Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

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

Abbas Tarassoli,*[a] Valiollah Nobakht,*[a], Elham Baladi,[a] Lucia Carlucci,[b] Davide M. Proserpio[b],[c]

[a] Department of Chemistry, Faculty of Sciences, Shahid Chamran University of Ahvaz, Ahvaz, Iran. Fax: +98 613 3331042 E-mail: tarassoli@scu.ac.ir (A. Tarassoli) and v.nobakht@scu.ac.ir (V. Nobakht)

[b] Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133, Milano, Italy.

[c] Samara Center for Theoretical Materials Science (SCTMS) Samara State University, Samara 443011, Russia

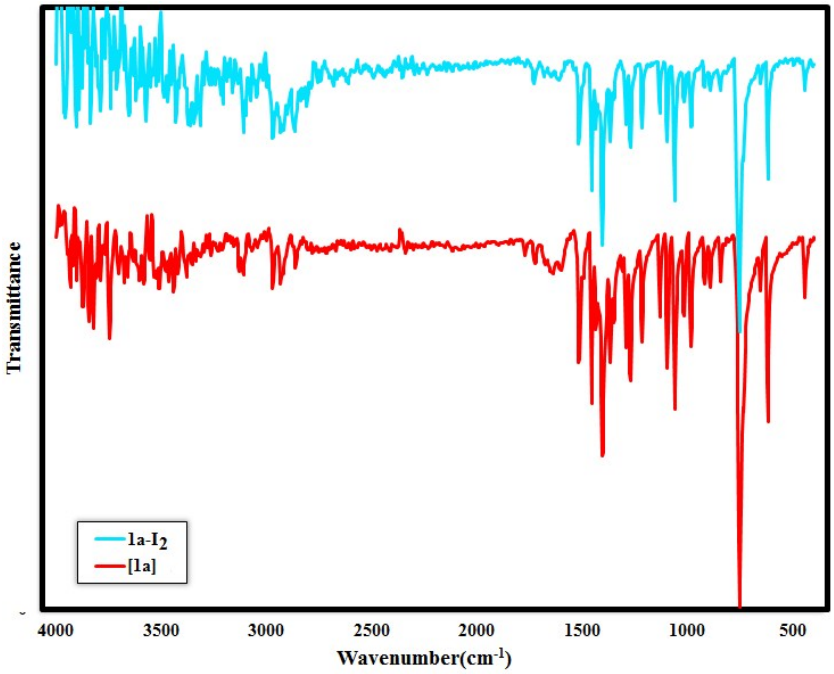
Table S1. Selected bond lengths (Å) and bond angles (°) for coordination polymers **1-3**.

(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)

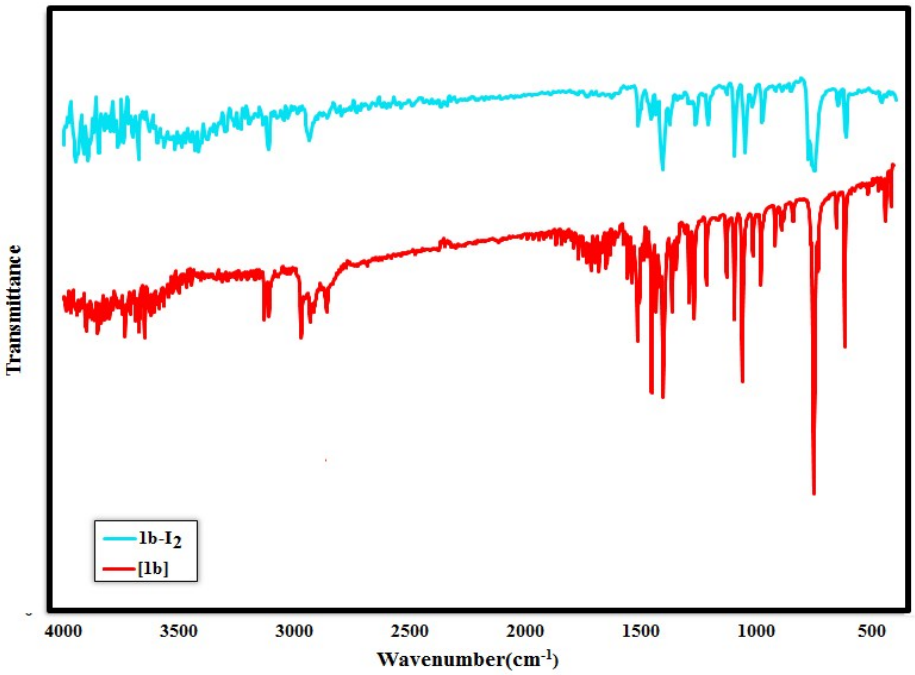
		I3–Cu4–I4	118.10(2)
		N13–Cu4–I3	100.72(9)
N1–Cu1–I1	100.91(9)	N13–Cu4–I4	113.60(8)
N1–Cu1–I2	108.32(8)	Cu1–I1–Cu2	64.34(2)
N1–Cu1–N12d	119.05(11)	Cu1–I2–Cu2	64.62(2)
I1–Cu1–I2	115.25(2)	Cu3–I3–Cu4	61.93(2)
N12d–Cu1–I1	103.46(9)	Cu3–I4–Cu4	61.33(2)
		(3)	
Cu1–N3	1.9938(18)	N1–Cu1–N3	115.18(7)
Cu1–I1	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 (˚), N-to-N and Cu···Cu separation (Å) for the bpmb linker ligands in the structure of **2**.

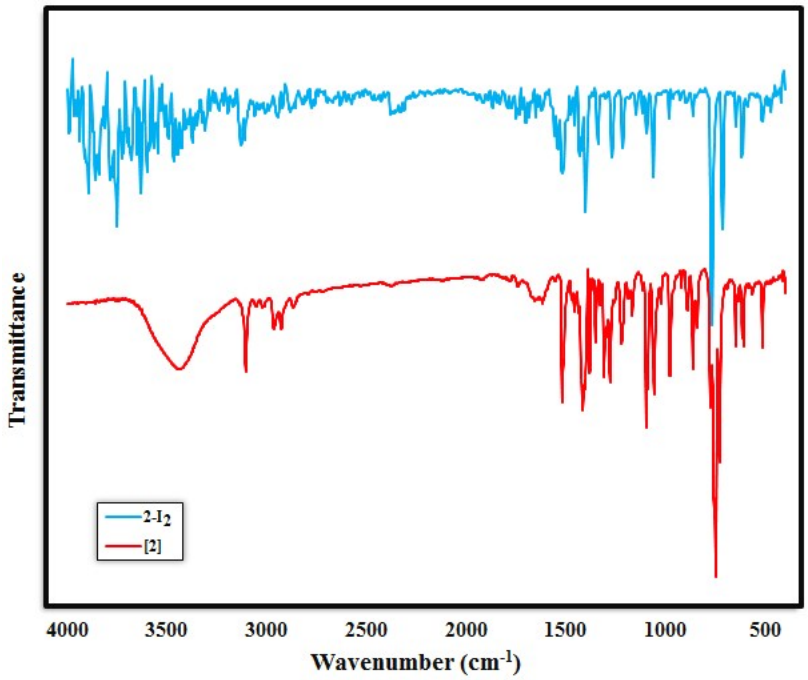
Ligand color	Dihedral angle	N-to-N	Cu···Cu
Red	82.13	9.39	10.49
Green	88.56	8.97	9.41
Blue	88.43	9.12	9.96
Yellow	79.03	9.22	9.87


Transmittance
1a-I2
[1a]
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

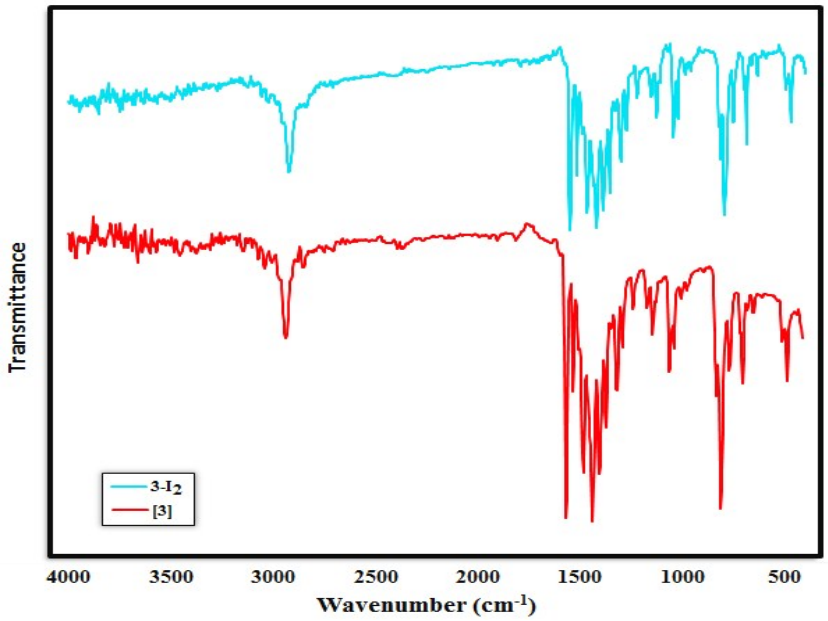
(**a**)


Transmittance
1b-I2
[1b]
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

(**b**)



(**c**)



(**d**)

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

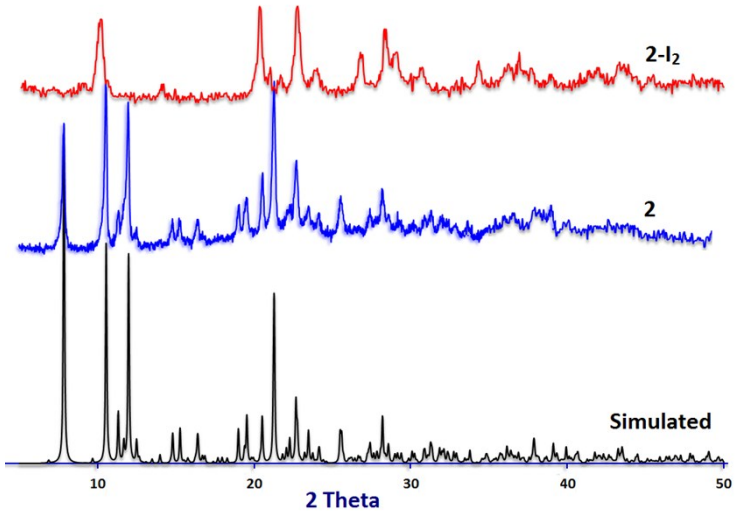


Figure S2. Powder X-ray diffraction patterns for **2**. Simulated from the single-crystal structure (black), experimental before (blue) and after (red) iodine sorption.

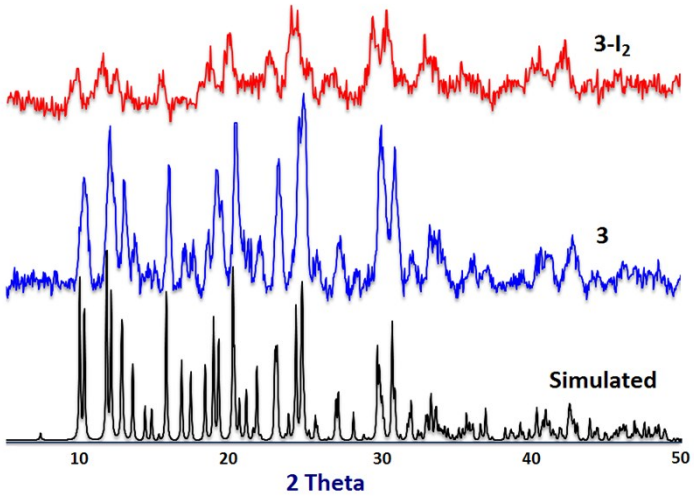
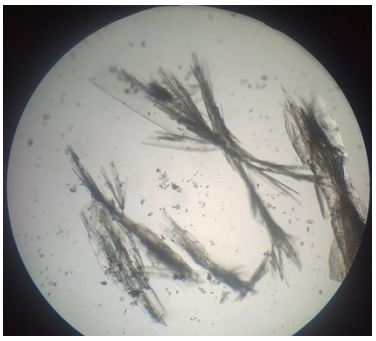
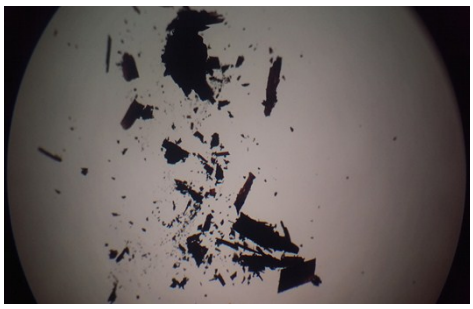


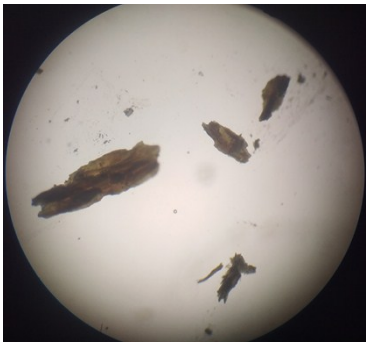
Figure S3. Powder X-ray diffraction patterns for **3**. Simulated from the single-crystal structure (black), experimental before (blue) and after (red) iodine sorption.

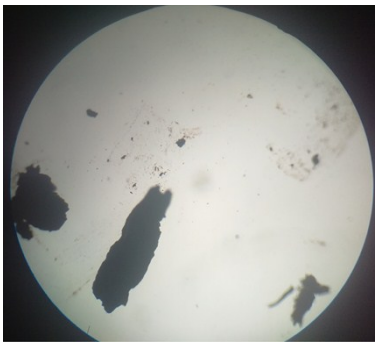
Compound 1a:


a


b

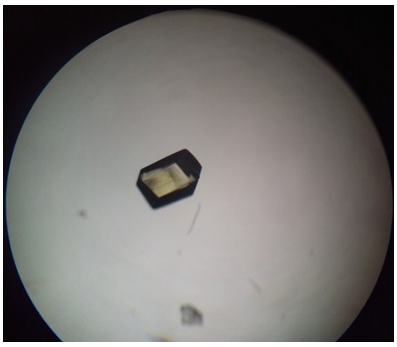

c

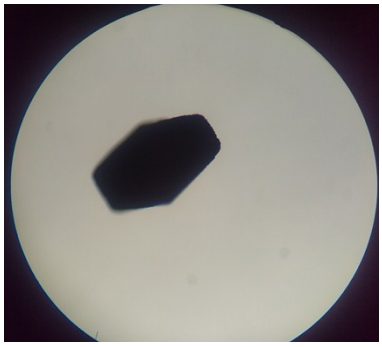

d

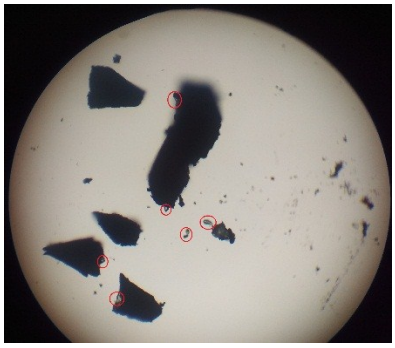

e

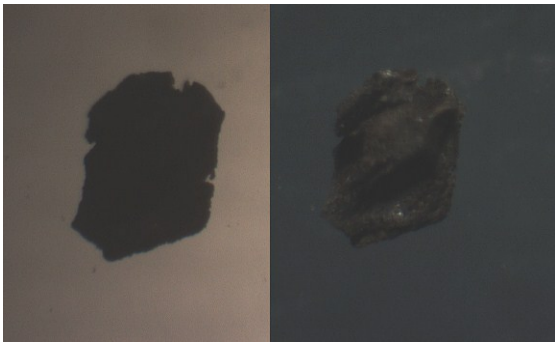
a) Crystals of **1a.**
b) Crystals of **1a-I_2** obtained by exposition to iodine vapors for 7 h at 58 °C.
c) Cracked crystals of **1a-I_2** at higher magnification. Direct microscopic observation show some transparent crystalline parts which is difficult to observe in photo.
d) Crystals of iodine released **1a-I_2** in DMF which show fluorescent emission under UV irradiation.
e) Crystals of iodine released **1a-I_2** re-exposed to iodine vapors. This iodine sorption test evidence the reversibility of the process.

Compound 1b:


(**a**)


(**b**)

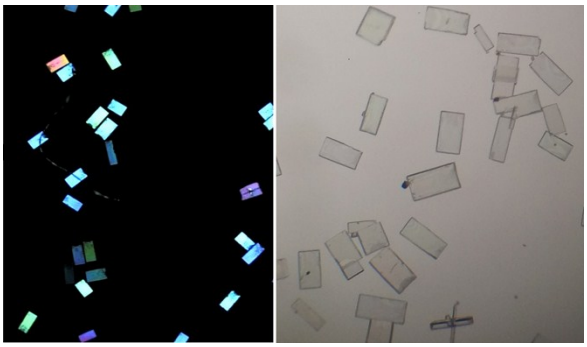

(**c**)



(**d**)

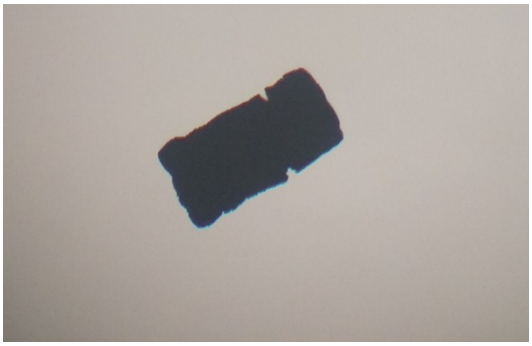
a) Crystal of **1b.**
b) Crystal of **1b-I_2** obtained by exposition to iodine vapors for 1 h at 58 °C at higher magnification.
c) Cracked crystals of **1b-I_2**. Microscopic observation shows some residual crystalline parts at the center of the crystals evidenced by red circles in the picture.
d) Crystals of **1b-I_2** 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:

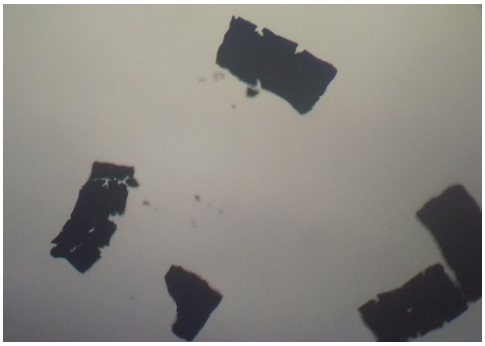


(**a**)

(**b**)



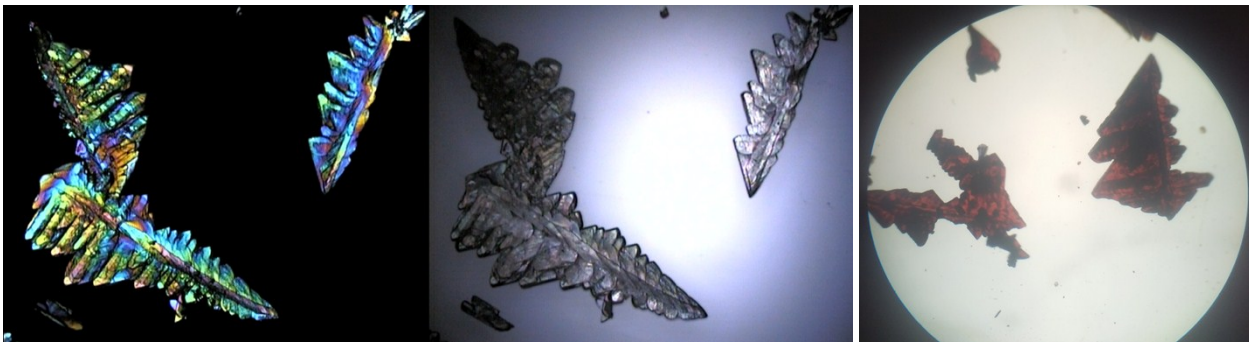
(**c**)



(**d**)

a) Crystals of **2**.
b) Crystals of **2-I_2** obtained by exposition to iodine vapors for 1 h at 58 °C , showing some residual crystalline parts.
c) Crystal of **2-I_2** obtained by exposition to iodine vapors for 7 h at 58 °C at higher magnification
d) Cracked crystals of **2-I_2** at higher magnification which show no interior crystalline part.

Compound 3:



(**a**) (**b**)

(**c**) (**d**) (**e**)

a) Crystals of **3**.
b) Crystals of **3-I_2** obtained by exposition of to iodine vapors for 1 h at 58 °C , showing some residual crystalline parts.
c) Crystals of **3-I_2** obtained by exposition to iodine vapors for 7 h at 58 °C.
d) Cracked crystals of **3-I_2** at higher magnification which show no interior crystalline part.
e) Crystals of iodine released **3-I_2** in DMF which show spongy texture.

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

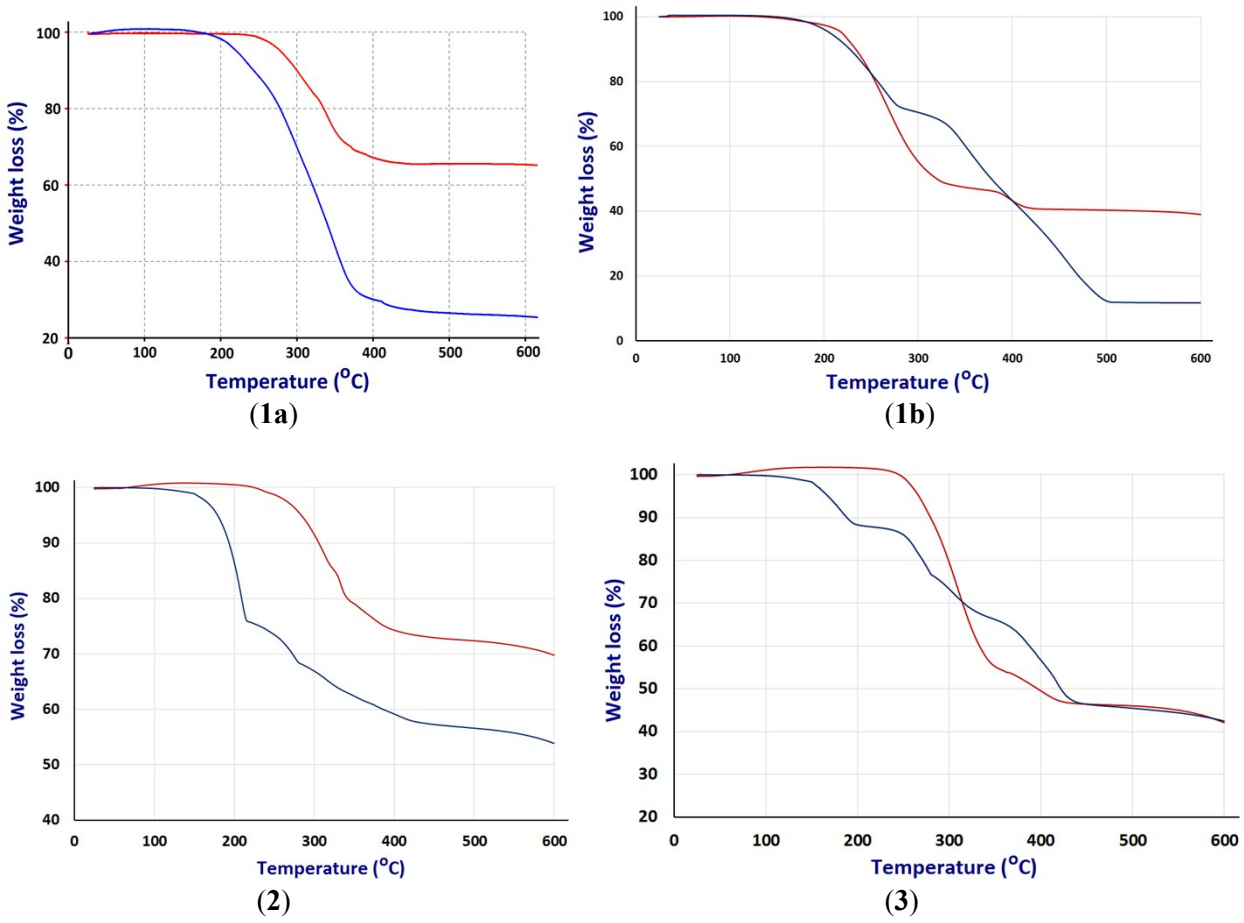
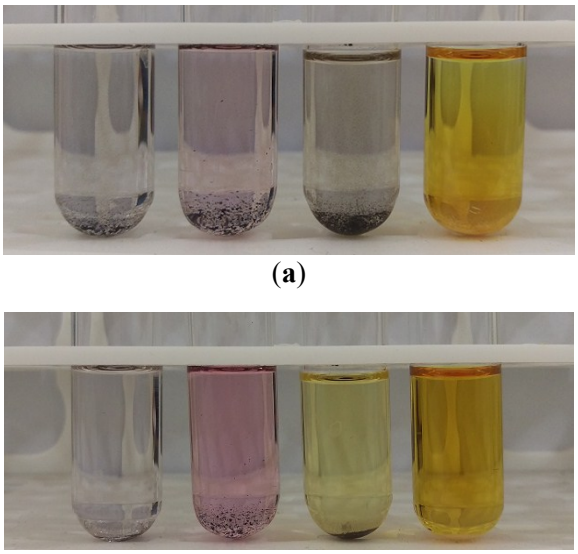


Figure S5. TGA curves for compounds **1-3** before (red) and after iodine sorption (blue).

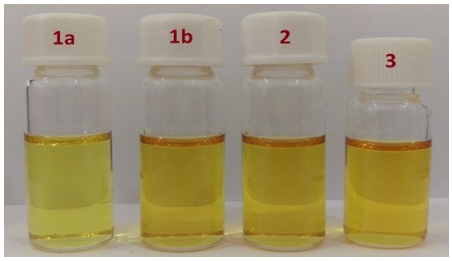


(**a**)

(**b**)

(**c**)

Figure S6. Visual detection of iodine release for **1a-I_2** in cyclohexane, CCl_4, EtOH and DMF (left to right) after a) 2 min., b) 20 min and c) 40 min.



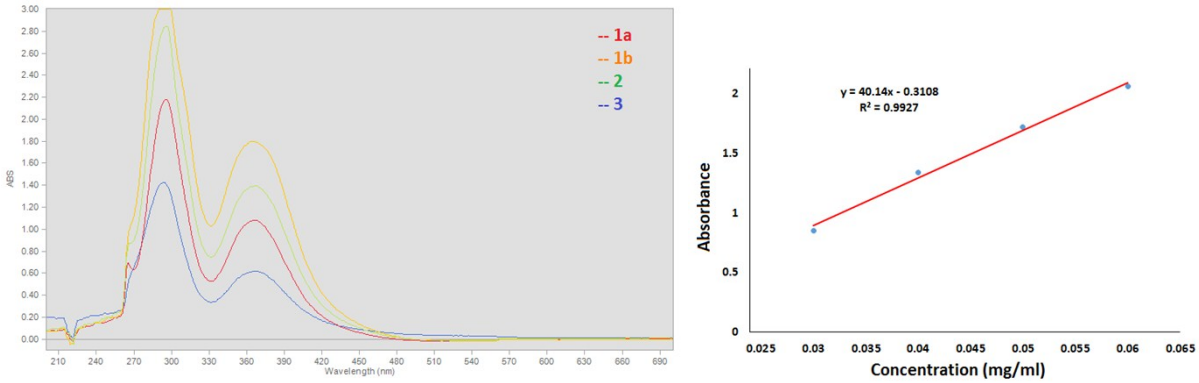
(**a**)

(**b**)

Figure S7. a) DMF solutions obtained by suspending compounds (**1-3**)-**I_2** 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-I_2	9.2	10	5	1.078	1.73	23.0%
1b-I_2	7.2	10	5	1.798	2.63	57.7%
2-I_2	7.8	10	6.67	1.391	2.82	56.6%
3-I_2	7.9	10	16.67	0.619	3.82	93.6%



(**a**) (**b**)

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.

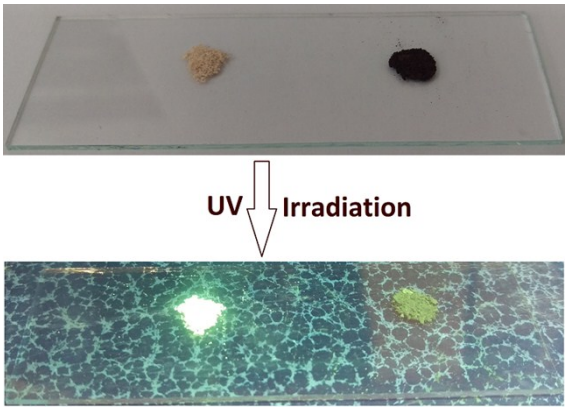


Figure S9. View of iodine loaded (right) and iodine released (left) powders of **1a** before and after UV irradiation.