Supplementary Information

Rare stoichiometry of carboxyl-carboxylate benzbetaine complexes: in vitro versus in silico†

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Table S1. Crystal data and structure refinement for the 3:2 complex of 3-trimethylammonium-benzoate with hydroiodic acid.

	1-I	**1**-II
Empirical formula	$C_{30}H_{41}I_2N_3O_6$	$C_{30}H_{41}I_2N_3O_6$
Formula weight	793.46	793.46
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pccn$
Unit cell dimensions	a = 18.7965(10) Å	a = 37.3738(17) Å
	b = 13.9047(8) Å	b = 13.9167(11) Å
	c = 12.8843(6) Å	c = 12.8674(7) Å
	β= 96.010(4)°	β= 90°
Volume	3348.9(3) Å^3	6692.6(7) Å^3
Z	4	8
Calculated density	1.574 g/cm^3	1.575 g/cm^3
Absorption coefficient	1.921 mm^{-1}	1.923 mm^{-1}
F(000)	1584	3168
Crystal size	0.20 x 0.15 x 0.08 mm	0.25 x 0.21 x 0.11 mm
θ range for data collection (°)	2.16 to 29.12	2.18 to 27.91
Limiting indices *h, k, l*	-25 / 21, -18 / 16, -17 / 14	-47 / 38, -17 / 17, -16 / 15
Reflections collected / unique	22456/7982, R_{int} = 0.0415	16812 / 7338 [R(int) = 0.0511]
θ_{Max}(°) / Completeness (%)	29.12 / 88.8	27.91 / 91.5
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7982 /0 /370	7338 / 0 / 372
Goodness-of-fit on F^2	1.021	1.038
Final R_1 / wR_2 indices [$I>2\sigma_I$]	0.0553/ 0.0715	0.0639/ 0.0823
R_1/ wR_2 indices (all data)	0.1164/0.1651	0.1384/ 0.1033
Largest diff. peak and hole	5.906 and -1.556 e.Å^{-3}	1.158 and -0.874 e.Å^{-3}

Table S2. Crystal data and structure refinement for 3-trimethylammonium-benzoate with hydroiodic acid.

Empirical formula	$C_{10}H_{14}INO_2$
Formula weight	307.12
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.1929(2) Å b = 11.3278(3) Å c = 13.1285(3) Å β= 105.735(3)°
Volume	1172.76(5) $Å^3$
Z	4
Calculated density	1.739 g/cm^3
Absorption coefficient	2.708 mm^{-1}
F(000)	600
Crystal size	0.30 x 0.20 x 0.05 mm
θ range for data collection (°)	2.41 to 26.52
Limiting indices *h, k, l*	-10/10, -10/13, -16/16
Reflections collected / unique	7686/2371, R_{int} = 0.1033
θ_{Max}(°) / Completeness (%)	26.52 / 97.5
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2371 /0 /128
Goodness-of-fit on F^2	1.017
Final R_1 / wR_2 indices [$I>2\sigma_I$]	0.0675/ 0.1846
R_1/ wR_2 indices (all data)	0.0765/ 0.1988
Largest diff. peak and hole	2.442 and -1.653 $e.Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide polymorphs **1**-I and **1**-II. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	1-I				**1**-II			
Atom	x	y	z	U(eq)	y	z		U(eq)
C(1)	5139(4)	8793(6)	8189(6)	28(2)	2559(1)	-1199(4)	7428(4)	28(1)
C(2)	5673(4)	8722(6)	9028(6)	29(2)	2814(1)	-1288(4)	8206(4)	29(1)
C(3)	6378(4)	8637(5)	8842(6)	26(2)	3169(1)	-1372(4)	7918(4)	26(1)
C(4)	6575(5)	8651(6)	7826(6)	31(2)	3269(1)	-1339(4)	6891(4)	35(1)
C(5)	6034(5)	8726(7)	7001(6)	34(2)	3010(1)	-1253(3)	6133(3)	39(2)
C(6)	5322(4)	8790(6)	7173(6)	31(2)	2659(1)	-1184(3)	6401(3)	35(1)
C(7)	4386(5)	8928(7)	8428(7)	35(2)	2174(1)	-1055(4)	7750(5)	33(1)
O(1)	3926(3)	8927(6)	7570(5)	48(2)	1953(1)	-1069(3)	6971(3)	48(1)
O(2)	4214(4)	9063(8)	9279(5)	67(3)	2088(1)	-939(4)	8644(3)	64(2)
N(1)	6973(4)	8529(5)	9697(5)	31(2)	3458(1)	-1490(3)	8721(3)	32(1)
C(8)	6689(6)	8523(9)	10753(7)	49(3)	3316(2)	-1528(5)	9799(4)	56(2)
C(9)	7366(6)	7604(9)	9559(9)	60(3)	3658(2)	-2403(4)	8505(5)	57(2)
C(10)	7479(7)	9371(10)	9697(10)	66(3)	3713(2)	-654(5)	8651(5)	62(2)
C(11)	1553(4)	10186(6)	7272(8)	35(2)	780(1)	232(4)	7027(4)	32(1)
C(12)	1163(5)	10839(7)	6588(8)	41(2)	582(1)	867(4)	6427(4)	34(1)
C(13)	447(5)	10998(7)	6745(8)	41(2)	226(1)	1031(4)	6659(4)	34(1)
C(14)	136(6)	10544(9)	7530(11)	62(3)	68(2)	563(4)	7477(5)	54(2)
C(15)	533(6)	9916(9)	8227(11)	66(4)	261(2)	-62(5)	8087(6)	66(2)
C(16)	1243(6)	9742(8)	8083(9)	53(3)	620(2)	-237(4)	7850(5)	52(2)
C(17)	2345(4)	10048(6)	7167(7)	33(2)	1174(1)	73(4)	6815(5)	34(1)
O(11)	2660(3)	9449(5)	7783(6)	47(2)	1329(1)	-547(3)	7362(3)	52(1)
O(12)	2622(3)	10559(5)	6533(6)	48(2)	1319(1)	593(3)	6151(3)	49(1)
N(11)	-5(4)	11671(6)	6031(6)	44(2)	5(1)	1704(3)	6018(4)	42(1)
C(18)	434(7)	12325(10)	5390(10)	69(4)	222(2)	2349(5)	5333(5)	67(2)
C(19)	-522(8)	11104(9)	5321(13)	100(6)	-244(2)	1141(5)	5339(6)	97(3)
C(20)	-407(6)	12367(8)	6665(10)	55(3)	-208(2)	2364(5)	6702(5)	64(2)
C(21)	5104(4)	11204(6)	6824(6)	26(2)	2570(1)	1210(4)	6090(4)	32(1)
C(22)	5629(4)	11292(6)	6143(6)	28(2)	2836(1)	1278(4)	5341(4)	31(1)
C(23)	6340(4)	11370(5)	6540(6)	27(2)	3189(1)	1361(4)	5638(4)	27(1)
C(24)	6543(5)	11341(6)	7605(6)	34(2)	3281(2)	1340(4)	6679(4)	37(2)
C(25)	6022(5)	11255(7)	8295(7)	35(2)	3020(2)	1267(4)	7420(4)	39(2)
C(26)	5307(4)	11199(6)	7907(6)	30(2)	2664(1)	1215(4)	7132(4)	35(1)
C(27)	4340(5)	11077(7)	6399(7)	35(2)	2193(2)	1083(5)	5748(5)	39(2)
O(21)	3894(3)	11078(6)	7106(5)	46(2)	1964(1)	1086(3)	6519(3)	51(1)
O(22)	4175(4)	10944(9)	5480(6)	71(3)	2111(1)	954(4)	4862(3)	72(2)
N(21)	6919(4)	11480(5)	5833(5)	31(2)	3484(1)	1460(3)	4859(3)	33(1)
C(28)	6629(5)	11506(8)	4700(7)	46(2)	3351(2)	1491(5)	3768(4)	54(2)
C(29)	7315(6)	12417(8)	6111(9)	52(3)	3683(2)	2384(5)	5064(5)	67(2)
C(30)	7425(6)	10650(8)	5984(9)	53(3)	3736(2)	622(5)	4955(5)	70(2)
I(1)	-1519(1)	13383(1)	3987(1)	52(1)	-758(1)	3393(1)	4195(1)	55(1)
I(2)	1481(1)	13527(1)	8045(1)	53(1)	739(1)	3543(1)	7854(1)	58(1)

H(1)	3538	9134	7709	57	1760	-845	7153	58
H(2)	5551	8732	9710	35	2748	-1292	8903	34
H(4)	7053	8612	7703	37	3509	-1374	6708	42
H(5)	6155	8732	6319	41	3076	-1242	5436	47
H(6)	4969	8832	6613	38	2485	-1127	5887	42
H(81)	6361	7992	10786	75	3153	-2059	9840	83
H(82)	6442	9113	10852	75	3196	-949	10002	83
H(83)	7078	8449	11290	75	3515	-1641	10255	83
H(91)	7548	7607	8886	90	3480	-2898	8551	85
H(92)	7048	7072	9598	90	3837	-2506	9028	85
H(93)	7759	7550	10094	90	3768	-2420	7830	85
H(101)	7673	9401	9037	99	3897	-770	9156	93
H(102)	7862	9289	10245	99	3587	-75	8825	93
H(103)	7227	9955	9808	99	3819	-588	7975	93
H(12)	1373	11149	6058	50	689	1183	5871	41
H(14)	-344	10653	7602	74	-173	670	7621	65
H(15)	324	9626	8770	80	154	-366	8651	79
H(16)	1514	9325	8530	64	752	-669	8248	63
H(181)	710	11939	4962	101	368	2022	4834	100
H(182)	754	12708	5856	101	371	2716	5793	100
H(183)	122	12739	4961	101	60	2772	4978	100
H(191)	-798	10696	5726	148	-107	777	4845	146
H(192)	-265	10716	4869	148	-400	1573	4977	146
H(193)	-835	11534	4908	148	-383	711	5760	146
H(201)	-702	12016	7095	84	-51	2684	7181	96
H(202)	-701	12781	6202	84	-383	2001	7083	96
H(203)	-70	12752	7099	84	-327	2833	6277	96
H(21)	3517	10826	6868	69	1768	902	6309	62
H(22)	5503	11298	5426	33	2777	1267	4639	38
H(24)	7024	11380	7859	40	3520	1375	6874	44
H(25)	6154	11234	9010	42	3082	1253	8120	47
H(26)	4958	11159	8366	36	2487	1183	7638	41
H(281)	6381	10917	4518	70	3225	916	3576	81
H(282)	7018	11580	4278	70	3557	1567	3329	81
H(283)	6306	12038	4580	70	3196	2035	3687	81
H(291)	7502	12398	6832	78	3515	2904	5007	100
H(292)	6993	12943	5987	78	3864	2450	4539	100
H(293)	7703	12478	5685	78	3793	2397	5738	100
H(301)	7172	10061	5809	80	3612	40	4782	106
H(302)	7627	10624	6699	80	3849	552	5621	106
H(303)	7801	10726	5541	80	3914	752	4437	106

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3-trimethylammonium-benzoic acid iodide. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	y	z		U(eq)
C(1)	4722(9)	4472(7)	6228(5)	39(2)
C(2)	3230(8)	3970(6)	5630(5)	33(1)
C(3)	3210(8)	2815(6)	5270(5)	32(1)
C(4)	4679(9)	2161(7)	5481(6)	42(2)
C(5)	6159(9)	2659(8)	6058(6)	45(2)
C(6)	6227(9)	3822(8)	6435(5)	42(2)
C(7)	4815(10)	5688(7)	6658(6)	45(2)
O(1)	3436(7)	6306(5)	6246(5)	53(1)
O(2)	6026(9)	6055(7)	7321(7)	80(2)
N(1)	1537(8)	2301(5)	4665(4)	37(1)
C(8)	690(11)	3107(8)	3766(7)	53(2)
C(9)	442(11)	2154(9)	5403(7)	58(2)
C(10)	1729(12)	1109(8)	4197(6)	54(2)
I(1)	3649(1)	9251(1)	6928(1)	41(1)
H(1)	3528	6961	6522	40
H(2)	2232	4408	5469	39
H(4)	4657	1388	5238	50
H(5)	7192	2223	6169	54
H(6)	7244	4157	6820	51
H(81)	539	3873	4041	80
H(82)	-394	2788	3398	80
H(83)	1386	3176	3287	80
H(91)	297	2904	5706	87
H(92)	972	1612	5956	87
H(93)	-645	1850	5019	87
H(101)	2414	1185	3712	81
H(102)	630	811	3828	81
H(103)	2263	572	4753	81

Table S5. Experimental and calculated by the B3LYP/6-31G(d,p) approach selected bond lengths (Å), bond and torsion angles (°) for [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide.

Parameters	X-Ray		B3LYP/6-31G(d,p)	
	1-I	**1**-II	**4**-I	**4**-II
Bond length				
A	*Cation*	*Cation*	*Cation*	*Cation*
C(1)-C(2)	1.398(10)	1.390(6)	1.400	1.400
C(2)-C(3)	1.378(11)	1.381(6)	1.388	1.387
C(3)-C(4)	1.398(11)	1.374(7)	1.399	1.399
C(4)-C(5)	1.396(10)	1.378(6)	1.393	1.393
C(5)-C(6)	1.381(11)	1.359(6)	1.395	1.395
C(1)-C(6)	1.389(11)	1.374(6)	1.395	1.395
C(1)-C(7)	1.492(12)	1.510(7)	1.514	1.506
C(7)-O(1)	1.329(10)	1.300(6)	1.312	1.322
C(7)-O(2)	1.190(11)	1.204(6)	1.224	1.220
N(1)-C(3)	1.493(10)	1.506(6)	1.512	1.511
N(1)-C(8)	1.512(12)	1.487(6)	1.513	1.514
N(1)-C(9)	1.503(12)	1.500(7)	1.519	1.520
N(1)-C(10)	1.510(10)	1.504(7)	1.503	1.508
Av.dif.[a]		0.0080		0.0015
R.m.s.[b]		0.0165		0.0039
Av.dif.[c]			0.0078	0.0164
R.m.s.[b]			0.0137	0.0107
B	*Zwitterion*	*Zwitterion*	*Zwitterion*	*Cation*
C(11)-C(12)	1.413(12)	1.387(7)	1.397	1.398
C(12)-C(13)	1.399(12)	1.382(7)	1.389	1.396
C(13)-C(14)	1.373(12)	1.372(8)	1.397	1.393
C(14)-C(15)	1.408(13)	1.378(8)	1.394	1.397
C(15)-C(16)	1.390(15)	1.398(8)	1.393	1.389
C(11)-C(16)	1.395(14)	1.380(7)	1.396	1.401
C(11)-C(17)	1.520(11)	1.514(7)	1.515	1.507
C(17)-O(11)	1.255(10)	1.256(6)	1.263	1.241
C(17)-O(12)	1.240(11)	1.243(6)	1.263	1.301
N(11)-C(13)	1.510(10)	1.498(7)	1.509	1.508
N(11)-C(18)	1.526(14)	1.497(7)	1.509	1.515
N(11)-C(19)	1.491(15)	1.496(7)	1.516	1.519
N(11)-C(20)	1.518(12)	1.501(7)	1.512	1.509
Av.dif.[a]		0.1030		-0.0016
R.m.s.[b]		0.0139		0.0133
Av.dif.[c]			-0.0020	-0.0132
R.m.s.[b]			0.0154	0.0123

Table S5 (continued)

Parameters	X-Ray		B3LYP/6-31G(d,p)	
	1-I	**1**-II	**4**-I	**4**-II
Bond length				
C	*Cation*	*Cation*	*Cation*	*Zwitterion*
C(21)-C(22)	1.391(11)	1.389(7)	1.400	1.400
C(22)-C(23)	1.386(11)	1.376(7)	1.388	1.388
C(23)-C(24)	1.384(11)	1.383(7)	1.399	1.400
C(24)-C(25)	1.395(12)	1.369(7)	1.393	1.394
C(25)-C(26)	1.386(12)	1.382(7)	1.395	1.395
C(21)-C(26)	1.407(11)	1.385(7)	1.395	1.394
C(21)-C(27)	1.494(11)	1.487(7)	1.513	1.526
C(27)-O(21)	1.301(10)	1.312(6)	1.303	1.270
C(27)-O(22)	1.206(11)	1.194(6)	1.230	1.252
N(21)-C(23)	1.499(10)	1.498(6)	1.512	1.514
N(21)-C(28)	1.504(12)	1.490(6)	1.514	1.514
N(21)-C(29)	1.517(11)	1.509(7)	1.519	1.518
N(21)-C(30)	1.498(12)	1.502(7)	1.508	1.508
Av.dif.[a]		0.0073		0.0
R.m.s.[b]		0.0108		0.0120
Av.dif.[c]			-0.0014	0.0147
R.m.s.[b]			0.0099	0.0227
Bond angles				
A	*Cation*	*Cation*	*Cation*	*Cation*
C(1)-C(2)-C(3)	119.8(7)	118.2(5)	119.52	119.39
C(2)-C(3)-C(4)	121.1(7)	121.1(5)	120.73	120.72
C(3)-C(4)-C(5)	118.1(7)	119.5(5)	119.35	119.44
C(4)-C(5)-C(6)	121.5(7)	120.3(3)	120.45	120.43
C(5)-C(6)-C(1)	119.5(7)	120.4(3)	119.74	119.60
C(6)-C(1)-C(2)	120.0(7)	120.5(5)	120.22	120.41
C(2)-C(1)-C(7)	117.9(7)	117.9(5)	117.19	116.98
C(6)-C(1)-C(7)	122.0(7)	121.5(4)	122.59	122.60
C(1)-C(7)-O(1)	112.2(7)	113.0(5)	112.68	112.23
C(1)-C(7)-O(2)	124.4(8)	122.3(5)	120.28	121.39
O(1)-C(7)-O(2)	123.4(9)	124.7(5)	127.03	126.37
C(2)-C(3)-N(1)	122.7(7)	120.9(5)	121.12	121.01
C(4)-C(3)-N(1)	116.2(7)	117.9(4)	118.14	118.26
C(3)-N(1)-C(8)	110.9(7)	112.8(4)	112.61	112.52
C(3)-N(1)-C(9)	109.7(7)	108.8(4)	110.31	110.16
C(3)-N(1)-C(10)	110.2(6)	109.2(4)	108.86	108.99
C(8)-N(1)-C(9)	109.2(8)	108.7(5)	107.21	107.02
C(8)-N(1)-C(10)	106.8(7)	108.1(5)	107.95	108.16
C(9)-N(1)-C(10)	109.9(7)	109.3(5)	108.86	109.96
Av.dif.[a]		0.0316		-0.0510
R.m.s.[b]		1.2889		0.4276
Av.dif.[c]			0.0584	-0.0389
R.m.s.[b]			1.7368	0.8930

Table S5 (continued)

Parameters	X-Ray		B3LYP/6-31G(d,p)	
	1-I	**1**-II	**4**-I	**4**-II
Bond angles				
B	*Zwitterion*	*Zwitterion*	*Zwitterion*	*Cation*
C(11)-C(12)-C(13)	117.2(9)	119.9(5)	119.84	119.31
C(12)-C(13)-C(14)	121.5(8)	120.2(5)	120.93	121.19
C(13)-C(14)-C(15)	121.2(7)	120.7(6)	118.93	118.88
C(14)-C(15)-C(16)	118.4(10)	119.3(6)	120.62	120.78
C(15)-C(16)-C(11)	120.3(10)	120.1(6)	120.00	119.90
C(16)-C(11)-C(12)	121.4(8)	119.9(5)	119.67	119.93
C(12)-C(11)-C(17)	118.5(8)	120.8(5)	119.08	121.72
C(16)-C(11)-C(17)	119.9(8)	119.3(5)	121.23	118.25
C(11)-C(17)-O(11)	115.6(8)	116.6(5)	117.47	119.16
C(11)-C(17)-O(12)	117.9(7)	117.6(5)	118.73	120.48
O(11)-C(17)-O(12)	126.4(8)	125.7(5)	123.80	120.35
C(12)-C(13)-N(11)	119.9(8)	121.1(5)	120.65	117.77
C(14)-C(13)-N(11)	118.6(7)	118.7(5)	118.38	121.02
C(13)-N(11)-C(18)	113.2(7)	113.5(4)	112.83	108.66
C(13)-N(11)-C(19)	109.6(4)	109.7(4)	108.70	110.66
C(13)-N(11)-C(20)	110.4(7)	110.6(4)	110.55	113.27
C(18)-N(11)-C(19)	109.9(6)	107.9(5)	107.25	109.09
C(18)-N(11)-C(20)	103.8(8)	105.4(5)	107.60	107.86
C(19)-N(11)-C(20)	109.9(5)	109.5(5)	109.84	107.19
Av.dif.[a]		-0.1579		0.0331
R.m.s.[b]		1.2821		2.2170
Av.dif.[c]			0.1368	0.0542
R.m.s.[b]			1.7795	2.5054
C	*Cation*	*Cation*	*Cation*	*Zwitterion*
C(21)-C(22)-C(23)	119.5(7)	119.9(5)	119.43	119.58
C(22)-C(23)-C(24)	121.3(8)	120.4(5)	120.70	120.80
C(23)-C(24)-C(25)	119.6(8)	119.9(5)	119.42	119.22
C(24)-C(25)-C(26)	119.6(8)	120.1(5)	120.43	120.44
C(25)-C(26)-C(21)	120.6(7)	120.3(5)	119.67	119.87
C(26)-C(21)-C(22)	119.3(7)	119.3(5)	120.33	120.08
C(22)-C(21)-C(27)	119.7(7)	118.7(5)	122.10	118.09
C(26)-C(21)-C(27)	120.9(7)	121.8(5)	117.55	121.82
C(21)-C(27)-O(21)	114.1(7)	113.3(5)	112.90	115.60
C(21)-C(27)-O(22)	121.1(8)	123.7(5)	120.07	116.73
O(21)-C(27)-O(22)	124.7(8)	122.9(5)	127.02	127.63
C(22)-C(23)-N(21)	121.1(7)	121.9(5)	120.93	120.83
C(24)-C(23)-N(21)	117.6(7)	117.7(5)	118.37	118.36
C(23)-N(21)-C(28)	112.5(7)	112.8(4)	112.48	112.52
C(23)-N(21)-C(29)	108.4(7)	108.9(4)	109.46	109.72
C(23)-N(21)-C(30)	109.5(7)	109.6(4)	109.77	109.52
C(28)-N(21)-C(29)	109.0(8)	107.7(5)	107.70	107.47
C(28)-N(21)-C(30)	107.8(8)	108.0(5)	107.47	107.61
C(29)-N(21)-C(30)	109.8(8)	109.8(5)	109.91	109.95
Av.dif.[a]		0.0158		-0.0068
R.m.s.[b]		0.9382		1.7243
Av.dif.[c]			0.0679	0.0452
R.m.s.[b]			1.4768	2.1184

Table S5 (continued)

Parameters	X-Ray		B3LYP/6-31G(d,p)	
	1-I	**1**-II	**4**-I	**4**-II
Torsion angles				
A	*Cation*	*Cation*	*Cation*	*Cation*
C(1)-C(2)-C(3)-C(4)	2.0(12)	1.9(8)	0.05	0.92
C(2)-C(3)-C(4)-C(5)	-1.8(12)	-2.2(9)	-0.25	-0.90
C(3)-C(4)-C(5)-C(6)	0.5(12)	1.2(7)	0.04	-0.14
C(4)-C(5)-C(6)-C(1)	0.6(12)	0.0(4)	0.36	1.13
C(5)-C(6)-C(1)-C(2)	-0.5(12)	-0.3(6)	-0.57	-1.11
C(6)-C(1)-C(2)-C(3)	-0.9(12)	-0.7(8)	0.36	0.09
C(7)-C(1)-C(2)-C(3)	-177.3(8)	-176.8(5)	179.76	179.04
C(7)-C(1)-C(6)-C(5)	175.9(8)	175.8(4)	-179.93	180.00
C(2)-C(1)-C(7)-O(1)	-176.3(8)	-174.0(5)	-170.45	164.54
C(2)-C(1)-C(7)-O(2)	6.9(15)	6.2(9)	8.75	14.74
C(6)-C(1)-C(7)-O(1)	7.3(12)	9.9(8)	8.93	14.39
C(6)-C(1)-C(7)-O(2)	-169.5(10)	-170.0(6)	-171.87	-166.34
C(1)-C(2)-C(3)-N(1)	-178.2(7)	-178.9(5)	178.84	-179.62
C(5)-C(4)-C(3)-N(1)	178.4(7)	178.5(4)	-179.07	179.63
C(8)-N(1)-C(3)-C(2)	0.4(11)	1.5(7)	2.37	3.72
C(8)-N(1)-C(3)-C(4)	-179.7(8)	-179.2(5)	-178.82	-176.81
C(9)-N(1)-C(3)-C(2)	121.1(9)	122.2(6)	122.10	123.03
C(9)-N(1)-C(3)-C(4)	-59.0(10)	-58.6(6)	-59.09	-57.49
C(10)-N(1)-C(3)-C(2)	-117.7(8)	-118.6(6)	-117.30	-116.25
C(10)-N(1)-C(3)-C(4)	62.2(9)	60.6(7)	61.52	63.23
Av.dif.[a]		0.265		-36.0036
R.m.s.[b]		1.0373		157.799
Av.dif.[c]			1.1515	-33.115
R.m.s.[b]			163.92	97.1087
B	*Zwitterion*	*Zwitterion*	*Zwitterion*	*Cation*
C(11)-C(12)-C(13)-C(14)	0.1(15)	-0.3(9)	-0.43	0.36
C(12)-C(13)-C(14)-C(15)	1.7(15)	1.0(10)	-0.95	0.65
C(13)-C(14)-C(15)-C(16)	-2.0(17)	-1.5(11)	1.23	-1.08
C(14)-C(15)-C(16)-C(11)	0.6(19)	1.4(10)	-0.15	0.51
C(15)-C(16)-C(11)-C(12)	1.3(17)	-0.7(9)	-1.24	0.52
C(16)-C(11)-C(12)-C(13)	-1.6(15)	0.2(8)	1.52	-0.95
C(17)-C(11)-C(12)-C(13)	-175.9(9)	-177.4(5)	-176.75	175.32
C(17)-C(11)-C(16)-C(15)	175.5(11)	176.9(6)	176.99	-175.88
C(12)-C(11)-C(17)-O(11)	-178.9(9)	-176.8(5)	141.82	-142.33
C(12)-C(11)-C(17)-O(12)	4.5(13)	6.3(8)	-37.57	33.37
C(16)-C(11)-C(17)-O(11)	6.7(13)	5.6(8)	-36.42	30.00
C(16)-C(11)-C(17)-O(12)	-169.9(10)	-171.3(5)	144.19	-150.30
C(11)-C(12)-C(13)-N(11)	-178.9(8)	-179.2(5)	-177.88	178.79
C(15)-C(14)-C(13)-N(11)	-179.3(8)	-180.0(6)	176.37	-177.74
C(18)-N(11)-C(13)-C(12)	-16.3(13)	-15.6(7)	-5.12	-65.32
C(18)-N(11)-C(13)-C(14)	164.6(8)	165.4(6)	177.36	113.11
C(19)-N(11)-C(13)-C(12)	106.7(8)	105.1(6)	113.71	54.44
C(19)-N(11)-C(13)-C(14)	-72.4(9)	-73.8(7)	-63.82	-127.13
C(20)-N(11)-C(13)-C(12)	-132.2(10)	-133.9(6)	-125.67	174.84
C(20)-N(11)-C(13)-C(14)	48.8(12)	47.2(7)	56.81	-6.73
Av.dif.[a]		0.29		22.4874
R.m.s.[b]		1.3238		202.309
Av.dif.[c]			-47.9948	-25.2125
R.m.s.[b]			122.746	3.1416

Table S5 (continued)

Parameters	X-Ray		B3LYP/6-31G(d,p)	
	1-I	**1**-II	**4**-I	**4**-II
Torsion angles				
C	*Cation*	*Cation*	*Cation*	*Zwitterion*
C(21)-C(22)-C(23)-C(24)	1.2(12)	2.6(8)	-1.38	-0.78
C(22)-C(23)-C(24)-C(25)	-1.3(13)	-2.2(9)	1.37	0.94
C(23)-C(24)-C(25)-C(26)	-0.2(13)	0.0(9)	-0.37	-0.40
C(24)-C(25)-C(26)-C(21)	1.8(13)	1.7(9)	-0.59	-0.30
C(25)-C(26)-C(21)-C(22)	-1.8(13)	-1.3(9)	0.58	0.47
C(26)-C(21)-C(22)-C(23)	0.3(12)	-0.8(8)	0.40	0.07
C(27)-C(21)-C(22)-C(23)	-177.3(8)	-177.7(5)	179.07	178.50
C(27)-C(21)-C(26)-C(25)	175.8(8)	175.4(5)	-178.03	-177.88
C(22)-C(21)-C(27)-O(21)	-175.0(8)	-176.1(5)	-179.42	-176.47
C(22)-C(21)-C(27)-O(22)	8.4(14)	6.5(10)	-0.48	1.26
C(26)-C(21)-C(27)-O(21)	7.3(12)	7.1(9)	-0.77	1.91
C(26)-C(21)-C(27)-O(22)	-169.3(10)	-170.2(6)	178.16	179.64
C(21)-C(22)-C(23)-N(21)	-179.1(7)	-178.6(5)	179.81	179.84
C(25)-C(24)-C(23)-N(21)	179.0(8)	178.9(5)	-179.79	-179.66
C(28)-N(21)-C(23)-C(22)	0.7(11)	2.1(7)	-8.99	-5.95
C(28)-N(21)-C(23)-C(24)	-179.6(8)	-179.0(5)	172.17	174.65
C(29)-N(21)-C(23)-C(22)	121.3(9)	121.6(6)	110.70	113.64
C(29)-N(21)-C(23)-C(24)	-59.0(10)	-59.5(6)	-68.14	-65.76
C(30)-N(21)-C(23)-C(22)	-119.1(9)	-118.3(6)	-128.59	-125.59
C(30)-N(21)-C(23)-C(24)	60.6(10)	60.6(7)	52.57	55.01
Av.dif.[a]		0.045		-1.243
R.m.s.[b]		0.7654		1.3795
Av.dif.[c]			-25.319	-33.017
R.m.s.[b]			206.876	196.645

[a] Average differences between data of polymorph **1**-I and polymorph **1**-II or optimized structures **4**-I and **4**-II.

[b] Root-mean-square errors.

[c] Average differences between data of polymorph **1**-I and optimized structure **4**-I or polymorph **1**-II and optimized structure **4**-II**.**

Table S6. Experimental and calculated by the B3LYP/6-31G(d,p) approach selected bond lengths (Å), bond and torsion angles (°) for 3-trimethylammonium-benzoic acid iodide.

Bond length		*Bond angles*	
C(1)-C(2)	1.383(9)	C(1)-C(2)-C(3)	120.4(6)
C(2)-C(3)	1.391(10)	C(2)-C(3)-C(4)	120.6(6)
C(3)-C(4)	1.376(10)	C(3)-C(4)-C(5)	119.7(7)
C(4)-C(5)	1.387(11)	C(4)-C(5)-C(6)	120.2(7)
C(5)-C(6)	1.404(12)	C(5)-C(6)-C(1)	119.6(7)
C(1)-C(6)	1.399(11)	C(6)-C(1)-C(2)	119.4(7)
C(1)-C(7)	1.483(11)	C(2)-C(1)-C(7)	123.0(7)
C(7)-O(1)	1.315(10)	C(6)-C(1)-C(7)	117.6(7)
C(7)-O(2)	1.203(10)	C(1)-C(7)-O(1)	112.8(7)
N(1)-C(3)	1.502(8)	C(1)-C(7)-O(2)	123.0(8)
N(1)-C(8)	1.505(9)	O(1)-C(7)-O(2)	124.2(8)
N(1)-C(9)	1.498(9)	C(2)-C(3)-N(1)	118.0(6)
N(1)-C(10)	1.509(10)	C(4)-C(3)-N(1)	121.4(7)
		C(3)-N(1)-C(8)	109.9(6)
		C(3)-N(1)-C(9)	108.8(5)
		C(3)-N(1)-C(10)	112.4(6)
		C(8)-N(1)-C(9)	110.2(7)
		C(8)-N(1)-C(10)	107.5(6)
		C(9)-N(1)-C(10)	108.1(6)

Torsion angles	
C(1)-C(2)-C(3)-C(4)	-1.4(10)
C(2)-C(3)-C(4)-C(5)	-0.1(10)
C(3)-C(4)-C(5)-C(6)	0.7(10)
C(4)-C(5)-C(6)-C(1)	0.2(10)
C(5)-C(6)-C(1)-C(2)	-1.6(10)
C(6)-C(1)-C(2)-C(3)	2.3(10)
C(7)-C(1)-C(2)-C(3)	-178.3(6)
C(7)-C(1)-C(6)-C(5)	178.9(6)
C(2)-C(1)-C(7)-O(1)	-12.6(10)
C(2)-C(1)-C(7)-O(2)	166.7(9)
C(6)-C(1)-C(7)-O(1)	166.8(6)
C(6)-C(1)-C(7)-O(2)	-13.8(13)
C(1)-C(2)-C(3)-N(1)	177.4(6)
C(5)-C(4)-C(3)-N(1)	-178.9(6)
C(8)-N(1)-C(3)-C(2)	52.6(8)
C(8)-N(1)-C(3)-C(4)	-128.5(7)
C(9)-N(1)-C(3)-C(2)	-68.0(8)
C(9)-N(1)-C(3)-C(4)	110.8(17)
C(10)-N(1)-C(3)-C(2)	172.3(6)
C(10)-N(1)-C(3)-C(4)	-8.8(9)

Table S7. Experimental (**1, 2**) and calculated (**3, 4**) geometry of the hydrogen bonds for 3:2. 2:1 and 1:1 complexes of 3-trimethylammonium-benzoate with hydroiodic acid; bonds in Å and angles in deg.

Comp	D-H···A	H···A	D···A	∠DH···A
X-ray				
1-I	O(1)-H(1)···O(11)	1.7199	2.529(9)	168.73
	O(21)-H(21)···O(12)	1.7337	2.533(9)	164.34
	C(29)-H(293)···I(1)[a]	3.0297	3.919(9)	154.73
	C(24)-H(24)···I(1)[b]	2.9817	3.903(8)	170.80
	C(18)-H(181)···I(2)[e]	3.0618	3.958(13)	155.95
	C(9)-H(93)···I(2)[c]	3.0522	3.914(10)	150.15
	C(4)-H(4)···I(2)[d]	3.0155	3.937(9)	171.14
1-II	O(1)-H(1)···O(11)	1.6841	2.493(5)	168.58
	O(21)-H(21)···O(12)	1.7440	2.549(5)	166.58
	C(19)-H(192)···I(1)	3.0354	3.960(6)	162.16
	C(20)-H(202)···I(1)[f]	3.1062	3.952(6)	147.76
	C(9)-H(92)···I(1)[g]	3.0077	3.928(6)	160.99
	C(4)-H(4)···I(1)[h]	2.9941	3.916(5)	171.10
	C(24)-H(24)···I(2)[i]	3.0460	3.968(5)	171.21
	C(29)-H(292)···I(2)[j]	3.0376	3.920(6)	153.47
	C(18)-H(181)···I(2)[k]	3.0036	3.931(7)	162.79
2	O(1)-H(1)···I(1)	2.6450	3.446(6)	166.00
	C(10)-H(101)···I(1)[l]	3.1504	4.087(9)	165.57
	C(5)-H(5)···O(2)[m]	2.4754	3.223(10)	137.45
	C(8)-H(83)···O(2)[n]	2.6098	3.502(13)	154.66
B3LYP/6-31G(d,p)				
3	O(1)-H(1)···O(11)	1.481	2,503	164.82
4-I	O(1)-H(1)···O(11)	1.413	2.480	174.22
	O(21)-H(21)···O(12)	1.400	2.443	161.92
4-II	O(1)-H(1)···O(11)	1.603	2.585	162.31
	O(12)-H(21)···O(21)	1.461	2.494	165.55

Symmetry codes: (a)=-1+x,y,z; (b)=-1-x,2.5-y,-0.5+z; (c)=1-x,2-y,2-z; (d)=1-x,0.5+y,1.5-z; (e)=x,2.5-y,0.5+z; (f)=x,0.5-y,-0.5+z; (g)=-0.5+x,-y,1.5-z; (h)=-0.5+x,0.5+y,1-z; (i)=0.5-x,0.5-y,z; (j)=0.5-x,y,0.5+z; (k)=x,0.5-y,0.5+z; (l)=x,1+y,z; (m)=1.5-x,1-y,1-z; (n)=1-x,1-y,1-z

Table S8. Experimental (**1**) and calculated (**2', 3, 4**) by the B3LYP/6-31G(d,p) approach, distances between positively charged nitrogen atoms and the iodine anions (in Å) in complexes of 3-trimethylammonium-benzoate with hydroiodic acid

Comp.	N(1)···I(1)	N(11)···I(1)	N(11)···I(2)	N(21)···I(2)
1-I	5.279(4)	4.374(8)	4.435(7)	5.204(5)
1-II	4.763(7)	4.375(5)	4.433(4)	4.825(3)
2'	4.306			
3	4.438	4.495		
4-I	4.357	5.019	4.678	4.323
4-II	4.270	4.793	4.555	4.408

The shortest interionic N···I distances (A) in experimentally determined structures **1**-I and **1**-II.

Comp		D···A
1-I	N(11)···I(1)	4.374(8)
	N(11)···I(2)	4.435(7)
	N(11)···I(1)^{e}	4.988(3)
	N(11)···I(2)^{e}	4.994(8)
	N(1)···I(2)^{d}	4.804(7)
	N(21)···I(2)^{d}	5.204(5)
	N(1)···I(2)^{c}	4.828(7)
	N(21)···I(1)^{b}	4.762(5)
	N(1)···I(1)^{b}	5.279(4)
	N(21)···I(1)^{a}	4.770(6)
1-II	N(11)···I(1)	4.375(5)
	N(11)···I(2)	4.433(4)
	N(11)···I(1)^{f}	4.985(2)
	N(11)···I(2)^{f}	4.921(5)
	N(1)···I(2)^{g}	5.202(6)
	N(21)···I(2)^{g}	4.825(3)
	N(21)···I(2)^{i}	4.848(6)
	N(21)···I(1)^{h}	5.265(4)
	N(1)···I(1)^{h}	4.763(7)
	N(1)···I(1)^{g}	4.774(8)

Symmetry codes: (a)=-1+x, y, z; (b)=-1-x, 2.5-y, -0.5+z, (c)=1-x, 2-y, 2-z, (d)=1-x, 0.5+y, 1.5-z, (e)=x, 2.5-y, 0.5+z, (f)=x,0.5-y,0.5+z, (g)=-0.5+x, -y, 1.5-z, (h)=-0.5+x, 0.5+y, 1-z, (i)=0.5-x, 0.5-y, z,

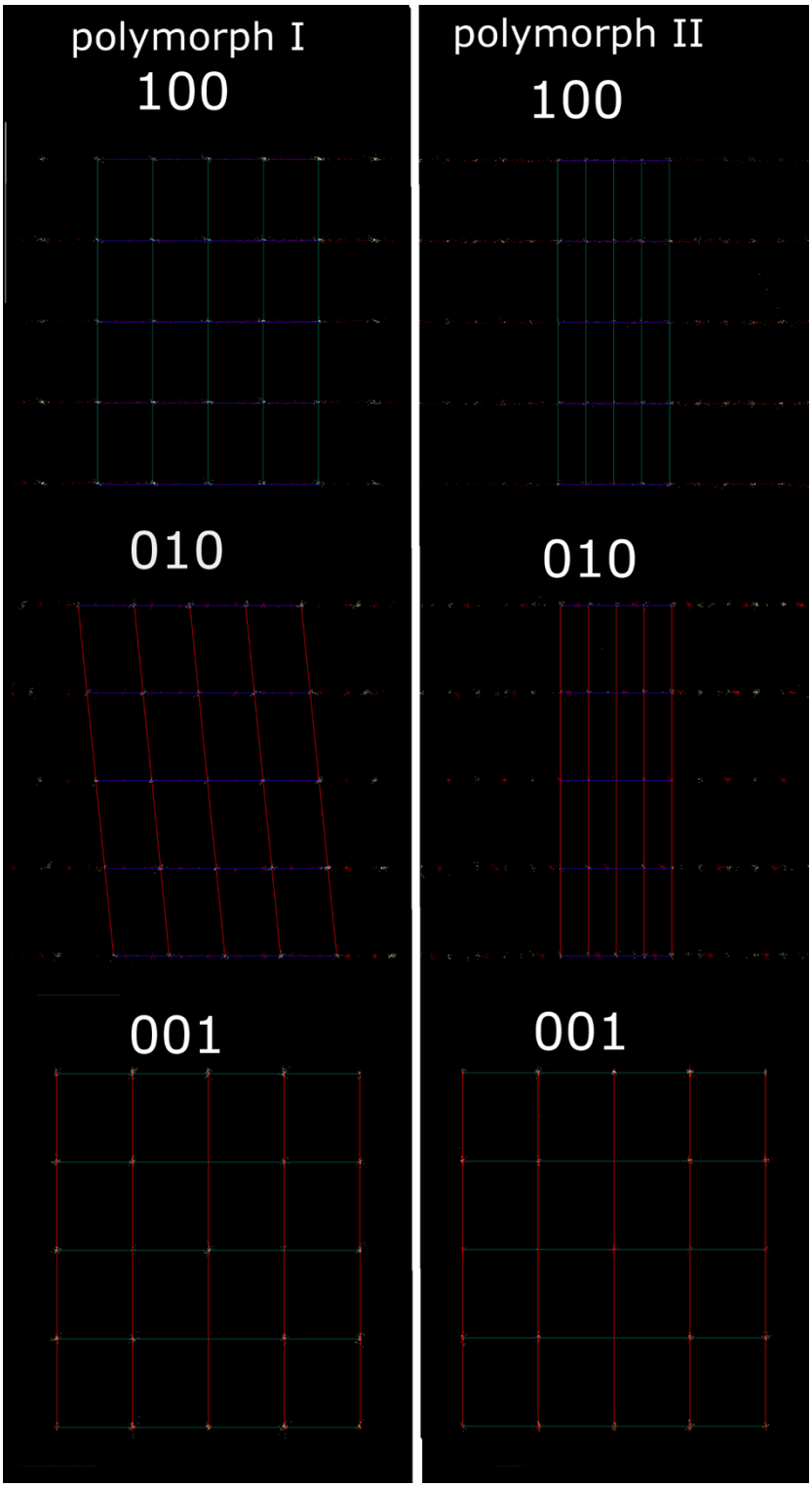

Figure S1. The reciprocal space projections for the diffraction pattern measured for an agglomerate of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide polymorphs **1**-I and **1**-II (space groups $P2_1/c$ and *Pccn*, respectively). According to the summed intensities of the reflections, their volume in the sample are 77.27% and 18.99%, respectively.

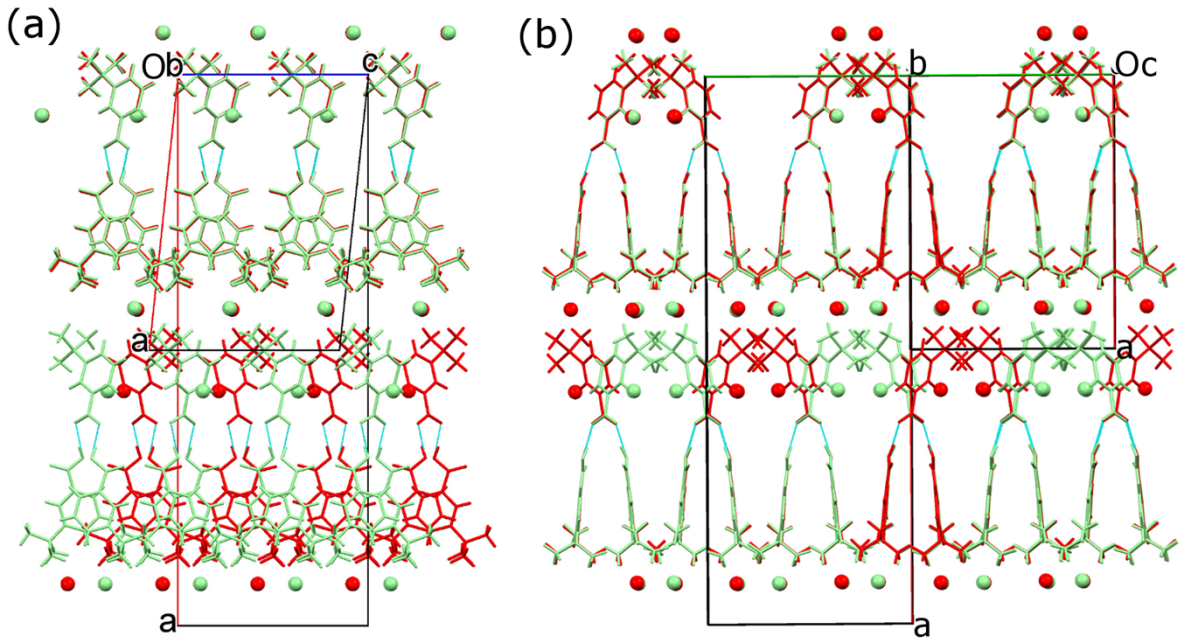

Figure S2. Structures of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide projected down the 010 (a) and 001 (c) in polymorph **1**-I (green) and polymorph **1**-II (red).

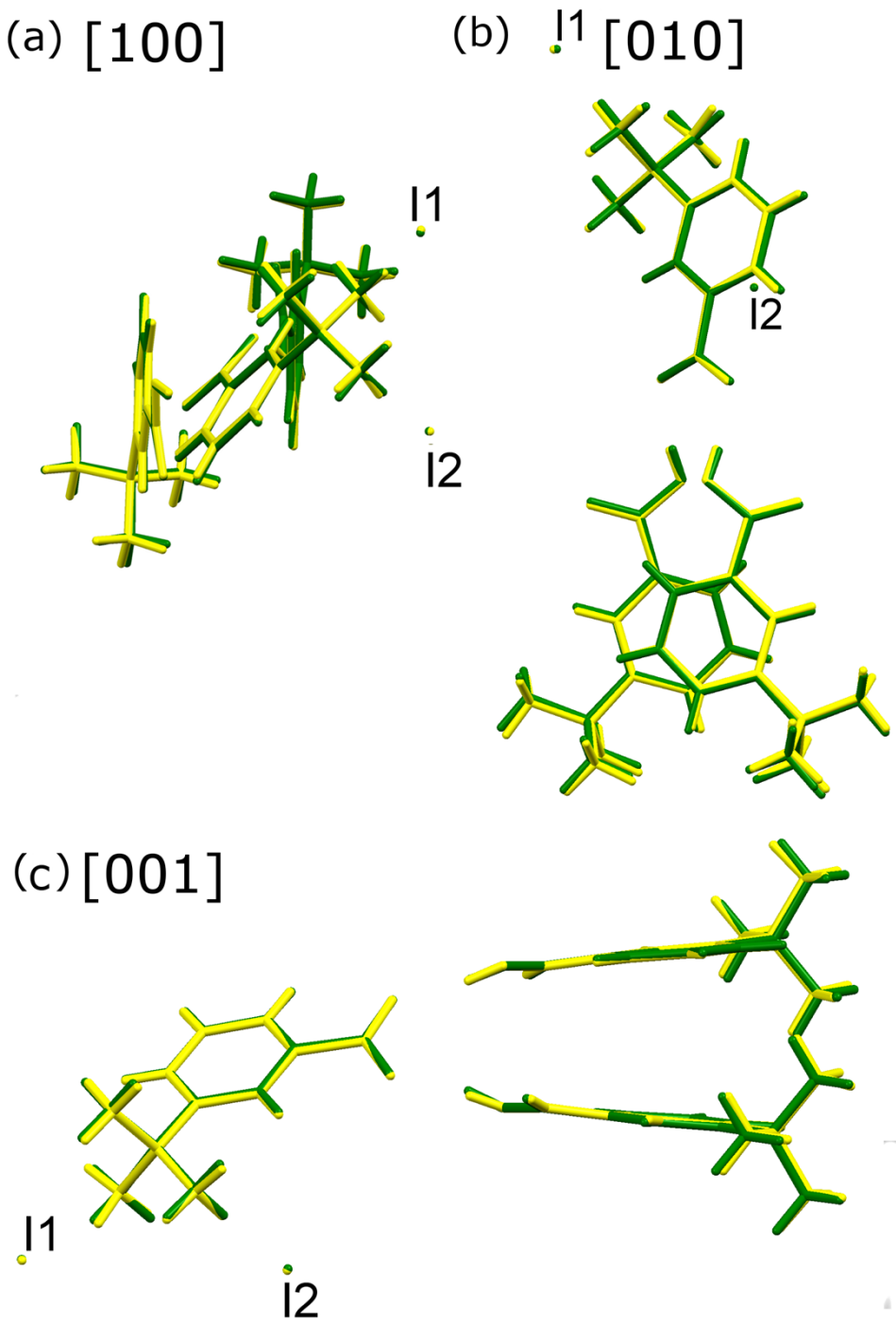

Figure S3. Aggregates of polymorph **1**-I (green) supperimposed with that in polymorph **1**-II (yellow), viewed in three crystallographic directions (a) [100]; (b) [010] and (c) [001].

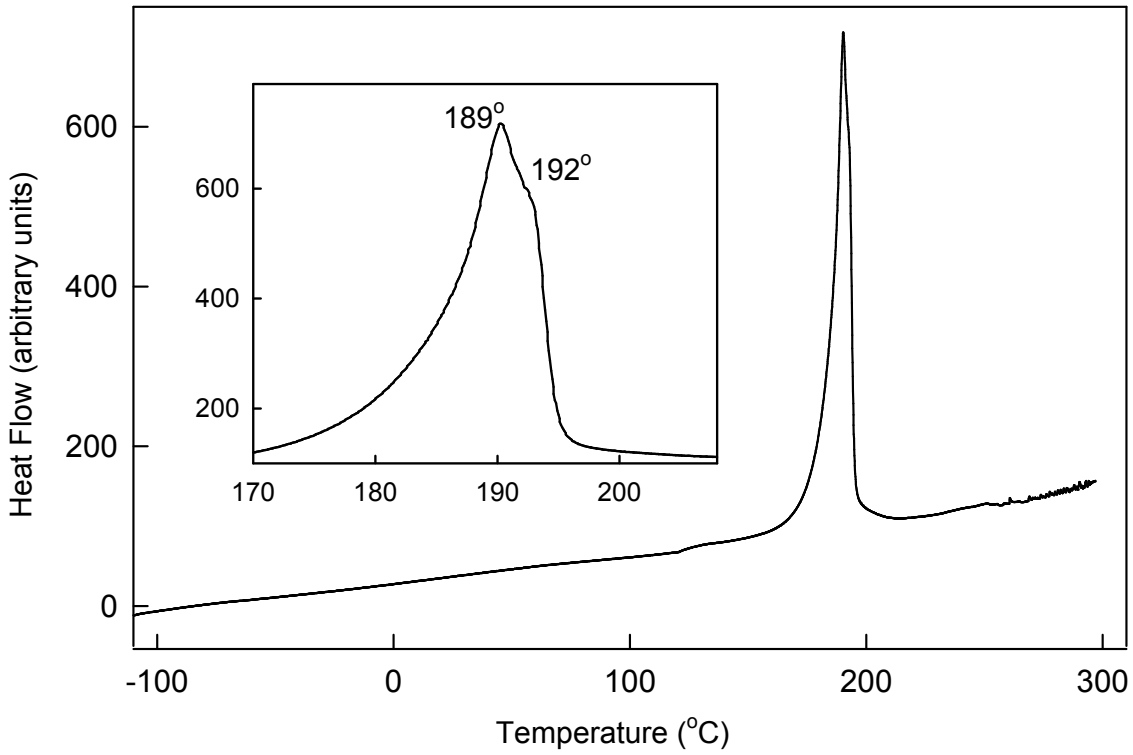

Figure S4. The different scanning calorymetry diagram for [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide (**1**-I).

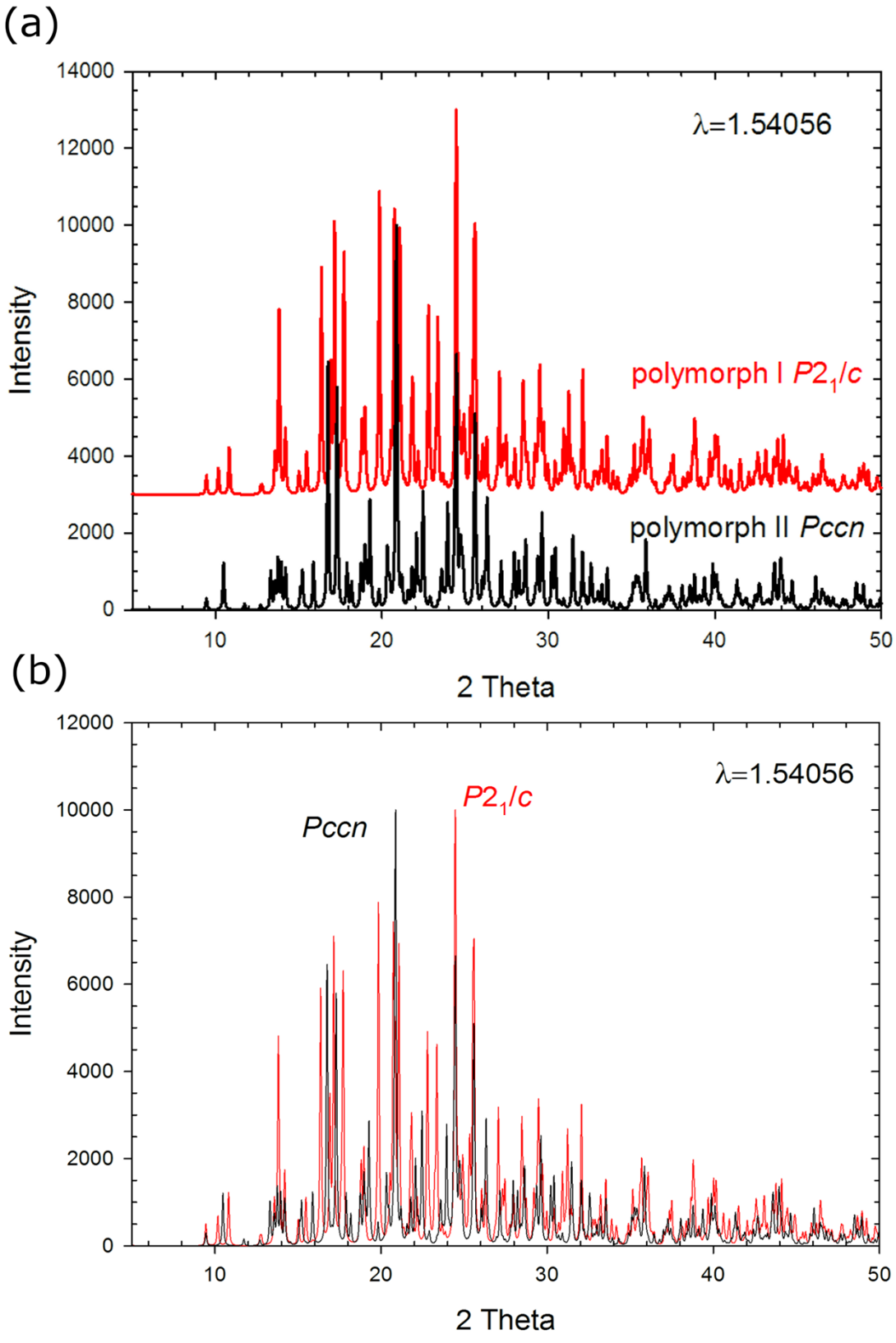

Figure S5. X-Ray powder diffraction (XRPD) of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide polymorphs **1**-I and **1**-II (space groups $P2_1/c$ and *Pccn*, respectively): (a) separate and (b) overlaid plots.

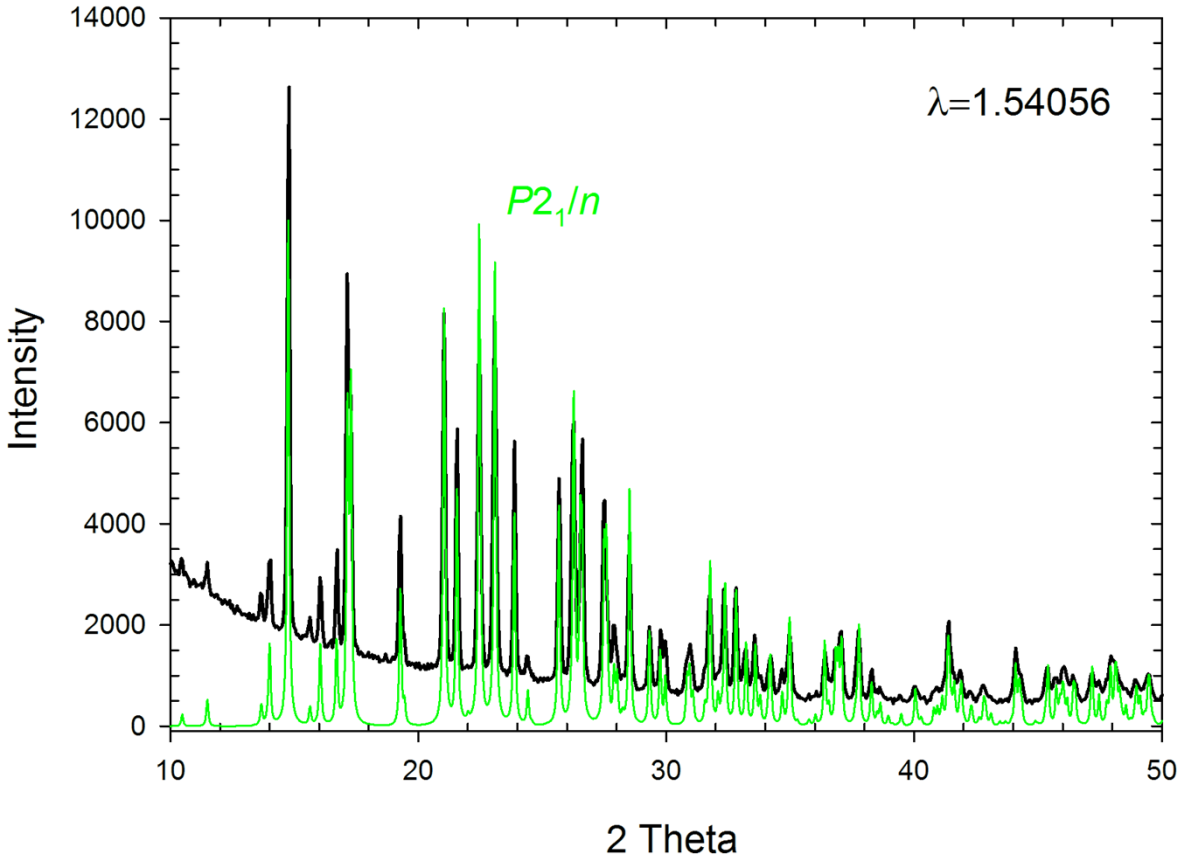

Figure S6. X-Ray powder diffraction (XRPD) of 3-trimethylammonium-benzoic acid iodide **2** (space group $P2_1/n$): measured experimentally (black) and calculated from the structure (green).