Table S1. Bond lengths for triiodides 2a, 2b, 2c

Atom	Atom	Length/Å	Atom	Atom	Length/Å
2a					
I5	C3	2.169(3)	C7	C6	1.376(5)
I3	I1	2.917(2)	C6	C5	1.387(5)
I1	I3[1]	2.917(2)	C5	C10	1.386(4)
I4	I2	2.9172(12)	C4	C11	1.524(4)
I2	I4[2]	2.9173(12)	C4	C3	1.529(4)
S2	C10	1.742(4)	C11	C12	1.390(5)
S2	C1	1.717(3)	C11	C16	1.390(5)
S1	C1	1.705(4)	C12	C13	1.385(5)
S1	C2	1.803(4)	C13	C14	1.383(7)
N1	C5	1.411(4)	C14	C15	1.377(6)
N1	C4	1.475(4)	C9	C10	1.392(5)
N1	C1	1.344(4)	C15	C16	1.386(5)
C8	C7	1.384(6)	C3	C2	1.522(5)
C8	C9	1.372(6)			
Symmetry transformation [1]*2-X,1-Y,2-Z;* [2]*-X,-Y,1-Z*					
2b					
I1	I2[1]	2.9126(16)	C5	C10	1.397(5)
I1	I2	2.9126(16)	C6	C7	1.387(7)
I5	C11	2.144(4)	C4	C11	1.536(6)
S2	C1	1.721(4)	C4	C3	1.514(6)
S2	C10	1.746(4)	C10	C9	1.383(6)
S1	C1	1.703(5)	C9	C8	1.374(7)
S1	C2	1.805(6)	C7	C8	1.392(7)
N1	C5	1.405(5)	C3	C2	1.523(8)
N1	C1	1.332(5)	I3	I4[2]	2.9318(17)
N1	C4	1.488(5)	I3	I4	2.9318(17)
C5	C6	1.399(6)			
Symmetry transformation [1]1-X,1-Y,1-Z; [2]2-X,2-Y,-Z					
2c					
I1	I3	2.9303(4)	N4	C8	1.298(6)
I1	I3[1]	2.9303(4)	N4	C10	1.501(6)
I2	I5	2.9159(5)	N4	C12	1.476(6)
I2	I5[2]	2.9159(5)	C6	C7	1.509(7)
I4	C7	2.167(5)	C7	C10	1.530(7)
S1	C6	1.815(5)	C10	C3	1.615(8)
S1	C8	1.714(4)	C10	C1	1.521(7)
S2	C8	1.722(4)	C12	C2	1.495(8)
S2	C2	1.806(6)			
Symmetry transformation: [1]*2-x,-y,2-z;* [2]*3-x,1-y,2-z*					

Table S2. Bond angles for triiodides 2a, 2b, 2c

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
2a								
I3	I1	I3[1]	180.000(15)		C16	C11	C4	117.9(3)
I4	I2	I4[2]	180.0		C13	C12	C11	120.3(4)
C1	S2	C10	90.46(16)		C14	C13	C12	119.9(4)

C1	S1	C2	100.49(17)		C15	C14	C13	120.2(4)
C5	N1	C4	121.5(2)		C8	C9	C10	117.4(4)
C1	N1	C5	113.2(3)		C5	C10	S2	111.4(2)
C1	N1	C4	125.2(3)		C5	C10	C9	120.8(3)
C9	C8	C7	121.5(4)		C9	C10	S2	127.8(3)
C6	C7	C8	121.9(4)		S1	C1	S2	118.78(19)
C7	C6	C5	116.9(3)		N1	C1	S2	113.2(2)
C6	C5	N1	126.6(3)		N1	C1	S1	128.1(2)
C10	C5	N1	111.8(3)		C14	C15	C16	120.1(4)
C10	C5	C6	121.6(3)		C15	C16	C11	120.2(4)
N1	C4	C11	111.3(2)		C4	C3	I5	111.8(2)
N1	C4	C3	110.8(3)		C2	C3	I5	111.4(2)
C11	C4	C3	110.3(2)		C2	C3	C4	112.5(3)
C12	C11	C4	122.8(3)		C3	C2	S1	113.9(2)
C12	C11	C16	119.2(3)					
2b								
I2	I1	I2[1]	180.0		C11	C4	N1	108.2(3)
C10	S2	C1	90.78(19)		C3	C4	N1	110.2(4)
C2	S1	C1	100.1(2)		C3	C4	C11	114.0(4)
C1	N1	C5	113.0(3)		C5	C10	S2	109.9(3)
C4	N1	C5	120.8(3)		C9	C10	S2	127.8(3)
C4	N1	C1	126.1(4)		C9	C10	C5	122.3(4)
C6	C5	N1	127.5(4)		C8	C9	C10	117.2(4)
C10	C5	N1	112.9(3)		C4	C11	I5	110.8(3)
C10	C5	C6	119.7(4)		C8	C7	C6	120.8(4)
C7	C6	C5	118.1(4)		C7	C8	C9	121.9(4)
S1	C1	S2	119.0(2)		C2	C3	C4	112.8(4)
N1	C1	S2	113.4(3)		C3	C2	S1	111.3(4)
N1	C1	S1	127.5(3)		I4[2]	I3	I4	180.0
2c								
I3[1]	I1	I3	180.0		S2	C8	S1	116.0(3)
I5[2]	I2	I5	180.0		N4	C8	S1	127.8(3)
C8	S1	C6	102.3(2)		N4	C8	S2	116.1(3)
C2	S2	C8	91.1(2)		C7	C10	N4	107.2(4)
C10	N4	C8	123.1(4)		C3	C10	N4	108.5(4)
C12	N4	C8	114.3(4)		C3	C10	C7	109.8(4)
C12	N4	C10	122.5(4)		C1	C10	N4	110.5(4)
C7	C6	S1	113.9(3)		C1	C10	C7	111.6(5)
C6	C7	I4	111.0(3)		C1	C10	C3	109.1(4)
C10	C7	I4	110.6(3)		C2	C12	N4	108.7(4)
C10	C7	C6	113.6(4)		C12	C2	S2	107.8(3)

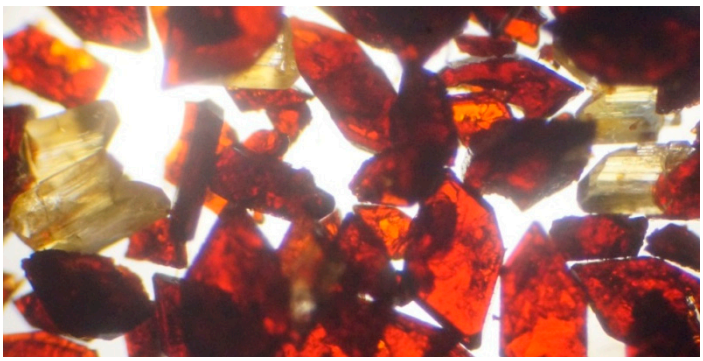

Fig. S1 Crystal habit of triiodide **2c** (ruby-red) and corresponding monoiodide (light yellow) under 4x microscope magnification

Table S3. Local properties at bond critical points (BCP) of noncovalent interactions formed by triiodide anions in 2a, 2b, 2c crystals

Type of interaction	Distance. Å	$\rho(r_{bcp})$, a.u.	$g(r_{bcp})$	$v(r_{bcp})$	$\nabla^2\rho(r_{bcp})$	$\eta(r_{bcp})$
2c, I_3^-						
H...I	2.894	0.0114	0.0064	-0.0057	0.0284	0.062
I...I	3.011	0.0412	0.0154	-0.0207	0.0402	0.457
H...I	3.148	0.0073	0.0042	-0.0033	0.0206	0.034
S...I	3.753	0.0077	0.0046	-0.0036	0.0227	0.034
I...I	4.779	0.0026	0.0012	-0.0008	0.0062	0.014
S...I	4.109	0.0049	0.0049	-0.0019	0.0130	0.025
I...I	3.011	0.0412	0.0154	-0.0207	0.0402	0.457
H...I	3.322	0.0056	0.0033	-0.0024	0.0171	0.023
I...I	4.195	0.0063	0.0033	-0.0026	0.0160	0.034
H...I	2.895	0.0113	0.0064	-0.0058	0.0284	0.061
H...I	3.074	0.0084	0.0048	-0.0039	0.0230	0.041
H...I	3.148	0.0073	0.0042	-0.0033	0.0206	0.034
S...I	3.754	0.0077	0.0046	-0.0036	0.0227	0.033
I...I	4.775	0.0026	0.0012	-0.0008	0.0062	0.014
2c, I_3^-						
I...I	3.000	0.0418	0.0157	-0.0212	0.0404	0.460
H...I	3.151	0.0074	0.0043	-0.0033	0.0213	0.033
H...I	3.162	0.0074	0.0045	-0.0035	0.0220	0.031
H...I	3.168	0.0071	0.0042	-0.0032	0.0211	0.030
H...I	3.364	0.0065	0.0037	-0.0029	0.0188	0.029
H...I	3,330	0.0064	0.0038	-0.0028	0.0195	0.026
H...I	3.625	0.0033	0.0018	-0.0012	0.0095	0.014
I...I	4.482	0.0038	0.0019	-0.0014	0.0098	0.019
I...I	4.334	0.0043	0.0023	-0.0017	0.0114	0.020
I...I	4.779	0.0026	0.0012	-0.0008	0.0062	0.012
S...I	4.082	0.0053	0.0029	-0.0022	0.0144	0.025

N...I	3.997	0.0043	0.0026	-0.0022	0.0122	0.015
H...I	3.113	0.0072	0.0043	-0.0034	0.0209	0.031
H...I	3.118	0.0071	0.0043	-0.0033	0.0208	0.030
I...I	4.068	0.0071	0.0038	-0.0031	0.0183	0.037
I...I	4.071	0.0071	0.0038	-0.0031	0.0182	0.036
I...I	4.165	0.0062	0.0033	-0.0026	0.0157	0.033
I...I	2.999	0.0419	0.0157	-0.0213	0.0403	0.460
H...I	3.154	0.0074	0.0045	-0.0035	0.0221	0.031
H...I	3.215	0.0065	0.0038	-0.0028	0.0188	0.029
H...I	3.633	0.0033	0.0018	-0.0012	0.0094	0.014
2b, I_3^-						
I...I	3.038	0.0405	0.0150	-0.0209	0.0360	0.457
H...I	3,390	0.0048	0.0026	-0.0018	0.0132	0.023
H...I	3.697	0.0028	0.0015	-0.0010	0.0080	0.011
H...I	3.424	0.0045	0.0025	-0.0017	0.0132	0.019
I...I	3.038	0.0405	0.0150	-0.0209	0.0360	0.457
H...I	3,390	0.0048	0.0026	-0.0018	0.0132	0.023
H...I	3.697	0.0028	0.0015	-0.0010	0.0080	0.011
2b, I_3^-						
I...I	3.034	0.0408	0.0151	-0.0212	0.0360	0.458
H...I	3,240	0.0060	0.0033	-0.0025	0.0164	0.029
I...I	3.034	0.0408	0.0151	-0.0212	0.0360	0.458
H...I	3,180	0.0068	0.0037	-0.0029	0.0181	0.035
H...I	3.241	0.0060	0.0033	-0.0025	0.0164	0.029
S...I	3.721	0.0083	0.0050	-0.0040	0.0245	0.036
2a, I_3^-						
H...I	2.877	0.0118	0.0058	-0.0049	0.0265	0.085
H...I	2.986	0.0100	0.0051	-0.0043	0.0237	0.064
I...I	2.996	0.0433	0.0164	-0.0235	0.0373	0.466
C...I	3.742	0.0063	0.0039	-0.0030	0.0192	0.024
S...I	3.797	0.0072	0.0047	-0.0033	0.0244	0.026
H...I	2.877	0.0118	0.0058	-0.0049	0.0265	0.085
H...I	2.986	0.0100	0.0051	-0.0043	0.0237	0.064
I...I	2.996	0.0433	0.0164	-0.0235	0.0373	0.466
C...I	3.742	0.0063	0.0039	-0.0030	0.0192	0.024
2a, I_3^-						
I...I	3.000	0.0433	0.0164	-0.0235	0.0371	0.466
H...I	3.049	0.0088	0.0042	-0.0035	0.0192	0.064
H...I	3.348	0.0052	0.0028	-0.0022	0.0136	0.025
S...I	3.772	0.0075	0.0050	-0.0035	0.0256	0.027
S...I	3,920	0.0058	0.0036	-0.0024	0.0194	0.022
I...I	3.927	0.0083	0.0041	-0.0035	0.0192	0.053

C...I	3.904	0.0049	0.0032	-0.0023	0.0162	0.016
S...I	3.775	0.0072	0.0050	-0.0035	0.0261	0.023
I...I	4.342	0.0044	0.0023	-0.0017	0.0115	0.021
I...I	3,000	0.0433	0.0164	-0.0235	0.0371	0.466
H...I	3.049	0.0088	0.0042	-0.0035	0.0192	0.064
H...I	3.327	0.0056	0.0032	-0.0025	0.0156	0.025
H...I	3.348	0.0052	0.0028	-0.0022	0.0136	0.025
S...I	3,920	0.0058	0.0036	-0.0024	0.0194	0.022
I...I	3.927	0.0083	0.0041	-0.0035	0.0192	0.053

$\rho(r_{bcp})$ –electron density at BCP; $g(r_{bcp})$ – density of kinetic energy at BCP; $v(r_{bcp})$ – virial density at BCP; $\eta(r_{bcp})$ – ELF at BCP.

Table S4. Local properties at bond critical points of noncovalent interactions formed by organic cations in 2a, 2b, 2c

Type of interaction	Distance. Å	$\varrho(r_{bcp})$, a.u.	$g(r_{bcp})$	$v(r_{bcp})$	$\nabla^2\rho(r_{bcp})$	$\eta(r_{bcp})$
2a						
H...H	2.8774	0.0118	0.0058	-0.0049	0.0265	0.085
H...H	3.2627	0.0064	0.0035	-0.0028	0.0168	0.032
C...I	3.5906	0.0056	0.0035	-0.0026	0.0175	0.021
H...H	3.2929	0.0055	0.0031	-0.0025	0.0151	0.024
H...H	3.5512	0.0038	0.0111	-0.0016	0.0220	0.015
H...H	2.1525	0.0076	0.0049	-0.0038	0.0236	0.029
H...H	2.5315	0.0049	0.0036	-0.0027	0.0181	0.012
H...S	3.2712	0.0031	0.0020	-0.0011	0.0109	0.089
H...C	2.5732	0.0100	0.0057	-0.0048	0.0267	0.051
2b						
H...H	3.3867	0.0051	0.0029	-0.0021	0.0150	0.021
H...H	3.4009	0.0050	0.0028	-0.0020	0.0145	0.021
H...I	2.9468	0.010	0.0061	-0.0051	0.0282	0.048
H...H	2.3715	0.0073	0.0057	-0.0038	0.0303	0.019
C...C	3.0799	0.0042	0.0026	-0.0019	0.0135	0.015
H...H	2.1651	0.0090	0.0074	-0.0050	0.0391	0.022
H...H	2.6768	0.0028	0.0018	-0.0011	0.0977	0.0078
H...H	2.4377	0.0039	0.0026	-0.0017	0.0140	0.011
H...H	3.1356	0.0076	0.0047	-0.0035	0.0235	0.032
H...H	3.2185	0.0068	0.0040	-0.0030	0.0199	0.030
H...H	3.2646	0.0059	0.0035	-0.0026	0.0174	0.025
2c						
H...H	3.3079	0.0057	0.0033	-0.0024	0.0172	0.0232
H...H	3.2748	0.0058	0.0033	-0.0024	0.0169	0.026
H...H	3.4753	0.0041	0.0024	-0.0017	0.0124	0.016
I...I	4.0612	0.0071	0.0039	-0.0031	0.0182	0.037
H...I	2.9514	0.0110	0.0082	-0.0064	0.0396	0.039

H...H	3.0730	0.0084	0.0048	-0.0039	0.0229	0.041
S...H	3.6463	0.0077	0.0046	-0.0036	0.0227	0.033
H...H	2.9512	0.0113	0.0081	-0.0064	0.0396	0.039
H...H	2.3277	0.0053	0.0036	-0.0024	0.0194	0.016
H...H	2.3772	0.0049	0.0032	-0.0021	0.0173	0.015
H...H	2.3234	0.0053	0.0037	-0.0024	0.0195	0.016