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Bi- or trinuclear 2-iodobenzoate complexes of Zn^{II}: crystal structures and luminescence

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Experimental

All experiments were performed in air. All reagents were obtained from commercial sources and used as purchased.

Synthesis of 1-4

1: 50 mg (0.2 mmol) of 2-IBA were dissolved in 5 ml of EtOH, followed by addition of 0.32 µl (0.4 mmol) pf Py. After that, solution of 30 mg (0.1 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ in 5 ml of EtOH was added. Slow partial evaporation of the mixture (within 2 days) results in formation of colorless crystals of **1**. Yield 83%. For $C_{38}H_{26}I_4N_2O_8Zn_2$ calcd, %: C, 35.80; H, 2.06; N, 2.20; found, %: C, 35.92, H, 2.11; N, 2.27.

2: the procedure was the same as for **1**, using 70 mg (0.28 mmol) of 2-IBA and 55 µl (0.65 mmol) of 3-MePy in 2 ml of EtOH and 42 mg (0.14 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ in 2 ml of EtOH, respectively. Yield 79%. For $C_{40}H_{30}I_4N_2O_8Zn_2$ calcd, %: C, 36.87; H, 2.32; N, 2.15; found, %: C, 36.97; H, 2.39; N, 2.14.

3: the procedure was the same as for **1**, using 50 mg (0.2 mmol) of 2-IBA and 46 µl (0.4 mmol) of 3,5-MePy in 3 ml of EtOH and 30 mg (0.14 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ in 3 ml of EtOH, respectively. Yield 84%. For $C_{42}H_{34}I_4N_2O_8Zn_2$ calcd, %: C, 37.90; H, 2.58; N, 2.11; found, %: C, 37.95; H, 2.62; N, 2.12.

4: the procedure was the same as for **1**, using 70 mg (0.28 mmol) of 2-IBA and 71 µl (0.56 mmol) of 2,4,6-MePy in 2 ml of EtOH and 42 mg (0.14 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ in 2 ml of EtOH, respectively. Yield 79%. For $C_{58}H_{50}I_6N_2O_{14}Zn_3$ calcd, %: C, 35.66; H, 2.58; N, 1.44; found, %: C, 35.70; H, 2.63; N, 1.45.

Luminescence

Photoluminescence (PL) spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon). The photoluminescence quantum yields (PL QY) were recorded using a Fluorolog 3 Quanta-phi device. Luminescence decay kinetics recorded by a Time-Correlated Single Photon Counting technique using a NanoLED pulsed light source and a NanoLED-C2 controller.

Computational details

The DFT calculations based on the experimental X-ray structures **1-4** have been carried out using the dispersion-corrected hybrid functional ωB97XD [Phys. Chem. Chem. Phys. 2008, 10, 6615.] with the help of Gaussian-09 [M. J. Frisch et al., in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [Mol. Phys. 2010, 108, 1965. || J. Chem. Phys. 2009, 130, 064108. || Chem. Phys. Lett. 2013, 582, 158. || J. Mol. Struct. - Theochem 2010, 961, 107.] for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader [Chem. Rev. 1991, 91, 893.] has been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Cartesian atomic coordinates for model supramolecular associates presented in Table S4.

The Hirshfeld surfaces analysis was performed in CrystalExplorer program (version 17.5) [M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, CrystalExplorer17 (2017). University of Western Australia. http://hirshfeldsurface.net || CrystEngComm 2009, 11, 19.]. The normalized contact distances (d_{norm} [Chem. Commun. 2007, 3814.]) based on Bondi's van der Waals radii [J. Phys. Chem. 1966, 70, 3006.] were mapped into the Hirshfeld surfaces.

Table S1. Crystal data and structure refinement for **1**-**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{38}H_{26}I_4N_2O_8Zn_2$	$C_{40}H_{30}I_4N_2O_8Zn_2$	$C_{42}H_{34}I_4N_2O_8Zn_2$	$C_{58}H_{50}I_6N_2O_{14}Zn_3$
M, g/mol	1276.95	1305.00	1333.05	1956.51
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, *P*-1
a,b,c, Å	10.7465 (4), 15.3117 (5), 23.6517 (8)	10.4789 (5), 21.4721 (10), 9.5766 (4)	3.9466 (7), 11.0012 (6), 14.7094 (8)	11.0413 (2), 12.4026 (2), 12.7793 (3)
α,β,γ°	90, 95.121 (3), 90	90, 97.893 (4), 90	90, 105.402 (6), 90	111.367 (2), 91.582 (2), 100.367 (2)
V, Å^3	3876.3 (2)	2134.36 (17)	2175.8 (2)	1594.80 (6)
Z	**4**	**2**	**2**	**1**
μ (mm^{-1})	4.48	4.07	3.99	4.09
T_{min}, T_{max}	0.845, 1.000	0.911, 1.000	0.842, 1.000	0.865, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19519, 7353, 6373	9830, 4052, 3245	10647, 4129, 3635	12896, 6066, 5207
R_{int}	0.026	0.024	0.027	0.025
θ values (°)	θ_{max} = 25.7, θ_{min} = 1.9	θ_{max} = 25.7, θ_{min} = 2.0	θ_{max} = 25.7, θ_{min} = 2.3	θ_{max} = 25.7, θ_{min} = 1.8
Range of *h*, *k*, *l*	h = −13→13, k = −14→18, l = −20→28	h = −12→12, k = −20→26, l = −11→11	h = −17→15, k = −13→10, l = −17→17	h = −13→13, k = −14→15, l = −15→13
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.059, 1.02	0.030, 0.068, 1.03	0.027, 0.062, 1.08	0.032, 0.068, 1.04
No. of reflections	7353	4052	4129	6066
No. of parameters	487	253	262	380
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, −1.59	1.23, −0.99	0.82, −1.14	1.17, −1.33

Table S2. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues, energy density – H_b, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to noncovalent interactions I···I and I···O in the X-ray structures **1**, **2**, **3** and **4**, and estimated strength for these interactions E_{int} (kcal/mol).

Contact*	% vdW radii sum**	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}***
1								
I···I 4.020	102/99	0.006	0.025	-0.006	0.001	-0.004	0.005	1.7
2								
I···I 3.787	96/93	0.008	0.032	-0.008	0.002	-0.005	0.007	2.1
3								
I···I 4.189	106/103	0.004	0.018	-0.004	0.001	-0.002	0.003	0.9
4								
I···O 3.648	104/103	0.004	0.019	-0.004	0.001	-0.002	0.003	0.9

* The sum of Bondi's van der Waals (vdW) radii[1] for I···I and I···O contacts is 3.96 and 3.50 Å, respectively. The sum of Alvarez's vdW radii[2] for I···I and I···O contacts is 4.08 and 3.54 Å, respectively. **Bondi/Alvarez *** $E_{int} = 0.68(-V(\mathbf{r}))$ (this empirical correlation between the interaction energy and the potential energy density of electrons at the bond critical points (3, –1) was specifically developed for noncovalent interactions involving iodine atoms)[3]

References

1. Bondi, A. van der Waals Volumes and Radii of Metals in Covalent Compounds. *J. Phys. Chem.* **1966**, *70*, 3006–3007.

2. Alvarez, S. A cartography of the van der Waals territories. *Dalton Trans.* **2013**, *42*, 8617–8636.

3. Bartashevich, E. V; Tsirelson, V.G. Interplay between non-covalent interactions in complexes and crystals with halogen bonds. *Russ. Chem. Rev.* **2014**, *83*, 1181–1203.

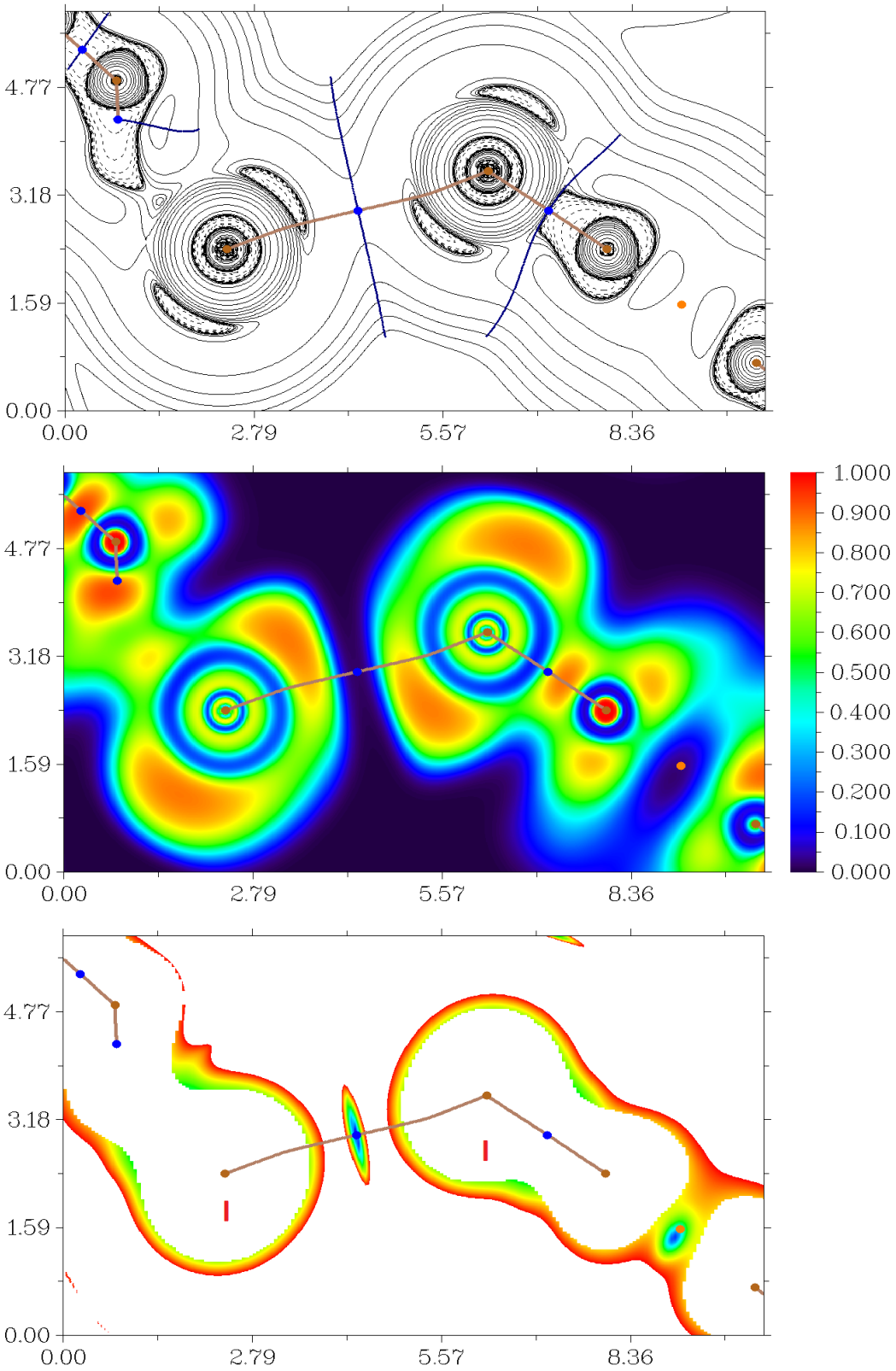

Figure S1. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for noncovalent interactions I···I in the X-ray structure **1**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

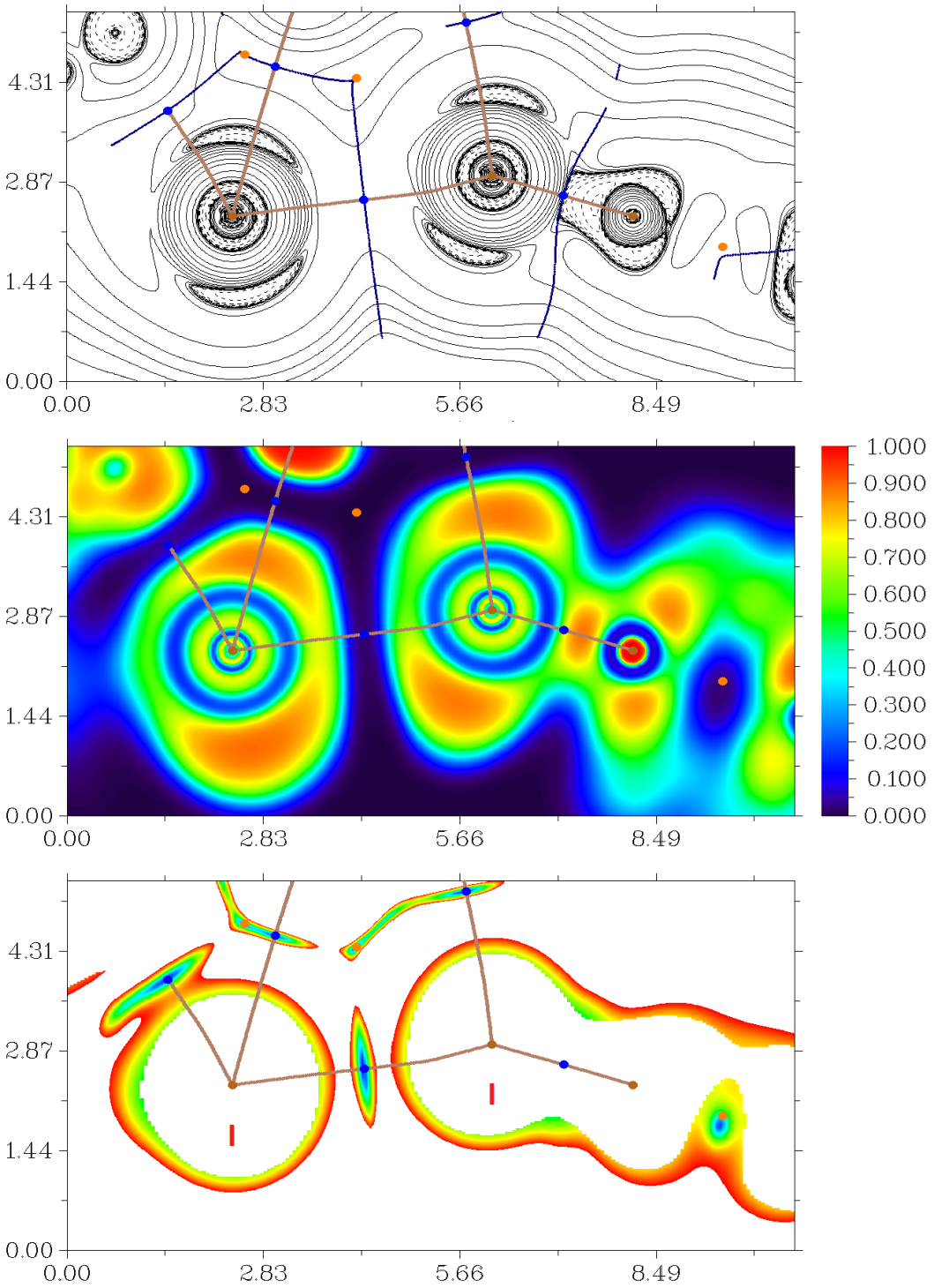

Figure S2. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for noncovalent interactions I···I in the X-ray structure **2**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

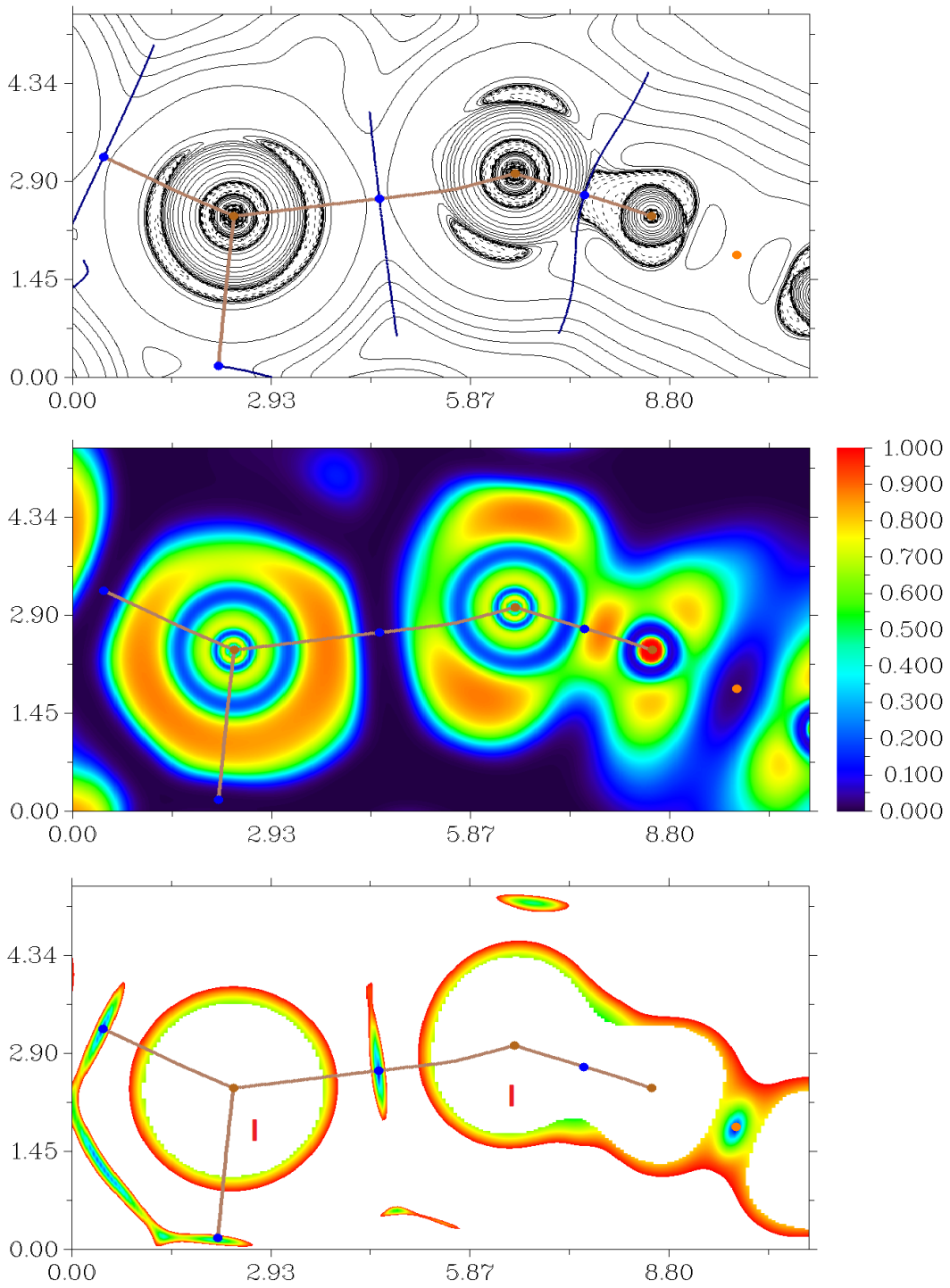

Figure S3. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for noncovalent interactions I···I in the X-ray structure **3**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

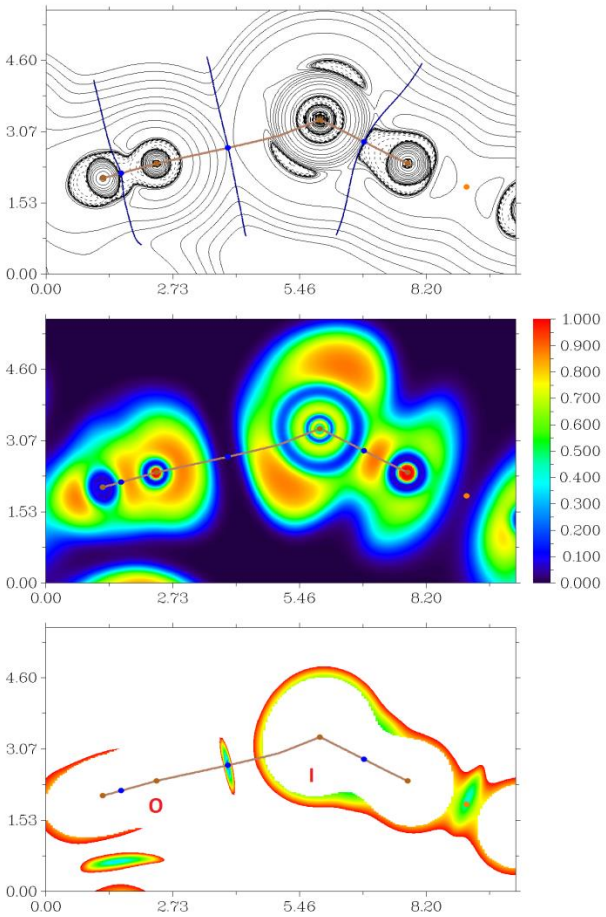

Figure S4. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for noncovalent interactions I···O in the X-ray structure **4**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

Table S3. Partial contributions of different interatomic contacts to the Hirshfeld surfaces of X-ray structures **1**-**4**.

X-ray structure	Contributions of different interatomic contacts to the Hirshfeld surfaces
1	H–H 31.3%, C–H 28.7%, I–H 19.6%, O–H 9.5%, C–C 4.8%, I–C 2.4%, I–I 1.6%, N–H 1.4%, N–C 0.5%, O–C 0.2%
2	H–H 31.6%, C–H 31.4%, I–H 19.3%, O–H 8.7%, C–C 3.9%, I–I 2.2%, I–C 1.8%, N–H 1.1%
3	H–H 47.4%, C–H 18.3%, I–H 12.0%, O–H 9.3%, C–C 5.6%, I–C 4.0%, N–H 1.8%, I–I 1.1%, N–C 0.4%
4	H–H 29.6%, C–H 22.1%, O–H 19.7%, I–H 18.5%, I–C 6.3%, C–C 2.0%, I–O 0.4%, I–N 0.4%, N–C 0.2%, O–C 0.2%, O–N 0.2%, I–I 0.2%, Zn–H 0.2%

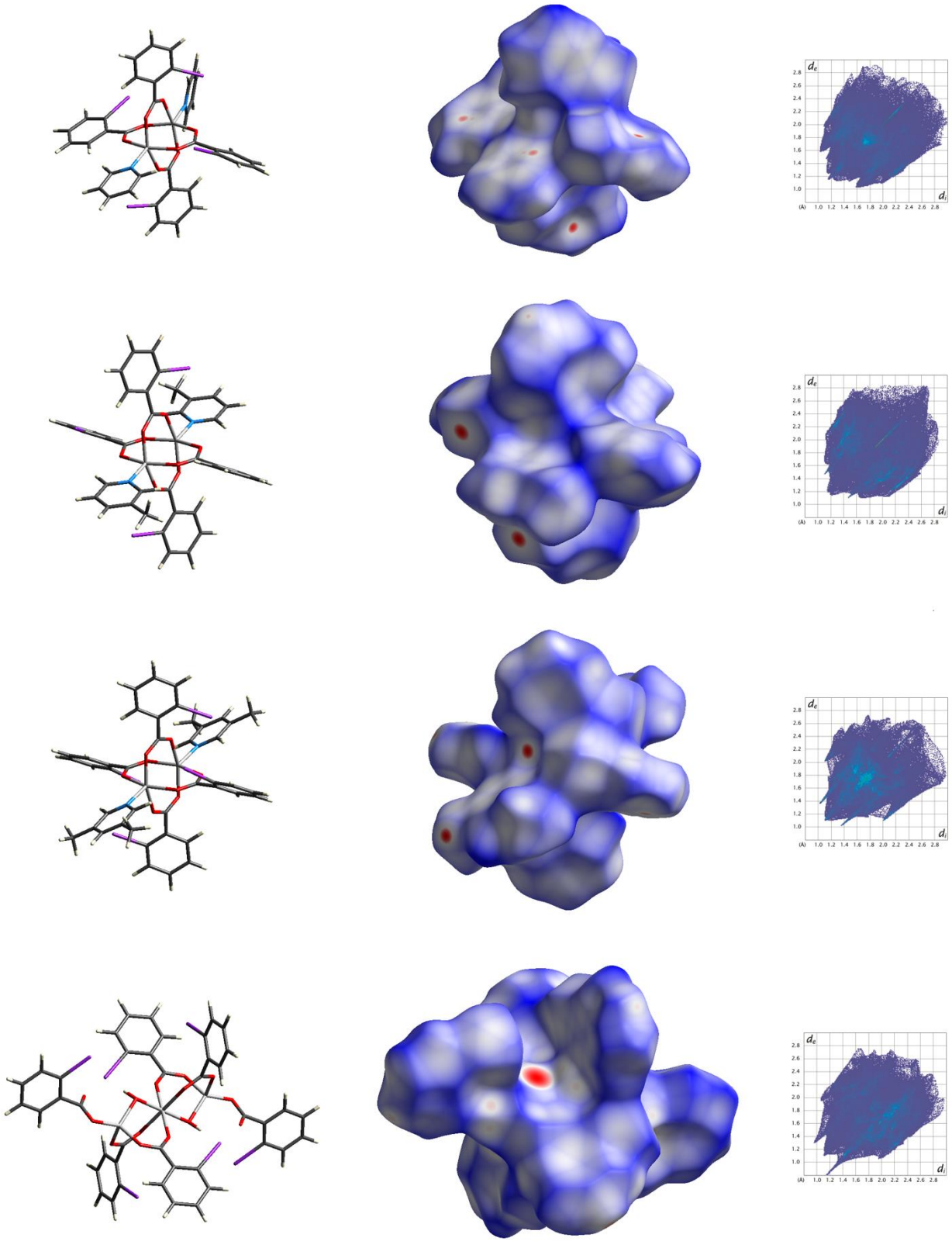

Figure S5. Visualization of Hirshfeld surfaces for the X-ray structures **1-4** (from top to bottom) and appropriate fingerprint plots.

Table S4. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1			
C	6.567999	8.027924	12.654035
H	5.782438	7.605321	12.977712
C	7.071556	9.111993	13.342615
H	6.639077	9.427414	14.127308
C	8.212935	9.732117	12.873825
H	8.587214	10.471672	13.338139
C	8.797655	9.262047	11.721402
H	9.577004	9.680057	11.371105
C	8.238398	8.173385	11.078759
H	8.641147	7.856433	10.278047
C	3.905001	1.330587	8.001470
H	3.894023	2.048705	7.380500
C	3.149018	0.209770	7.743282
H	2.632330	0.156179	6.949401
C	3.146170	-0.823769	8.638459
H	2.610094	-1.592417	8.480625
C	3.925375	-0.739555	9.764733
H	3.952851	-1.451549	10.393477
C	4.668515	0.402698	9.962379
H	5.211398	0.462413	10.739770
C	7.348868	3.206270	11.915043
C	8.046879	2.526431	13.071941
C	8.495127	1.218811	12.866757
H	8.391410	0.820707	12.009508
C	9.085697	0.496099	13.879485
H	9.407994	-0.382792	13.712700
C	9.209195	1.054976	15.139565
H	9.592852	0.551221	15.846991
C	8.774240	2.339628	15.364302
H	8.859918	2.722420	16.230974
C	8.211845	3.083776	14.336968
C	4.708394	5.721982	8.270259
C	4.108443	6.337513	7.026434
C	3.438705	7.557855	7.148931
H	3.407987	7.989645	7.995345
C	2.815508	8.150418	6.056580
H	2.362811	8.980312	6.155520
C	2.858786	7.527232	4.830187
H	2.419422	7.920742	4.084834
C	3.533713	6.339044	4.673767
H	3.568225	5.921034	3.820993
C	4.166709	5.748012	5.764705
C	4.092473	4.598104	11.881356
C	3.011684	4.562887	12.921175

C	1.984581	3.610499	12.990198
C	1.049864	3.650309	14.006930
H	0.373312	2.984250	14.049569
C	1.092373	4.645570	14.959587
H	0.444474	4.668537	15.653821
C	2.081904	5.613269	14.902108
H	2.111084	6.308420	15.547813
C	3.023172	5.558147	13.896211
H	3.702714	6.221144	13.868178
C	8.016931	4.402114	8.609484
C	9.321490	4.218373	7.878736
C	9.821254	2.916879	7.818194
H	9.285477	2.200291	8.136689
C	11.076174	2.644331	7.305587
H	11.400300	1.751658	7.286271
C	11.854323	3.674808	6.824783
H	12.725773	3.495661	6.490034
C	11.367148	4.968647	6.828788
H	11.889657	5.674516	6.466477
C	10.114859	5.235070	7.360005
N	4.660082	1.432869	9.109134
N	7.146685	7.550199	11.544958
O	4.285141	3.573598	11.194425
O	4.762606	5.657214	11.790425
O	6.802853	2.430732	11.088653
O	7.359436	4.444374	11.845078
O	4.561900	4.483419	8.417963
O	5.281069	6.498285	9.062961
O	7.201645	3.461516	8.521379
O	7.876648	5.447137	9.287462
Zn	5.548744	3.175953	9.647182
Zn	6.417486	5.879846	10.652136
I	1.640363	2.106124	11.552496
I	7.654133	5.039999	14.860647
I	5.359374	4.070615	5.351981
I	9.503699	7.244884	7.262949
C	12.813865	7.283776	10.903257
H	13.599426	7.706379	10.579580
C	12.310308	6.199707	10.214678
H	12.742787	5.884286	9.429984
C	11.168930	5.579583	10.683468
H	10.794650	4.840028	10.219153
C	10.584210	6.049653	11.835890
H	9.804861	5.631643	12.186187
C	11.143467	7.138315	12.478533
H	10.740717	7.455267	13.279246
C	15.476863	13.981113	15.555822
H	15.487842	13.262995	16.176793

C	16.232846	15.101930	15.814010
H	16.749535	15.155521	16.607891
C	16.235695	16.135469	14.918833
H	16.771771	16.904117	15.076667
C	15.456490	16.051255	13.792559
H	15.429013	16.763249	13.163815
C	14.713350	14.909002	13.594913
H	14.170467	14.849287	12.817523
C	12.032997	12.105430	11.642249
C	11.334986	12.785270	10.485351
C	10.886738	14.092889	10.690535
H	10.990455	14.490993	11.547785
C	10.296167	14.815601	9.677807
H	9.973871	15.694492	9.844592
C	10.172669	14.256724	8.417727
H	9.789012	14.760479	7.710302
C	10.607624	12.972072	8.192991
H	10.521946	12.589280	7.326318
C	11.170019	12.227924	9.220324
C	14.673471	9.589718	15.287034
C	15.273421	8.974187	16.530859
C	15.943159	7.753845	16.408361
H	15.973877	7.322055	15.561947
C	16.566356	7.161282	17.500712
H	17.019053	6.331388	17.401772
C	16.523079	7.784468	18.727105
H	16.962443	7.390958	19.472458
C	15.848151	8.972656	18.883525
H	15.813639	9.390666	19.736299
C	15.215156	9.563688	17.792587
C	15.289391	10.713596	11.675936
C	16.370180	10.748813	10.636117
C	17.397283	11.701201	10.567095
C	18.332000	11.661391	9.550362
H	19.008552	12.327450	9.507723
C	18.289491	10.666130	8.597705
H	18.937391	10.643163	7.903472
C	17.299961	9.698431	8.655185
H	17.270780	9.003280	8.009479
C	16.358692	9.753553	9.661081
H	15.679151	9.090556	9.689114
C	11.364933	10.909586	14.947809
C	10.060375	11.093327	15.678556
C	9.560610	12.394821	15.739098
H	10.096387	13.111409	15.420604
C	8.305690	12.667369	16.251705
H	7.981564	13.560042	16.271022
C	7.527542	11.636892	16.732509

H	6.656091	11.816039	17.067258
C	8.014717	10.343053	16.728504
H	7.492207	9.637184	17.090816
C	9.267006	10.076630	16.197287
N	14.721782	13.878831	14.448158
N	12.235179	7.761501	12.012334
O	15.096723	11.738102	12.362867
O	14.619258	9.654486	11.766867
O	12.579011	12.880968	12.468639
O	12.022428	10.867326	11.712215
O	14.819964	10.828281	15.139329
O	14.100795	8.813415	14.494331
O	12.180220	11.850184	15.035913
O	11.505216	9.864563	14.269830
Zn	13.833120	12.135747	13.910110
Zn	12.964379	9.431854	12.905156
I	17.741502	13.205576	12.004796
I	11.727731	10.271701	8.696646
I	14.022490	11.241085	18.205311
I	9.878166	8.066816	16.294343
2			
C	8.351596	8.593134	-0.316828
H	7.997535	9.177176	-1.020680
H	7.723164	7.858789	-0.152723
H	9.215475	8.228109	-0.599507
C	8.535453	9.393829	0.957125
C	9.766511	9.895847	1.344148
H	10.533469	9.733303	0.808196
C	9.880744	10.632769	2.508065
H	10.721654	10.976538	2.784104
C	8.740616	10.857582	3.264089
H	8.812090	11.375919	4.056160
C	7.453702	9.654715	1.790933
H	6.603997	9.306008	1.548095
C	4.180227	13.050742	3.687159
C	3.949602	14.429036	3.136030
C	5.059602	15.100469	2.619998
H	5.906552	14.669739	2.633279
C	4.959429	16.378703	2.087841
H	5.729948	16.816949	1.745401
C	3.735901	17.004185	2.062229
H	3.659215	17.875523	1.693228
C	2.622239	16.374194	2.566877
H	1.779880	16.814802	2.543163
C	2.718738	15.096819	3.110418
C	5.830727	11.939991	6.642009
C	6.408662	12.736176	7.786954
C	5.897234	12.465842	9.079878

H	5.210417	11.818244	9.181377
C	6.369489	13.113870	10.178342
H	6.027794	12.904732	11.040608
C	7.348692	14.077109	10.031311
H	7.687655	14.523728	10.798719
C	7.840843	14.401123	8.779176
H	8.491374	15.086297	8.682420
C	7.375147	13.716592	7.663637
N	7.546735	10.372527	2.918803
O	5.254617	12.489247	3.375074
O	3.318842	12.553663	4.435595
O	6.592269	11.594290	5.714290
O	4.626524	11.665362	6.726433
Zn	5.883812	10.684088	4.036144
I	8.158929	14.334774	5.810572
I	0.896293	14.299989	3.812278
C	0.812211	12.878966	9.802702
H	1.166272	12.294924	10.506554
H	1.440643	13.613311	9.638596
H	-0.051668	13.243991	10.085381
C	0.628354	12.078271	8.528749
C	-0.602703	11.576253	8.141725
H	-1.369661	11.738797	8.677677
C	-0.716936	10.839331	6.977809
H	-1.557847	10.495562	6.701770
C	0.423192	10.614518	6.221785
H	0.351717	10.096181	5.429714
C	1.710105	11.817385	7.694941
H	2.559810	12.166092	7.937779
C	4.983580	8.421358	5.798715
C	5.214205	7.043064	6.349844
C	4.104205	6.371631	6.865875
H	3.257256	6.802361	6.852595
C	4.204378	5.093397	7.398033
H	3.433859	4.655151	7.740473
C	5.427907	4.467915	7.423645
H	5.504592	3.596577	7.792645
C	6.541568	5.097906	6.918996
H	7.383928	4.657298	6.942711
C	6.445069	6.375281	6.375456
C	3.333080	9.532109	2.843865
C	2.755145	8.735924	1.698920
C	3.266573	9.006258	0.405995
H	3.953390	9.653856	0.304497
C	2.794319	8.358230	-0.692469
H	3.136013	8.567368	-1.554735
C	1.815115	7.394991	-0.545438
H	1.476153	6.948372	-1.312845

C	1.322964	7.070977	0.706698
H	0.672433	6.385803	0.803453
C	1.788660	7.755508	1.822236
N	1.617072	11.099573	6.567070
O	3.909190	8.982853	6.110800
O	5.844966	8.918437	5.050279
O	2.571538	9.877810	3.771583
O	4.537283	9.806738	2.759441
Zn	3.279995	10.788012	5.449729
I	1.004878	7.137326	3.675302
I	8.267514	7.172111	5.673596
C	18.830496	8.593134	-0.316828
H	18.476435	9.177176	-1.020680
H	18.202064	7.858789	-0.152723
H	19.694375	8.228109	-0.599507
C	19.014353	9.393829	0.957125
C	20.245411	9.895847	1.344148
H	21.012369	9.733303	0.808196
C	20.359644	10.632769	2.508065
H	21.200554	10.976538	2.784104
C	19.219516	10.857582	3.264089
H	19.290990	11.375919	4.056160
C	17.932602	9.654715	1.790933
H	17.082897	9.306008	1.548095
C	14.659127	13.050742	3.687159
C	14.428502	14.429036	3.136030
C	15.538502	15.100469	2.619998
H	16.385452	14.669739	2.633279
C	15.438329	16.378703	2.087841
H	16.208848	16.816949	1.745401
C	14.214801	17.004185	2.062229
H	14.138115	17.875523	1.693228
C	13.101139	16.374194	2.566877
H	12.258780	16.814802	2.543163
C	13.197638	15.096819	3.110418
C	16.309627	11.939991	6.642009
C	16.887562	12.736176	7.786954
C	16.376134	12.465842	9.079878
H	15.689317	11.818244	9.181377
C	16.848389	13.113870	10.178342
H	16.506694	12.904732	11.040608
C	17.827592	14.077109	10.031311
H	18.166555	14.523728	10.798719
C	18.319743	14.401123	8.779176
H	18.970274	15.086297	8.682420
C	17.854047	13.716592	7.663637
N	18.025635	10.372527	2.918803
O	15.733517	12.489247	3.375074

O	13.797742	12.553663	4.435595
O	17.071169	11.594290	5.714290
O	15.105424	11.665362	6.726433
Zn	16.362712	10.684088	4.036144
I	18.637829	14.334774	5.810572
I	11.375193	14.299989	3.812278
C	11.291111	12.878966	9.802702
H	11.645172	12.294924	10.506554
H	11.919543	13.613311	9.638596
H	10.427232	13.243991	10.085381
C	11.107254	12.078271	8.528749
C	9.876197	11.576253	8.141725
H	9.109239	11.738797	8.677677
C	9.761964	10.839331	6.977809
H	8.921053	10.495562	6.701770
C	10.902092	10.614518	6.221785
H	10.830617	10.096181	5.429714
C	12.189005	11.817385	7.694941
H	13.038710	12.166092	7.937779
C	15.462480	8.421358	5.798715
C	15.693105	7.043064	6.349844
C	14.583105	6.371631	6.865875
H	13.736156	6.802361	6.852595
C	14.683278	5.093397	7.398033
H	13.912759	4.655151	7.740473
C	15.906807	4.467915	7.423645
H	15.983492	3.596577	7.792645
C	17.020468	5.097906	6.918996
H	17.862828	4.657298	6.942711
C	16.923969	6.375281	6.375456
C	13.811980	9.532109	2.843865
C	13.234045	8.735924	1.698920
C	13.745473	9.006258	0.405995
H	14.432290	9.653856	0.304497
C	13.273219	8.358230	-0.692469
H	13.614913	8.567368	-1.554735
C	12.294015	7.394991	-0.545438
H	11.955053	6.948372	-1.312845
C	11.801864	7.070977	0.706698
H	11.151333	6.385803	0.803453
C	12.267560	7.755508	1.822236
N	12.095972	11.099573	6.567070
O	14.388090	8.982853	6.110800
O	16.323866	8.918437	5.050279
O	13.050438	9.877810	3.771583
O	15.016183	9.806738	2.759441
Zn	13.758895	10.788012	5.449729
I	11.483778	7.137326	3.675302

I	18.746414	7.172111	5.673596
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C	3.782324	10.971497	3.366600
H	2.992412	11.513856	3.160974
H	3.794886	10.180510	2.789428
H	4.591970	11.501755	3.212026
C	3.734295	10.540250	4.811657
C	4.215189	9.287213	5.161931
H	4.569064	8.728352	4.479819
C	3.696066	9.618349	7.385532
H	3.691613	9.294914	8.277525
C	3.181465	10.882387	7.137362
C	2.583530	11.682174	8.254835
H	1.617027	11.523757	8.290288
H	2.752636	12.634878	8.101679
H	2.989670	11.411545	9.104285
C	3.230373	11.329036	5.815681
H	2.908454	12.199231	5.607218
C	9.658260	7.150780	6.702001
H	9.205208	7.751446	7.283428
C	11.000010	7.355402	6.428306
H	11.465446	8.079281	6.829632
C	11.653757	6.500609	5.568929
H	12.575593	6.632623	5.381738
C	10.974904	5.453295	4.980412
H	11.428237	4.874632	4.377714
C	9.631423	5.243172	5.265453
C	8.955248	6.081463	6.140429
C	7.510168	5.914245	6.536082
C	5.228324	6.101266	9.579352
C	5.207961	6.376296	11.055608
C	4.588959	5.571008	12.001489
C	4.634829	5.895543	13.348696
H	4.226734	5.324581	13.989683
C	5.280230	7.056170	13.759949
H	5.306624	7.281694	14.681722
C	5.881211	7.883460	12.833921
H	6.316872	8.681047	13.110453
C	5.841979	7.534722	11.498059
H	6.258664	8.102384	10.861326
N	4.200384	8.833964	6.424618
O	6.817517	6.954959	6.549980
O	7.127007	4.767920	6.853172
O	5.112792	7.100174	8.831298
O	5.387922	4.913136	9.201000
Zn	4.793899	6.947148	6.834879
I	8.699624	3.692223	4.178611
I	3.385795	3.917527	11.482034

C	6.257610	0.029703	10.814529
H	7.047522	-0.512656	11.020155
H	6.245048	0.820690	11.391701
H	5.447964	-0.500555	10.969103
C	6.305639	0.460950	9.369472
C	5.824745	1.713987	9.019198
H	5.470869	2.272848	9.701310
C	6.343868	1.382851	6.795597
H	6.348321	1.706286	5.903604
C	6.858469	0.118813	7.043767
C	7.456403	-0.680974	5.926294
H	8.422907	-0.522557	5.890841
H	7.287297	-1.633678	6.079450
H	7.050264	-0.410345	5.076844
C	6.809561	-0.327836	8.365448
H	7.131480	-1.198031	8.573910
C	0.381674	3.850420	7.479127
H	0.834726	3.249754	6.897701
C	-0.960076	3.645798	7.752823
H	-1.425512	2.921919	7.351497
C	-1.613823	4.500591	8.612199
H	-2.535659	4.368577	8.799390
C	-0.934970	5.547905	9.200716
H	-1.388303	6.126568	9.803414
C	0.408511	5.758028	8.915676
C	1.084686	4.919737	8.040700
C	2.529766	5.086955	7.645046
C	4.811610	4.899934	4.601776
C	4.831973	4.624904	3.125521
C	5.450975	5.430192	2.179639
C	5.405105	5.105657	0.832432
H	5.813200	5.676619	0.191445
C	4.759703	3.945030	0.421180
H	4.733310	3.719506	-0.500594
C	4.158722	3.117740	1.347207
H	3.723062	2.320153	1.070675
C	4.197955	3.466478	2.683070
H	3.781270	2.898816	3.319802
N	5.839549	2.167236	7.756510
O	3.222417	4.046241	7.631149
O	2.912927	6.233280	7.327956
O	4.927142	3.901026	5.349831
O	4.652012	6.088064	4.980129
Zn	5.246034	4.054052	7.346250
I	1.340310	7.308977	10.002517
I	6.654139	7.083673	2.699094
C	15.184243	16.472097	3.723964
H	15.974155	17.014456	3.929591

H	15.171681	15.681110	4.301136
H	14.374597	17.002355	3.878539
C	15.232272	16.040850	2.278907
C	14.751378	14.787813	1.928633
H	14.397502	14.228952	2.610746
C	15.270501	15.118949	-0.294967
H	15.274954	14.795514	-1.186960
C	15.785102	16.382987	-0.046798
C	16.383037	17.182774	-1.164271
H	17.349540	17.024357	-1.199723
H	16.213930	18.135478	-1.011114
H	15.976897	16.912145	-2.013720
C	15.736194	16.829636	1.274883
H	16.058113	17.699831	1.483346
C	9.308307	12.651380	0.388563
H	9.761359	13.252046	-0.192863
C	7.966557	12.856002	0.662259
H	7.501121	13.579881	0.260933
C	7.312810	12.001209	1.521635
H	6.390974	12.133223	1.708826
C	7.991663	10.953895	2.110152
H	7.538330	10.375232	2.712850
C	9.335144	10.743772	1.825111
C	10.011319	11.582063	0.950136
C	11.456399	11.414845	0.554482
C	13.738243	11.601866	-2.488788
C	13.758606	11.876896	-3.965044
C	14.377608	11.071608	-4.910925
C	14.331738	11.396143	-6.258132
H	14.739833	10.825181	-6.899119
C	13.686336	12.556770	-6.669385
H	13.659943	12.782294	-7.591158
C	13.085355	13.384060	-5.743357
H	12.649695	14.181647	-6.019889
C	13.124588	13.035322	-4.407495
H	12.707903	13.602984	-3.770762
N	14.766182	14.334564	0.665946
O	12.149050	12.455559	0.540585
O	11.839560	10.268520	0.237392
O	13.853775	12.600774	-1.740734
O	13.578645	10.413736	-2.110436
Zn	14.172668	12.447748	0.255686
I	10.266943	9.192823	2.911953
I	15.580772	9.418127	-4.391470
C	12.708957	5.530303	-3.723964
H	11.919045	4.987944	-3.929591
H	12.721519	6.321290	-4.301136
H	13.518603	5.000045	-3.878539

C	12.660928	5.961550	-2.278907
C	13.141822	7.214587	-1.928633
H	13.495698	7.773448	-2.610746
C	12.622699	6.883451	0.294967
H	12.618246	7.206886	1.186960
C	12.108098	5.619413	0.046798
C	11.510163	4.819626	1.164271
H	10.543660	4.978043	1.199723
H	11.679270	3.866922	1.011114
H	11.916303	5.090255	2.013720
C	12.157006	5.172764	-1.274883
H	11.835087	4.302569	-1.483346
C	18.584893	9.351020	-0.388563
H	18.131841	8.750354	0.192863
C	19.926643	9.146398	-0.662259
H	20.392079	8.422519	-0.260933
C	20.580390	10.001191	-1.521635
H	21.502226	9.869177	-1.708826
C	19.901537	11.048505	-2.110152
H	20.354870	11.627168	-2.712850
C	18.558056	11.258628	-1.825111
C	17.881881	10.420337	-0.950136
C	16.436801	10.587555	-0.554482
C	14.154957	10.400534	2.488788
C	14.134594	10.125504	3.965044
C	13.515592	10.930792	4.910925
C	13.561462	10.606257	6.258132
H	13.153367	11.177219	6.899119
C	14.206864	9.445630	6.669385
H	14.233257	9.220106	7.591158
C	14.807845	8.618340	5.743357
H	15.243505	7.820753	6.019889
C	14.768612	8.967078	4.407495
H	15.185297	8.399416	3.770762
N	13.127018	7.667836	-0.665946
O	15.744150	9.546841	-0.540585
O	16.053640	11.733880	-0.237392
O	14.039425	9.401626	1.740734
O	14.314555	11.588664	2.110436
Zn	13.720532	9.554652	-0.255686
I	17.626257	12.809577	-2.911953
I	12.312428	12.584273	4.391470
4			
C	6.590533	3.241301	-0.074587
H	6.066534	2.669691	-0.623926
C	7.168824	4.365633	-0.606168
H	7.071825	4.553421	-1.533178
C	7.896393	5.229634	0.200083

H	8.281647	6.014692	-0.171669
C	8.060141	4.947863	1.542649
C	6.771865	2.943889	1.264428
H	6.379728	2.155568	1.623156
C	7.518062	3.774415	2.099092
C	7.744439	3.325214	3.505590
C	10.060837	0.686186	4.996146
C	11.001966	-0.348439	4.391163
C	11.868976	-1.050771	5.221091
H	11.899794	-0.853994	6.150469
C	12.694498	-2.044381	4.689511
H	13.260746	-2.549399	5.261345
C	12.687342	-2.290657	3.343393
H	13.269287	-2.950971	2.985849
C	11.844695	-1.593369	2.489786
H	11.839789	-1.772847	1.556856
C	11.008331	-0.624337	3.030838
C	6.023167	0.116709	7.388851
C	4.848341	-0.568953	8.054214
C	4.568553	-1.924648	7.735740
H	5.105672	-2.390431	7.105894
C	3.506480	-2.557959	8.350195
H	3.310855	-3.463208	8.139457
C	2.728001	-1.885199	9.270101
H	1.992204	-2.329408	9.673818
C	2.997839	-0.594522	9.607519
H	2.471925	-0.149794	10.262227
C	4.047744	0.067768	8.984776
H	8.388835	2.469210	7.363988
O	8.152426	2.861041	6.866742
O	8.854212	0.320895	5.063630
O	6.919573	2.482554	3.980342
O	8.746244	3.769531	4.101102
O	10.550222	1.755108	5.375001
O	5.827027	0.535711	6.201378
O	7.080569	0.228264	7.992650
Zn	9.748957	3.701152	5.919605
Zn	7.418151	1.530255	5.637832
I	4.356872	2.068186	9.516830
I	9.734507	0.444844	1.728880
I	9.052641	6.457904	2.632685
C	12.907381	4.161002	11.913797
H	13.431380	4.732612	12.463136
C	12.329090	3.036670	12.445377
H	12.426089	2.848882	13.372387
C	11.601521	2.172670	11.639127
H	11.216267	1.387611	12.010878
C	11.437773	2.454440	10.296561

C	12.726049	4.458414	10.574782
H	13.118186	5.246735	10.216054
C	11.979852	3.627888	9.740118
C	11.753475	4.077089	8.333620
C	9.437077	6.716117	6.843063
C	8.495947	7.750742	7.448047
C	7.628938	8.453074	6.618118
H	7.598120	8.256297	5.688740
C	6.803416	9.446684	7.149699
H	6.237168	9.951702	6.577865
C	6.810572	9.692960	8.495817
H	6.228627	10.353274	8.853361
C	7.653219	8.995673	9.349424
H	7.658125	9.175150	10.282354
C	8.489582	8.026641	8.808372
C	13.474747	7.285594	4.450359
C	14.649573	7.971257	3.784995
C	14.929361	9.326951	4.103470
H	14.392242	9.792734	4.733316
C	15.991434	9.960262	3.489015
H	16.187059	10.865512	3.699753
C	16.769913	9.287502	2.569108
H	17.505710	9.731711	2.165391
C	16.500074	7.996825	2.231691
H	17.025988	7.552097	1.576983
C	15.450170	7.334535	2.854433
H	11.109079	4.933094	4.475221
O	11.345488	4.541263	4.972468
O	10.643702	7.081409	6.775580
O	12.578340	4.919749	7.858867
O	10.751670	3.632772	7.738107
O	8.947692	5.647195	6.464208
O	13.670887	6.866593	5.637832
O	12.417345	7.174040	3.846559
Zn	12.079762	5.872048	6.201378
I	15.141042	5.334117	2.322379
I	9.763407	6.957460	10.110330
I	10.445272	0.944399	9.206525

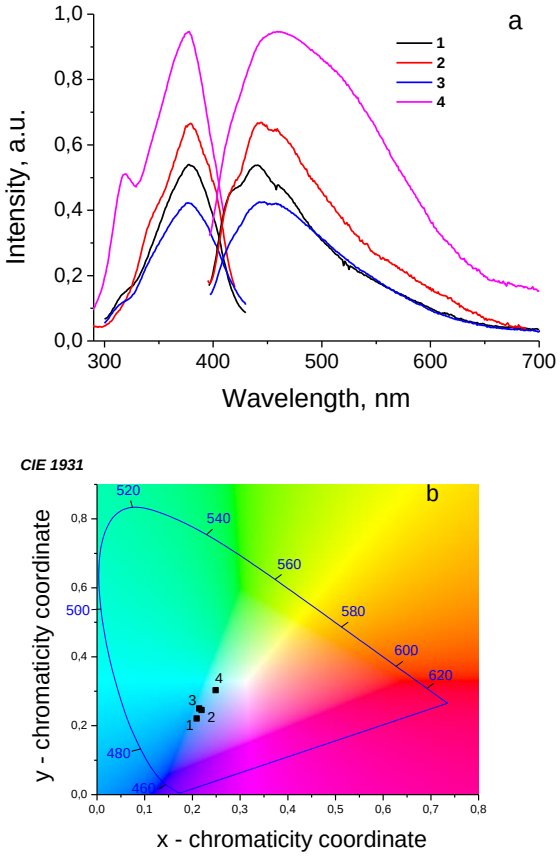

Figure S6. The excitation (λ_{em} = 460 nm) and emission (λ_{ex} = 380 nm) spectra (a) and CIE chromaticity coordinate (b) of **1**-**4** in the solid state at 300 K.

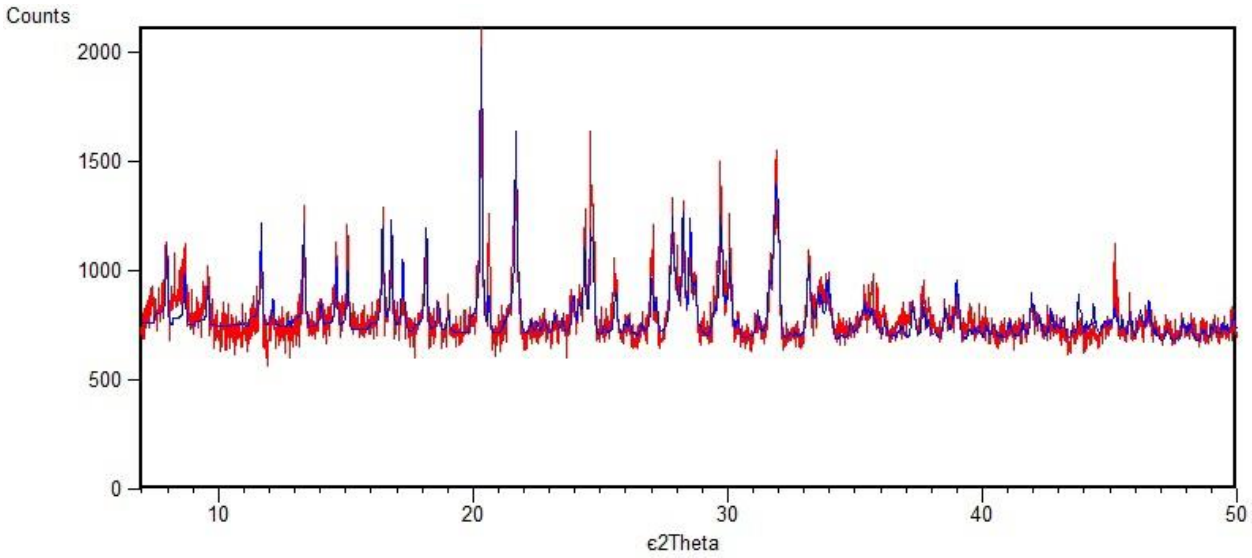

Figure S7. Calculated (blue) and experimental (red) PXRD patterns for **1**

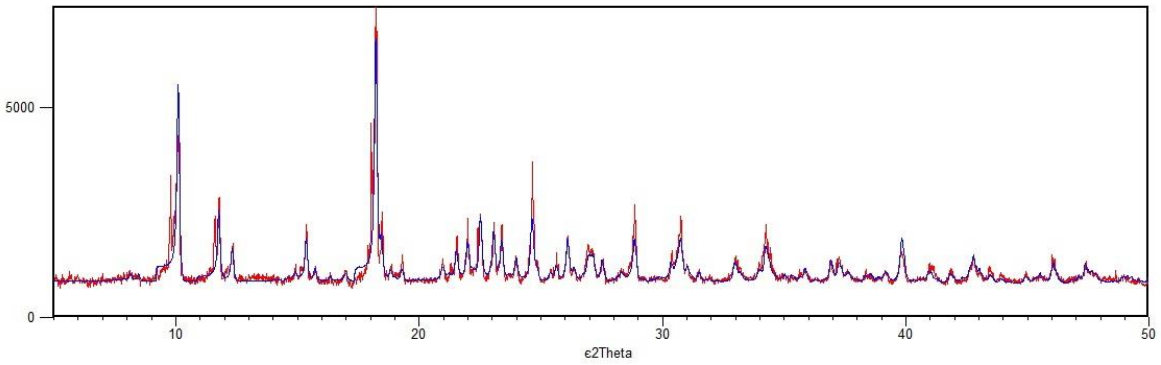

Figure S8. Calculated (blue) and experimental (red) PXRD patterns for **2**

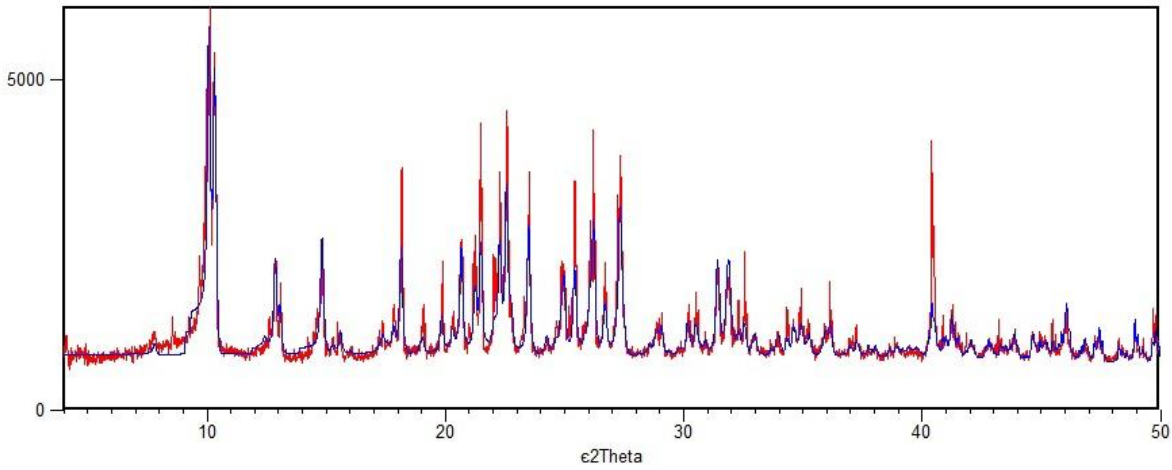

Figure S9. Calculated (blue) and experimental (red) PXRD patterns for **3**

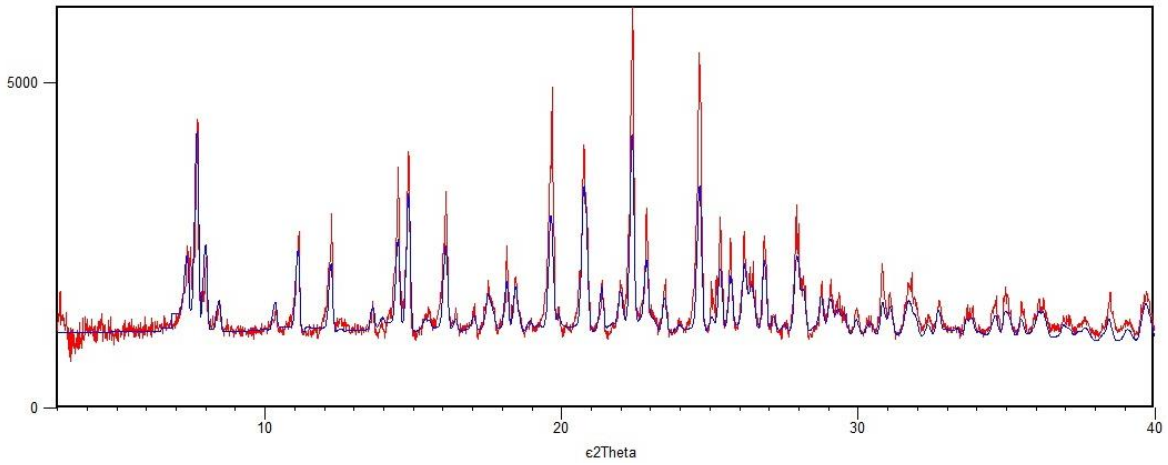

Figure S10. Calculated (blue) and experimental (red) PXRD patterns for **4**