Electronic Supporting information for:

N…I halogen bonding supported stabilization of a discrete pseudo-linear polyiodide  $[I_{12}]^{2-}$ 

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## **Experimental details**

## Syntheses and crystallizations

All solvents and reagents were purchased from Sigma-Aldrich and were used without further purification. The two dicationic N-donors were prepared according to a literature method using 1,4-diazabicyclo[2.2.2]octane and 1,6-diiodohexane and 1,8-diiodooctane for synthesis of  $1 \cdot 2I^-$  and  $2 \cdot 2I^-$ , respectively.<sup>1</sup> The syntheses of the corresponding PF<sub>6</sub><sup>-</sup> salts,  $1[PF_6]_2$  and  $2[PF_6]_2$ , were carried out by an anion metathesis reaction which involved dissolving one equivalent of the halide salt of 1 or 2 and three equivalents of KPF<sub>6</sub> separately in minimum amount of water after which the two solutions were combined. The resulting fine white precipitates were filtered, washed with cold water (until a negative AgNO<sub>3</sub> test resulted) and dried in air.

<u>The polyiodides  $1 \cdot I_4^{2-}$ ,  $1 \cdot 2I_3^{-}$  and  $2 \cdot 2I_3^{-}$ </u> were crystallized by dissolving 0.02 mmol of the corresponding iodide salt  $(1 \cdot 2I^{-} \text{ or } 2 \cdot 2I^{-})$  in methanol (ca. 2-3 ml) into which 0.02 or 0.04 mmol of  $I_2$ , dissolved in acetonitrile (ca. 3-4 ml), was added. In case of 1, crystals of both  $I_4^{2-}$  and  $I_3^{-}$  salts were obtained by a slow evaporation of the solvent (structure of  $1 \cdot 2I_3^{-}$  is shown in Fig. S3 and powder X-ray diffraction (PXRD) analyses of iodide salts of cation 1 are shown in Fig. S6). In case of 2, both 1:1 and 1:2 reactions led to a crystallization of a triiodide species, but with two different polymorphs, I and II, respectively (see powder X-ray characterization in Fig. S7). Both polymorphs I and II could be also characterized by single crystal X-ray, despite the poor crystal quality of polymorph II (the CCDC data consist of cifs of only polymorph I whereas II is presented in the ESI only). These two structures exhibit similar  $I_3^{-} \cdots I_3^{-}$  units but distinct intermolecular packing (Fig. S4 and Fig. S5). Crystallizations were also carried out by passing  $I_2$  vapors into acetonitrile/methanol solutions of  $1 \cdot 2I^{-}$  and  $2 \cdot 2I^{-}$ . Consequently, good quality single crystals, corresponding to  $1 \cdot I_4^{2-}$  and  $2 \cdot 2I_3^{-}$  (polymorph I), were obtained.

<u>The polyiodides  $[I_2 \cdots 1 \cdots I_2] \cdot I_{16}^{2-}$  and  $2 \cdot I_{12}^{2-}$  were crystallized by dissolving 0.02 mmol of the corresponding PF<sub>6</sub><sup>-</sup> salt (1[PF<sub>6</sub>]<sub>2</sub> or 2[PF<sub>6</sub>]<sub>2</sub>) into acetonitrile (ca. 5 ml) together with 10 equivalents of I<sub>2</sub>. After a prolonged standing of the solution and eventual evaporation of the solvent,  $[I_2 \cdots 1 \cdots I_2] \cdot I_{16}^{2-}$  was obtained only in single crystal quantities together with a yellow precipitate, which was subsequently characterized as the  $[I_2 \cdots 1 \cdots I_2]$ [PF<sub>6</sub>]<sub>2</sub> complex by PXRD. Conversely, crystals of  $2 \cdot I_{12}^{2-}$  could be obtained as a single product upon standing the corresponding solution for several days. Further attempts to obtain  $2 \cdot I_{12}^{2-}$  by mixing 5-10 equivalents of I<sub>2</sub> with  $2 \cdot 2I^-$  in methanol led to an instant precipitation of dark brown powder [ $2(5I_2) \cdot 2I^-$ ] with similar chemical composition to  $2 \cdot I_{12}^{2-}$  (calcd. (%) for  $C_{20}H_{40}N_4I_{12}$ : C, 12.92; H, 2.17; N, 3.01. Found ( $2 \cdot I_{12}^{2-}$ ): C, 12.71; H, 2.13; N, 3.04; [ $2(5I_2) \cdot 2I^-$ ]: C, 13.12; H, 2.29; N, 3.07). However, this amorphous product is not crystallographically equivalent to  $2 \cdot I_{12}^{2-}$  (see comparison of PXRD graphs of  $2 \cdot I_{12}^{2-}$  and  $2(5I_2) \cdot 2I^-$  in Fig. S8).</u>

<u>Complexes  $[I_2 \cdots 1 \cdots I_2][PF_6]_2$  and  $[I_2 \cdots 2 \cdots I_2][PF_6]_2$ </u> could be obtained by an addition of  $I_2$  (0.04 mmol in 2-3 ml CHCl<sub>3</sub>) to a MeCN solution (1 ml) of  $\mathbf{1}[PF_6]_2$  and  $\mathbf{2}[PF_6]_2$  (0.02 mmol), respectively. The resulting fine orange/yellow precipitates were isolated by centrifugation, washed with CHCl<sub>3</sub> and recrystallized from MeCN to obtain single crystals of  $[I_2 \cdots 1 \cdots I_2][PF_6]_2$  and  $[I_2 \cdots 2 \cdots I_2][PF_6]_2$  (Fig. S1 and Fig. S2).

## Single crystal X-ray diffraction measurements

Single crystal measurements and data reductions were carried out using one of the two following methods:

- 1) For well-diffracting crystals, the data collection was carried out using Bruker-Nonius KappaCCD diffractometer equipped with Apex II detector using Mo  $K_{\alpha}$  ( $\lambda = 0.71073$  Å) radiation. Data collection and processing were done with programs COLLECT<sup>2</sup> and DENZO-SMN,<sup>3</sup> respectively, and semi-empirical absorption corrections were carried out with SADABS.<sup>4</sup>
- 2) For weakly diffracting crystals, Agilent SuperNova diffractometer, equipped with multilayer optics monochromated dual source (Cu and Mo) and Atlas detector, was used. Data acquisitions, reductions and analytical face-index based absorption corrections were made using program CrysAlisPRO.<sup>5</sup>

The structures were solved by using either SHELXS<sup>6</sup> or Superflip<sup>7</sup> program and full matrix least-squares refinements on  $F^2$  were performed using SHELXL-2013,<sup>6</sup> all in the Olex<sup>2</sup> program package.<sup>8</sup> All heavy atoms (excluding hydrogens) were refined using anisotropic displacement parameters. Hydrogen atoms were refined with a riding model with isotropic displacement parameters 1.2 times to their host carbon atoms. All anisotropic thermal ellipsoids in ESI are presented at the 50 % probability level. The refined structures of  $1 \cdot I_4^{2-}$ ,  $2 \cdot 2I_3^-$  (I),  $2 \cdot 2I_3^-$  (II),  $[I_2 \cdots 1 \cdots I_2][PF_6]_2$  and  $[I_2 \cdots 2 \cdots I_2][PF_6]_2$  show significant amount of residual electron density. This unrefined electron density lies close to iodine atoms, hence it can be accounted for absorption. The CheckCif report of structure  $1 \cdot 2I_3^-$  contains several C-level alerts related to anisotropic displacement parameters is not beneficial as the data in question is measured at the room temperature and, consequently, exhibits larger thermal displacement parameters. All crystallographic data are presented in Table S1.

## **Powder X-ray diffraction measurements (PXRD)**

All powder X-ray measurements (Fig. S6 - Fig. S8) were conducted with PANalytical X'Pert PRO diffractometer using a Johansson monochromator to produce pure Cu  $K_{\alpha l}$  radiation (1.5406 Å; 45 kV, 30 mA). The lightly hand ground samples were prepared on a Si-plate (zero-background producing) using white petrolatum jelly as an adhesive. The data were collected with X'Celerator detector with 20 range of 2–70° using a step size of 0.0167° while rotating the sample. The program X'pert HighScore Plus v. 2.2d was used for data analysis, and the simulated PXRD patterns were generated by the program Mercury.<sup>9</sup>

Identification code	$1 \cdot I_4^{2-}$	1·2I <sub>3</sub> -	$2 \cdot 2I_3^{-}(I)$	$2 \cdot 2I_3^{-}$ (II)	$[I_2 \cdots 1 \cdots I_2] \cdot {I_{16}}^{2-}$	$2 \cdot I_{12}^{2-}$	$[I_2 \cdots 1 \cdots I_2][PF_6]_2$	$[I_2 \cdots 2 \cdots I_2][PF_6]_2$
Empirical formula	$C_{18}H_{36}N_4I_4$	$C_{18}H_{36}N_4I_6$	$C_{20}H_{40}N_4I_6$	$C_{20}H_{40}N_4I_6$	$C_{18}H_{36}N_4I_{20}$	$C_{20}H_{40}N_4I_{12}$	$C_{18}H_{36}N_4F_{12}P_2I_4\\$	$C_{20}H_{40}N_4P_2F_{12}I_4$
Formula weight (g/mol)	816.11	1069.91	1097.96	1097.96	2846.51	1859.36	1106.05	1134.1
Temperature/K	123	298	123	123	123	123	123	123
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	triclinic	triclinic	triclinic	triclinic
Space group	Pnma	Pbam	Pbca	Pbam	Pl	Pl	Pl	Pl
a/Å	28.9478(14)	23.6028(6)	16.8096(2)	30.718(5)	9.2353(4)	8.8468(5)	7.3275(5)	8.1603(6)
b/Å	14.3498(9)	25.1893(8)	15.32770(10)	6.6794(14)	9.5741(4)	9.2378(4)	8.5017(6)	9.2796(8)
c/Å	6.3034(4)	7.6207(2)	22.8613(3)	7.4035(13)	15.2398(7)	13.5621(8)	13.4868(9)	11.8828(5)
α/°	90	90	90	90	92.225(4)	102.188(3)	84.830(6)	96.851(5)
$\beta/^{\circ}$	90	90	90	90	94.475(4)	92.217(2)	86.312(6)	90.584(5)
γ/°	90	90	90	90	92.593(4)	106.349(3)	74.381(6)	111.270(7)
Volume/Å <sup>3</sup>	2618.4(3)	4530.8(2)	5890.27(11)	1519.0(5)	1340.80(10)	1033.87(10)	805.17(10)	831.15(10)
Z	4	6	8	2	1	1	1	1
$\rho_{calc}/g\;cm^{\text{-}3}$	2.07	2.353	2.476	2.4	3.525	2.986	2.281	2.266
$\mu/\text{mm}^{-1}$	4.771	6.183	6.344	6.15	11.553	9.004	32.151	31.229
F(000)	1536	2940	4048	1012	1232	824	522	538
Crystal size/mm3	0.20×0.15×0.05	0.22×0.2×0.04	0.25×0.2×0.05	0.22×0.12×0.02	0.28×0.18×0.12	0.24×0.20×0.15	0.23×0.16×0.12	0.20×0.12×0.08
Radiation	$Mo K_{\alpha}$ ( $\lambda = 0.71073$ )	$Mo K_{\alpha}$ ( $\lambda = 0.71073$ )	$Mo K_{\alpha}$ ( $\lambda = 0.71073$ )	$Mo K_{\alpha}$ ( $\lambda = 0.71073$ )	$Mo K_{\alpha}$ ( $\lambda = 0.71073$ )	Mo $K_{\alpha}$ ( $\lambda = 0.71073$ )	$Cu K_{\alpha}$ ( $\lambda = 1.54184$ )	$Cu K_{\alpha}$ ( $\lambda = 1.54184$ )
2\overline{O} range for data collection/°	6.306 to 51.998	3.234 to 52	4.31 to 52	5.304 to 49.996	6.296 to 52	4.724 to 49.992	6.586 to 135.862	7.506 to 137.958
Index ranges	$-35 \le h \le 35,$ $-17 \le k \le 16,$ $-6 \le l \le 7$	$-29 \le h \le 17,$ $-31 \le k \le 31,$ $-9 \le l \le 8$	$\begin{array}{l} -20 \leq h \leq 16, \\ -18 \leq k \leq 18, \\ -28 \leq l \leq 28 \end{array}$	$\begin{array}{l} -36 \leq h \leq 26, \\ -4 \leq k \leq 7, \\ -8 \leq l \leq 8 \end{array}$	$-11 \le h \le 9$ , $-11 \le k \le 11$ , $-18 \le l \le 18$	$-10 \le h \le 10,$ $-10 \le k \le 10,$ $-16 \le l \le 16$	$\begin{array}{l} -8 \leq h \leq 3, \\ -10 \leq k \leq 10, \\ -16 \leq l \leq 15 \end{array}$	$-9 \le h \le 9$ , $-11 \le k \le 10$ , $-7 \le l \le 14$
Reflections collected	15764	20815	37444	4673	8950	13721	5322	5124
Independent reflections	2638 [R <sub>int</sub> = 0.0525, R <sub>sigma</sub> = 0.0357]	4796 [R <sub>int</sub> = 0.0465, R <sub>sigma</sub> = 0.0433]	5750 [ $R_{int} = 0.0457$ , $R_{sigma} = 0.0334$ ]	1402 [R <sub>int</sub> = 0.1152, R <sub>sigma</sub> = 0.1442]	5226 [ $R_{int} = 0.0318$ , $R_{sigma} = 0.0553$ ]	3625 [Rint = 0.0474, $R_{sigma} = 0.0468$ ]	2922 [ $R_{int} = 0.0541$ , $R_{sigma} = 0.0554$ ]	3050 [R <sub>int</sub> = 0.0474, R <sub>sigma</sub> = 0.0611]
Data/restraints/para meters	2638/6/124	4796/24/263	5750/0/271	1402/108/103	5226/0/190	3625/0/163	2922/48/218	3050/0/190
Goodness-of-fit on F2	1.199	1.119	1.052	1.048	1.016	1.129	1.123	1.056
Final R indexes $[I \ge 2\sigma (I)]$ Final R indexes [all data] Largest diff	R1 = 0.0563,wR2 = 0.1465R1 = 0.0625,wR2 = 0.1497	R1 = 0.0543,wR2 = 0.0878R1 = 0.0886,wR2 = 0.1011	R1 = 0.0582, wR2 = 0.1562 R1 = 0.0676, wR2 = 0.1649	R1 = 0.1406,wR2 = 0.3297R1 = 0.2435,wR2 = 0.4013	R1 = 0.0330,wR2 = 0.0617R1 = 0.0406,wR2 = 0.0666	R1 = 0.0408,wR2 = 0.0737R1 = 0.0514,wR2 = 0.0780	R1 = 0.0643,wR2 = 0.1750R1 = 0.0692,wR2 = 0.1783	R1 = 0.0442,wR2 = 0.1094R1 = 0.0512,wR2 = 0.1167
peak/hole / e Å-3	3.54/-1.14	1.01/-0.83	2.78/-4.13	1.96/-1.49	1.14/-1.33	0.94/-0.93	2.29/-2.88	1.57/-2.42

Table S1. Single crystal X-ray data for structures of iodide salts and  $I_2$  complexes of cations 1 and 2.



**Fig. S1.** An illustration of the ion pair (left) and packing (right) in structure of  $[I_2 \cdots 1 \cdots I_2][PF_6]_2$ . Interatomic distances (Å): (N1-I1) = 2.517(9) and (I1-I2) = 2.778(1). Symmetry code(s): (') = -x, -y, -z. Disordered F atoms are omitted for clarity.



**Fig. S2.** An illustration of the ion pair (left) and packing (right) in structure of  $[I_2 \cdots 2 \cdots I_2][PF_6]_2$ . Interatomic distances (Å): (N1–I1) = 2.503(6) and (I1-I2) = 2.771(1). Symmetry code(s): (') = -x, -y, -z.



**Fig. S3.** An illustration of the asymmetric unit with symmetry-completed molecular fragments (a) and packing viewed along crystallographic *c*- (b) and *a*-axis (c) in structure of  $1 \cdot 2I_3^-$ . Interatomic distances (Å): (I1–I2) = 2.938(2), (I2–I3) = 2.915(2), (I4–I5) = 2.943(2), (I5–I6) = 2.911(2), (I7A-I8A) = 2.938(4) and (I8A–I9A) = 2.907(5). Disordered C and I atoms are omitted from the figure.



**Fig. S4.** An illustration of the asymmetric unit (left) and packing viewed along crystallographic *b*-axis (right) in structure of  $2 \cdot 2I_3^{-}(I)$ . Interatomic distances (Å): (I1-I2) = 2.802(1), (I2-I3) = 2.809(1), (I3-I4) = 3.590(1), (I4-I5) = 2.846(1) and (I5-I6) = 2.856(1).



**Fig. S5.** An illustration of the asymmetric unit with symmetry-completed molecular fragments (a) and packing viewed along crystallographic *c*- (b) and *b*-axis (c) in structure of  $2 \cdot 2I_3^{-}(II)$ . Interatomic distances (Å): (I1A–I2A) = 2.743(8), (I2A–I3A) = 2.935(10), (I3A–I3B') = 3.60(2), (I3B'–I2B') = 2.77(2) and (I2B'–I1B') = 2.68(2). Disordered I atoms are omitted from the figure.



Fig. S6. PXRD analyses of iodide salts of cation 1. List of PXRD graphs: measured (a) and simulated (b) graphs of  $1 \cdot 2I_3^-$ ; measured (c) and simulated (d) graphs of  $1 \cdot I_4^{2-}$ . Small variations in the measured and simulated patterns of  $1 \cdot I_4^{2-}$  are mainly due to different temperatures used in single crystal and powder X-ray analyses and arise also because of the PXRD measuring technique (preferred orientation of only lightly ground crystalline sample).



Fig. S7. PXRD analyses of triiodide salts of cation 2. List of PXRD graphs: measured (a) and simulated (b, c) graphs of  $2 \cdot 2I_3^-$ . The two simulated graphs (b) and (c) correspond to the two different polymorphs (I and II) of  $2 \cdot 2I_3^-$  of which (b) represents the PXRD pattern of the bulk sample.



Fig. S8. PXRD analyses of dodecaiodide salts of cation 2. List of PXRD graphs: measured (a) and simulated (b) graphs of  $2 \cdot I_{12}^{2-}$ . Graph (c) corresponds to the bulk sample obtained by an addition of  $I_2$  into a solution of  $2 \cdot 2I^-$ .

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