Electronic Supplementary Material (ESI) for CrystEngComm.

Halobismuthates with halopyridinium cations: appearance or non-appearance of unusual colouring via intermolecular charge transfer in solid state

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XRD powder analysis was performed on Shimadzu XRD-7000 diffractometer (CuK-alpha radiation, Ni – filter, 5 – 50° 2θ range, 0.03° 2θ step, 1s per step, room temperature). Samples were slightly ground in an agate mortar, and the resulting powder was put in a hole of a quartz sample holder and slightly pressed. Indexing of the diffraction patterns was carried out using single-crystal data.

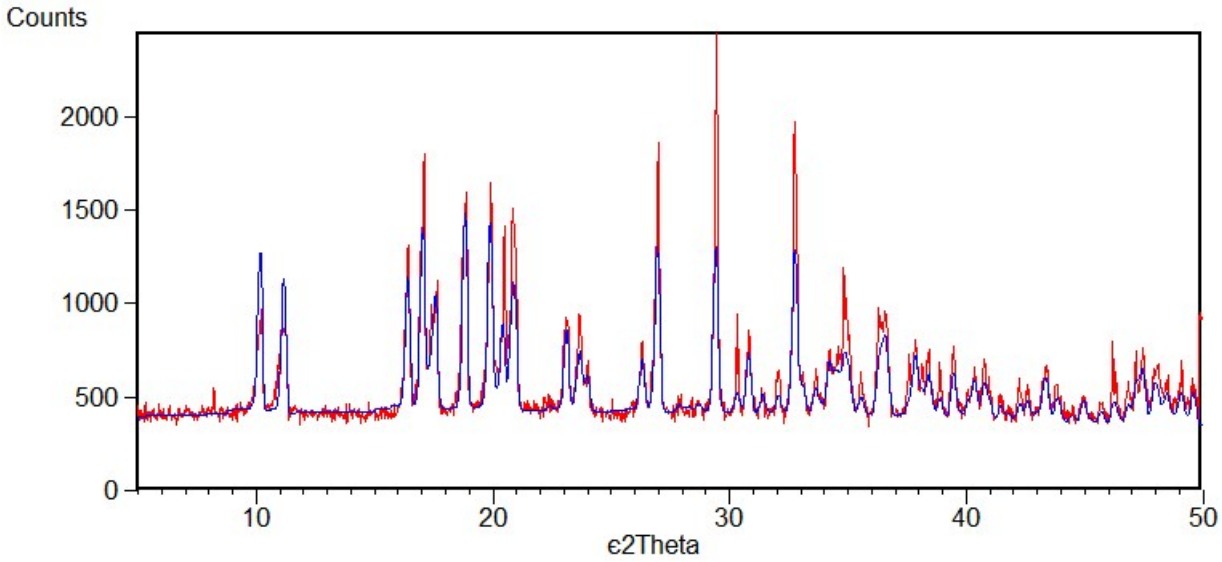

Figure 1S. PXRD for **2**: theoretical (blue) and experimental (red)

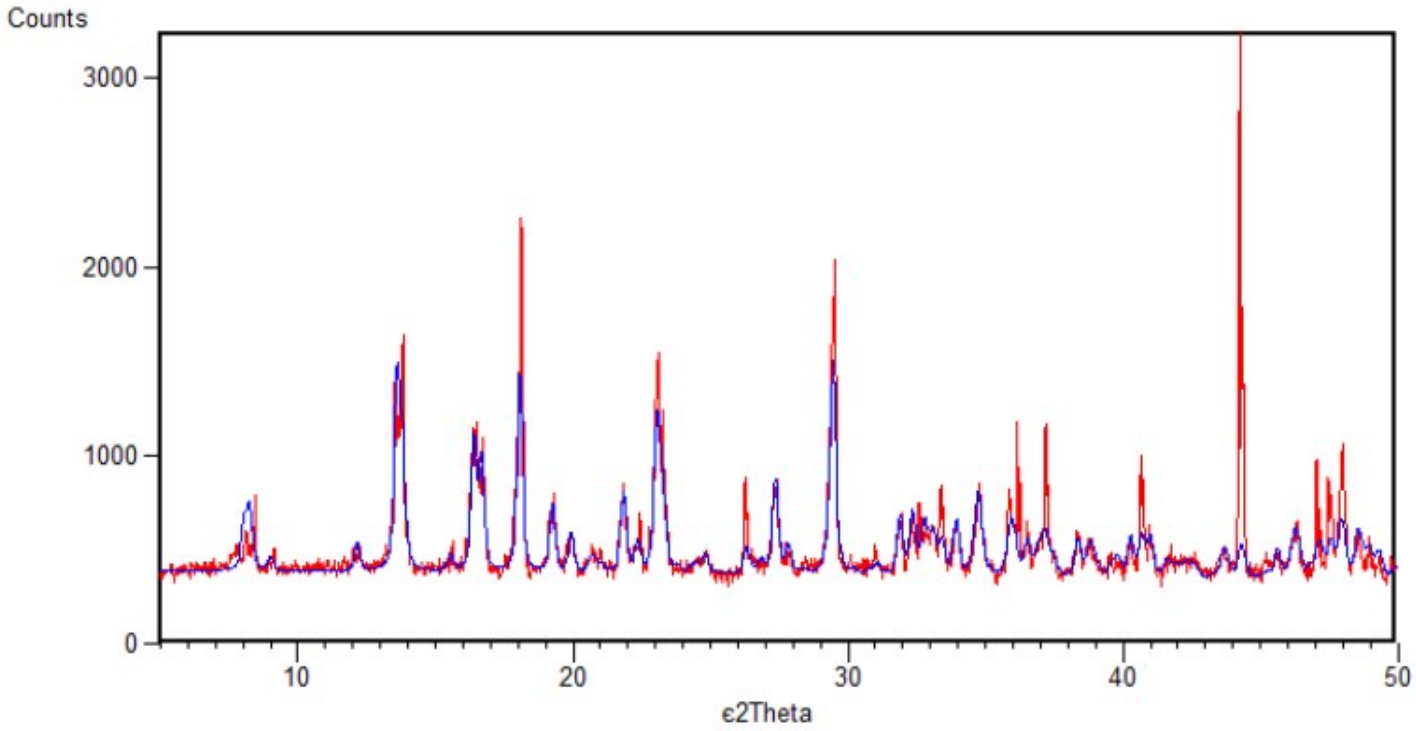

Figure 2S. PXRD for **3**: theoretical (blue) and experimental (red)

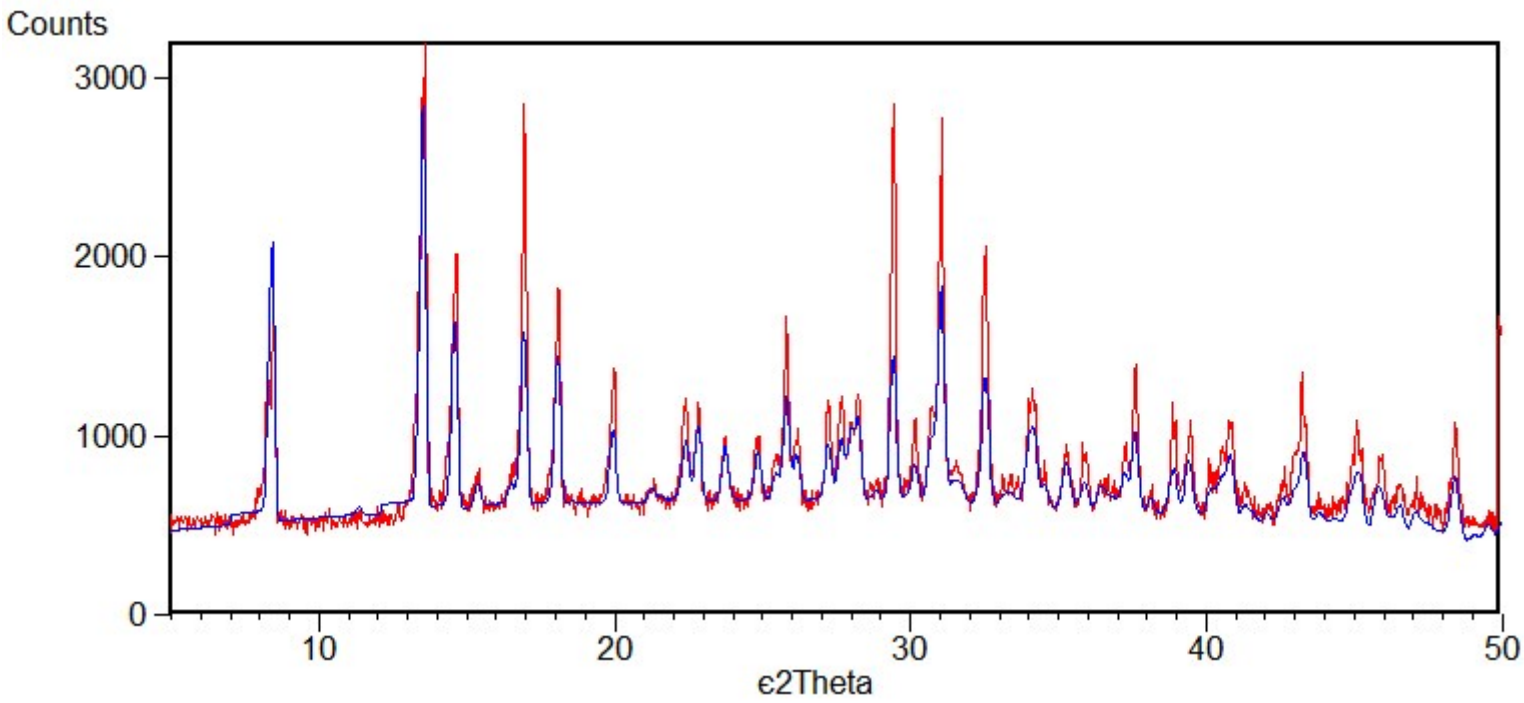

Figure 3S. PXRD for **5**: theoretical (blue) and experimental (red)

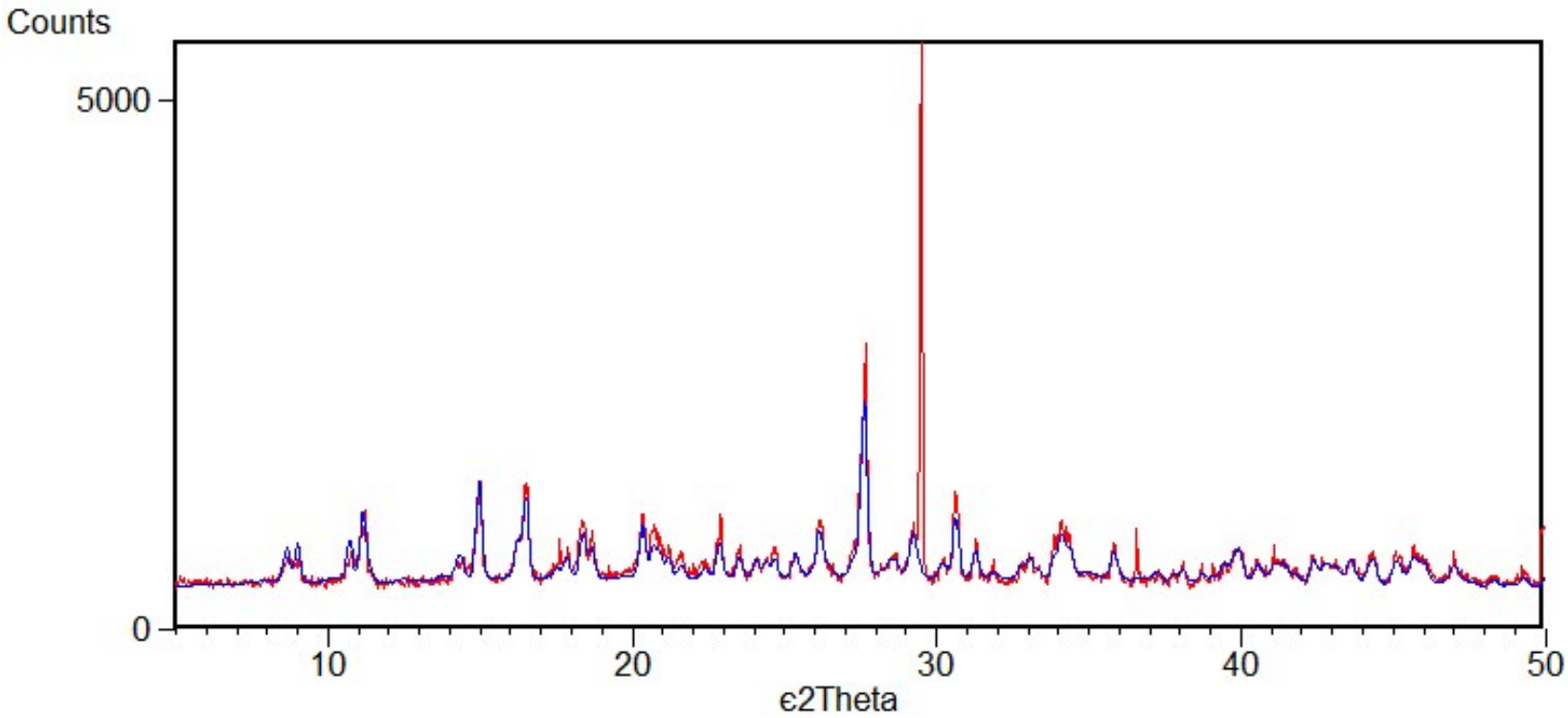

Figure 4S. PXRD for **6**: theoretical (blue) and experimental (red)

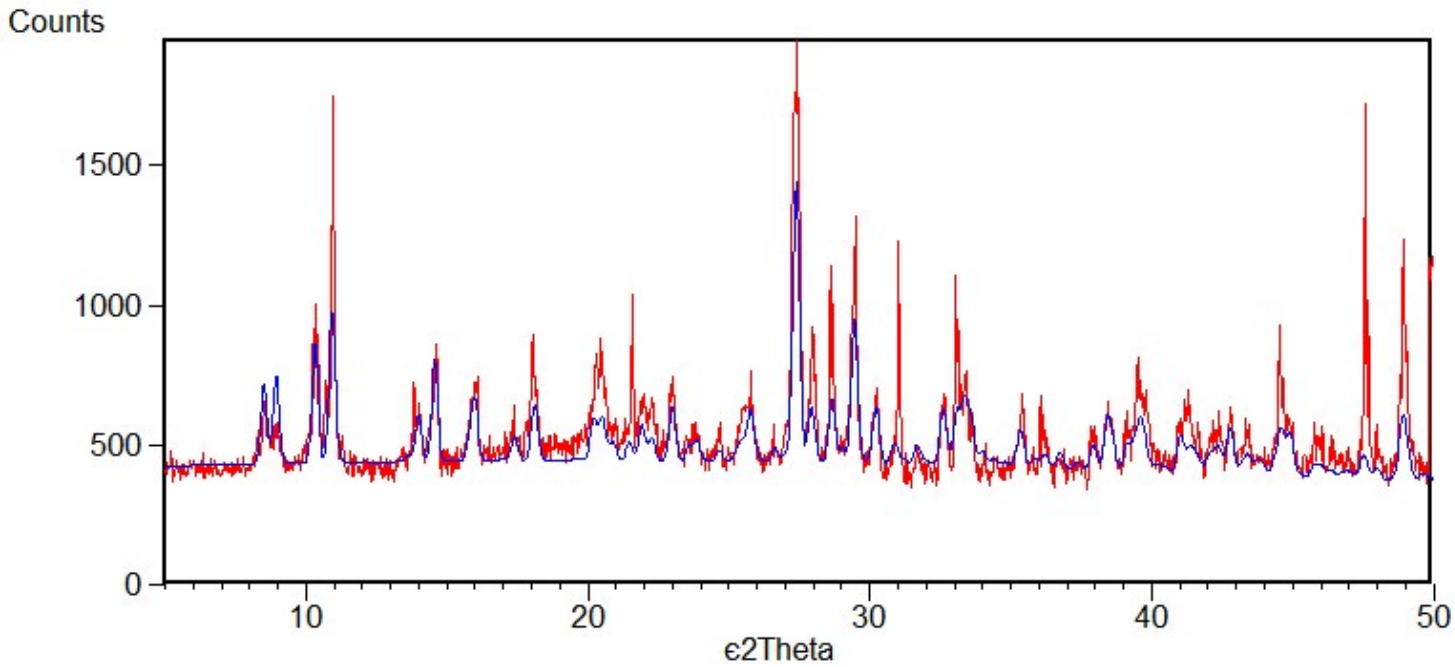

Figure 5S. PXRD for **7**: theoretical (blue) and experimental (red)

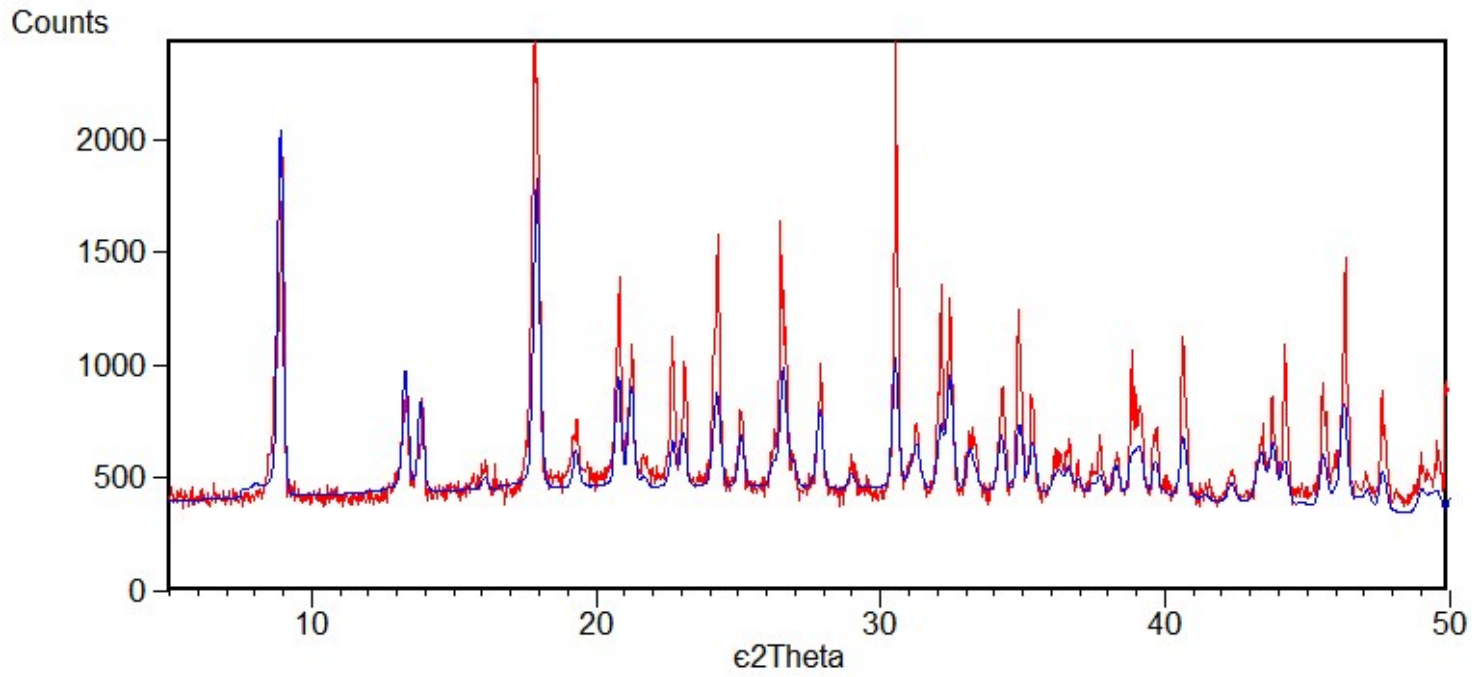

Figure 6S. PXRD for **8**: theoretical (blue) and experimental (red)

Table 1S. Crystal data and structure refinement for **1–9**.

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{10}H_9BiBr_2Cl_4N_2$	$C_{10}H_{10}BiBr_2Cl_5N_2$	$C_{10}H_{12}BiBr_2Cl_5N_2O$	$C_{15}H_{21}Bi_2Br_{12}N_3O_3$	$C_{10}H_{12}BiBr_7N_2O$	$C_{20}H_{20}Bi_2Br_4Cl_{10}N_4$	$C_{10}H_{10}BiBr_7N_2$	$C_{12}H_{14}BiBr_2Cl_5N_2$	$C_{18}H_{25}Bi_2Br_{12}N_3O_2$
M, g/mol	667.79	704.25	722.27	1668.23	944.57	1408.50	926.55	732.30	1692.29
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Orthorhombic*	*Triclinic*	*Triclinic*	*Orthorhombic*	*Monoclinic*
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	*Pnna*	$P2_1$
a, Å	7.12752(19)	5.5707(3)	11.5904(7)	9.3220(3)	8.2817(4)	8.8204(4)	9.1733(3)	21.9138(9)	8.1878(7)
b, Å	17.6661(4)	15.7750(8)	7.6333(4)	20.3199(7)	20.8514(11)	10.4344(4)	10.5445(3)	8.3002(3)	12.1235(9)
c, Å	13.3872(3)	10.5170(6)	21.9998(11)	9.6981(3)	12.0986(5)	10.4924(4)	10.7330(4)	11.1021(4)	19.5314(15)
α, deg.	90	90	90	90	90	99.470(3)	100.260(3)	90	90
β, deg.	93.272(3)	104.307(5)	96.548(5)	100.515(3)	90	97.092(4)	97.127(3)	90	99.969(8)
γ, deg.	90	90	90	90	90	108.757(4)	108.312(3)	90	90
V, Å^3	1682.90(7)	895.55(9)	1933.69(18)	1806.19(10)	2089.25(17)	885.70(7)	951.67(6)	2019.35(13)	1909.5(3)
Z	4	2	4	2	4	1	2	4	2
D(calc.), g/cm^3	2.636	2.612	2.481	3.067	3.003	2.641	3.233	2.409	2.943

μ, mm^{-1}	15.847	15.041	13.939	23.026	21.825	15.208	23.950	13.346	21.780
$F(000)$	1216	644	1328	1484	1688	644	824	1352	1512
Crystal size, mm	0.36 × 0.21 × 0.18	0.19 × 0.16 × 0.10	0.62 × 0.25 × 0.21	0.45 × 0.25 × 0.06	0.65 × 0.18 × 0.06	0.43 × 0.15 × 0.14	0.16 × 0.12 × 0.06	0.27 × 0.15 × 0.04	0.46 × 0.25 × 0.17
θ range for data collection, deg.	3.26–29.06	3.78–28.98	3.48–28.91	3.35–25.35	3.37–25.68	3.32–28.95	3.37–29.14	3.34–28.96	3.36–29.04
Index ranges	$-9 \le h \le 8$, $-22 \le k \le 24$, $-10 \le l \le 18$	$-6 \le h \le 4$, $-21 \le k \le 16$, $-14 \le l \le 12$	$-11 \le h \le 15$, $-7 \le k \le 10$, $-29 \le l \le 23$	$-9 \le h \le 11$, $-24 \le k \le 20$, $-10 \le l \le 11$	$-8 \le h \le 10$, $-25 \le k \le 24$, $-8 \le l \le 14$	$-10 \le h \le 12$, $-14 \le k \le 13$, $-12 \le l \le 9$	$-11 \le h \le 9$, $-10 \le k \le 14$, $-12 \le l \le 14$	$-27 \le h \le 18$, $-11 \le k \le 10$, $-14 \le l \le 10$	$-9 \le h \le 10$, $-16 \le k \le 16$, $-19 \le l \le 25$
Reflections collected / independent	8384 / 3763	3882 / 1962	10104 / 4309	7353 / 5242	8918 / 2852	7177 / 3893	7197 / 4174	5990 / 2237	9858 / 6912
R_{int}	0.0335	0.0325	0.0369	0.0381	0.048	0.0371	0.0250	0.0272	0.0427
Reflections with $I > 2\sigma(I)$	3252	1651	3696	4817		3444	3614	1920	6447
Goodness-of-fit on F^2	1.061	1.051	1.100	1.000	1.035	1.030	1.013	1.050	1.078
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0292$, $wR_2 = 0.0564$	$R_1 = 0.0353$, $wR_2 = 0.0762$	$R_1 = 0.0344$, $wR_2 = 0.0750$	$R_1 = 0.0423$, $wR_2 = 0.0845$	$R_1 = 0.0384$, $wR_2 = 0.0899$	$R_1 = 0.0363$, $wR_2 = 0.0627$	$R_1 = 0.0301$, $wR_2 = 0.0525$	$R_1 = 0.0249$, $wR_2 = 0.0495$	$R_1 = 0.0481$, $wR_2 = 0.0991$
R indices (all	$R_1 = 0.0380$,	$R_1 = 0.0465$,	$R_1 = 0.0431$,	$R_1 = 0.0479$,	$R_1 = 0.0422$,	$R_1 = 0.0445$,	$R_1 = 0.0390$,	$R_1 = 0.0329$,	$R_1 = 0.0533$,

data)	$wR_2 = 0.0595$	$wR_2 = 0.0814$	$wR_2 = 0.0790$	$wR_2 = 0.0883$	$wR_2 = 0.0929$	$wR_2 = 0.0680$	$wR_2 = 0.0560$	$wR_2 = 0.0522$	$wR_2 = 0.1050$
Largest diff. peak / hole, e/Å^3	0.927 / −1.583	1.870 / −2.241	2.309 / −2.222	2.658 / −3.256	1.972 / −2.868	1.830 / −1.450	1.659 / −1.605	0.705 / −1.481	1.564 / −2.303

Diffuse reflectance spectra were recorded in the wavelength interval of 400-1000 nm at room temperature. $BaSO_4$ powder was used as a white reference.

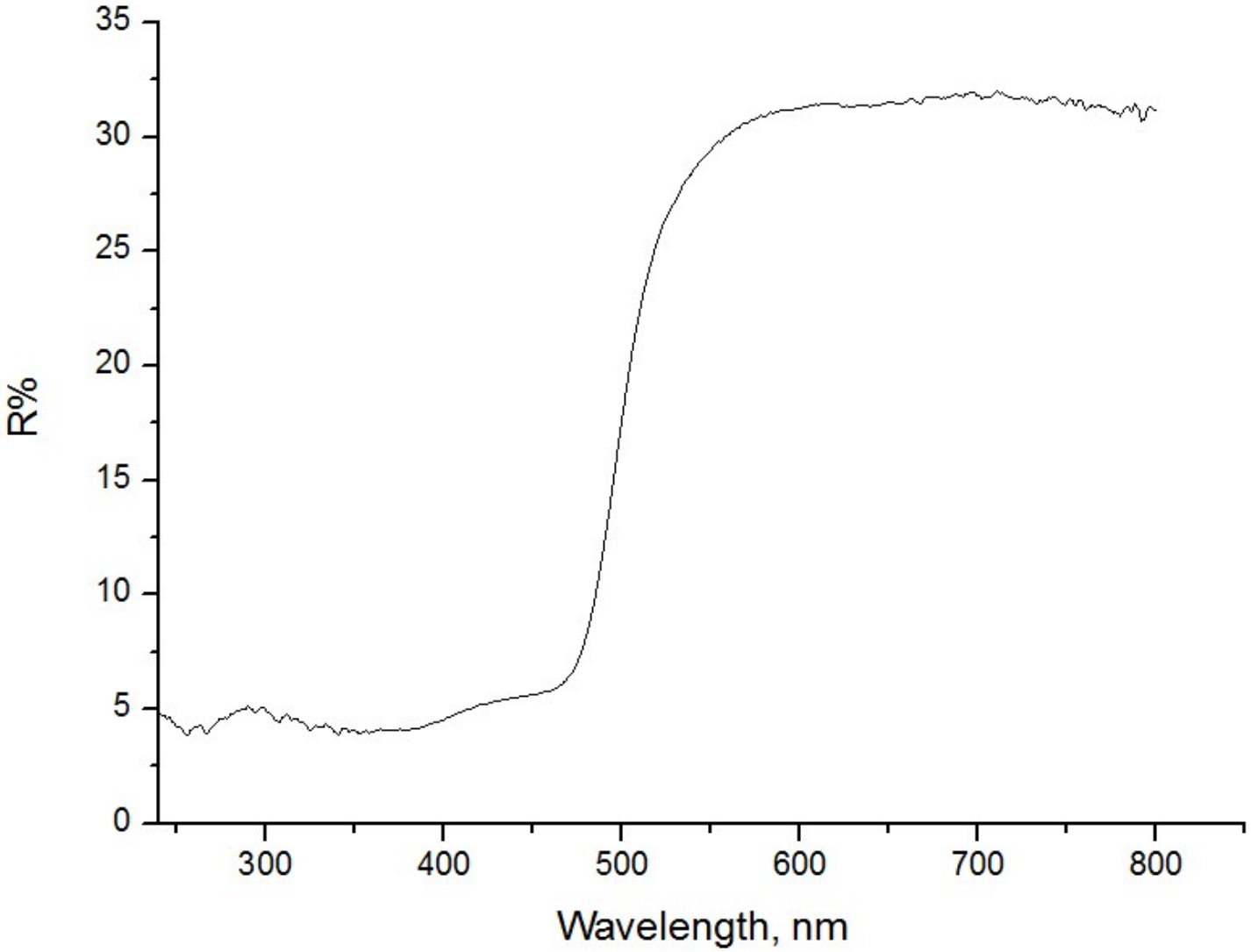

Figure 7S. Diffuse reflectance spectrum of **2**

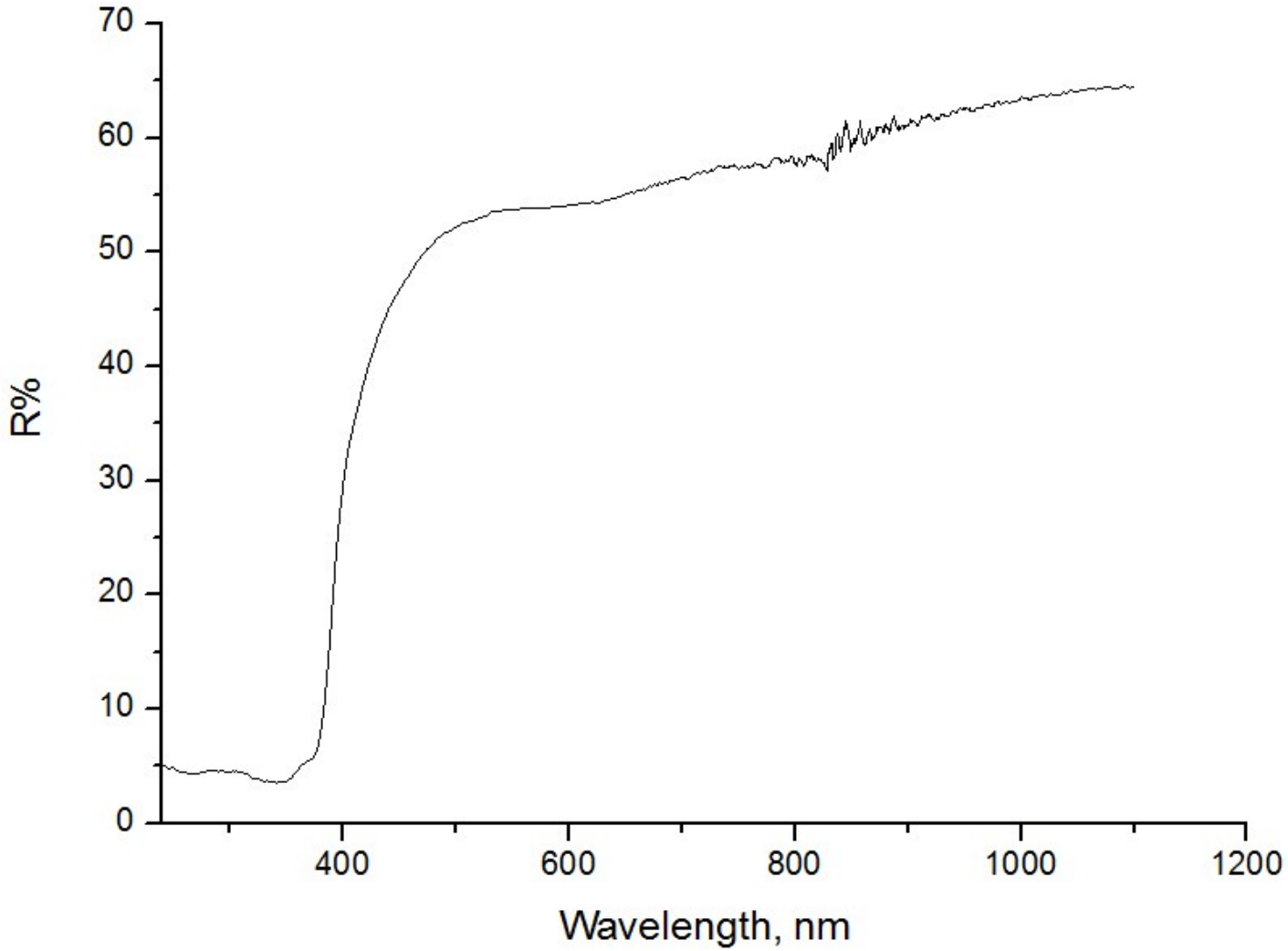

Figure 8S. Diffuse reflectance spectrum of **3**

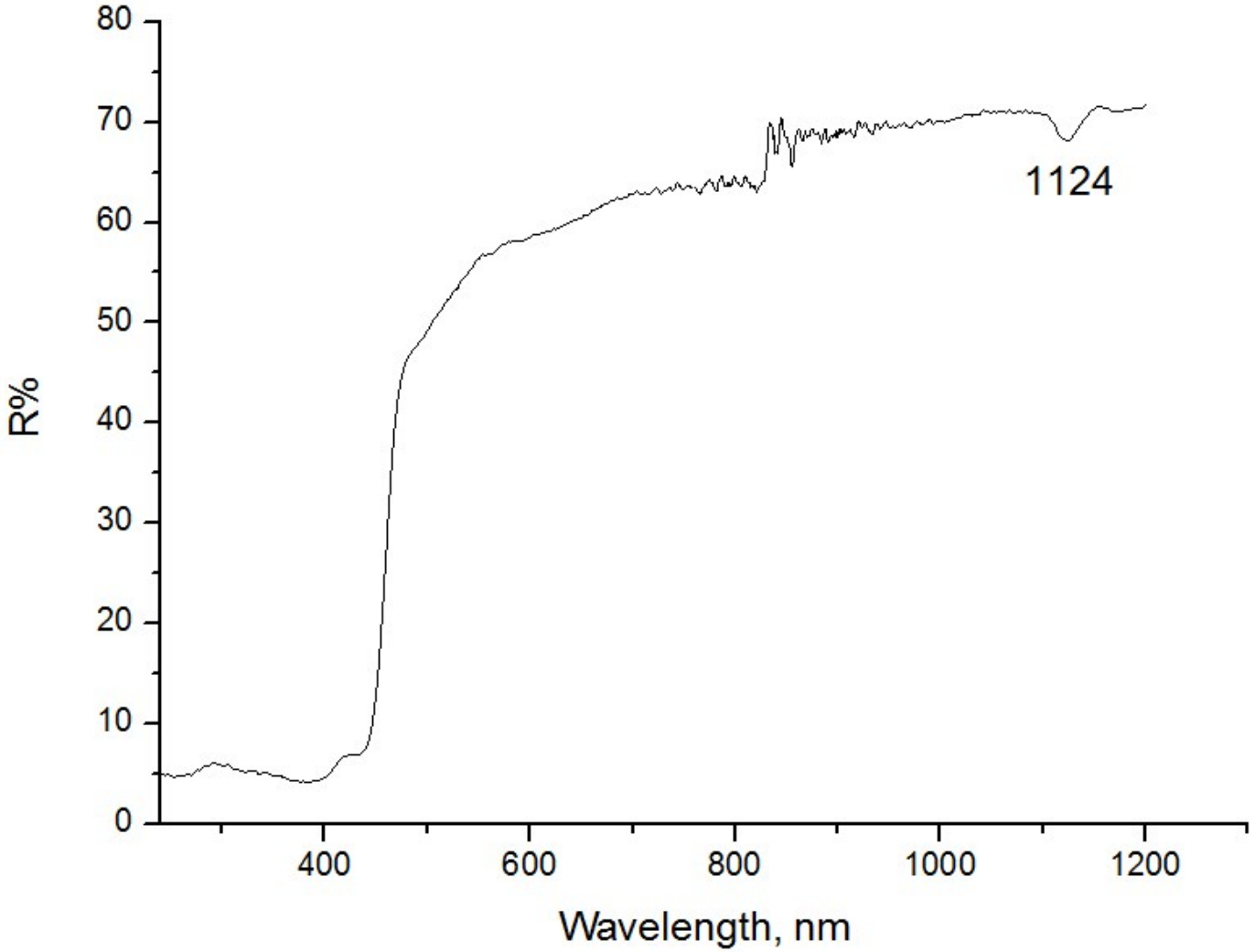

Figure 9S. Diffuse reflectance spectrum of **5**

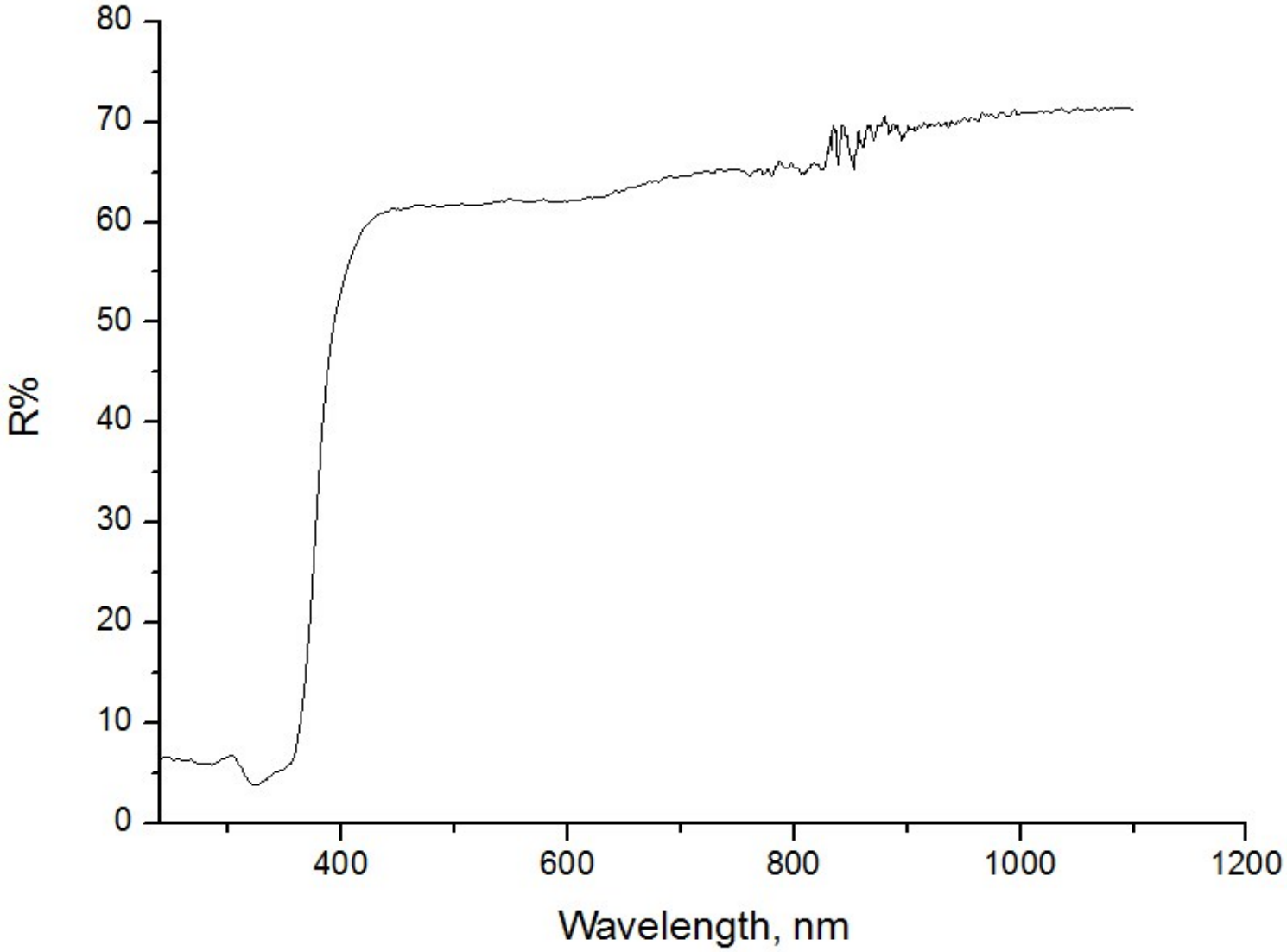

Figure 10S. Diffuse reflectance spectrum of **6**

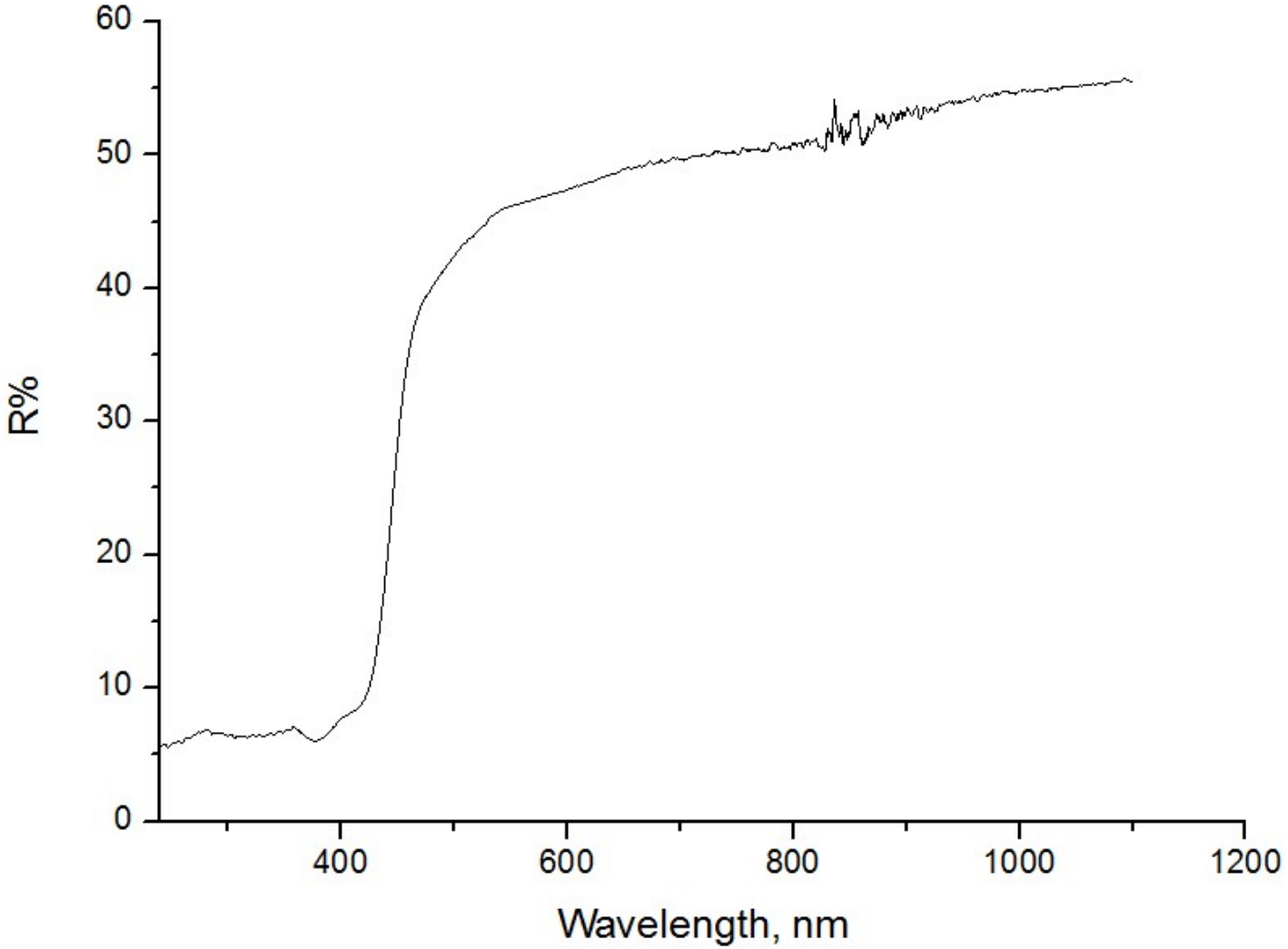

Figure 11S. Diffuse reflectance spectrum of **7**

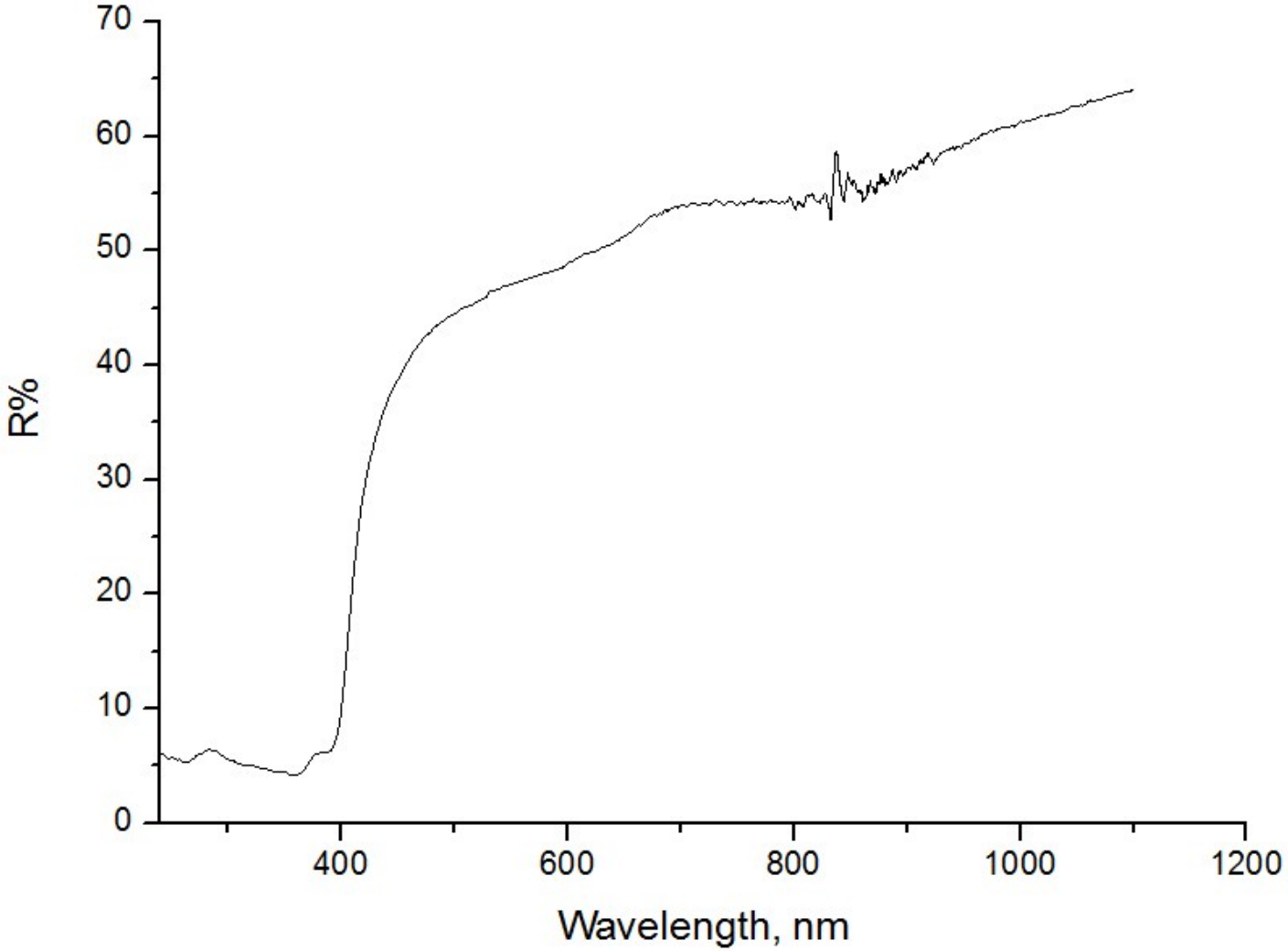

Figure 12S. Diffuse reflectance spectrum of **8**

Computational details

The single point quantum chemical calculations based on the experimental X-ray geometries of **1–9** have been carried out at the DFT level of theory using the M06 functional with the help of Gaussian-09 [1] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using DZP-DKH basis sets for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader [2] has been performed by using the Multiwfn program [3]. The Wiberg bond indices were computed by using the Natural Bond Orbital (NBO) partitioning scheme [4]. The Cartesian atomic coordinates of model supramolecular associates are presented in Table 2S.

References:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J.;, D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, **2010**.
2. Bader, R. F. W. A quantum theory of molecular structure and its applications. *Chem. Rev.* **1991,** 91, (5) 893–928.
3. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012,** 33, (5), 580–592.
4. Glendening, E. D.; Landis, C. R.; Weinhold, F. Natural bond orbital methods. *WIREs Computational Molecular Science*, **2012,** 2, (1) 1–42.

Table 2S. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1			
Bi	5.341758	7.717612	0.147687
Cl	4.401670	5.757912	-1.159446
Cl	6.298140	6.256979	1.968987
Cl	6.651178	10.074447	1.359125
Cl	4.035644	9.679786	-1.647684
Cl	7.603862	7.591653	-1.359125
Cl	3.091876	7.986314	1.647684
N	4.887375	9.138674	6.095948
Br	5.401845	10.300573	8.545688
C	4.940684	10.315236	6.709419
C	4.695237	11.534197	6.090602
H	4.747186	12.352102	6.572531
C	4.375840	11.512997	4.758074
H	4.206869	12.325991	4.296260
C	4.301200	10.320536	4.093815
H	4.071742	10.293683	3.171764

C	4.567315	9.149273	4.787478
H	4.521649	8.321652	4.322817
N	5.235869	6.617721	7.405755
H	5.167697	7.375102	6.962492
Br	4.633234	5.524896	4.942249
C	5.023311	5.448225	6.760207
C	5.097721	4.262830	7.428476
H	4.924284	3.443688	6.980950
C	5.431730	4.276963	8.779716
H	5.501193	3.460877	9.261858
C	5.662641	5.481791	9.415908
H	5.897847	5.502937	10.336542
C	5.547275	6.644220	8.703533
H	5.691147	7.477424	9.135475
Bi	8.149192	9.948488	13.217689
Cl	9.089280	11.908188	14.524823
Cl	7.192811	11.409121	11.396389
Cl	6.839773	7.591653	12.006251

Cl	9.455306	7.986314	15.013060
Cl	5.887088	10.074447	14.724502
Cl	10.399075	9.679786	11.717693
2			
Bi	1.485883	7.887500	5.095411
Cl	1.486569	5.322485	4.295431
Cl	1.409738	7.048112	7.626403
Cl	4.271233	7.887500	5.095411
Cl	1.485197	10.452515	5.895390
Cl	1.562029	8.726888	2.564418
Cl	-1.299467	7.887500	5.095411
N	-2.067691	4.052598	11.002010
H	-1.446577	3.585863	10.589221
Br	-0.776860	6.129376	9.745176
C	-2.083262	5.376120	10.866472
C	-3.017386	6.136475	11.495246
H	-3.018908	7.081729	11.396385
C	-3.966429	5.510208	12.282997

H	-4.631031	6.022374	12.728916
C	-3.943616	4.128318	12.418534
H	-4.584464	3.684661	12.961980
C	-2.978930	3.415288	11.755112
H	-2.954926	2.467731	11.827243
3			
Bi	0.503730	3.952370	4.279243
Cl	-0.756013	2.060380	3.081518
Cl	-1.116990	3.848710	6.313189
Cl	-0.999809	5.751768	3.182931
Cl	2.256313	4.042596	2.103231
Cl	2.281465	2.080074	5.490955
Cl	2.259356	5.896724	5.437189
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H	-5.205046	4.795667	9.922711
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C	-3.257131	3.086143	11.876707
H	-2.444213	2.594551	11.879111
C	-4.008270	3.205223	13.028533
H	-3.719939	2.792887	13.833741
C	-5.181434	3.927333	13.000120
H	-5.703462	4.026833	13.786378
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N	6.658060	3.514371	-3.781138
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H	6.483540	3.504440	-1.776239
C	4.652960	3.834970	-2.589970
C	3.981215	3.964736	-3.816108
H	3.044455	4.120410	-3.837112
C	4.694953	3.863976	-4.985419
H	4.248219	3.948156	-5.820439
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Br	8.319447	8.560367	2.644122
Br	4.768607	7.945894	4.251764
Br	5.503909	11.333627	2.012889
Br	4.736116	11.634768	5.938548
Br	8.399943	12.372178	4.500634
Br	6.064465	15.468117	5.953805
Br	6.888023	15.135887	1.898467
Br	3.220006	14.467159	3.308729
N	-0.818848	11.641271	10.940736
H	-0.705788	11.508500	11.802808
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H	1.145967	11.431386	10.443025
C	0.040390	11.710358	8.772422

C	-1.237913	11.962325	8.276590
H	-1.383077	12.082436	7.348820
C	-2.273466	12.035477	9.134761
H	-3.159257	12.173530	8.818382
C	-2.028946	11.905429	10.479230
H	-2.751516	12.007395	11.097600
Br	1.536397	11.597786	7.608169
N	12.394478	15.174901	-3.088465
H	12.236672	15.184411	-3.954055
C	11.369261	15.327301	-2.240782
H	10.495517	15.484089	-2.576613
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C	12.871669	15.075334	-0.390945
H	13.029565	15.009579	0.541506
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H	14.819615	14.925210	-0.991179
C	13.647126	15.010310	-2.660332
H	14.349521	14.905602	-3.293158

Br	10.137538	15.468524	0.287011
5			
Bi	5.802822	13.448944	6.079909
Br	5.997359	12.911187	8.805724
Br	4.168759	11.226394	5.839994
Br	7.961033	11.960780	5.532448
Br	5.583771	13.951463	3.205403
Br	7.481274	15.898775	6.208155
Br	3.340424	15.378325	6.208155
N	9.694558	14.026737	15.207940
H	9.754095	14.778826	15.660948
C	8.897030	13.997545	14.150523
H	8.387176	14.760581	13.902888
C	8.828292	12.836122	13.423397
C	9.548800	11.735168	13.816601
H	9.492302	10.926571	13.319470
C	10.335562	11.803978	14.921203
H	10.835743	11.045487	15.202980

C	10.410097	12.986252	15.627762
H	10.961617	13.055166	16.399459
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N	1.951997	12.535862	-2.999243
H	1.900874	11.755206	-3.400590
C	2.716398	12.669311	-1.895851
H	3.180123	11.914678	-1.552081
C	2.838139	13.862011	-1.276402
C	2.172290	14.937943	-1.791803
H	2.257890	15.789848	-1.379966
C	1.374762	14.791983	-2.909713
H	0.906233	15.536545	-3.269961
C	1.275382	13.570091	-3.484397
H	0.710396	13.450592	-4.241261
Br	3.954843	13.973566	0.241367
6			
Bi	0.917717	4.739969	6.669157
Br	1.229517	6.542238	8.760284

Br	0.919991	6.909095	4.807891
Br	-1.788102	4.670558	6.870518
Br	1.071807	2.592881	8.511769
Br	3.841966	4.577024	6.142386
Bi	3.610960	2.816164	3.694240
Br	3.299160	1.013895	1.603114
Br	3.608685	0.647038	5.555507
Br	6.316779	2.885575	3.492880
Br	3.456869	4.963253	1.851628
Br	0.686711	2.979109	4.221012
N	8.182024	3.474084	11.867127
H	8.914455	3.115513	12.196797
C	8.304229	4.470555	10.990383
H	9.166551	4.774565	10.734065
C	7.185728	5.055948	10.458741
H	7.255045	5.783151	9.851819
C	5.951483	4.556668	10.833896
C	5.843691	3.522880	11.758311

H	4.993544	3.194021	12.025459
C	6.995007	2.990710	12.272335
H	6.955481	2.287448	12.909881
Br	4.369678	5.260079	10.069803
Bi	10.091017	4.739969	6.669157
Br	10.402817	6.542238	8.760284
Br	10.093291	6.909095	4.807891
Br	7.385198	4.670558	6.870518
Br	10.245107	2.592881	8.511769
Br	13.015266	4.577024	6.142386
Bi	12.784260	2.816164	3.694240
Br	12.472460	1.013895	1.603114
Br	12.781985	0.647038	5.555507
Br	15.490079	2.885575	3.492880
Br	12.630169	4.963253	1.851628
Br	9.860011	2.979109	4.221012
7			
Bi	7.379910	2.075050	8.326575

Cl	9.238858	3.904912	8.619670
Cl	5.478450	0.000000	7.993401
Cl	7.236156	2.565758	5.694267
Cl	9.238858	0.245188	8.033480
Cl	7.236156	1.584342	10.958883
Cl	5.478450	4.150100	8.659749
N	13.247988	2.554802	4.938214
H	13.041691	3.119057	4.295636
C	12.260771	1.972128	5.646528
C	12.563182	1.126337	6.694566
H	11.869018	0.739805	7.216609
C	13.893349	0.847450	6.977670
C	14.877279	1.430954	6.194972
H	15.790602	1.229990	6.356219
C	14.537396	2.293345	5.193562
H	15.216789	2.709526	4.676316
C	14.237396	-0.102092	8.086770
H	15.053027	0.203455	8.536527

H	13.500632	-0.132637	8.732046
H	14.384876	-0.997543	7.716603
Br	10.496272	2.347048	5.174800
8			
Bi	4.317203	8.915743	6.123172
Bi	4.857809	6.349562	3.117853
Br	4.507647	8.132201	8.737414
Br	6.086846	11.105611	6.628515
Br	2.065380	10.409722	6.589081
Br	4.553803	9.354978	3.122470
Br	2.661664	6.688050	5.255606
Br	6.522341	6.981317	5.553002
Br	5.030363	3.652083	3.443719
Br	7.055316	6.515048	1.570468
Br	3.193907	6.123216	0.960479
N	7.831418	-1.597877	3.751119
H	7.484889	-1.349552	4.520271
C	7.591617	-0.900776	2.693111

C	8.049106	-1.259632	1.394647
H	7.799990	-0.784027	0.610201
C	8.921746	-2.404090	1.367716
C	9.142274	-3.092705	2.535372
H	9.692008	-3.867578	2.513538
C	8.610876	-2.718089	3.695333
H	8.780324	-3.224342	4.482202
C	9.507362	-2.896304	-0.240456
H	9.619367	-3.869579	-0.263771
H	10.364179	-2.462416	-0.425742
H	8.851245	-2.628557	-0.920217
Br	6.577996	0.686675	2.883937
N	4.822047	2.855084	9.398957
H	5.246193	3.608196	9.235254
C	4.209489	2.202840	8.379422
C	3.515920	1.057169	8.598718
H	3.039449	0.625342	7.897779
C	3.521417	0.529797	9.918343

C	4.161597	1.235385	10.887863
H	4.154782	0.898654	11.776070
C	4.794736	2.383480	10.639712
H	5.223137	2.857169	11.343768
C	2.800725	-0.734684	10.245363
H	2.526384	-0.721118	11.186663
H	3.390028	-1.499665	10.087105
H	2.003565	-0.813669	9.676982
Br	4.329385	2.966620	6.681800
N	1.690945	14.867048	2.910483
H	2.063313	14.859216	2.111341
C	1.828673	13.830489	3.710722
C	1.300126	13.808666	4.947629
H	1.445463	13.056209	5.508931
C	0.556442	14.869473	5.405458
C	0.381084	16.022418	4.539816
H	-0.129655	16.778051	4.809434
C	0.978587	15.961800	3.329839

H	0.899407	16.706486	2.744549
C	-0.026833	14.936152	6.767403
H	-0.207057	15.871965	6.999164
H	0.610214	14.559317	7.411576
H	-0.859890	14.425389	6.793565
Br	2.869270	12.399916	3.082265
9			
Bi	0.785534	4.767533	6.514924
Cl	0.747374	6.838788	4.764209
Cl	-1.766141	4.710437	6.703451
Cl	0.946687	2.741875	8.276513
Cl	1.050164	6.476772	8.481200
Cl	3.579028	4.544660	5.970379
Bi	3.384209	2.849639	3.648288
Cl	3.422369	0.778384	5.399003
Cl	5.935883	2.906735	3.459761
Cl	3.223056	4.875297	1.886699
Cl	3.119578	1.140399	1.682012

Cl	0.590715	3.072512	4.192833
N	7.799624	3.550307	11.659236
H	8.530672	3.184803	11.984053
C	6.602237	3.106342	12.091173
H	6.556722	2.439678	12.766569
C	5.467953	3.612541	11.561670
H	4.620152	3.278231	11.828972
C	5.556778	4.620590	10.628687
C	6.800581	5.092777	10.211995
H	6.873066	5.788505	9.569670
C	7.913509	4.517830	10.761825
H	8.776240	4.814800	10.498171
Br	3.987297	5.320370	9.851912

The DFT calculations followed by the topological analysis of the electron density distribution within the framework of Bader's theory (QTAIM method) [10.1021/cr00005a013] were carried out for 9 model supramolecular clusters **UXENUI02**, **UXEPAQ02**, **UXEPIY02**, **UXERAS02**, **UXEREW02**, **UXEROG02**, **UXERUM02**, **UXESAT02**, and **UXESOH02** obtained from the experimental X-ray geometries of substituted-pyridinium iodo- and bromoplumbates reported by Ruben et al.

[*CrystEngComm*, 2016, 18, 8207]. Results are summarized in **Table 3S**, the contour line diagram of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces and RDG isosurface for Br8···I5 contact in **UXEREW02** are shown in **Figure 13S**.

Table 3S. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, 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 different intermolecular non-covalent interactions in model supramolecular clusters **UXENUI02**, **UXEPAQ02**, **UXEPIY02**, **UXERAS02**, **UXEREW02**, **UXEROG02**, **UXERUM02**, **UXESAT02**, and **UXESOH02 (Refcodes from CSD)** bond lengths – *l* (Å), Wiberg bond indices (WI), as well as energies for these contacts E_{int} (kcal/mol), defined by different approaches.

Contact	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}^a	E_{int}^b	*l*	WI
UXENUI02 (3-ClPyH){[PbI_3]} (2.77)									
Cl5···I1	0.008	0.027	0.001	-0.004	0.005	1.3	1.3	3.674	0.02
UXEPAQ02 (4-ClPyH){[PbI_3]} (2.80)									
Cl8···I2	0.012	0.038	0.001	-0.007	0.008	2.2	2.2	3.461	0.04
Cl20···I6	0.012	0.037	0.001	-0.007	0.008	2.2	2.2	3.439	0.03
UXEPIY02 (4-ClPyH){[$PbBr_3$]} (3.49)									
Cl11···Br2	0.012	0.036	0.001	-0.007	0.008	2.2	2.2	3.267	0.03
Cl26···Br5	0.013	0.035	0.001	-0.007	0.008	2.2	2.2	3.292	0.04

UXERAS02 (2-BrPyH){[PbI_3]} (2.79)									
Br6···I1	0.018	0.045	0.001	-0.010	0.011	3.1	3.0	3.370	0.10
UXEREW02 (3-BrPyH)$_2${[PbI_4]} (2.07)									
Br8···I5	0.011	0.031	0.001	-0.006	0.007	1.9	1.9	3.581	0.05
UXEROG02 (3-BrPyH){[$PbBr_3$]} (3.36)									
Br8···Br2	0.014	0.038	0.001	-0.008	0.009	2.5	2.4	3.275	0.04
UXERUM02 (3-BrPyH)$_2${[$PbBr_4$]} (2.76)									
Br8···Br3	0.012	0.030	0.000	-0.007	0.007	2.2	1.9	3.386	0.04
UXESAT02 (4-BrPyH){[$PbBr_3$]} (3.42)									
Br8···Br4	0.016	0.041	0.000	-0.009	0.010	2.8	2.7	3.245	0.07
Br20···Br2	0.014	0.038	0.001	-0.008	0.009	2.5	2.4	3.276	0.05
UXESOH02 (4-ClPyH){[Pb_3I_{10}]} (2.63)									
Cl14···I11	0.012	0.038	0.001	-0.007	0.008	2.2	2.2	3.474	0.03
Cl38···I6	0.011	0.036	0.001	-0.006	0.008	1.9	2.2	3.519	0.03
Cl26···I6	0.006	0.019	0.001	-0.003	0.004	0.9	1.1	3.824	0.01

[a] $E_{int} = -V(\mathbf{r})/2$ [10.1016/S0009-2614(98)00036-0]

[b] $E_{int} = 0.429G(\mathbf{r})$ [10.1002/jcc.23062]

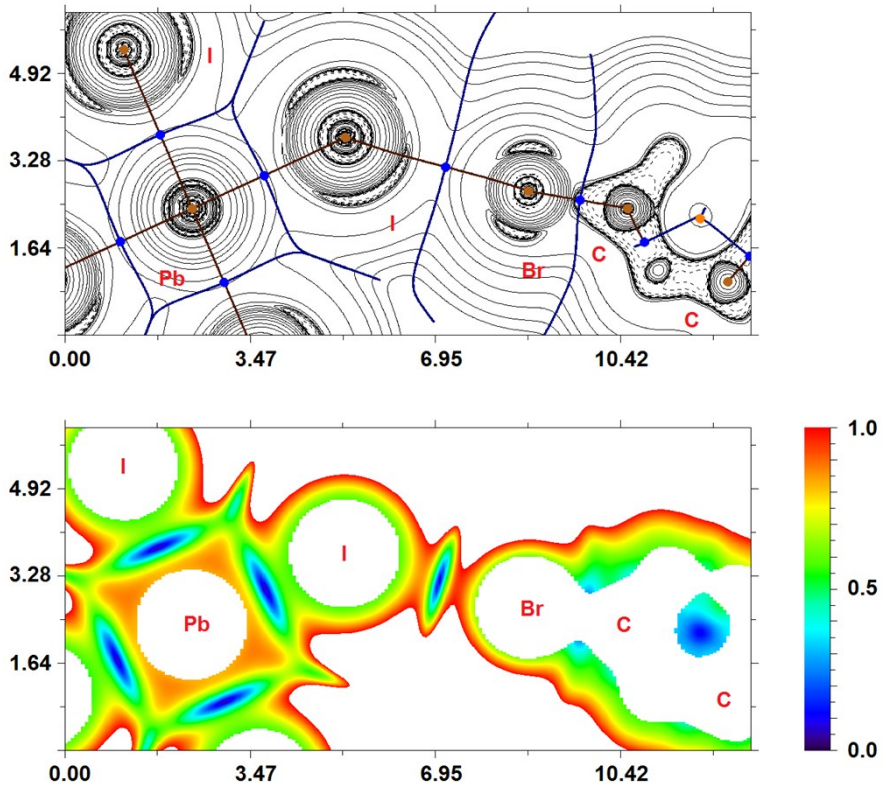

Figure 13S. Contour line diagram of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, bond paths and selected zero-flux surfaces (top) and RDG isosurface (bottom) referring to Br8···I5 non-covalent interactions in **UXEREW02**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange. Length units – Å, RDG isosurface values are given in a.u.

The QTAIM analysis demonstrates the presence of appropriate bond critical points (BCP's) (3, –1) for various intermolecular contacts in model supramolecular clusters **UXENUI02**, **UXEPAQ02**, **UXEPIY02**, **UXERAS02**, **UXEREW02**, **UXEROG02**, **UXERUM02**, **UXESAT02**, and **UXESOH02** (**Table 1**). The low magnitude of the electron density (0.006–0.018 a.u.), positive values of the Laplacian (0.019–0.045 a.u.), and zero or very close to zero positive energy density (0.000–0.001 a.u.) in these BCP's as well as small values of the Wiberg bond indices for these intermolecular contacts (0.01–0.10) are typical for non-covalent interactions. We have defined energies for these intermolecular contacts according to procedures proposed by Espinosa et al.[10.1016/S0009-2614(98)00036-0] and Vener et al.[10.1002/jcc.23062], and one can state that their estimated strength vary from 0.9 to 3.1 kcal/mol. The balance between the Lagrangian kinetic energy G(**r**) and potential energy density V(**r**) at the BCPs (3, –1) reveals the nature of these interactions, if the ratio –G(**r**)/V(**r**) > 1 is satisfied, than the nature of appropriate interaction is purely non-covalent, in case the –G(**r**)/V(**r**) < 1 some covalent component takes place [E. Espinosa, I. Alkorta, J. Elguero, E. Molins, *Journal of Chemical Physics* **2002**, *117*, 5529-5542.]. Based on this criterion one can state that a covalent contribution in all discussed above intermolecular contacts is absent.

Table 4S. Cartesian atomic coordinates for model supramolecular clusters

Atom	X	Y	Z
UXENUI02			
I	0.892511	12.377538	1.833963
Pb	2.584283	11.041873	4.195325
I	3.007239	8.534907	2.231028
I	5.132631	12.366345	2.596198
Cl	-1.672465	13.235874	4.321091
N	-5.031953	13.854441	6.182774
C	-4.043160	13.928080	5.276345
C	-2.909274	13.184327	5.500000
C	-2.790519	12.430263	6.635595
C	-3.833321	12.396389	7.542024
C	-4.966404	13.109215	7.289232
H	-5.763558	14.322786	6.039447
H	-4.125721	14.475955	4.505369
H	-1.996441	11.933936	6.799398

H	-3.760356	11.879443	8.335838
H	-5.699262	13.078286	7.892468
I	2.303014	13.556793	6.168599
I	4.428406	9.725355	6.533769
I	0.188286	9.714162	5.771534
UXEPAQ02			
Pb	7.925643	5.831024	7.894589
I	10.158048	3.463779	8.637863
I	7.338069	3.941667	5.431307
I	6.069152	4.056484	9.606482
I	9.631518	8.207913	6.100964
I	5.505702	7.596419	7.111753
I	8.368055	8.106981	10.248460
Cl	12.114391	6.233006	9.332590
N	14.444969	9.752322	10.502063
C	14.963108	8.546792	10.694801
C	14.298128	7.457658	10.341206
C	13.033196	7.632252	9.784728

C	12.502471	8.871038	9.584744
C	13.224090	9.910288	9.929644
H	14.900176	10.464000	10.751318
H	15.821080	8.461989	11.091871
H	14.669426	6.588845	10.462935
H	11.638206	8.974132	9.206513
H	12.886355	10.786584	9.774584
Cl	3.662637	10.345110	6.176320
N	1.191511	13.867752	5.401019
C	2.353653	14.034032	5.982132
C	3.121422	12.953212	6.276312
C	2.678801	11.714426	5.877793
C	1.497779	11.564774	5.179298
C	0.740499	12.687164	4.970619
H	0.677567	14.577768	5.286536
H	2.659922	14.911159	6.195159
H	3.941635	13.050486	6.745840
H	1.220879	10.720072	4.853237

H	-0.096496	12.627303	4.528625
UXEPIY02			
Pb	12.292373	1.629495	5.223822
Br	14.569600	3.204040	5.931855
Br	14.034215	0.016821	3.616272
Br	11.943209	3.864873	3.038702
Br	10.322728	-0.783388	4.560635
Br	12.945937	-0.132968	7.464932
Br	10.797234	4.029881	6.910464
N	18.789216	9.371817	7.604908
C	16.785749	8.490706	6.781360
C	17.595492	9.548039	7.013747
Cl	16.320197	5.832955	6.766411
C	17.281144	7.225110	7.119749
C	19.298538	8.170302	7.950091
C	18.498743	7.056898	7.691883
H	19.268695	10.089522	7.778859
H	15.922289	8.596439	6.396766

H	17.316956	10.420339	6.759616
H	20.165977	8.083793	8.346917
H	18.801153	6.184598	7.917476
N	6.169564	5.406817	2.749237
C	7.574179	3.228070	3.443681
C	7.383183	5.591050	3.311859
C	6.334695	3.091899	2.833494
C	8.077532	4.445605	3.696453
C	5.670189	4.221323	2.554901
Cl	8.485388	1.852736	3.844583
H	5.698043	6.109303	2.511414
H	7.747269	6.459345	3.438245
H	5.972599	2.240425	2.626928
H	8.911150	4.522502	4.146278
H	4.804739	4.154839	2.183897
UXERAS02			
I	-1.343754	4.882132	0.602100
Pb	-3.840039	2.628786	0.027169

I	-5.529904	0.138468	-0.602100
I	-2.231553	0.891458	1.911051
I	-1.785309	1.783317	-2.358588
Br	-4.020378	6.761744	1.414006
C	-5.492229	7.721683	2.098066
C	-6.773191	7.299952	1.900335
N	-5.199198	8.824207	2.775787
C	-6.136896	9.569264	3.356906
C	-7.752750	8.083166	2.434662
C	-7.451347	9.187698	3.192381
H	-6.978312	6.501677	1.420345
H	-4.358619	9.071220	2.843710
H	-5.904983	10.339424	3.865573
H	-8.662819	7.869288	2.276175
H	-8.150434	9.687750	3.604447
I	-5.971459	3.237283	2.358588
I	-6.417703	4.129142	-1.911051
UXEREW02			

Pb	0.000000	0.000000	0.000000
I	0.610188	1.937573	-2.554594
I	-3.067620	0.283408	-0.745553
I	-0.610188	-1.937573	2.554594
I	3.067620	-0.283408	0.745553
I	0.186292	-2.453627	-2.116792
I	-0.186292	2.453627	2.116792
Br	5.914469	-2.202626	-0.270940
N	9.490072	-4.048686	0.321391
C	8.404009	-3.310087	0.487693
C	7.484102	-3.221384	-0.548421
C	7.730760	-3.916950	-1.681699
C	8.818055	-4.672237	-1.812498
C	9.752833	-4.786408	-0.756764
H	10.083530	-4.050443	0.971648
H	8.255070	-2.848132	1.304251
H	7.111603	-3.871282	-2.402026
H	8.968627	-5.135069	-2.624384

H	10.514717	-5.351116	-0.816558
UXEROG02			
Pb	2.114286	7.645276	11.483098
Br	-0.233363	9.056894	10.869566
Br	0.462903	5.940911	13.205241
Br	1.430492	5.750955	9.285004
Br	3.359327	9.968811	9.750548
Br	2.391738	9.778855	13.670784
Br	4.055593	5.028994	12.086223
Br	-1.971811	11.651023	9.882008
N	-4.496818	14.103289	7.857001
C	-3.905960	13.008506	8.384984
C	-2.811219	13.185733	9.185376
C	-2.366030	14.442438	9.494514
C	-2.963563	15.551722	8.928271
C	-4.057596	15.346299	8.124819
H	-5.187582	14.000175	7.322897
H	-4.243029	12.139285	8.204399

H	-1.642600	14.552803	10.100547
H	-2.629197	16.425776	9.088962
H	-4.511662	16.093072	7.751405
UXERUM02			
Pb	4.162468	6.003750	4.503230
Br	5.940877	6.003750	2.212627
Br	3.893062	8.939103	4.050754
Br	6.343551	6.003750	6.448822
Br	3.893062	3.068397	4.050754
Br	1.840327	6.003750	2.310323
Br	2.243001	6.003750	7.120028
Br	2.194614	11.868213	4.016380
N	0.262435	15.201495	5.300897
C	1.016936	14.096805	5.210438
C	1.139953	13.433991	4.061609
C	0.451061	13.875867	2.921826
C	-0.303441	15.021383	2.994193
C	-0.369049	15.691401	4.233481

H	0.187805	15.609750	6.076131
H	1.467997	13.779807	5.982054
H	0.501087	13.388362	2.112218
H	-0.771724	15.350388	2.236146
H	-0.868496	16.495904	4.313990
UXESAT02			
Pb	12.729562	5.615030	4.100681
Br	10.473055	7.221487	4.854090
Br	10.937482	4.029667	2.507733
Br	14.693763	3.168553	3.444697
Br	12.089591	3.873240	6.333965
Br	13.067162	7.904275	1.925362
Br	14.196925	8.044118	5.781529
Br	16.421020	5.788123	2.618493
C	18.705911	7.153941	1.676358
C	16.984693	8.525797	2.608424
C	17.487973	7.285974	2.257368
N	19.013918	9.454860	1.793376

C	17.785915	9.635197	2.351255
C	19.487002	8.260121	1.425993
H	19.023984	6.290090	1.440960
H	16.127104	8.619186	3.008463
H	19.521225	10.161720	1.668194
H	17.477908	10.508709	2.563521
H	20.334525	8.178003	1.005543
Br	8.654000	9.853777	5.556609
C	7.655895	11.375780	5.978828
C	8.173267	12.631705	5.746152
C	6.373538	11.222815	6.520379
C	5.666933	12.349927	6.782990
C	7.446531	13.722589	6.078158
N	6.226580	13.559157	6.592495
H	9.034883	12.732340	5.355636
H	6.011176	10.360575	6.697267
H	4.775121	12.291156	7.101389
H	7.800840	14.594490	5.947532

H	5.767589	14.274873	6.818367
UXESOH02			
Pb	4.683714	7.206551	3.289368
Pb	8.994385	11.836535	3.625736
I	7.011462	4.912835	3.292568
I	4.736449	6.839494	6.599359
I	2.705165	4.500315	3.622062
I	4.497349	7.533745	0.201489
I	2.303484	9.329616	3.446648
I	6.625621	9.657482	3.567541
I	11.337904	13.966990	3.835403
I	7.018103	14.402577	4.111562
I	8.714037	12.407613	0.561799
I	9.015182	11.924772	6.924112
I	10.967984	9.329616	3.446648
Cl	8.546676	8.969278	0.092448
N	8.669171	4.591016	-0.722990
C	9.239403	5.150896	0.320012

C	9.297550	6.382632	0.663729
C	8.573049	7.256045	-0.201489
C	7.987248	6.808141	-1.363014
C	7.956448	5.486824	-1.564503
H	8.719323	3.735519	-0.885367
H	9.659286	4.539507	0.920923
H	9.792191	6.689446	1.411609
H	7.617558	7.399374	-2.000668
H	7.457366	5.128501	-2.293419
Cl	5.880474	9.670247	-2.652544
N	7.928898	12.364390	-5.369090
C	7.247990	11.443947	-5.902444
C	6.617715	10.637720	-5.060931
C	6.743554	10.749696	-3.674212
C	7.439353	11.699252	-3.093449
C	8.149707	12.496522	-4.017929
H	8.283675	12.964581	-5.903629
H	7.187068	11.329732	-6.841146

H	6.053216	9.963624	-5.410573
H	7.463364	11.833624	-2.148821
H	8.786338	13.123587	-3.706213
Cl	4.182368	4.053531	-0.210971
N	4.790047	-0.264263	0.154080
C	5.215081	0.582275	1.114116
C	5.058782	1.885676	1.078559
C	4.438322	2.329101	-0.082966
C	3.837223	1.500478	-1.031150
C	4.208375	0.179162	-0.877070
H	4.917429	-1.130958	0.246528
H	5.664112	0.212754	1.864366
H	5.340358	2.463472	1.774289
H	3.242263	1.805053	-1.698434
H	4.011576	-0.432227	-1.587023