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Dimensional encapsulation of $I^{-}\cdots I_2\cdots I^{-}$ in an organic salt crystal matrix†

Antonio Abate,[a] Manuel Brischetto,[a] Manu Lahtinen,[b] Pierangelo Metrangolo,*[a] Tullio Pilati,[c] Stefano Radice,[d] Giuseppe Resnati,*[a,c] Kari Rissanen[e] and Giancarlo Terraneo[a]

Electronic Supplementary Information

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[a] *NFMLab and CNST-IIT@POLIMI, D.C.M.I.C. "Giulio Natta", Politecnico di Milano*
Via L. Mancinelli 7, 20131 Milan, Italy; Fax: +39 02 2399 3080;
Tel: +39 02 2399 3041 (P. M.), 3032 (G. R.);
E-mail: pierangelo.metrangolo@polimi.it; giuseppe.resnati@polimi.it.
[b] *Department of Chemistry, University of Jyväskylä, P.O. Box 35, Jyväskylä, FI–40014, Finland.*
[c] *ISTM-CNR, Università di Milano, Via Venezian 21, 20133 Milan, Italy.*
[d] *Solvay-Solexis S.p.A., Viale Lombardia 20, 20121 Bollate (MI), Italy.*
[e] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, Jyväskylä, FI–40014, Finland.*

† Electronic Supplementary Information (ESI) available: CIFs and characterization for **2**-**4**, experimental procedures. See http://www.rsc.org/suppdata/xx/b0/b000000x/.

Experimental procedures

General

Commercial HPLC-grade solvents were used without further purification. Starting materials were purchased from Sigma–Aldrich, Acros Organics, and Apollo Scientific. The mass spectra were recorded with a Finnigan Mod TSQ-70 instrument in FAB mode from an m-NBA matrix. The thermal transitions were determined by DSC (Mettler Toledo) on heating and cooling at a rate of 10°Cmin^{-1}.

Co-crystallization

Co-crystals by solvent/non-solvent

BTMAH^{2+}·2I$^-$ **1** and I_2, in right amount, are dissolved separately in acetonitrile (solvent) by using only as much solvent as necessary for complete dissolution. The saturated solutions were put together in the opened vial and placed in a closed cylindrical wide-mouth bottle containing chloroform (non-solvent). Solvents were allowed to mix by slow diffusion in gas and liquid phase at room temperature until crystals were formed, usually 2-3 days. The crystals were filtered off the mother liquor (from which one to two further crystal fractions could be obtained in the same manner) and dried in air at room temperature. The crystals were good for single crystal X-ray analysis.

Specifically, co-crystals **2** was obtained mixing 14 mg (0.03 mmol) of BTMAH^{2+}·2I$^-$ **1** and 8 mg (0.03 mmol) of I_2 in 8.5 ml of acetonitrile and 40 ml of chloroform. Co-crystal **3** was obtained mixing 18 mg (0.04 mmol) of BTMAH^{2+}·2I$^-$ **1** and 20 mg (0.08 mmol) of I_2 in 12 ml of acetonitrile and 45 ml of chloroform. Co-crystal **4** was obtained mixing 14 mg (0.03 mmol) of BTMAH^{2+}·2I$^-$ **1** and 30 mg (0.12 mmol) of I_2 in 15 ml of acetonitrile and 50 ml of chloroform.

Co-crystals by co-grinding

BTMAH^{2+}·2I$^-$ **1** and I_2 were put in vials and grind together until to obtain a very fine and evenly colored powder, usually were necessary 5 minutes. Specifically, co-crystals **2** was obtained mixing 68 mg (0.15 mmol) of BTMAH^{2+}·2I$^-$ **1** and 38 mg (0.15 mmol) of I_2. Co-crystals **3** was obtained mixing 45 mg (0.10 mmol) of BTMAH^{2+}·2I$^-$ **1** and 50 mg (0.20 mmol) of I_2. Co-crystals **4** was obtained mixing 45 mg (0.10 mmol) of BTMAH^{2+}·2I$^-$ **1** and 101 mg (0.40 mmol) of I_2.

Co-crystals by solid-gas reaction

Fine powders of BTMAH^{2+}·2I$^-$ **1** was scattered on the bottom of airtight container. A right amount of iodine was let evaporated in the container without touching **1**. Specifically, co-crystals **2** was obtained starting from 23 mg (0.05 mmol) of BTMAH^{2+}·2I$^-$ **1** and 13 mg (0.05 mmol) of I_2. Co-crystals **3** was obtained starting from 14 mg (0.03 mmol) of BTMAH^{2+}·2I$^-$ **1** and 15 mg (0.06 mmol) of I_2. Co-crystals **3** was obtained starting from 14 mg (0.03 mmol) of BTMAH^{2+}·2I$^-$ **1** and 30 mg (0.12 mmol) of I_2.

Thermal analysis

Thermal behaviours of co-crystals **2**, **3** and **4** have been investigated by DSC analysis. There was a good agreement between the data of crystals obtained from different procedures. Specifically, the thermal stability decrease from crystal **2** to crystal **4**. The melting points are 199.75, 141.53 and 104.36 °C for crystals **2**, **3** and **4** respectively (Figure SI1-SI3).

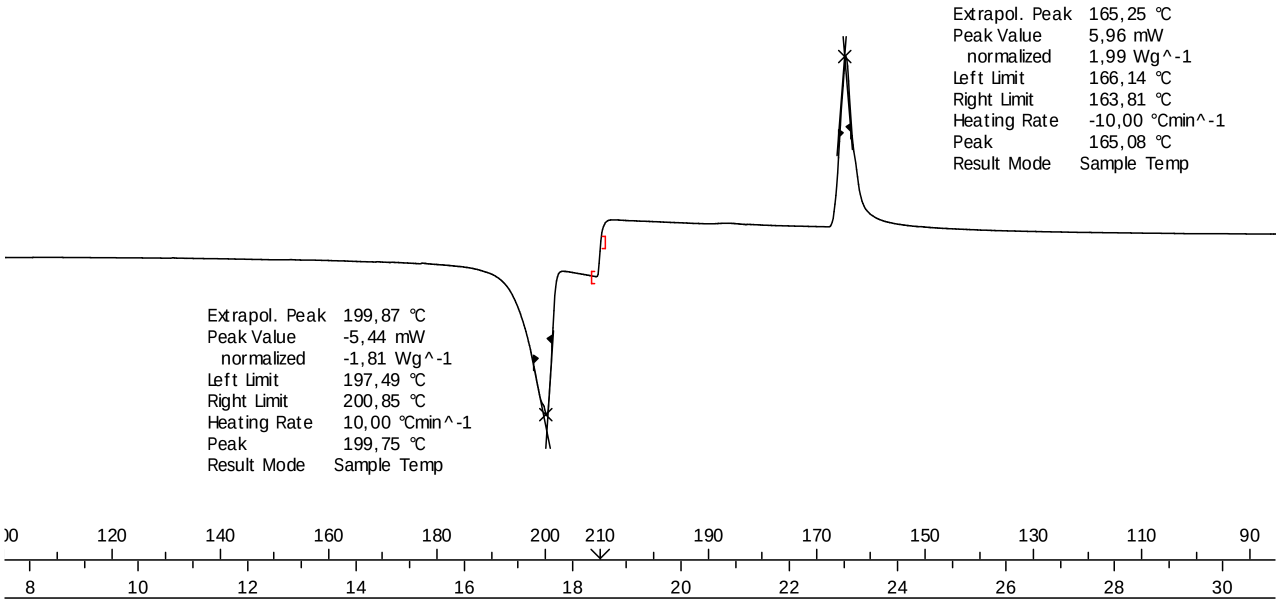

Figure SI1. DSC co-crystal **2**

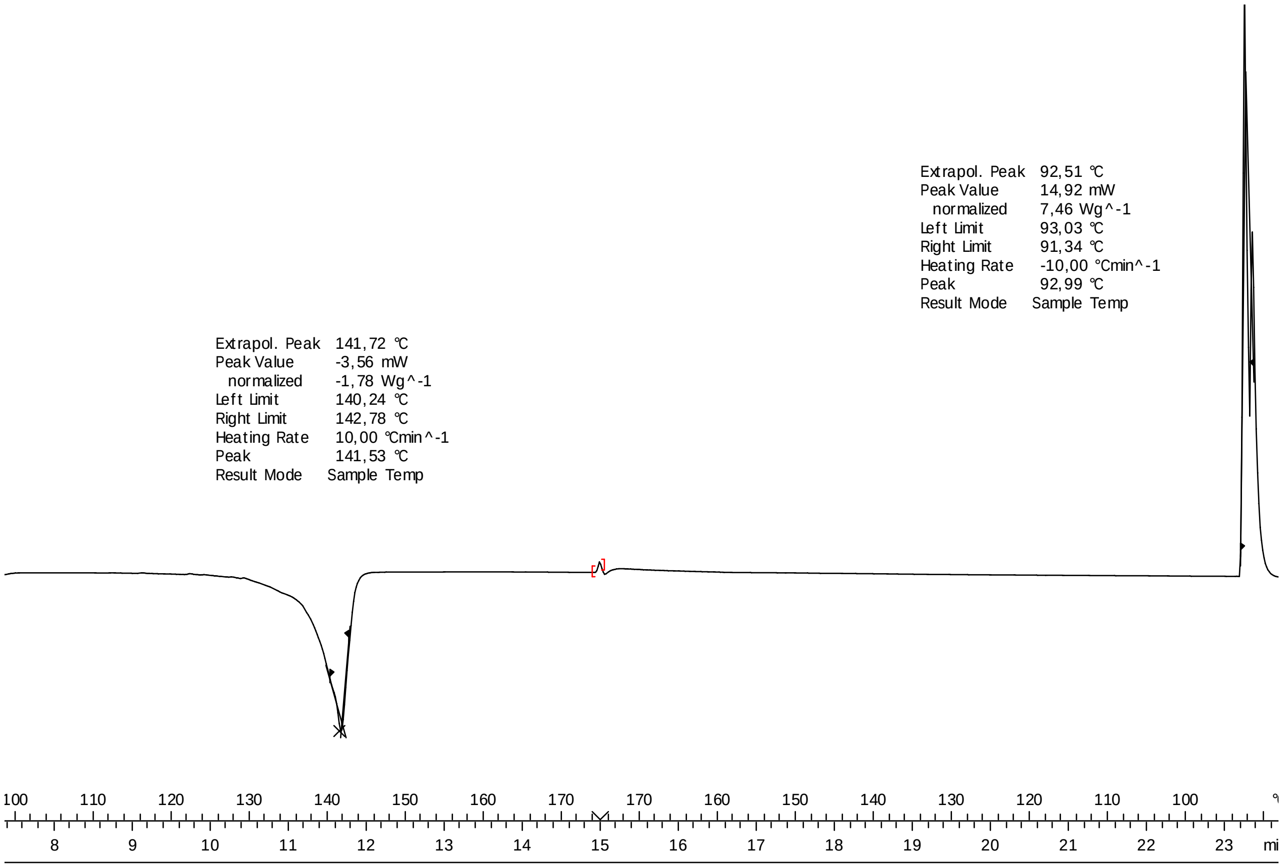

Figure SI2. DSC co-crystal **3**

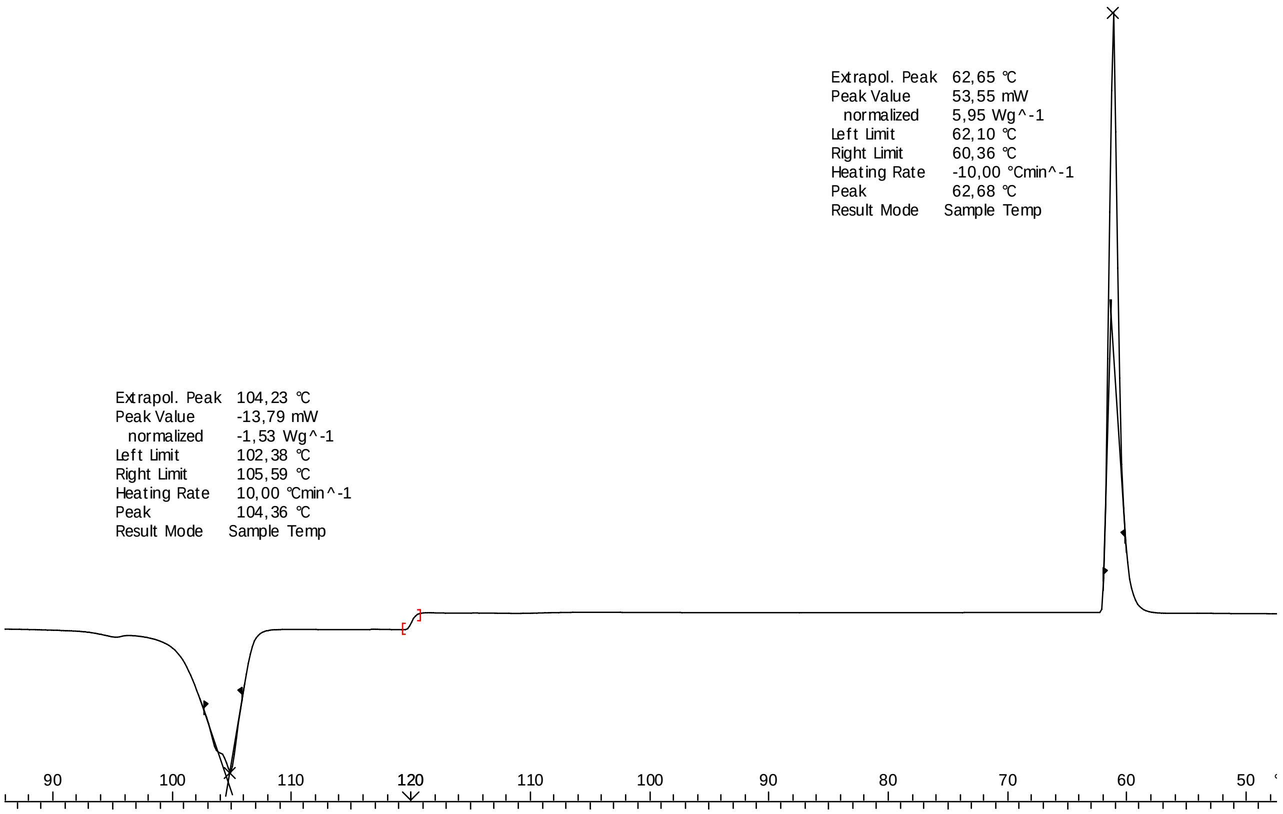

Figure SI3. DSC co-crystal **4**

FT-IR and Raman analyses for 2, 3 and 4

IR spectra were obtained using a Perkin–Elmer 2000 FTIR spectrometer equipment with U-ATR device. Absorptions are specified in wavenumbers, which have been rounded to the nearest 1 cm^{-1} by automatic assignment. Baseline corrections are not appropriate for the spectra of the complexes **2-4** due to the strong optical extinction. Selected IR data of the starting module (**1**) is reported to show the changes that occur upon the formation of cocrystals **2, 3, 4** (Figure SI4-SI6).

Diiodide salt of the bis(trimethylammonium) hexane **1:** IR (ṿ selected bands): 3011, 2947, 2851, 1488, 1472, 1394, 1061, 965, 945, 914 cm^{-1}; co-crystal **2** (ṿ selected bands): 3011, 2940, 2860, 1482, 1474, 1408, 1058, 966, 945, 911 cm^{-1}; co-crystal **3** (ṿ selected bands): 3012, 2936, 2871, 1479, 1468, 1404, 1055, 962, 947, 901 cm^{-1}; co-crystal **4** (ṿ selected bands): 3007, 2939, 2854, 1480, 1465, 1403, 1056, 965, 946, 907 cm^{-1}

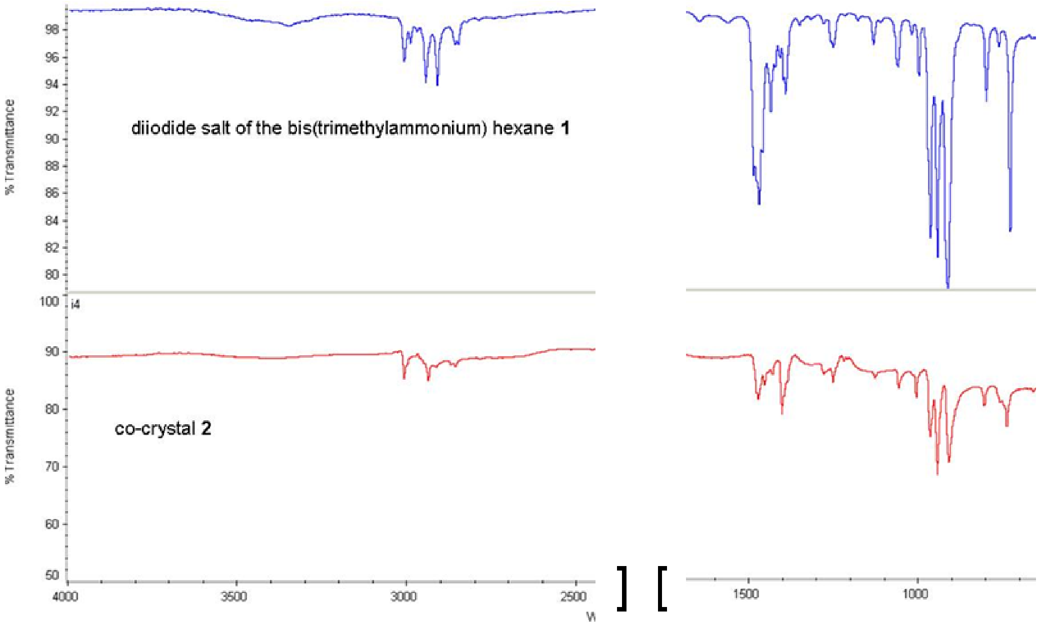

Figure SI4. IR spectra for **1** and co-crystal **2**

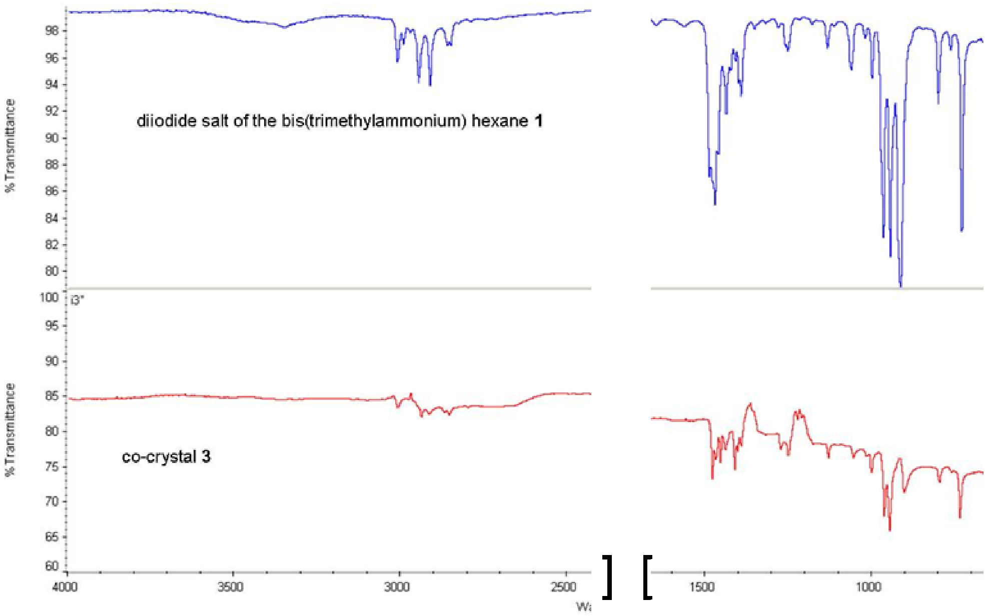

Figure SI5. IR spectra for **1** and co-crystal **3**

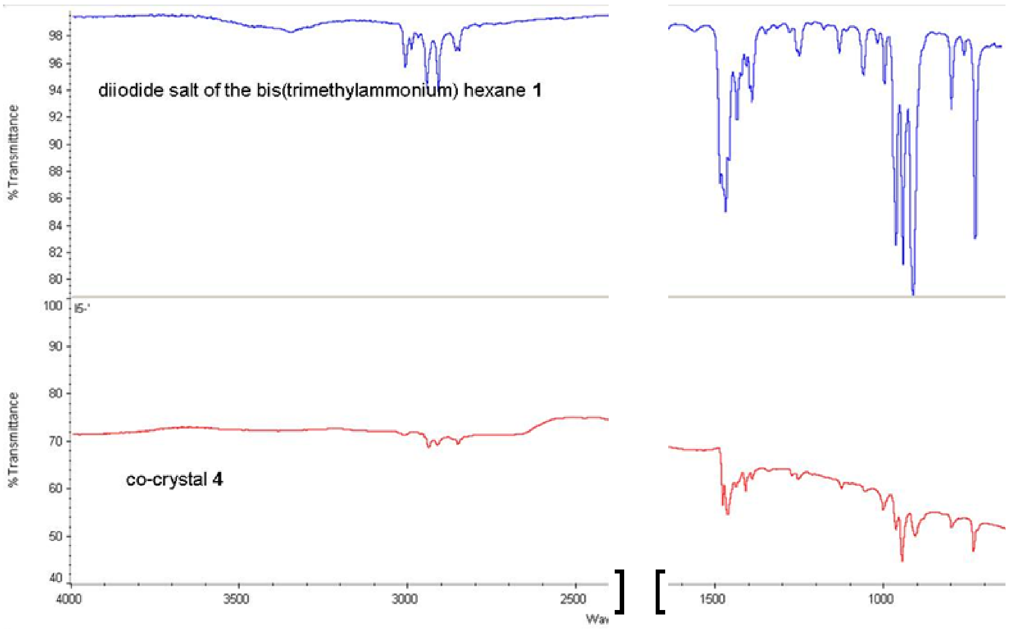

Figure SI6. IR spectra for **1** and co-crystal **4**

FT-Raman spectra have been colletcted with a Thermo Nicolet Nexus 870 spectrometer equipped with a FT-Raman module. Laser exciting line : Nd-YAg laser emitting at 1,064nm . Laser power at sample in the range of 100 mW ; collection parameters provided 2 cm^{-1} as spectral resolution, while 2048 scans have been coadded (Figure SI7).

co-crystal **2** Raman (y̤ diagnostic band): 161 cm^{-1}

co-crystal **3** Raman (y̤ diagnostic bands): 147 and 109 cm^{-1}

co-crystal **3** Raman (y̤ diagnostic bands): 164, 147 and 110 cm^{-1}

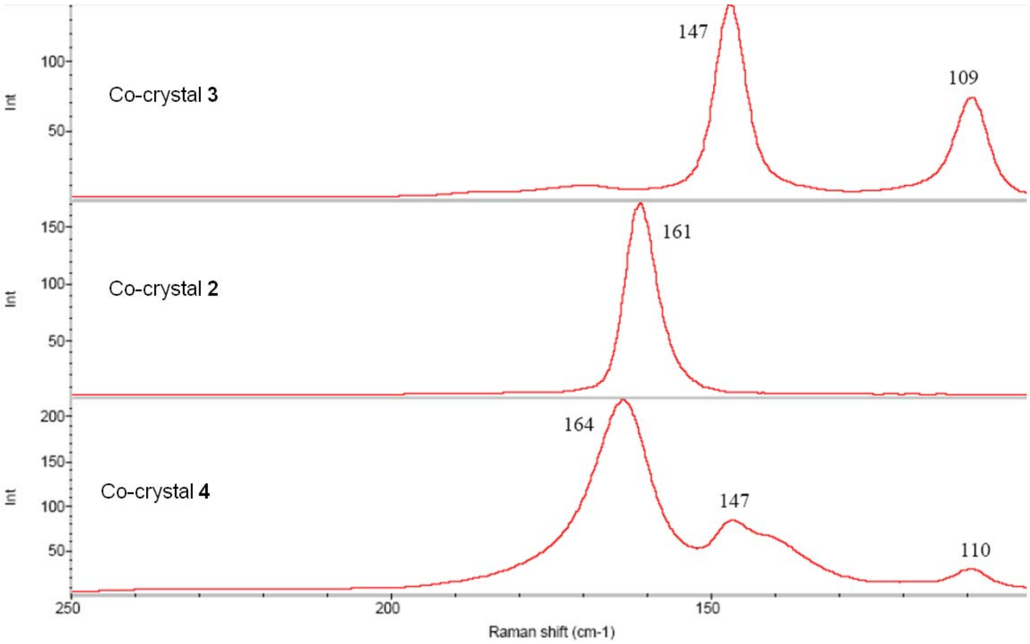

Figure SI7. Raman spectra for the co-crystals **2, 3** and **4**

XRay diffraction analyses of 1, 2, 3 and 4 (single crystal and powder).

Single crystal data collection, structure solution and refinement.

Data were collected on a Bruker KAPPA APEX II diffractometer with Mo-Kα radiation and CCD detector. All the compounds give stable crystals a room temperature, excluding pure **4** which was collected at low temperature (123K) using CRYOFLEX devices. The structures were solved by *SIR*2002[1] and refined by *SHELXL*-97[2] programs, respectively. The refinement was carried on by full-matrix least-squares on F^2. Hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms (Table SI1 and Figure SI8-10).

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table SI1. Crystal data and structure refinement for **2**, **3**, and **4**

	2	**3**	**4**
Formula	$C_{12}H_{30}I_4N_2$	$C_{12}H_{30}I_6N_2$	$C_{12}H_{30}I_{10}N_2$
M	709.98	963.78	1471.38
crystal color	red	intense red	dark red
dimension [mm^3]	0.04x0.18x0.36	0.07x0.32x0.46	0.12x0.25x0.46
crystal system	monoclinic	monoclinic	monoclinic
space group	*C2/m*	*C2/m*	*C2/m*
a [Å]	25.963(5)	21.891(4)	16.675(4)
b [Å]	7.5588(16)	7.6086(14)	7.736(2)
c [Å]	5.8260(12)	7.8147(15)	12.727(3)
β [°]	100.17(2)	92.79(2)	100.22(2)
V [Å^3]	1125.4(4)	1300.1(4)	1615.7(7)
Z	2	2	2
T [K]	295	295	123

ρ_{calc} [g cm^{-1}]	2.095	2.462	3.024
$\mu(\mathrm{MoK}_\alpha)$ [mm^{-1}]	5.530	7.165	9.593
θ_{max} [°]	30.56	30.65	31.33
data collected	6319	7324	15847
unique data	1737	2014	2726
R_{int}	0.0254	0.0358	0.0270
No. obs. data $I_o>2\sigma(I_o)$]	1514	1463	2464
no. parameters	75	60	71
no. restraints	16	-	-
R_{all}	0.0449	0.0422	0.0426
R_{obs}	0.0391	0.0286	0.0376
wR_{all}	0.1175	0.0822	0.0972
wR_{obs}	0.1113	0.0718	0.0923
goodness-of-fit	1.055	1.033	1.108
$\Delta\rho_{\mathrm{min,max}}$ [e Å^{-3}]	-1.66, 1.72	-0.77, 0.83	-2.08, 4.35
CCDC	743342	755088	755087

Note for Co-crystal 4. The large residues found in **4** (from -2.08 to 4.35 e Å^{-3}) are not surprising: in our experience,[3] the residues around heavy atoms become larger lowering the temperature of data collection and increasing the data resolution, especially for atoms lying on the molecular periphery; they are essentially due to 'banana' motion of atoms , not sufficiently taken in account from the usual anisotropic refinement. This is the case of **4**, the data of which were collected at 123 K and to a $2\theta_{\mathrm{max}} = 60$ °. These residues completely disappear, without any substantial change in the molecular geometry, when third and fourth cumulants are adopted for thermal motion, as allowed by code for refinement more sophisticated than SHELXL, such as VALRAY or XD.

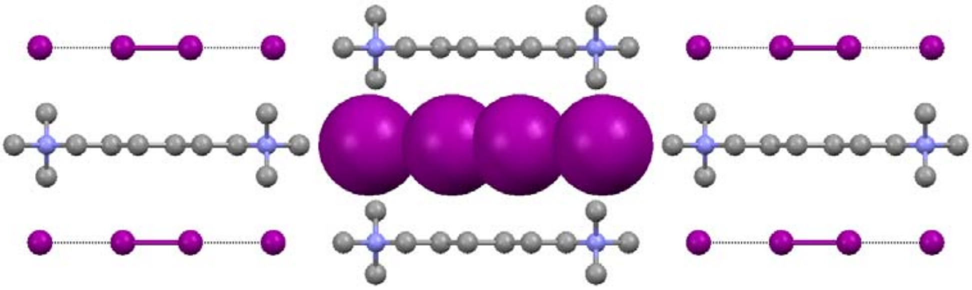

Figure SI8. The crystal packing of the complex **2** viewed down crystallographic *c* axis. Colour code: Carbon: gray, Nitrogen: pale blue, Iodine: purple. The hydrogen atoms are omitted for clarity. Central I_4^{-2} moiety is pictured in spacefill model.

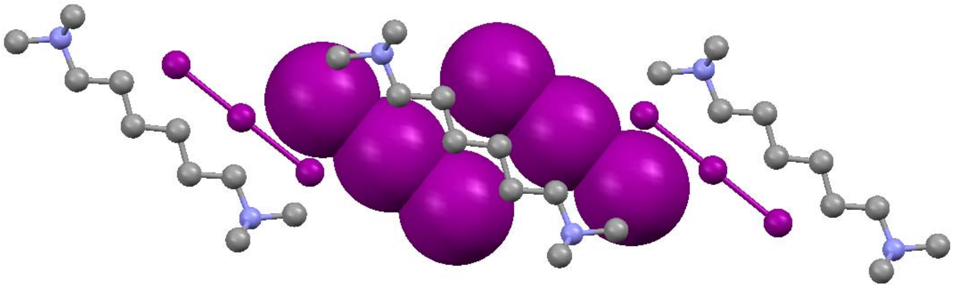

Figure SI9. The crystal packing of the complex **3** viewed down crystallographic *b* axis and rotating -90° along z axis. Colour code: Carbon: gray, Nitrogen: pale blue, Iodine: purple. The hydrogen atoms are omitted for clarity. Central I_3^- moieties are pictured in spacefill model.

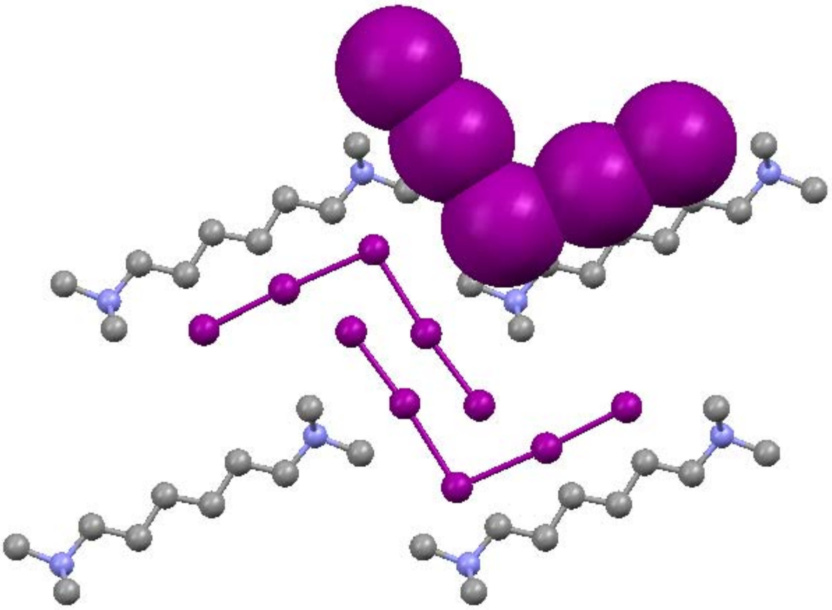

Figure SI9. The crystal packing of the complex **4** viewed down crystallographic *b* axis. Colour code: Carbon: gray, Nitrogen: pale blue, Iodine: purple. The hydrogen atoms are omitted for clarity. Central I_5^- moiety is pictured in spacefill model.

Powder data collection, structure solution and refinement

The X–ray powder diffraction data was measured with PANalytical X´Pert PRO diffractometer in Bragg–Brentano geometry using Johansson monochromator (α_1 setup) to produce pure CuKα_1 radiation (1.5406 Å; 45kV, 30mA) and step–scan technique in 2θ range of 3.5–72°. The data was collected by X´Celerator detector in continuous scanning mode with a step size of 0.0167° and using sample dependently counting times of 40 to 440 sec per step. Programmable divergence slit (PDS) was used in automatic mode to set irradiated length on sample to 10 mm together with 10 mm incident beam mask. Soller slits of 0.02° rad. were used on both incident and diffracted beam sides together with anti–scatter slits (4° and 13 mm, respectively). Before further analyses, the diffraction data were converted from automatic slit mode (ADS) to a fixed slit mode (FDS) data by the tools implemented in Highscore Plus v. 2.2c software package. Hand-ground powder samples were prepared on a silicon-made zero–background holder using petrolatum jelly as an adhesive. The simulated powder diffraction patterns were generated from the CIF-files of the known single crystal structures by the program Mercury[4]. To confirm the consistency of the measured diffraction pattern with an expected single crystal structure, Rietveld refinements were carried out for the XRD patterns by FULLPROF[5] program, when applicable, using the expected single crystal structure parameters as basis for a refinement. Typically, all global and profile parameters were refined together with atomic coordinates of the iodine atoms at final stage. Polynomial of Chebyshev type I with eight coefficients was used as a background function for each XRD pattern.

The diffraction patterns of compound **1** and co-crystal **2**, **3** and **4** together with the simulated XRD patterns originating from the single crystal structure CIF-files are illustrated in Figure SI10.

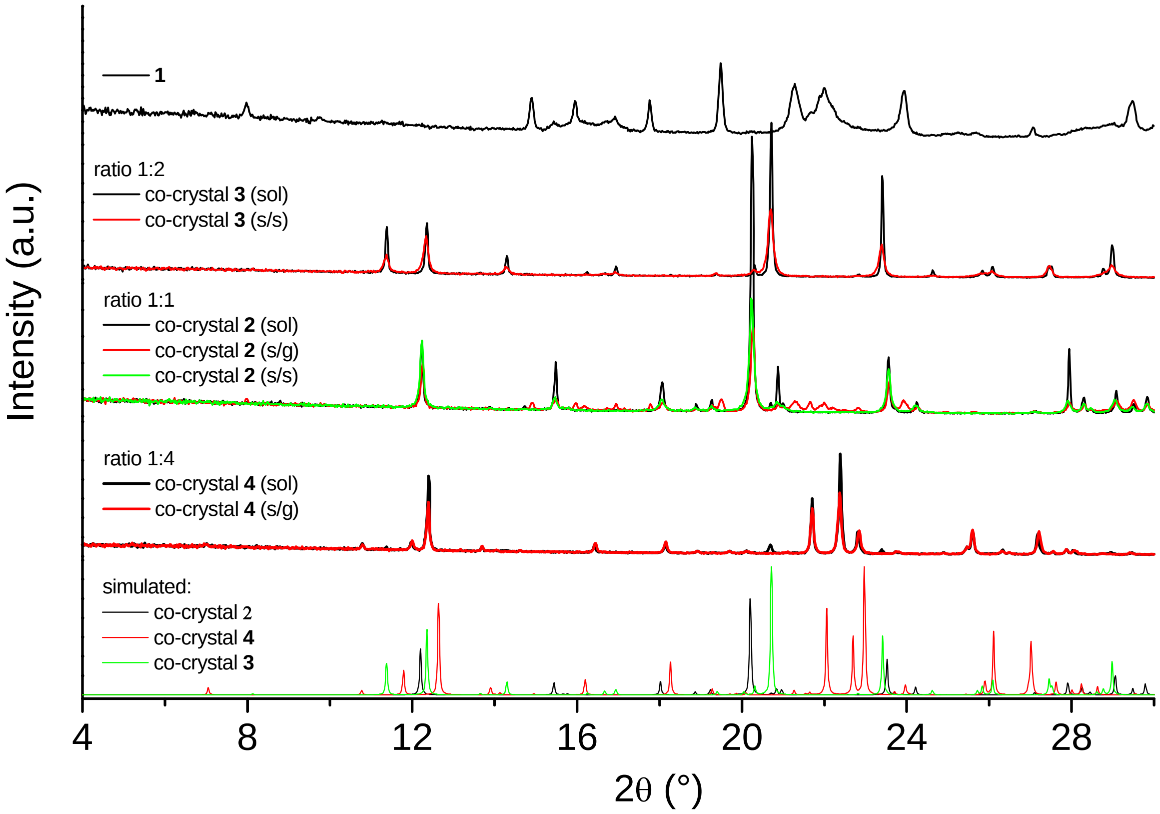

Figure SI10. XRD patterns of compound **1** and co-crystal **2**, **3** and **4**, and the simulated patterns of single crystal structure. Patterns are grouped by the mixing ratio of hexamethonium iodide and iodine. (sol: solution; s/s: solid/solid; s/g: solid/gas)

Diiodide salt of the bis(trimethylammonium) hexane (**1**)

Based on XRD data of hexamethonium iodide (further on hexameth), the bulk powder exhibits relatively low crystallinity due to low overall intensity gain, and clearly broadened diffraction line widths indicating decrease in average size of the diffracting crystallites. Broad diffraction humps at low 2θ-range below the observed reflections indicate also some degree of amorphous content to be present, as well. Therefore, the inadequate quality of the XRD pattern (mainly due to low crystallinity) prevents unit cell indexing, and as a consequence of that a structure solving of this phase.

Hexameth iodide/I_2 co-crystals with mixing ratio of 1:2 (**3**)

The co-crystals with mixing ratio 1:2 were prepared via two methods; from solution and by grinding in solid state. The consistency between both bulk powders ($\mathbf{3}_{\mathbf{pwd1}}$ and $\mathbf{3}_{\mathbf{pwd2}}$) and the expected single crystal structure ($\mathbf{3}_{\mathbf{sc}}$) can be confirmed as the XRD patterns corresponding to the bulk powders obtained either from a solution or by grinding via solid state are mutually consistent, as well as they match with the simulated diffraction pattern of $\mathbf{3}_{\mathbf{sc}}$ (Figures SI10 and SI11). By comparing the overall intensities and the full width maximums (fwhm) of the diffraction peaks on both experimental XRD patterns (Figure SI11), it can be concluded that in a sense of crystallinity, the bulk powder obtained from a solution is more crystalline to that of the powdery product obtained by grinding. For both XRD patterns the Rietveld refinement was successful revealing reasonable agreement between the calculated and measured profiles for $\mathbf{3_{pwd1}}$ and, in case of the $\mathbf{3_{pwd2}}$ excellent R-values for the refinement were obtained (Table SI2). Finally, it also can be noted that residual diffraction peaks relating to an impurity phase was not observed on neither of the powder patterns. Final Rietveld refinement plot is exemplified in Figure SI12.

Table SI2. Refined cell parameters of powder diffraction data ($\mathbf{3_{pwd1}}$ and $\mathbf{3_{pwd2}}$) compared to those of single crystal data of $\mathbf{3_{sc}}$.

	Cell Parameters		
	$\mathbf{3_{pwd1}}$	$\mathbf{3_{pwd2}}$	$\mathbf{3_{sc}}$
a	21.917(1)	21.913(2)	21.891(4)
b	7.6102(4)	7.6125(6)	7.6086(14)
c	7.8120(4)	7.8082(6)	7.8147(15)
α	90	90	90
β	92,817(3)	92.809(4)	92.79(2)
γ	90	90	90
V	1301.42	1300.95	1300.07
SG	C2/m (No. 12)	C2/m (No. 12)	C2/m (No. 12)
R_B (%)	19.2	4.14	
R_p (%)	13.75	7.65	
R_{wp} (%)	22.2	10.72	

$$R_B = 100\frac{\sum_{\mathbf{h}} \left| {}'I_{obs,\mathbf{h}}' - I_{calc,\mathbf{h}} \right|}{\sum_{\mathbf{h}} \left| {}'I_{obs,\mathbf{h}}' \right|} \qquad R_p = 100\frac{\sum_{i=1,n} \left| y_i - y_{c,i} \right|}{\sum_{i=1,n} y_i} \qquad R_{wp} = 100\left[\frac{\sum_{i=1,n} w_i \left| y_i - y_{c,i} \right|^2}{\sum_{i=1,n} w_i y_i^2} \right]^{1/2}$$

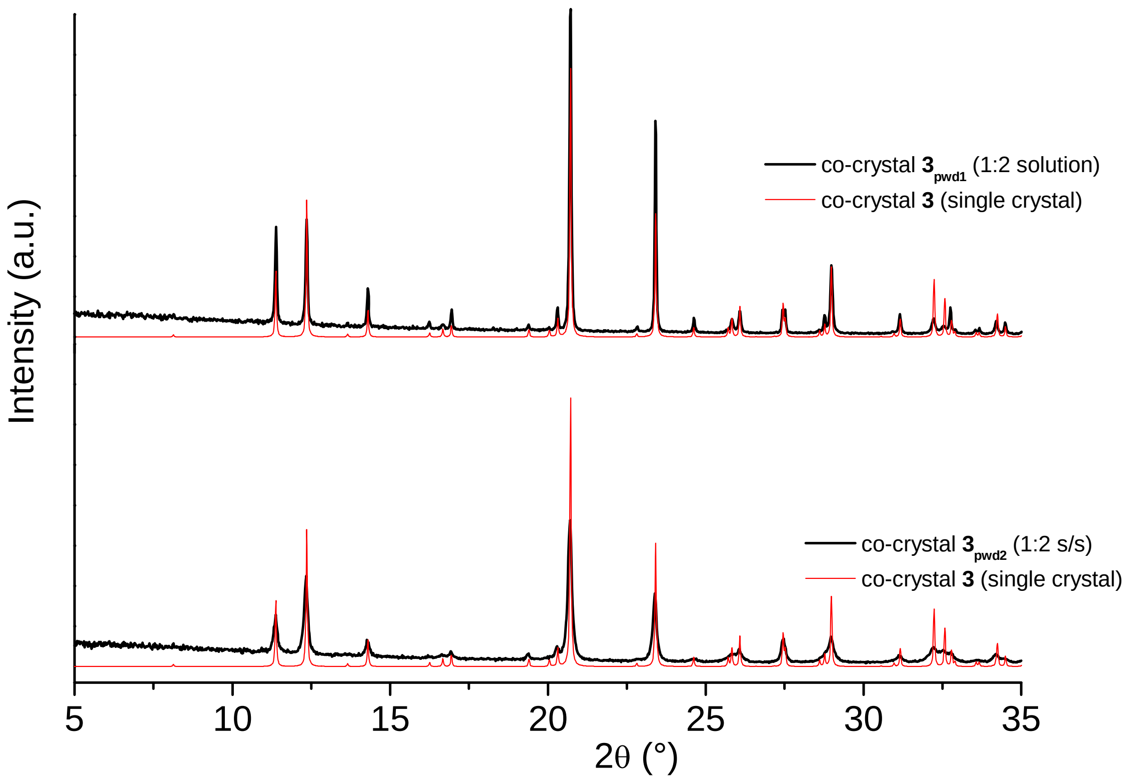

Figure SI11. XRD patterns of $\mathbf{3_{pwd1}}$ (1:2 solution) and $\mathbf{3_{pwd2}}$ (1:2 solid/solid reaction) compared to the simulated XRD pattern of expected single crystal structure $\mathbf{3_{sc}}$.

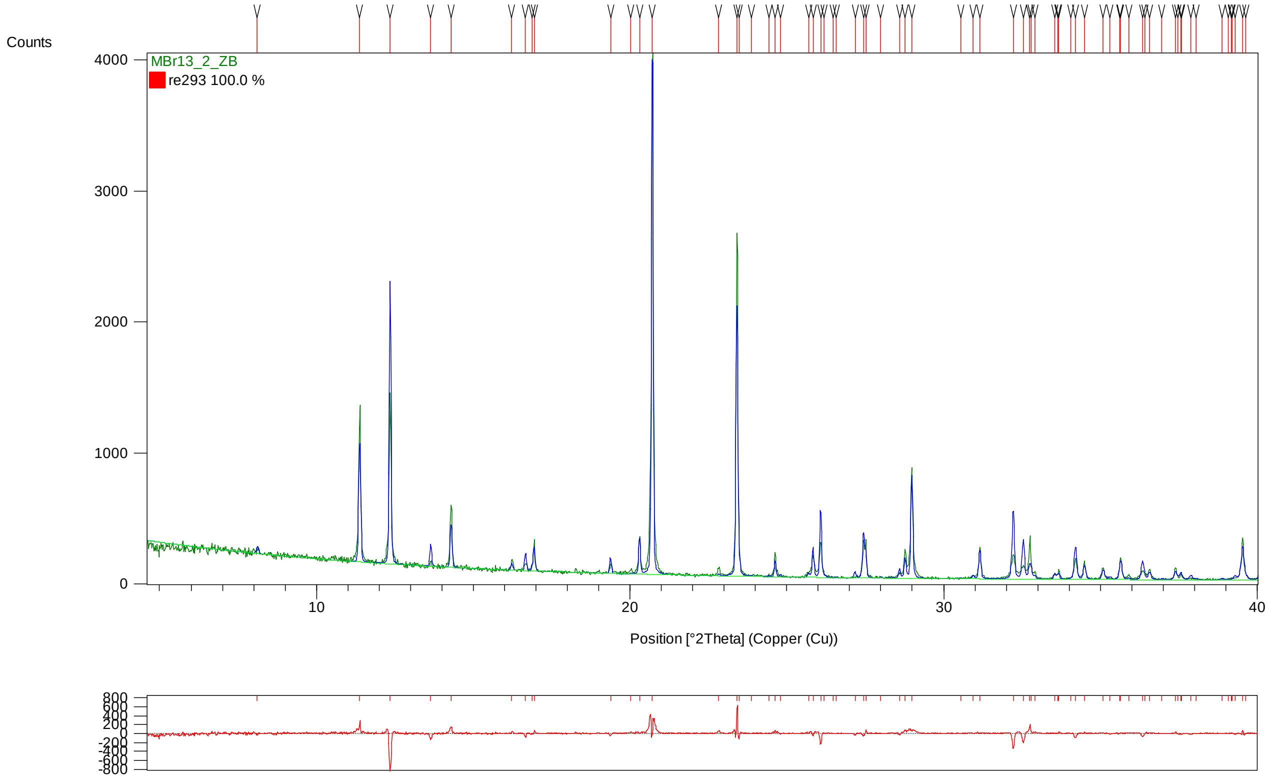

Figure SI12. Final Rietveld refinement plot of $\mathbf{3}_{\mathbf{pwd1}}$. The red tick marks on top represent the diffraction positions, green line the observed pattern, blue line the best fitted profile, and the red difference curve between observed and calculated profile at the lower graph.

Hexameth iodide/I_2 co-crystals with mixing ratio of 1:1 ($\mathbf{2}_{\mathbf{pwd1}}$, $\mathbf{2}_{\mathbf{pwd2}}$ and $\mathbf{2}_{\mathbf{pwd3}}$)

The co-crystals with mixing ratio 1:1 were prepared via three methods; from solution, solid/reaction and by grinding in solid state. The consistency between all three bulk powders ($\mathbf{2}_{\mathbf{pwd1}}$, $\mathbf{2}_{\mathbf{pwd2}}$ and $\mathbf{2}_{\mathbf{pwd3}}$) and the expected single crystal structure ($\mathbf{2}_{\mathbf{sc}}$) can be confirmed as the XRD patterns corresponding to the bulk powders are mutually consistent, as well as they match with the simulated diffraction pattern of $\mathbf{2}_{\mathbf{sc}}$ single crystal (Figures SI10 and SI13). In one case of powder $\mathbf{2}_{\mathbf{pwd}}$ some diffraction peaks corresponding to an impurity phase can also be observed (Figure SI13) in the powder pattern, which was identified as unreacted hexamethonium iodide. In sense of crystallinity, the highest degree is clearly presented by the bulk powder of an another batch $\mathbf{2}_{\mathbf{pwd1}}$ which is obtained from a solution. The Rietveld refinements were only carried out with the single phased patterns as no structural parameters are available for the hexamethonium iodide. For all the powder batches the refinements were successful revealing reasonable agreement between the calculated and measured profiles for both powder patterns (Table SI3). Final Rietveld refinement plot is exemplified in Figure SI14.

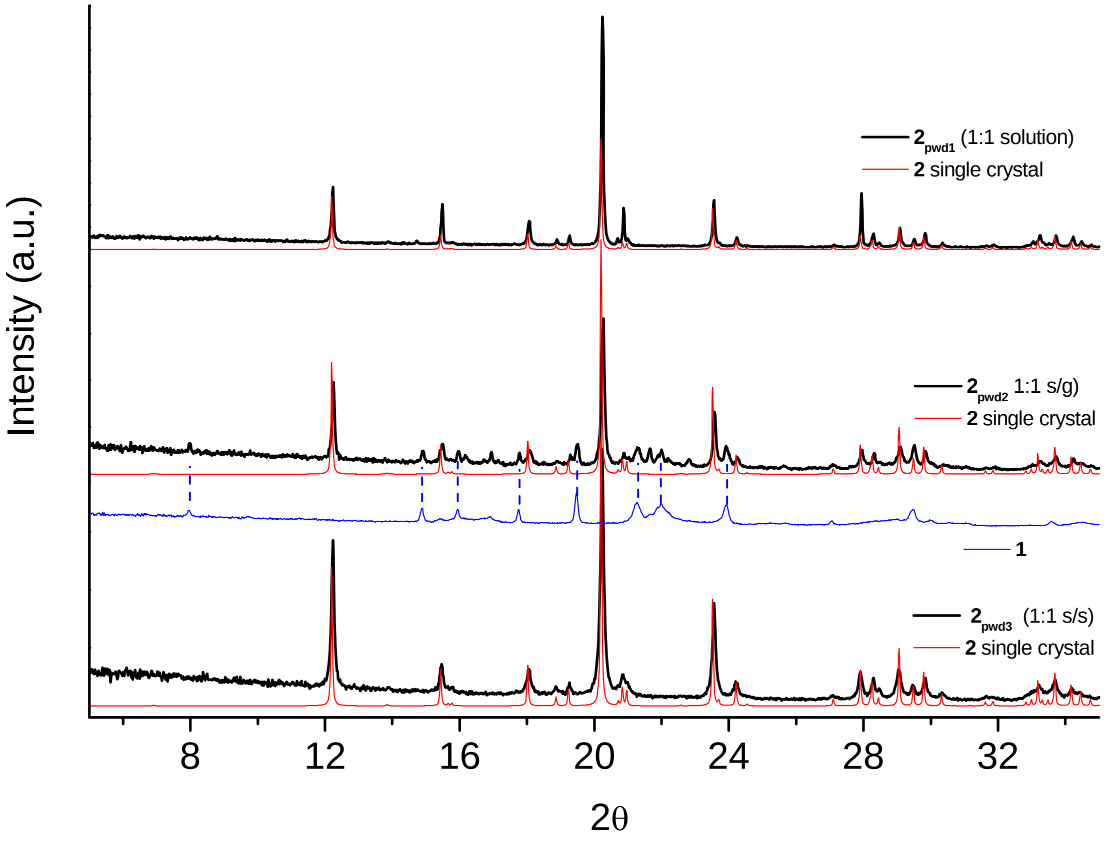

Figure SI13. XRD patterns of **1** (hexamethonium iodide), $\mathbf{2}_{\mathbf{pwd1}}$ (1:1 solution), $\mathbf{2}_{\mathbf{pwd2}}$ (1:1 solid/gas) and $\mathbf{2}_{\mathbf{pwd3}}$ (1:1 solid/solid) compared to the simulated diffraction pattern of the expected single crystal structure $\mathbf{2}_{\mathbf{sc}}$. Some diffraction peaks of hexamethonium iodide impurity on $\mathbf{2}_{\mathbf{pwd2}}$ pattern is pointed out by dashed blue lines.

Table SI3. Refined cell parameters of powder diffraction data ($\mathbf{2_{pwd1}}$, $\mathbf{2_{pwd2}}$ and $\mathbf{2_{pwd3}}$) compared to those of single crystal data of $\mathbf{2_{sc}}$.

	Cell Parameters		
	$\mathbf{2_{pwd1}}$	$\mathbf{2_{pwd3}}$	$\mathbf{2_{sc}}$
a	25.961(2)	25.995(3)	25.963(5)
b	7.5558(5)	7.5568(8)	7.5588(16)
c	5.8224(4)	5.8296(7)	5.8260(12)
α	90	90	90
β	100.213(5)	100.240(8)	100.17(2)
γ	90	90	90
V	1124.99	1126.93	1300.07
SG	C2/m (No. 12)	C2/m (No. 12)	C2/m (No. 12)
R_B (%)	15.67	11.13	
R_p (%)	11.46	9.02	
R_{wp} (%)	18.11	12.91	

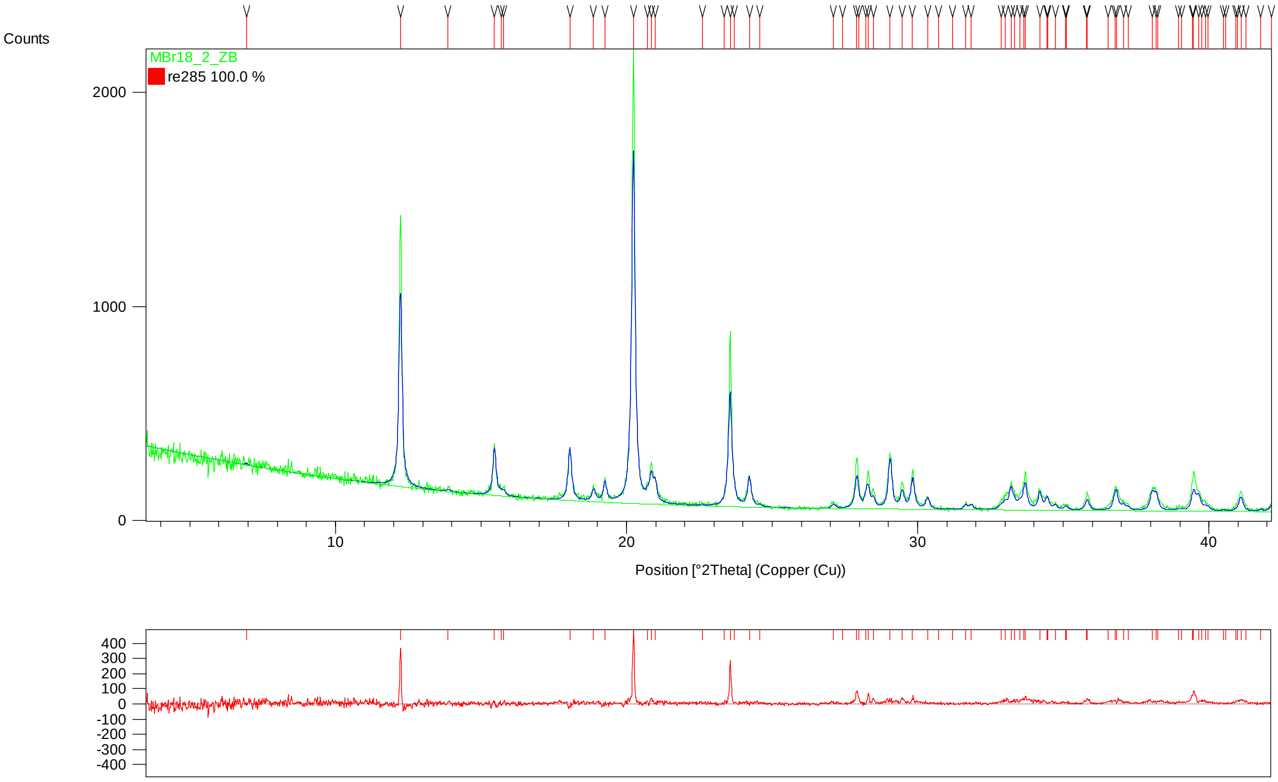

Figure SI14. Final Rietveld refinement plot of $\mathbf{2_{pwd3}}$. The red tick marks on top represent the diffraction positions, green line the observed pattern, blue line the best fitted profile, and the red difference curve between observed and calculated profile at the lower graph.

Hexameth iodide /I$_2$ co-crystals with mixing ratio of 1:4 ($\mathbf{4_{pwd1}}$ and $\mathbf{4_{pwd2}}$)

The co-crystals with mixing ratio 1:4 were prepared via two methods; from solution and by grinding in solid state. The consistency between both bulk powders ($\mathbf{4_{pwd1}}$ and $\mathbf{4_{pwd2}}$) and the expected single crystal structure (**4**) can NOT be confirmed. The XRD patterns corresponding to the bulk powders are mutually consistent but they differ from the simulated diffraction pattern of **4**

(Figures SI10 and SI15), although certain degree of resemblance is clearly observable. It looks just like the one of the cell axes might be elongated for some reason as the similar peak formations on both simulated and the experimental patterns can be observed but the peaks only differing somewhat on angular positions. Furthermore, in case of **4**$_{\mathbf{pwd1}}$ some diffraction peaks corresponding to an impurity phase can also be observed (Figure SI15), which was identified to be the strongest reflections corresponding to **3**$_{\mathbf{pwd1}}$ structure, as can be seen in Figure SI15. The overall crystallinity seems to be similar on both bulk powders. The **4**$_{\mathbf{pwd2}}$ was tried to index using all five indexing programs (ITO, TREOR, DICVOL, DICVOL04, McMaille) implemented in HighScore plus. At least one potential monoclinic cell candidate was found with figure of merit of 46 (using ITO) and having zero-unindexed lines out of first 20 peaks used for indexing. However, the space group could not be determined unambiguously. The lattice parameters for the cell are given in Table SI4.

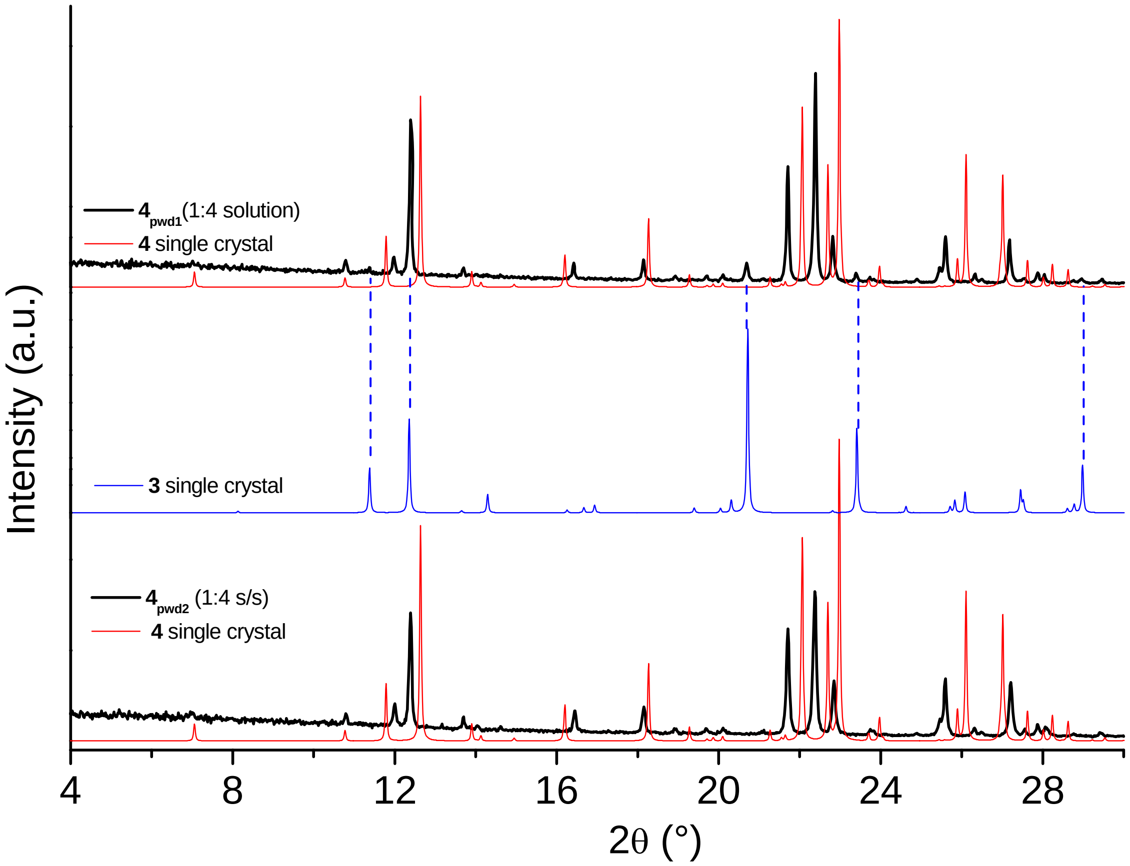

Figure SI15. XRD patterns of **4**$_{\mathbf{pwd1}}$ (1:4 solution) and **4**$_{\mathbf{pwd2}}$ (1:4 solid/solid) compared to simulated patterns of two single crystal structures (**4** and **3**). The peak positions of **3**$_{\mathbf{sc}}$ phase in **4**$_{\mathbf{pwd1}}$ pattern is pointed out by dashed blue lines.

Table 4. Cell parameters found for **4**$_{\mathbf{pwd2}}$ phase

Cell parameter			
a	12.89(1)	α	90.0
b	8.028(9)	*β*	98.01(1)
c	16.79(3)	*γ*	90.0
SG	-	V	1721.27

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