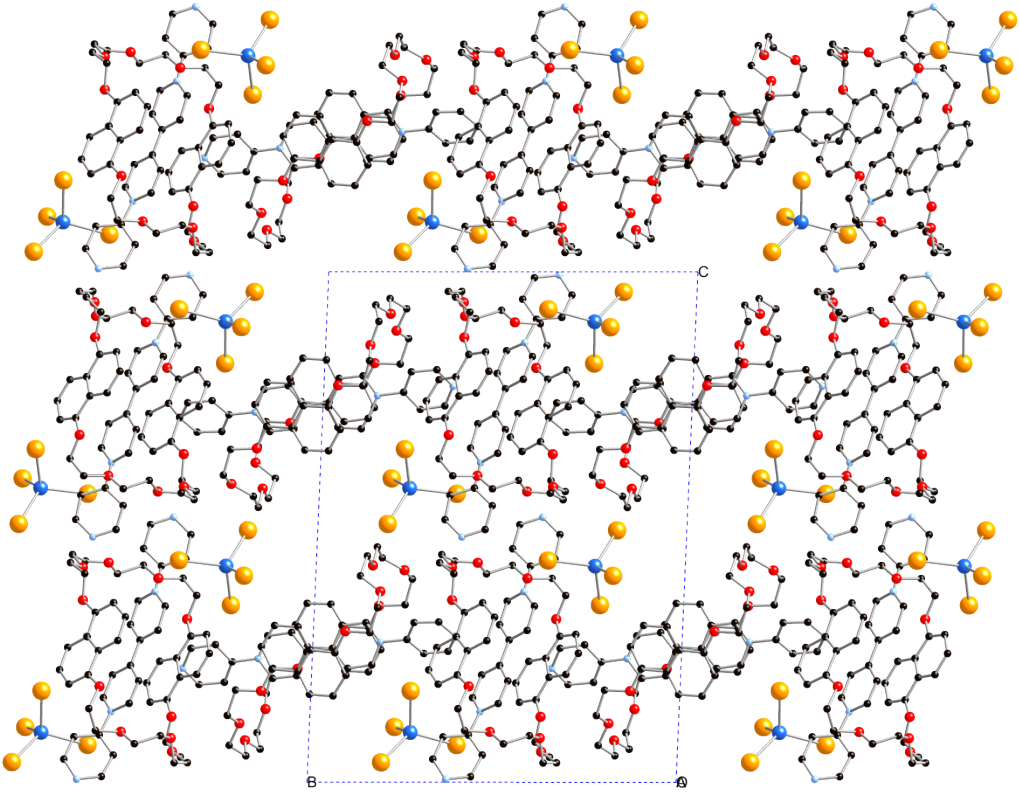

Figure S9. Packing diagram of **2**·$[CdBr_4]$·$0.5CHCl_3$·$1.5CH_3OH$·$0.5H_2O$. H-atoms and solvent molecules are omitted for clarity. Color code: Cd−blue; Br−orange; O−red; N−light blue; C−black.

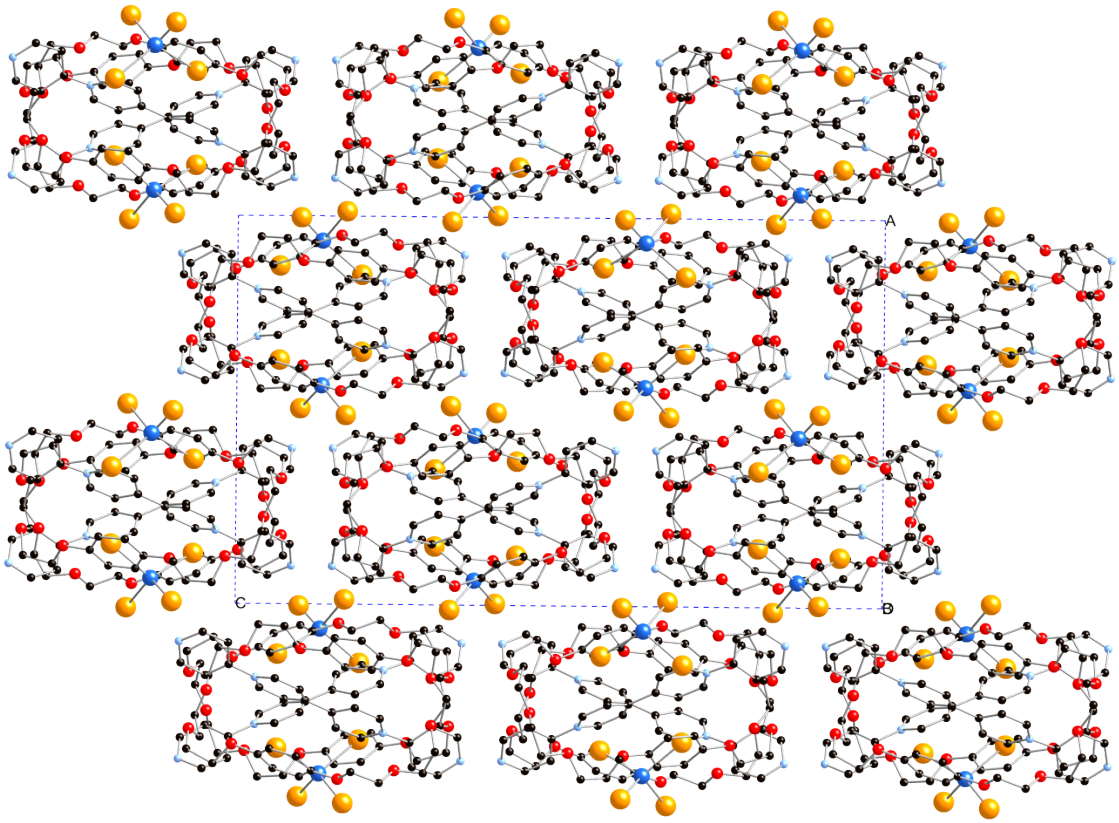

Figure S10. Packing diagram of **3**·[$CdBr_4$]. H-atoms are omitted for clarity. Color code: Cd−blue; Br−orange; O−red; N−light blue; C−black.

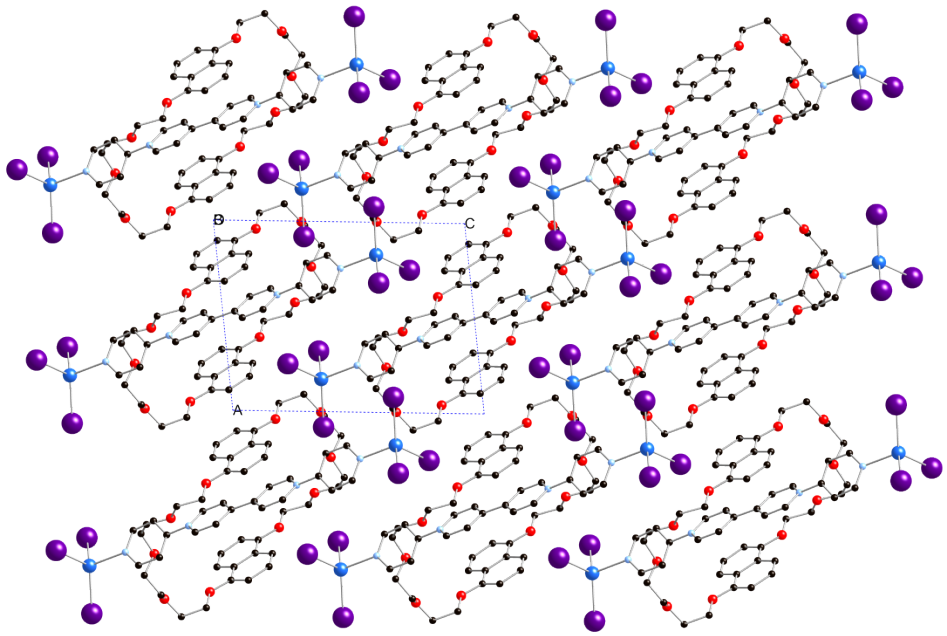

Figure S11. Packing diagram of **2**$(CdI_3)_2$·$2CH_3OH$. H-atoms and solvent molecules are omitted for clarity. Color code: Cd−blue; I−violet; O−red; N−light blue; C−black.

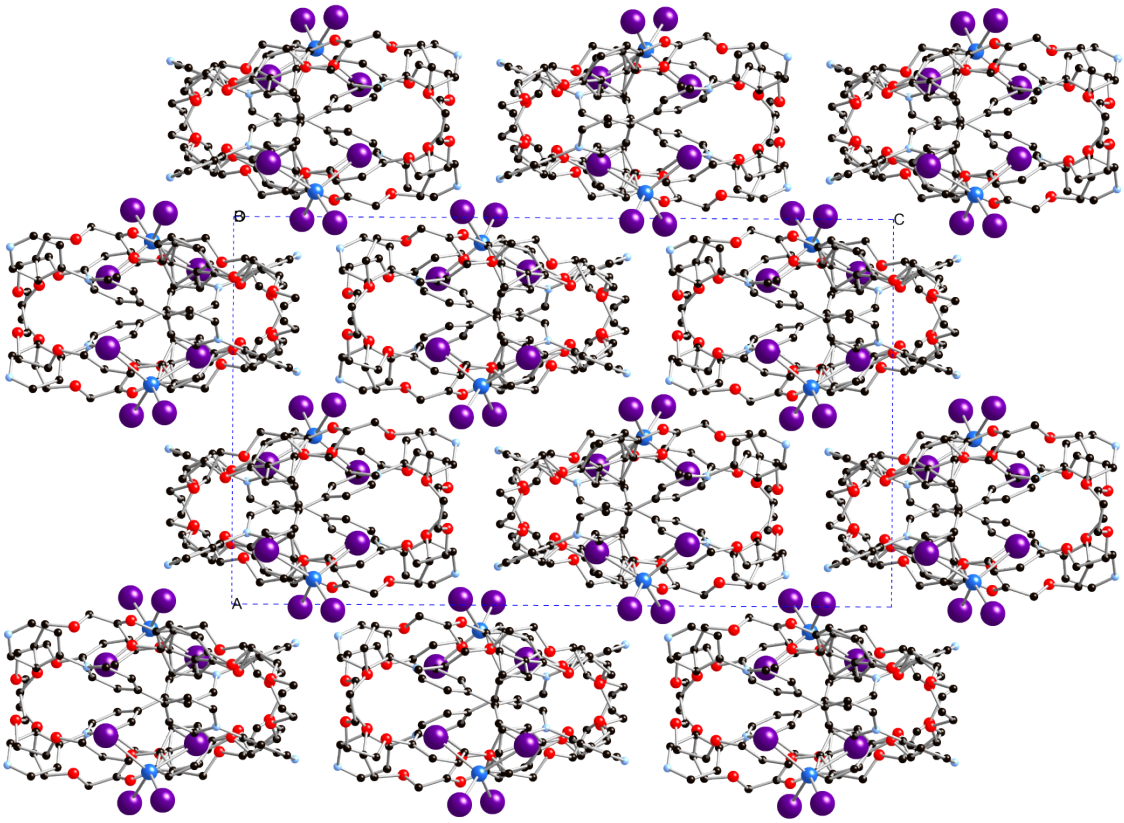

Figure S12. Packing diagram of **3**·[CdI_4]. H-atoms are omitted for clarity. Color code: Cd−blue; I−violet; O−red; N−light blue; C−black.

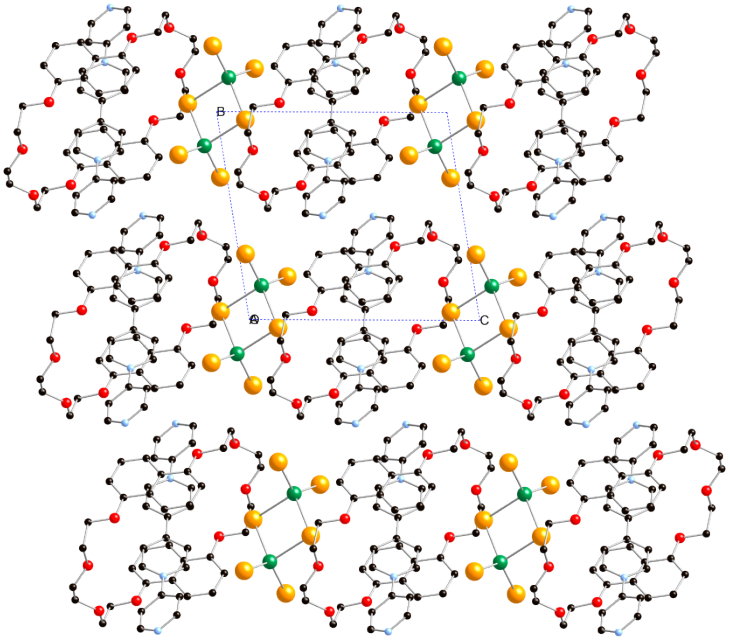

Figure S13. Packing diagram of **1**·[Hg_2Br_6]. H-atoms are omitted for clarity. Color code: Hg−green; Br−orange; O−red; N−light blue; C−black.

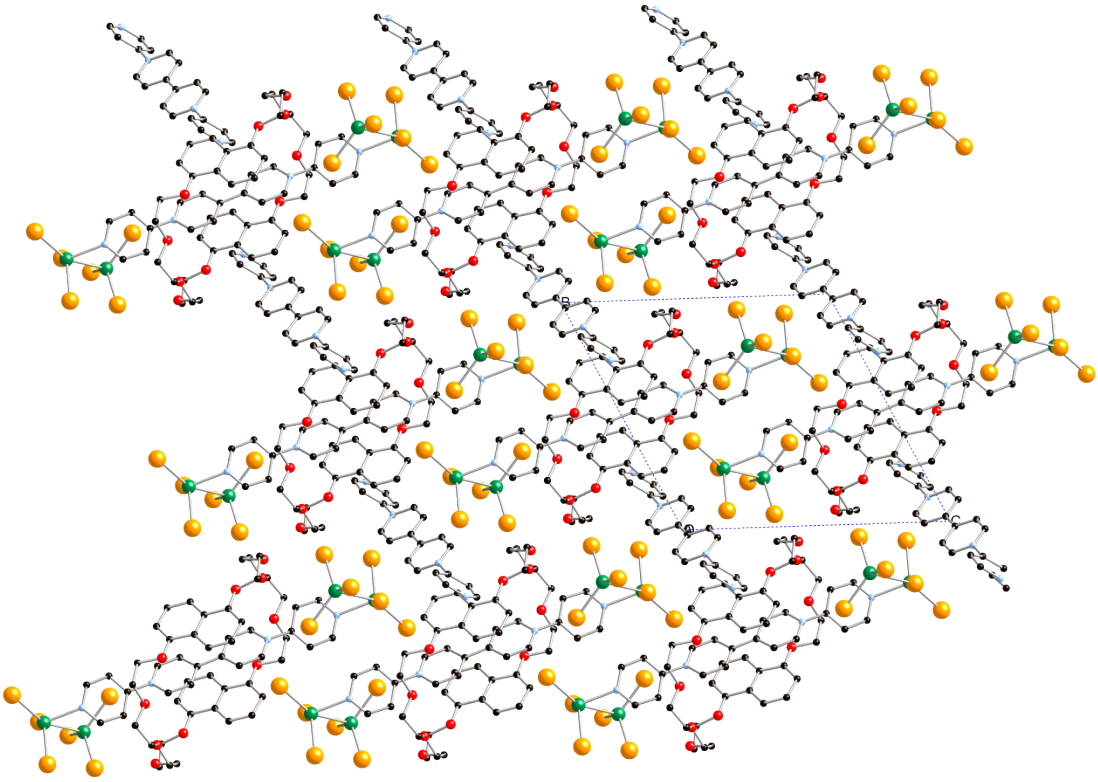

Figure S14. Packing diagram of **2**$(Hg_2Br_6)_2$·PyBP·CH_3OH. H-atoms and solvent molecules are omitted for clarity. Color code: Hg−green; Br−orange; O−red; N−light blue; C−black.

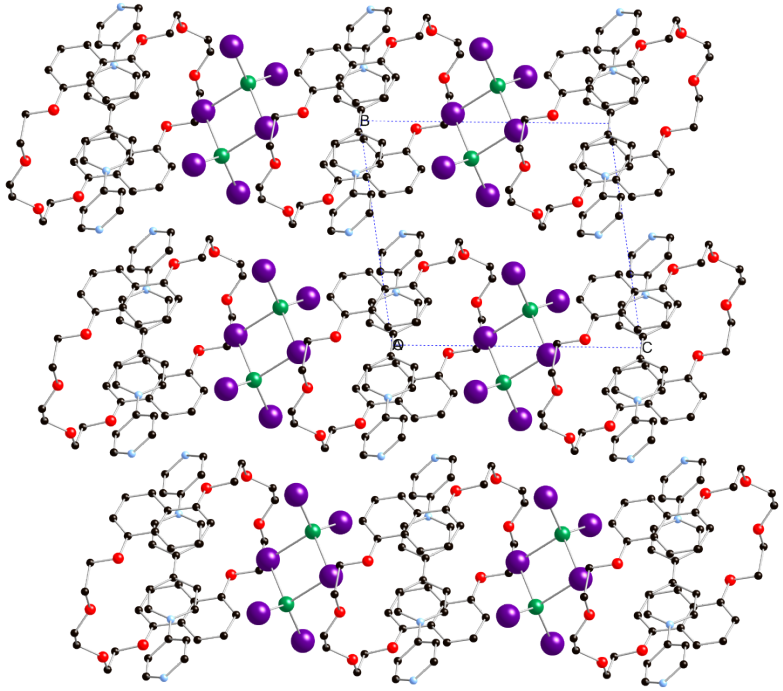

Figure S15. Packing diagram of **1**·$[Hg_2I_6]$. H-atoms are omitted for clarity. Color code: Hg−green; I−violet; O−red; N−light blue; C−black.

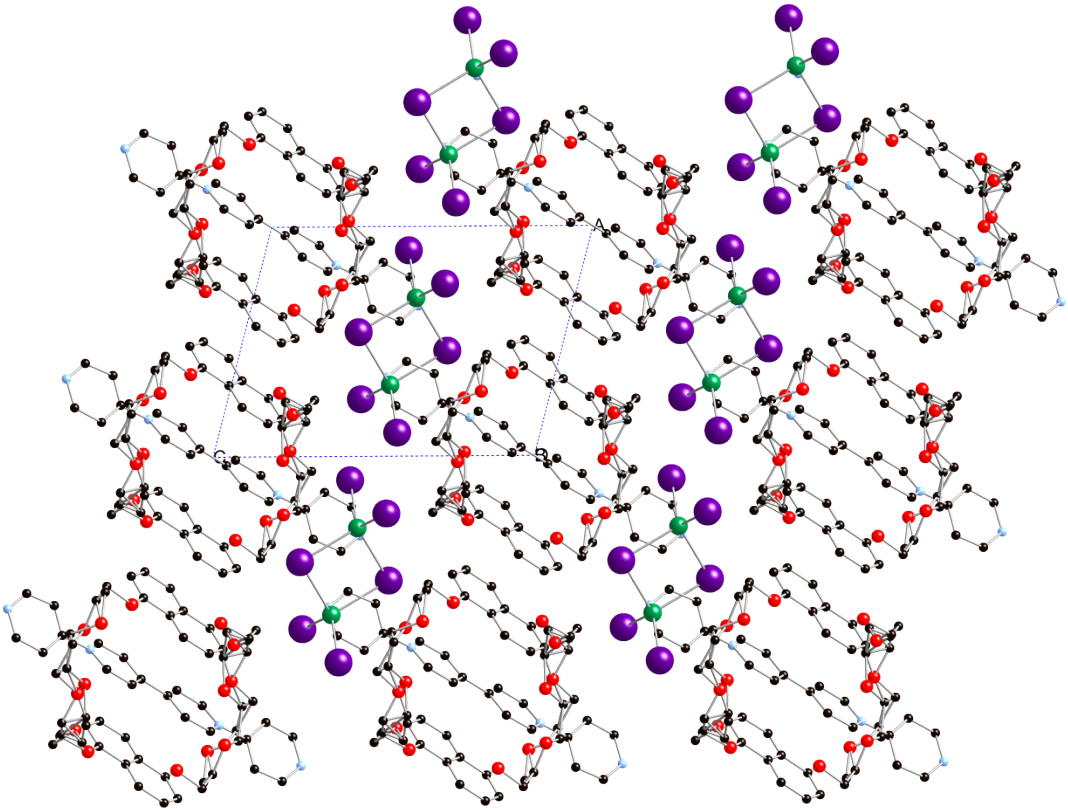

Figure S16. Packing diagram of **2**·$[Hg_2I_6]$·$3CH_3OH$. H-atoms and solvent molecules are omitted for clarity. Color code: Hg−green; I−violet; O−red; N−light blue; C−black.

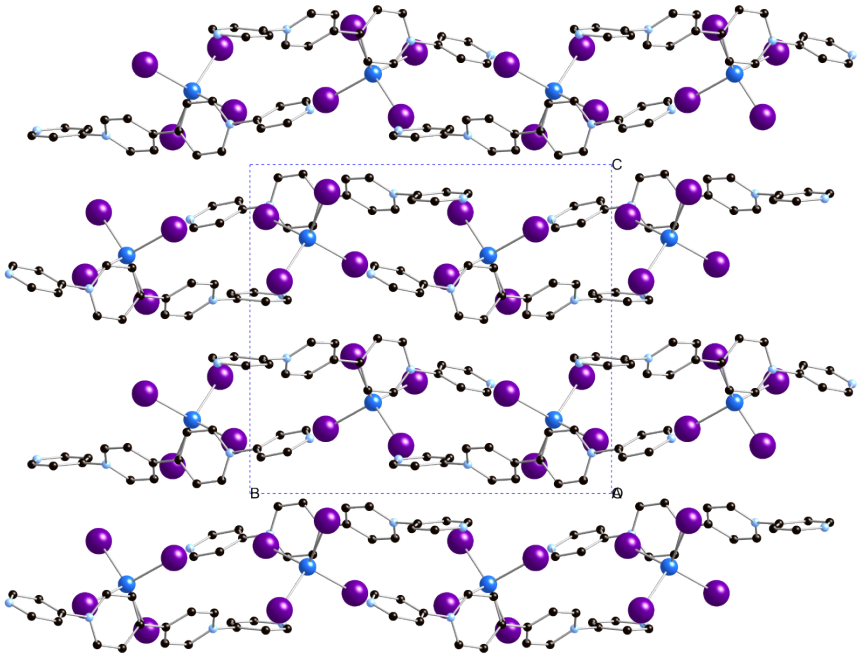

Figure S17. Packing diagram of PyBP·$[CdI_4]$. H-atoms are omitted for clarity. Color code: Cd−blue; I−violet; N−light blue; C−black.

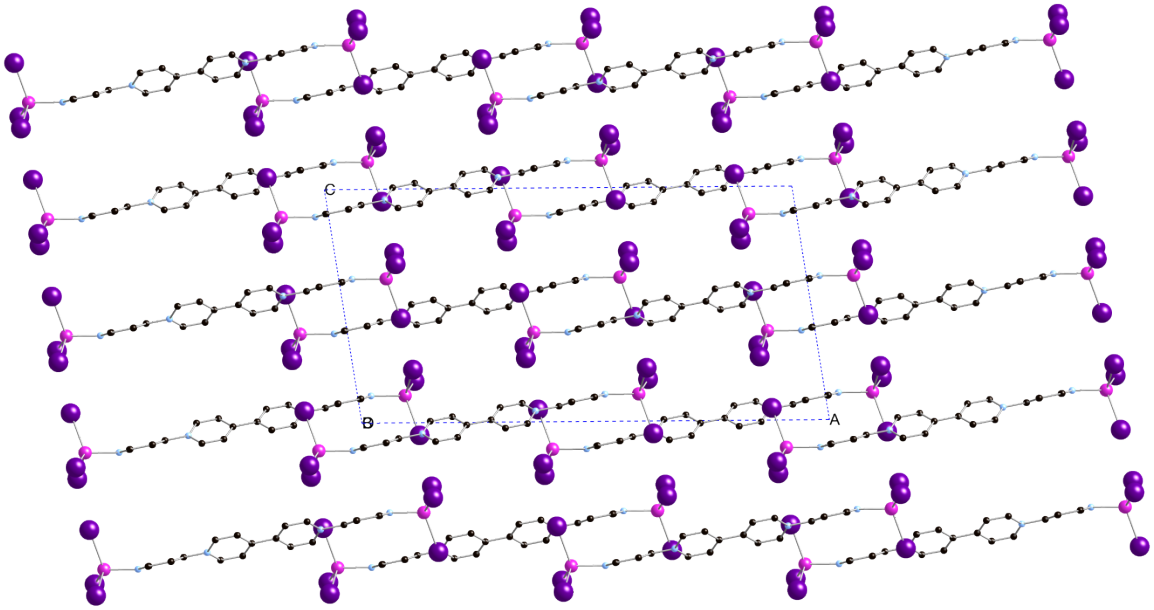

Figure S18. Packing diagram of $PyBP(ZnI_3)_2 \cdot 3CH_3OH$. H-atoms and solvent molecules are omitted for clarity. Color code: Zn−magenta; I−violet; N−light blue; C−black.