

Supporting Information

Capture of volatile iodine by newly prepared and characterized non-porous [Cu_nI_n]-based coordination polymers

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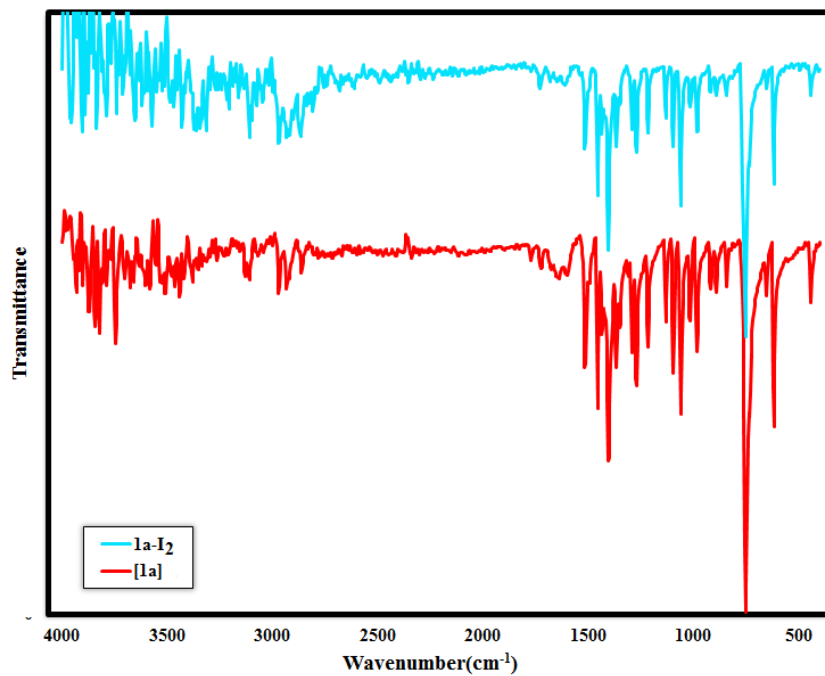
Table S1. Selected bond lengths (Å) and bond angles (°) for coordination polymers **1-3**.

(1a)			
I1–Cu1	2.6162(10)	Cu1–I1–Cu1a	73.58(3)
I1–Cu1a	2.7343(10)	Cu1–I1–Cu1c	66.25(3)
I1–Cu1c	2.7310(10)	Cu1a–I1–Cu1c	106.84(3)
Cu1–N1	2.032(4)	I1–Cu1–N1	121.10(12)
		I1–Cu1–I1a	106.42(3)
		I1–Cu1–I1c	113.76(3)
		I1a–Cu1–N1	104.45(13)
		I1c–Cu1–N1	103.22(13)
		I1a–Cu1–I1c	106.84(3)
(1b)			
Cu1–N3	2.053(2)	N1–Cu1–N3	124.20(9)
Cu1–I1	2.6940(4)	N3–Cu1–I1b	101.17(7)
Cu1b–I1	2.7140(5)	I1–Cu1–I1b	117.54(2)
Cu1–N1	2.044(2)	I1–Cu1–N1	100.92(6)
		I1–Cu1–N3	107.99(7)
		I1b–Cu1–N1	106.15(6)
		Cu1–I1–Cu1b	62.46(1)
(2)			
Cu1–I1	2.7603(13)	N12d–Cu1–I2	109.82(8)
Cu1–I2	2.6393(12)	N9–Cu2–I1	106.62(8)
Cu1–N1	2.054(3)	N9–Cu2–I2	100.74(8)
Cu1–N12d	2.047(3)	N9–Cu2–N6	117.97(11)
Cu2–I1	2.6421(12)	I1–Cu2–I2	115.76(2)
Cu2–I2	2.7429(13)	N19–Cu2–I1	114.39(8)
Cu2–N6	2.054(3)	N19–Cu2–I2	100.85(8)
Cu2–N9	2.056(3)	N16e–Cu3–N4a	116.59(12)
Cu3–I3	2.6303(12)	N16e–Cu3–I3	108.22(8)
Cu3–I4	2.7645(13)	N16e–Cu3–I4	100.96(8)
Cu3–N4a	2.047(3)	N4a–Cu3–I3	108.89(8)
Cu3–N16e	2.043(3)	N21–Cu3–I4	103.80(9)
Cu4–I3	2.7480(13)	I3–Cu3–I4	118.63(2)
Cu4–I4	2.6622(12)	N8–Cu4–I3	101.33(8)
Cu4–N8	2.051(3)	N8–Cu4–I4	103.51(8)
Cu4–N13	2.053(3)	N8–Cu4–N13	119.76(11)

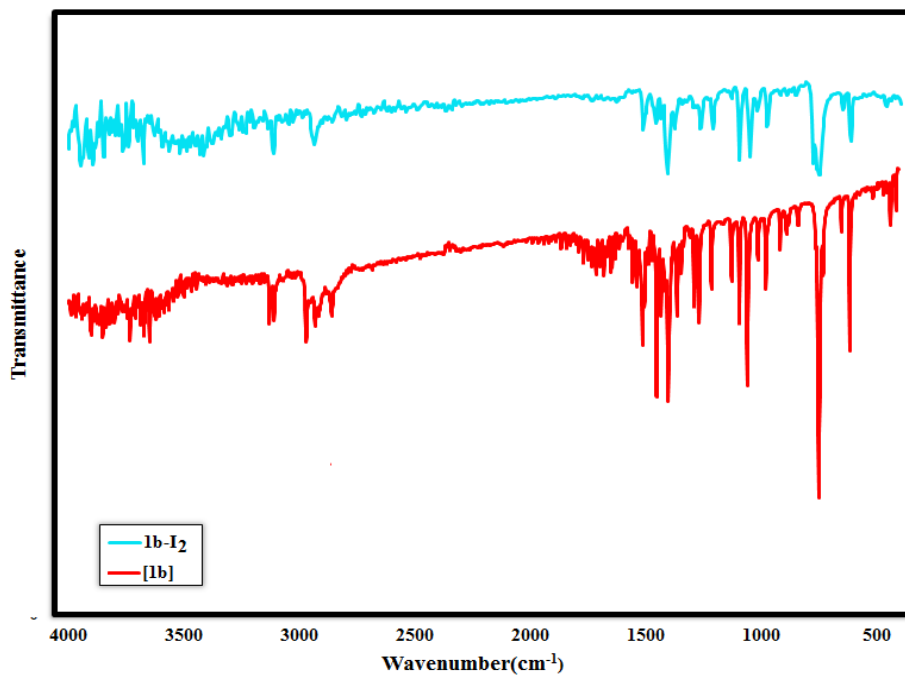
		I3–Cu4–I4	118.10(2)
		N13–Cu4–I3	100.72(9)
N1–Cu1–I1	100.91(9)	N13–Cu4–I4	113.60(8)
N1–Cu1–I2	108.32(8)	Cu1–I1–Cu2	64.34(2)
N1–Cu1–N12d	119.05(11)	Cu1–I2–Cu2	64.62(2)
I1–Cu1–I2	115.25(2)	Cu3–I3–Cu4	61.93(2)
N12d–Cu1–I1	103.46(9)	Cu3–I4–Cu4	61.33(2)
(3)			
Cu1–N3	1.9938(18)	N1–Cu1–N3	115.18(7)
Cu1–I1	2.5205(5)	N3–Cu1–I1	121.29(5)
Cu1–N1	1.9978(18)	I1–Cu1–N1	123.53(5)

Table S2. Dihedral angle between the pyrazolyl rings ($^{\circ}$), N-to-N and Cu \cdots Cu separation (\AA) for the bpmb linker ligands in the structure of **2**.

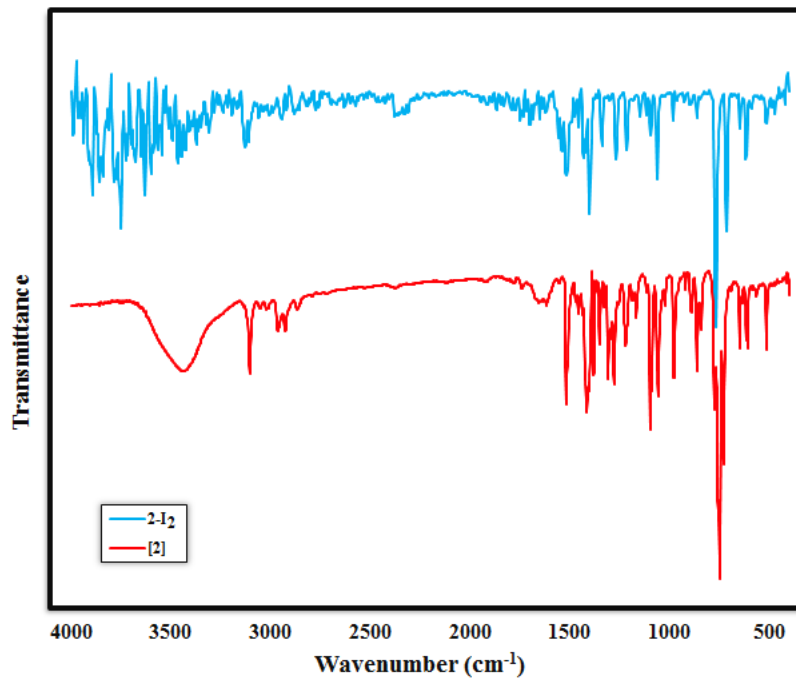
Ligand color	Dihedral angle	N-to-N	Cu \cdots Cu
Red	82.13	9.39	10.49
Green	88.56	8.97	9.41
Blue	88.43	9.12	9.96
Yellow	79.03	9.22	9.87



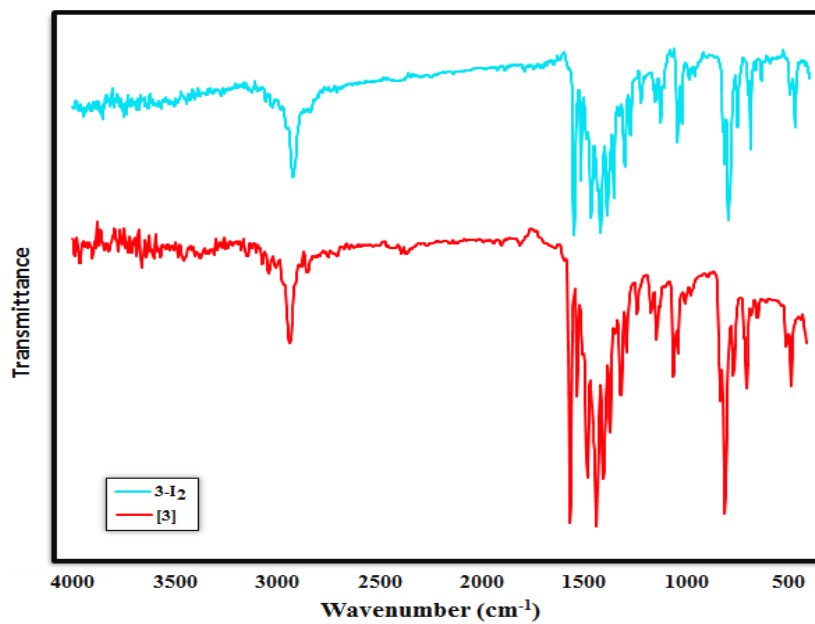
(a)



(b)



(c)



(d)

Figure S1. FT-IR spectra of compounds **1-3** before (red) and after (blue) iodine sorption.

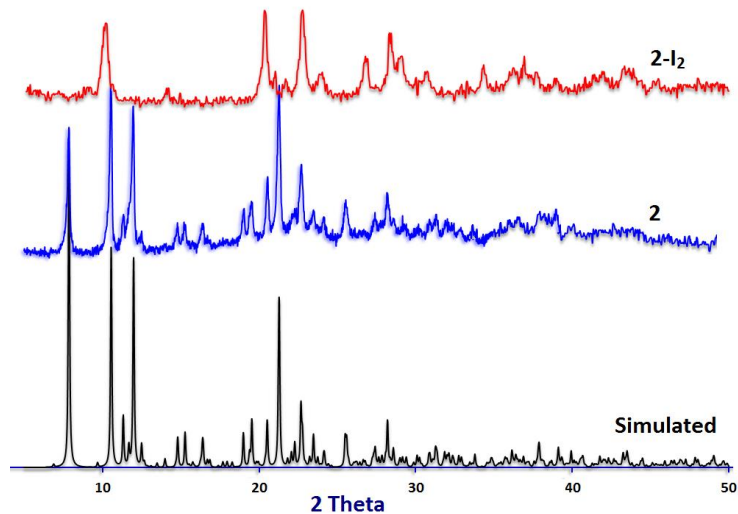


Figure S2. Powder X-ray diffraction patterns for **2**. Simulated from the single-crystal structure (black), experimental before (blue) and after (red) iodine sorption.

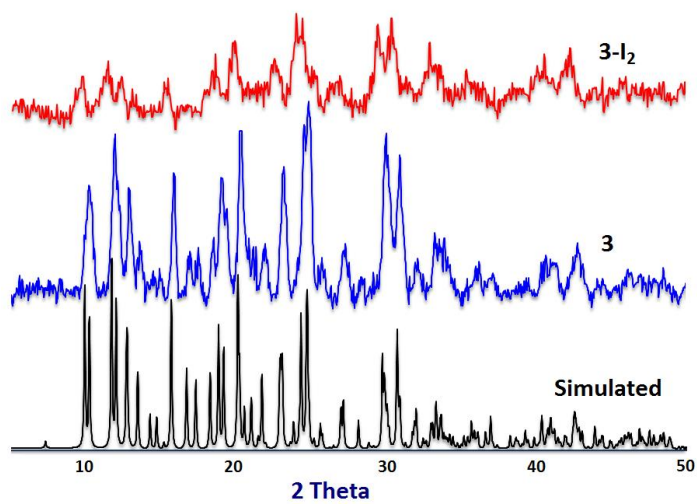
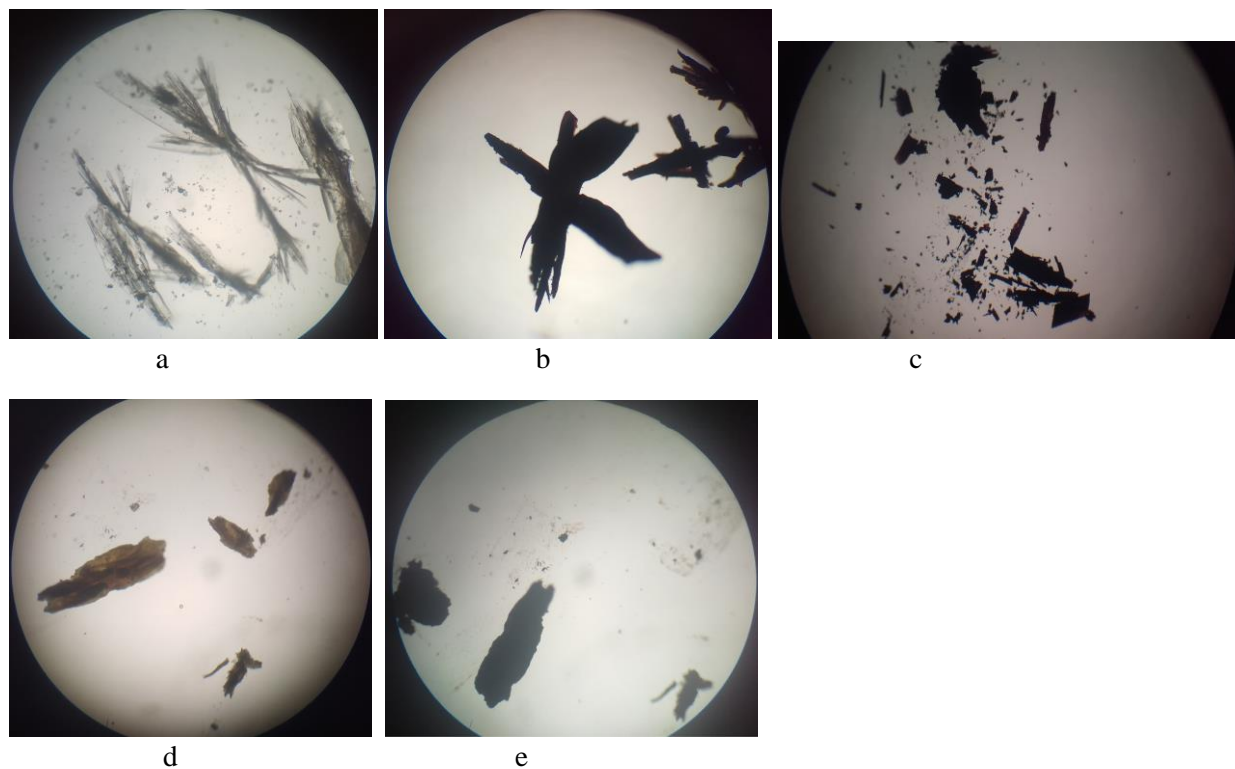
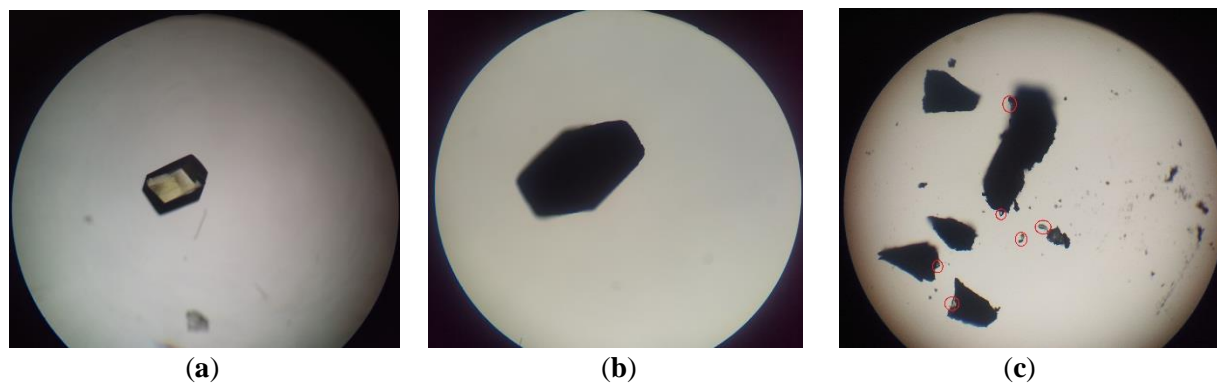


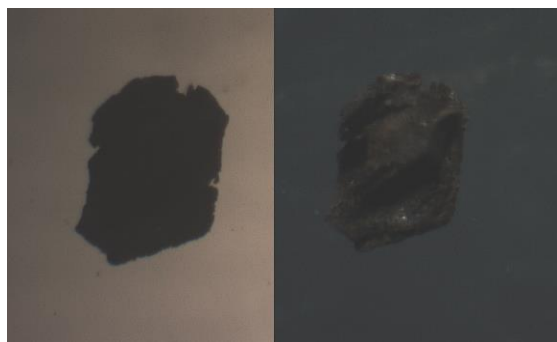
Figure S3. Powder X-ray diffraction patterns for **3**. Simulated from the single-crystal structure (black), experimental before (blue) and after (red) iodine sorption.

Compound 1a:



Compound 1b:

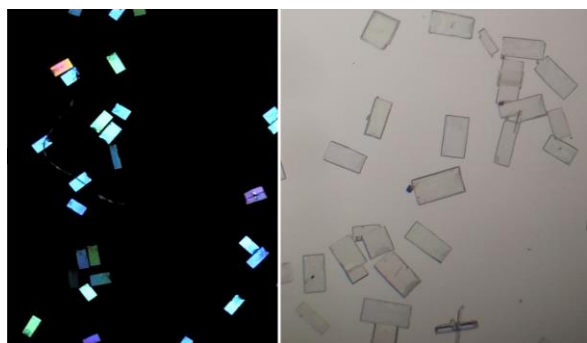




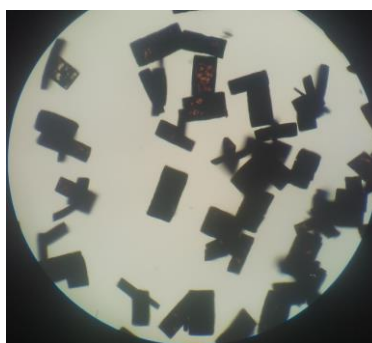
(d)

- a) Crystal of **1b**.
- b) Crystal of **1b-I₂** obtained by exposition to iodine vapors for 1 h at 58 °C at higher magnification.
- c) Cracked crystals of **1b-I₂**. Microscopic observation shows some residual crystalline parts at the center of the crystals evidenced by red circles in the picture.
- d) Crystals of **1b-I₂** obtained by exposition to iodine vapors for 7 h at 58 °C. The crystals show an amorphous and spongy texture with some cracks on the surface.

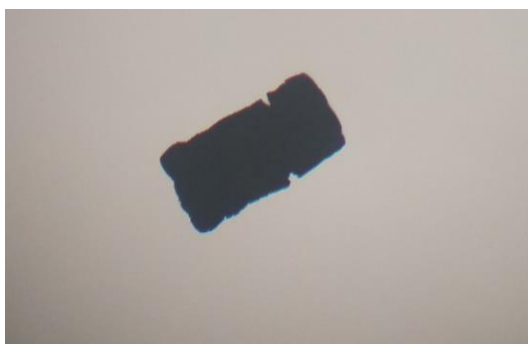
Compound 2:



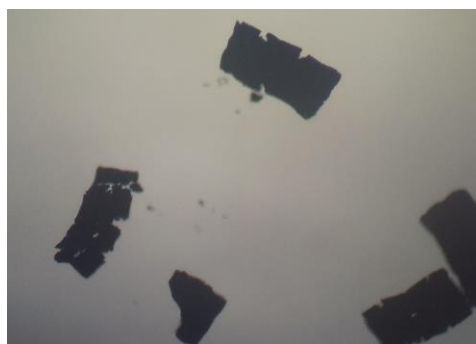
(a)



(b)



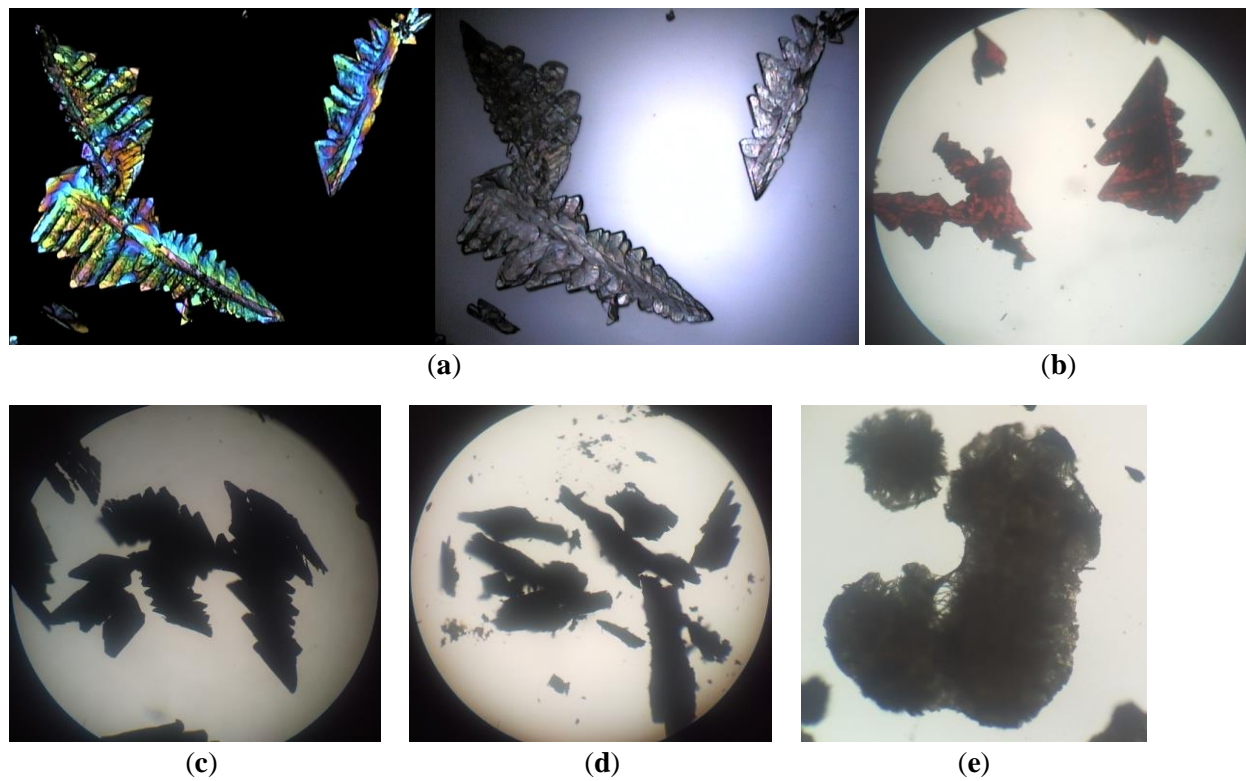
(c)



(d)

- a) Crystals of **2**.
- b) Crystals of **2-I₂** obtained by exposition to iodine vapors for 1 h at 58 °C , showing some residual crystalline parts.
- c) Crystal of **2-I₂** obtained by exposition to iodine vapors for 7 h at 58 °C at higher magnification
- d) Cracked crystals of **2-I₂** at higher magnification which show no interior crystalline part.

Compound 3:



- a) Crystals of **3**.
- b) Crystals of **3-I₂** obtained by exposition of to iodine vapors for 1 h at 58 °C , showing some residual crystalline parts.
- c) Crystals of **3-I₂** obtained by exposition to iodine vapors for 7 h at 58 °C.
- d) Cracked crystals of **3-I₂** at higher magnification which show no interior crystalline part.
- e) Crystals of iodine released **3-I₂** in DMF which show spongy texture.

Figure S4. Microscopic photos of **1-3** crystals during gaseous iodine sorption.

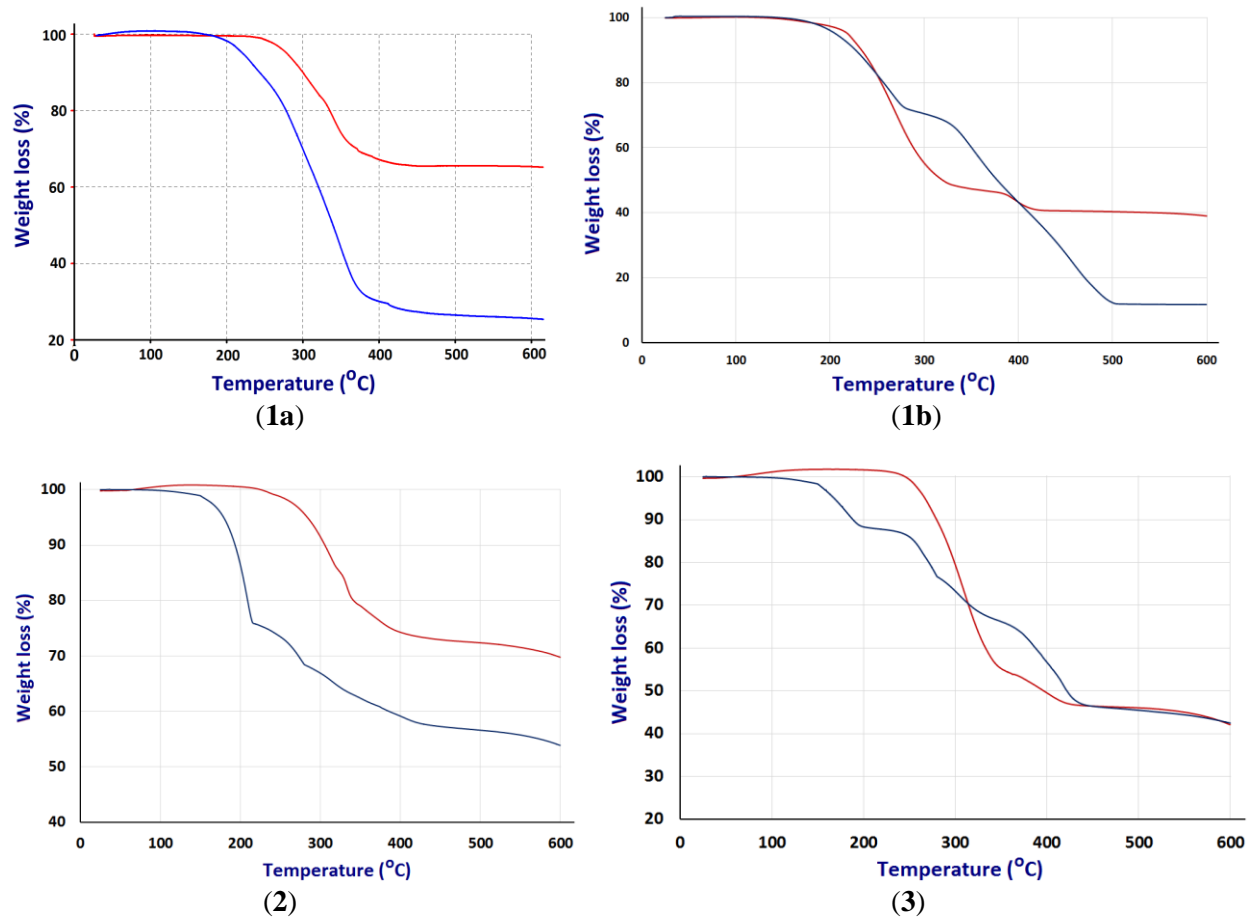
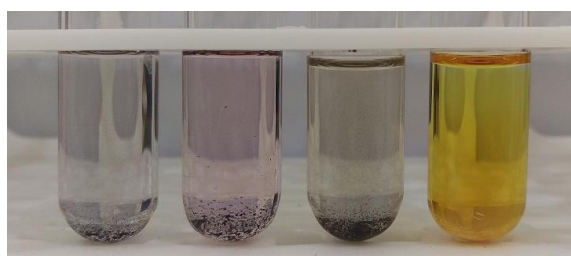


Figure S5. TGA curves for compounds **1-3** before (red) and after iodine sorption (blue).



(a)

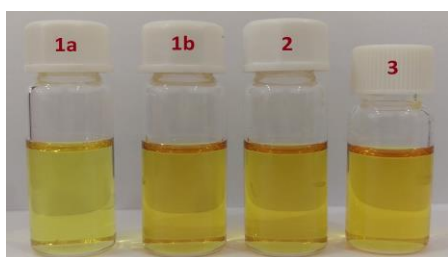


(b)



(c)

Figure S6. Visual detection of iodine release for **1a-I₂** in cyclohexane, CCl₄, EtOH and DMF (left to right) after a) 2 min, b) 20 min and c) 40 min.



(a)



(b)

Figure S7. a) DMF solutions obtained by suspending compounds (**1-3**)-I₂ in pure DMF, b) Solid materials of compounds **1-3** (left to right) recovered from DMF solutions after iodine release.

Table S3. Sample weight, absorbance, iodine content and iodine percent for compounds **1-3**, determined by UV-Vis spectroscopy.

Compound	Weight of sample (mg)	Solvent Volume (ml)	Times of Dilution	Absorbance	Iodine content (mg)	Iodine percent
1a-I₂	9.2	10	5	1.078	1.73	23.0%
1b-I₂	7.2	10	5	1.798	2.63	57.7%
2-I₂	7.8	10	6.67	1.391	2.82	56.6%
3-I₂	7.9	10	16.67	0.619	3.82	93.6%

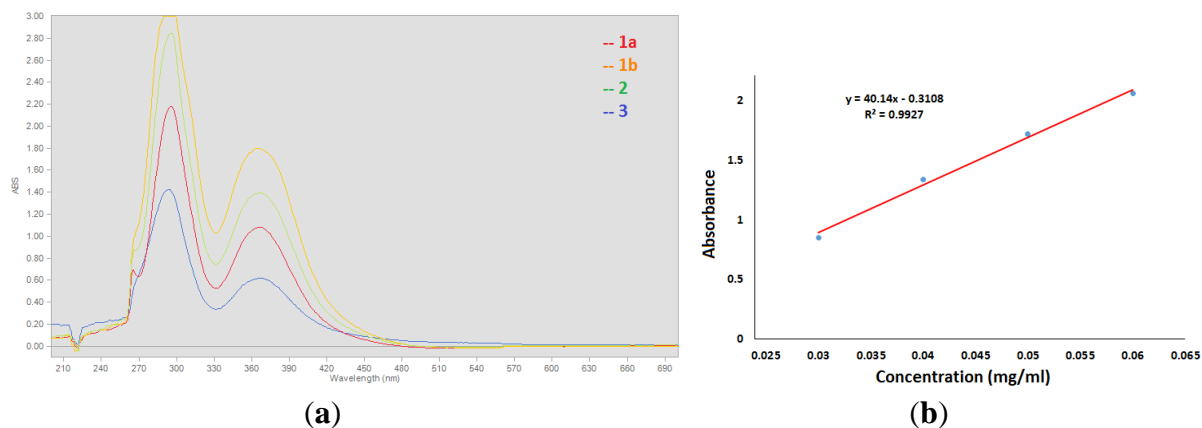


Figure S8. a) UV-Vis absorption spectra of the diluted solution of released iodine and b) Calibration curve obtained from UV-Vis spectra of standard iodine solution.

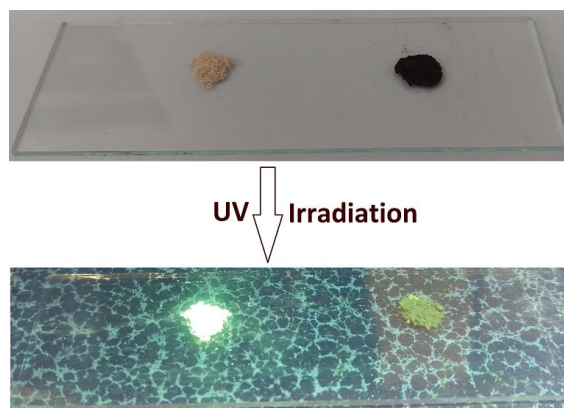


Figure S9. View of iodine loaded (right) and iodine released (left) powders of **1a** before and after UV irradiation.