Supplementary Materials

The crystal structures analysis of the methyl-substituted pyrazines with anilic acids: a combined diffraction, inelastic neutron scattering, 1H NMR studies and theoretical approach

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CAPTIONS OF FIGURES

CAPTION OF TABLES

Table S15. Comparison of the hydrogen bonds geometry with tunnelling frequencies and tunnelling activation energies for known supramolecular complexes of methyl derivatives of pyrazine. PT-the proton transfer, HB- the hydrogen bond without proton transfer, a,b- the number of protonated nitrogen atoms in pyrazine ring.

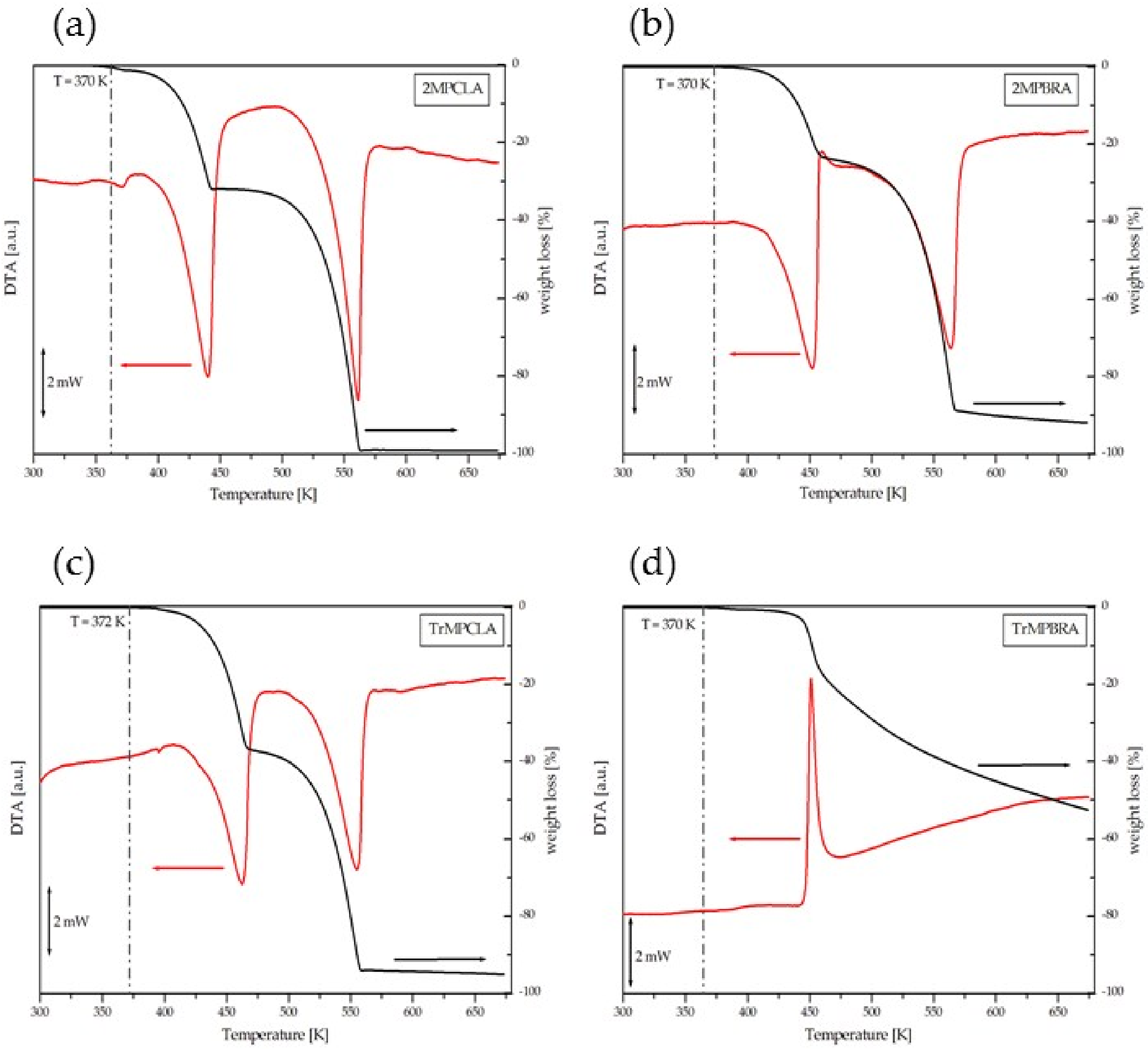

Fig. S1. Simultaneous curves of thermogravimetric analysis and differential thermal analysis (2 K min^{-1}).

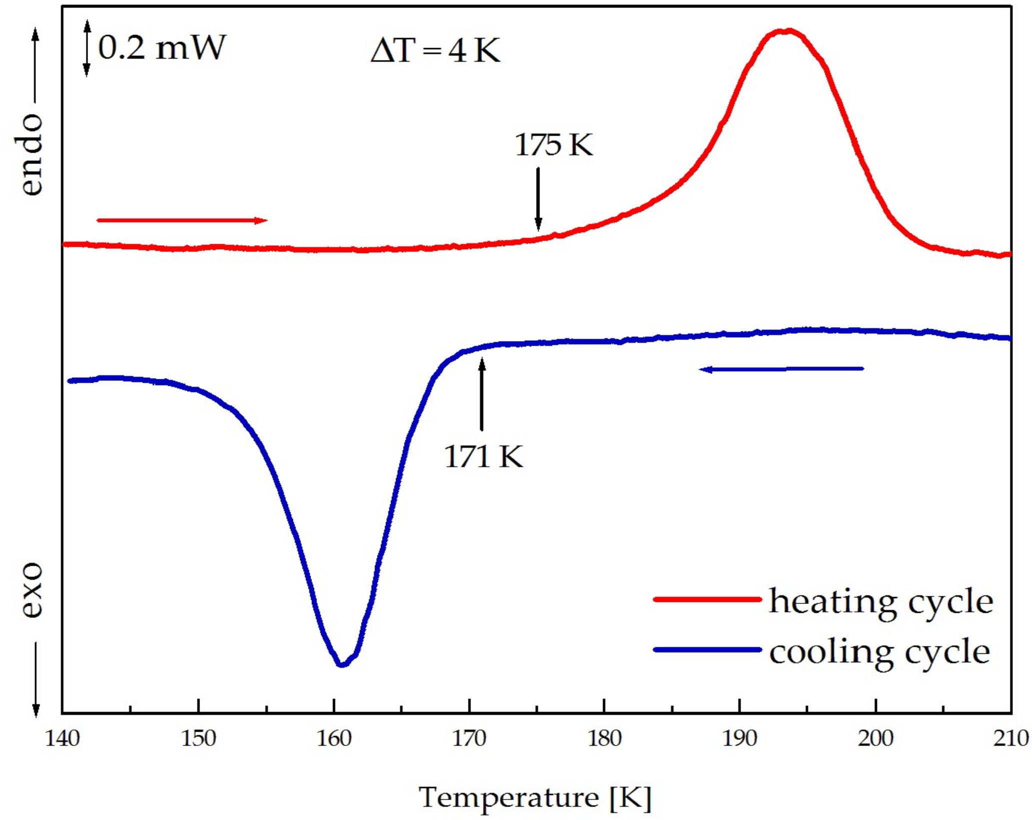

Fig. S2. DSC curves of TrMP·CLA on heating and cooling runs.

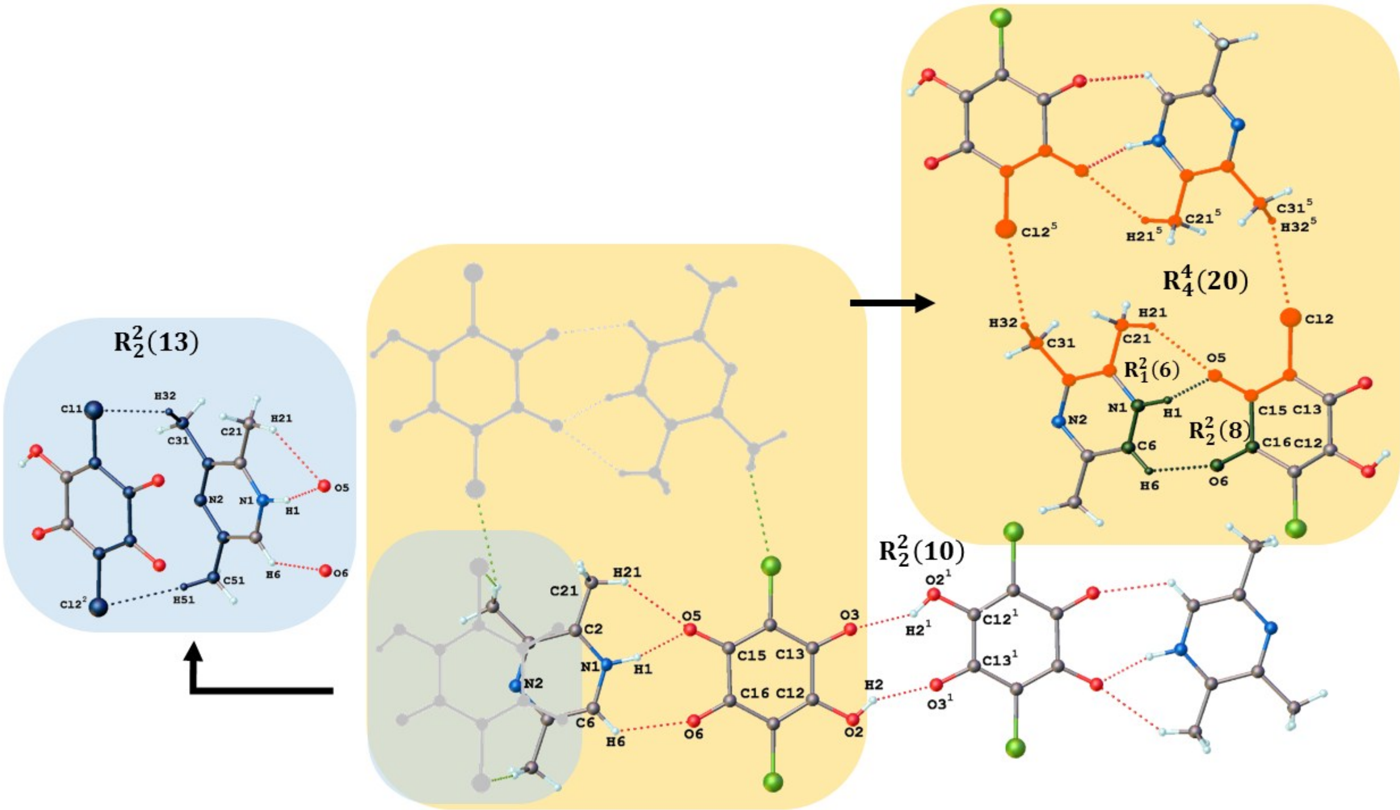

Fig. S3. The hydrogen bonding ring motifs between tetramethylpyrazine and chloranialic acid (**3a**); the graph set $R_2^2(10)$ is assigned to the ring motif formed by two CLA- molecules, the $R_2^2(8)$ (green) and $R_1^2(4)$ (green–orange) motifs present interaction between TrMPH+ cations and CLA- anions, the $R_2^2(13)$ (dark blue) and $R_4^4(20)$ (orange) rings are built by the unconventional hydrogen bonds.

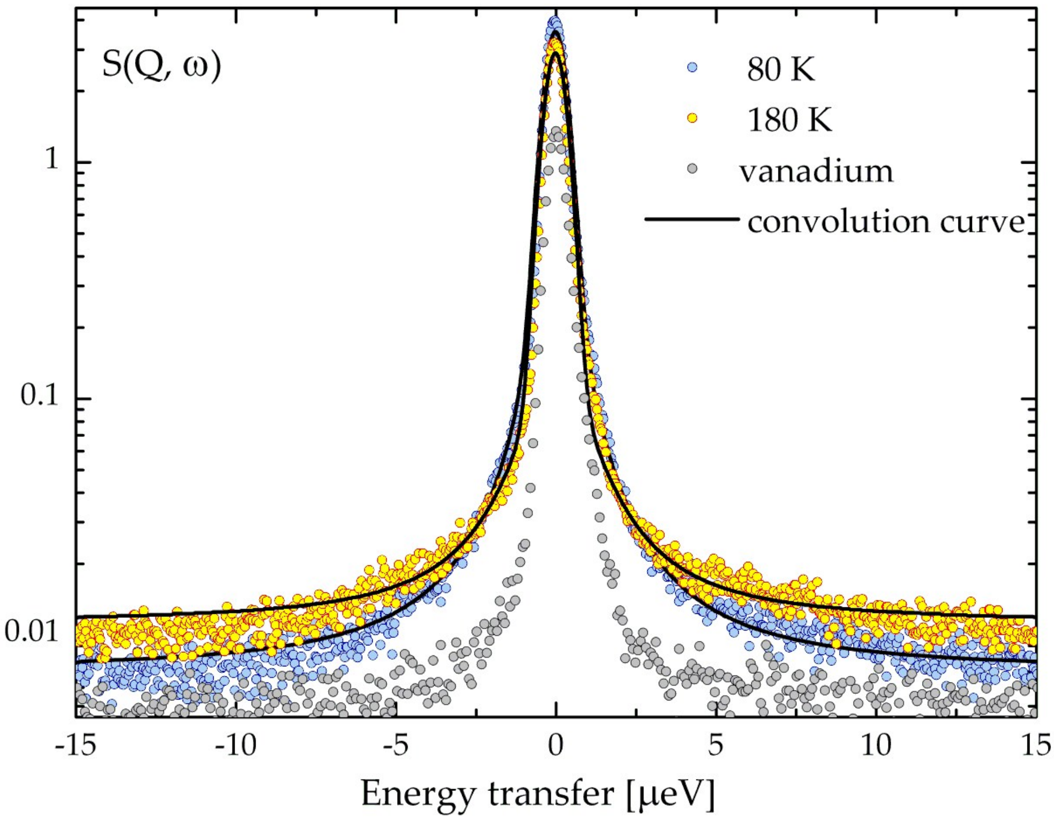

Fig. S4. Quasielastic spectra of TrMP·CLA **(3b)**. Sample temperatures T = 80 and 180 K. Solid lines are fitted with Dirac, Lorentzian components and resolution function obtained for vanadium.

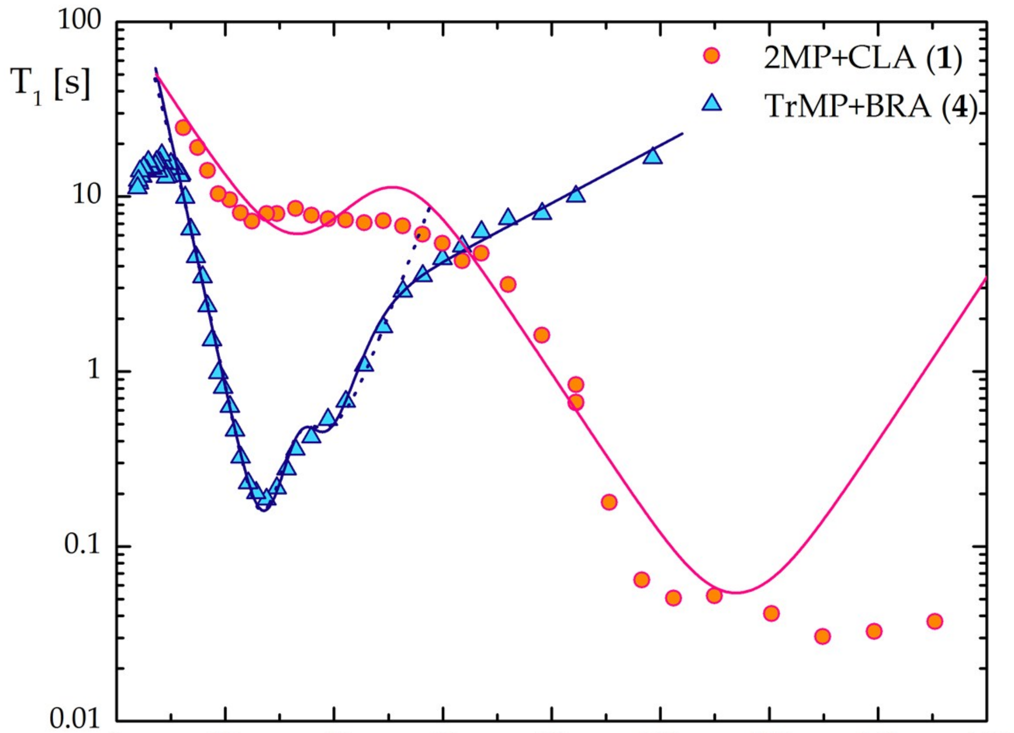

Fig. S5. The temperature dependence of the ^{1}H NMR spin–lattice relaxation time (T_1) for TrMP BRA **(4)** (triangles) and 2MP CLA **(1)** (circles).

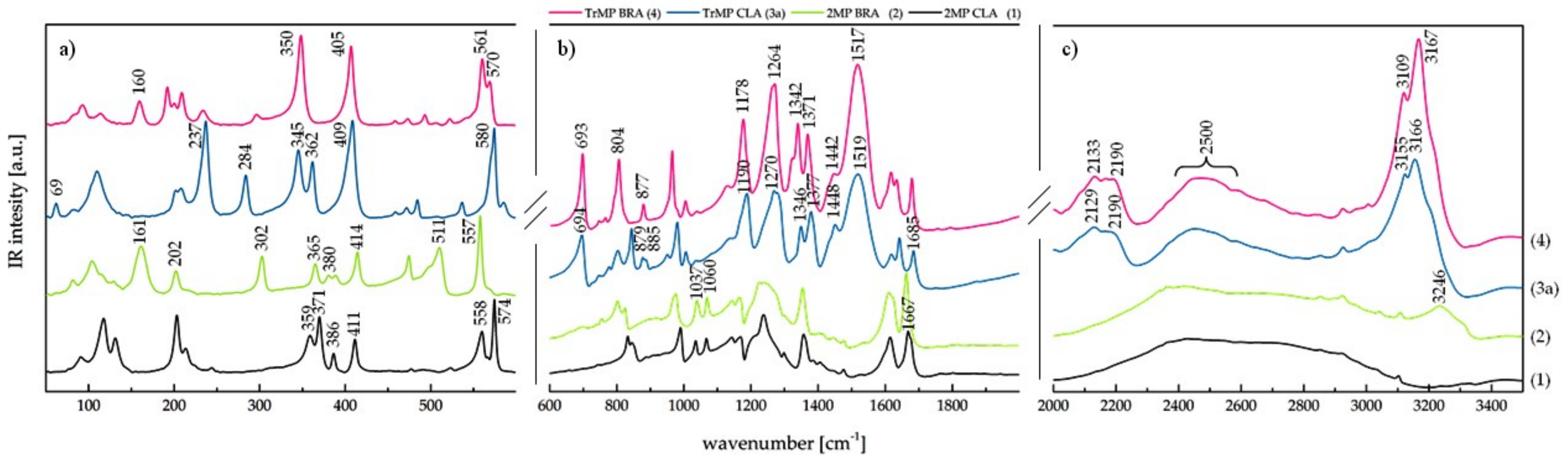

Fig. S6. Infrared spectra of the powdered **(1)**, **(2)**, **(3a)**, **(4)** complexes in KBr pellets at 300K: between 50 and 4000 cm-1.

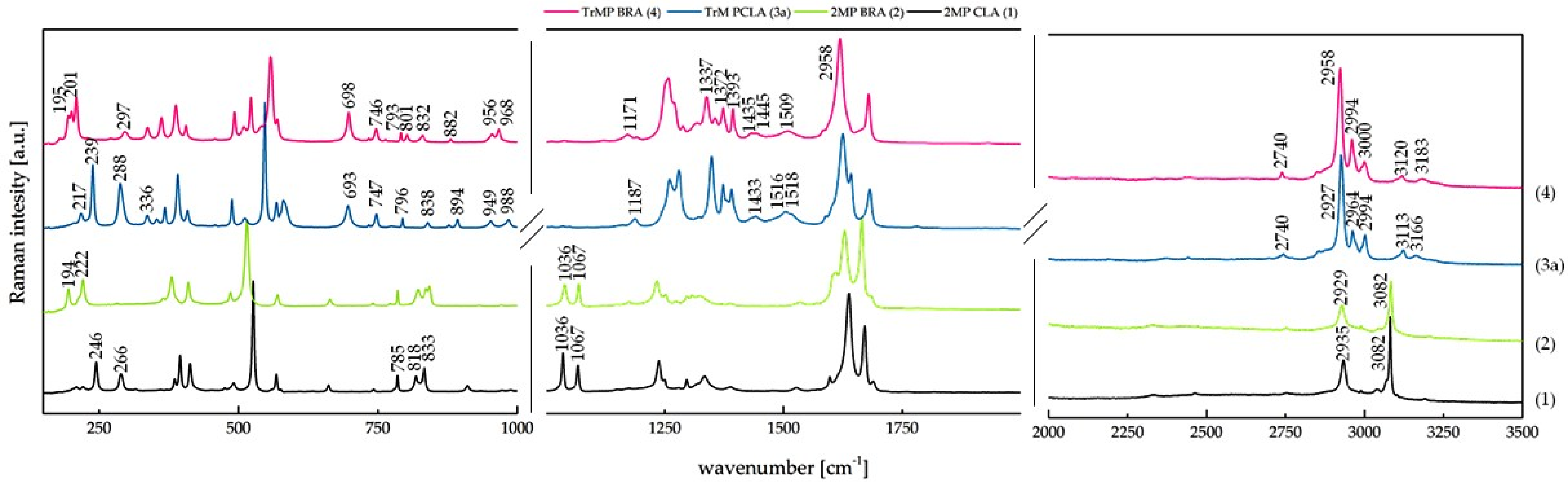

Fig. S7. Raman spectra of the powdered **(1)**, **(2)**, **(3a)**, **(4)** complexes in KBr pellets at 300K: between 50 and 4000 cm-1.

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Table S1. Crystal data and structure refinement for all complexes.

Complexes:	**2MP CLA (1)**	**2MP BRA (2)**	**TrMP CLA (3a)**	**TrMP CLA (3b)**	**TrMP BRA (4)**
Formula	$C_{11}H_8Cl_2N_2O_4$	$C_{11}H_8Br_2N_2O_4$	$C_{13}H_{12}Cl_2N_2O_4$		$C_{13}H_{12}Br_2N_2O_4$
Formula weight	303.09	392.01	331.16		420.06
T (K)	120(2)	100(2)	200(2)	100(2)	100(2)
λ [Å]	0.71073				
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$C2/c$	P-1	P-1	P-1
a (Å)	6.711(2)	20.001(2)	8.463(3)	13.379(7)	8.450(4)
b (Å)	14.834(5)	4.845(4)	8.976(3)	14.992(3)	9.153(2)
c (Å)	12.391(4)	16.024(4)	10.962(4)	16.043(4)	10.952(4)
α (°)	90	90	95.57(2)	113.90(4)	67.50(3)
β (°)	104.88(3)	125.35(3)	111.82(3)	103.69(3)	67.45(2)
γ (°)	90	90	109.33(2)	98.24(2)	72.56(3)
V (Å^3)	1192(2)	1266(3)	706(2)	2746(4)	711(2)
Z	4	4	2	8	2
μ (Mo K_α) (mm^{-1})	0.56	6.41	0.48	0.49	5.72
Crystal size (mm^3)	0.49×0.35×0.10	0.15×0.11×0.04	0.68×0.36×0.12	0.72×0.37×0.08	0.24×0.19×0.12
θ Range (°)	3.1 to 36.7	3.1 to 36.4	2.9 to 36.6	3.1 to 36.4	3.7 to 36.6
Index ranges	$-7 \leq h \leq 8$ $-17 \leq k \leq 17$ $-12 \leq l \leq 15$	$-25 \leq h \leq 25$, $-6 \leq k \leq 6$, $-20 \leq l \leq 20$	$-10 \leq h \leq 8$, $11 \leq k \leq 11$, $-14 \leq l \leq 14$	$-16 \leq h \leq 16$ $-16 \leq k \leq 18$ $-19 \leq l \leq 19$	$-10 \leq h \leq 10$ $-11 \leq k \leq 11$ $-14 \leq l \leq 13$
Absorption correction	none	analytical	analytical	analytical	analytical
T_{min}, T_{max}	-	0.569, 0.817	0.797, 0.951	0.799, 0.966	0.431, 0.644
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4947, 2198, 1943	5110, 1451, 1341	9923, 3238, 2776	25077, 10236, 6857	9479, 3247, 2920
R_{int}	0.018	0.047	0.041	0.042	0.029
Goodness-of-fit on F^2	1.13	1.23	1.07	1.04	1.07
Final R_1, wR_2 indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.033$, $wR_2 = 0.079$	$R_1 = 0.038$, $wR_2 = 0.090$	$R_1 = 0.046$, $wR_2 = 0.126$	$R_1 = 0.056$, $wR_2 = 0.141$	$R_1 = 0.027$, $wR_2 = 0.074$
Final R_1, wR_2 indices (all data)	$R_1 = 0.039$, $wR_2 = 0.081$	$R_1 = 0.041$, $wR_2 = 0.092$	$R_1 = 0.053$, $wR_2 = 0.133$	$R_1 = 0.090$, $wR_2 = 0.156$	$R_1 = 0.031$, $wR_2 = 0.077$
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max, min}$ (e Å^{-3})	0.33/-0.31	0.52/-0.61	0.46/-0.28	0.60/-0.38	0.71/-0.51

Table S2. Experimental and calculated (on the DFT method level in the solid state) bond lengths (Å) and angles (°) 2MP·CLA **(1)** complex.

	Experimental	Calculated
2MP		
N(1)–C(2)	1.349(3)	1.348
N(1)–C(6)	1.347(3)	1.348
N(2)–C(5)	1.338(3)	1.341
N(2)–C(3)	1.342(3)	1.341
C(5)–C(6)	1.378(3)	1.387
C(2)–C(3)	1.395(3)	1.401
C(2)–C(21)	1.496(3)	1.488
N1–C2–C3	119.55(18)	121.01
N1–C2–C21	119.46(18)	122.65
C2–N1–C6	117.76(17)	117.24
C3–N2–C5	116.93(18)	117.24
N2–C5–C6	121.44(19)	121.01
N2–C3–C2	122.61(18)	121.01
N1–C6–C5	121.69(19)	121.72
C3–C2–C21	120.98(18)	122.64
CLA		
Cl(1)–C(11)	1.718(2)	1.773
Cl(2)–C(14)	1.719(2)	1.779
C(13)–O(3)	1.217(2)	1.237
C(12)–O(2)	1.322(2)	1.283
C(15)–O(5)	1.323(2)	1.333
C(16)–O(6)	1.220(2)	1.253
C(14)–C(15)	1.348(3)	1.389
C(14)–C(13)	1.458(3)	1.426
C(15)–C(16)	1.506(3)	1.543
C(16)–C(11)	1.460(3)	1.447
C(12)–C(11)	1.349(3)	1.362
C(12)–C(13)	1.515(3)	1.509
O2–C12–C11	121.88(18)	122.60
O2–C12–C13	117.34(17)	116.36
O3–C13–C14	124.16(18)	126.01
O3–C13–C12	118.20(17)	116.14
O5–C15–C14	122.36(18)	124.46
O5–C15–C16	116.77(17)	117.46
O6–C16–C15	118.27(17)	118.38
O6–C16–C11	123.81(18)	123.54
C11–C16–C15	117.92(16)	118.06
C11–C12–C13	120.77(17)	121.01
C12–C11–Cl1	122.34(15)	119.32
C12–C11–C16	121.29(18)	121.76
C13–C14–Cl2	117.79(15)	116.19
C14–C15–C16	120.87(17)	121.02
C14–C13–C12	117.64(17)	118.07
C15–C14–Cl2	120.70(15)	120.56
C15–C14–C13	121.51(18)	123.23
C16–C11–Cl1	116.36(14)	118.86

Table S3. Experimental and calculated (on the DFT method level in the solid state) bond lengths (Å) and angles (°) 2MP·BRA **(2)** complex.

	Experimental	Calculated
2MP		
N(1)–C(2)	1.338(5)	1.352
N(1)–C(3)	1.331(5)	1.344
C(3)–C(2)^{2}	1.395(6)	1.389
C(2)–C(3)^{2}	1.395(6)	1.389
C(2)–C(21)	1.496(9)	1.495
N1–C2–C3^{2}	120.6(4)	119.40
N1–C3–C2^{2}	122.1(4)	120.79
N1–C2–C21	119.0(5)	119.27
C2–N1–C3	117.3(3)	118.05
BRA		
Br(1)–C(11)	1.881(4)	1.902
C(13)–O(3)	1.215(5)	1.241
C(12)–O(2)	1.319(5)	1.318
C(11)–C(13)^{1}	1.453 (5)	1.443
C(11)–C(12)	1.353(5)	1.352
C(13)–C(11)^{1}	1.453(5)	1.443
C(13)–C(12)	1.521(5)	1.521
O2–C12–C11	122.1(4)	121.94
O2–C12–C13	117.7(3)	118.04
O3–C13–C11^{1}	124.6 (4)	124.39
O3–C13–C12	117.7(3)	117.54
C11^{1}–C13–C12	117.7 (3)	118.03
C11–C12–C13	120.1(3)	119.97
C12–C11–C13^{1}	122.2(3)	121.98
C13^{1}–C11–Br1	116.8 (3)	117.44
Symmetry code: (1) -*x*+1/2, -*y*-1/2, -*z*+1; (2) -*x*, -*y*+1, -*z*+1.		

Table S4. Experimental and calculated (on the DFT method level in the solid state) bond lengths (Å) and angles (°) TrMP·CLA (**3a)** complex.

	Experimental	Calculated
TrMPH⁺		
N(1)–C(2)	1.345(2)	1.352
N(1)–C(6)	1.338(2)	1.351
N(2)–C(3)	1.333(2)	1.342
N(2)–C(5)	1.351(2)	1.353
C(5)–C(6)	1.385(2)	1.388
C(2)–C(3)	1.411(2)	1.415
C(2)–C(21)	1.490(2)	1.486
C(3)–C(31)	1.500(2)	1.491
C(5)–C(51)	1.489(3)	1.492
N1–C2–C3	116.89(16)	116.87
N1–C2–C21	119.54(16)	120.02
C2–N1–C6	122.15(15)	122.46
C3–N2–C5	119.64(15)	120.06
N2–C5–C6	119.77(16)	120.00
N2–C3–C2	121.71(15)	121.32
N1–C6–C5	119.81(16)	119.23
C3–C2–C21	123.56(16)	123.08
N2–C3–C31	117.95(15)	118.29
C2–C3–C31	120.34(16)	120.39
N2–C5–C51	118.23(16)	118.07
C6–C5–C51	121.99(16)	121.92
CLA⁻		
Cl(1)–C(11)	1.717(2)	1.779
Cl(2)–C(14)	1.729(2)	1.787
C(13)–O(3)	1.242(2)	1.263
C(12)–O(2)	1.328(2)	1.329
C(15)–O(5)	1.255(2)	1.266
C(16)–O(6)	1.220(2)	1.238
C(14)–C(15)	1.391(2)	1.398
C(14)–C(13)	1.411(2)	1.408
C(15)–C(16)	1.542(2)	1.554
C(16)–C(11)	1.450(2)	1.439
C(12)–C(11)	1.351(2)	1.361
C(12)–C(13)	1.509(2)	1.514
O2–C12–C11	121.63(15)	121.97
O2–C12–C13	116.62(13)	116.69
O3—C13—C12	116.10(14)	116.68
O3–C13–C14	125.45(15)	125.22
O5–C15–C14	125.66(15)	126.11
O5–C15–C16	116.73(14)	116.59
O6—C16—C11	123.03(15)	121.09
O6–C16–C15	117.81(15)	117.54
C11–C16–C15	119.15(14)	118.36
C11–C12–C13	121.73(14)	121.32
C12–C11–Cl1	121.87(13)	120.91
C12–C11–C16	120.13(14)	121.01
C13–C14–Cl2	117.54(12)	117.38

C14–C15–C16	117.61(14)	117.39
C14–C13–C12	118.45(14)	118.06
C15–C14–Cl2	119.71(12)	119.31
C15–C14–C13	122.74(14)	123.29
C16–C11–Cl1	117.93(12)	117.88

Table S5. Experimental bond lengths (Å) and angles (°) for the TrMP·CLA (**3b)** complex.

ionic pair A		**ionic pair B**		**ionic pair C**		**ionic pair D**	
	experimental		experimental		experimental		experimental
TrMPH⁺		**TrMPH⁺**		**TrMPH⁺**		**TrMPH⁺**	
N(1A)–C(2A)	1.345(4)	N(1B)–C(2B)	1.341(4)	N(1C)–C(2C)	1.332(4)	N(1D)–C(2D)	1.333(4)
N(1A)–C(6A)	1.340(4)	N(1B)–C(6B)	1.340(4)	N(1C)–C(6C)	1.348(4)	N(1D)–C(6D)	1.345(4)
N(2A)–C(3A)	1.331(4)	N(2B)–C(3B)	1.332(4)	N(2C)–C(3C)	1.330(4)	N(2D)–C(3D)	1.327(4)
N(2A)–C(5A)	1.343(4)	N(2B)–C(5B)	1.351(4)	N(2C)–C(5C)	1.342(4)	N(2D)–C(5D)	1.348(4)
C(2A)–C(3A)	1.407(5)	C(2B)–C(3B)	1.409(5)	C(2C)–C(3C)	1.415(5)	C(2D)–C(3D)	1.411(5)
C(2A)–C(21A)	1.494(5)	C(2B)–C(21B)	1.490(5)	C(2C)–C(21C)	1.487(4)	C(2D)–C(21D)	1.486(5)
C(3A)–C(31A)	1.499(5)	C(3B)–C(31B)	1.492(5)	C(3C)–C(31C)	1.492(4)	C(3D)–C(31D)	1.500(5)
C(5A)–C(6A)	1.388(5)	C(5B)–C(6B)	1.381(5)	C(5C)–C(6C)	1.390(5)	C(5D)–C(6D)	1.388(5)
C(5A)–C(51A)	1.490(5)	C(5B)–C(51B)	1.495(5)	C(5C)–C(51C)	1.487(5)	C(5D)–C(51D)	1.491(5)
N(1A)–C(2A)–C(3A)	116.8(3)	C(2B)–N(1B)–C(6B)	122.7(3)	C(2C)–N(1C)–C(6C)	122.7(3)	C(2D)–N(1D)–C(6D)	123.5(3)
N(1A)–C(2A)–C(21A)	119.4(3)	C(3B)–N(2B)–C(5B)	119.3(3)	C(3C)–N(2C)–C(5C)	120.2(3)	C(3D)–N(2D)–C(5D)	119.3(3)
C(2A)–N(1A)–C(6A)	122.3(3)	N(1B)–C(2B)–C(3B)	116.6(3)	N(1C)–C(2C)–C(3C)	116.6(3)	N(1D)–C(2D)–C(3D)	116.2(3)
C(3A)–N(2A)–C(5A)	119.7(3)	N(1B)–C(2B)–C(21B)	120.2(3)	N(1C)–C(2C)–C(21C)	120.2(3)	N(1D)–C(2D)–C(21D)	120.1(3)
C(3A)–C(2A)–C(21A)	123.8(3)	C(3B)–C(2B)–C(21B)	123.3(3)	C(3C)–C(2C)–C(21C)	123.2(3)	C(3D)–C(2D)–C(21D)	123.7(3)
N(2A)–C(3A)–C(2A)	121.8(3)	N(2B)–C(3B)–C(2B)	122.0(3)	N(2C)–C(3C)–C(2C)	121.7(3)	N(2D)–C(3D)–C(2D)	122.3(3)
N(2A)–C(3A)–C(31A)	118.4(3)	N(2B)–C(3B)–C(31B)	118.4(3)	N(2C)–C(3C)–C(31C)	118.8(3)	N(2D)–C(3D)–C(31D)	118.1(3)
C(2A)–C(3A)–C(31A)	119.7(3)	C(2B)–C(3B)–C(31B)	119.7(3)	C(2C)–C(3C)–C(31C)	119.5(3)	C(2D)–C(3D)–C(31D)	119.6(3)
N(2A)–C(5A)–C(6A)	120.1(3)	N(2B)–C(5B)–C(6B)	120.4(3)	N(2C)–C(5C)–C(6C)	119.5(3)	N(2D)–C(5D)–C(6D)	120.4(3)
N(2A)–C(5A)–C(51A)	117.6(3)	N(2B)–C(5B)–C(51B)	117.9(3)	N(2C)–C(5C)–C(51C)	118.7(3)	N(2D)–C(5D)–C(51D)	117.9(3)
C(6A)–C(5A)–C(51A)	122.3(3)	C(6B)–C(5B)–C(51B)	121.7(3)	C(6C)–C(5C)–C(51C)	121.7(3)	C(6D)–C(5D)–C(51D)	121.7(3)
N(1A)–C(6A)–C(5A)	119.2(3)	N(1B)–C(6B)–C(5B)	119.1(3)	N(1C)–C(6C)–C(5C)	119.2(3)	N(1D)–C(6D)–C(5D)	118.3(3)
CLA⁻		**CLA⁻**		**CLA⁻**		**CLA⁻**	
Cl(1A)–C(11A)	1.720(3)	Cl(1B)–Cl(11B)	1.716(3)	Cl(1C)–C(11C)	1.716(3)	Cl(1D)–C(11D)	1.713(3)
Cl(2A)–Cl(14A)	1.727(3)	Cl(2B)–C(14B)	1.732(3)	Cl(2C)–Cl(14C)	1.730(4)	Cl(2D)–Cl(14D)	1.727(3)
C(12A)–O(2A)	1.325(4)	C(12B)–O(2B)	1.324(4)	C(12C)–O(2C)	1.326(4)	C(12D)–O(2D)	1.327(4)
C(13A)–O(3A)	1.250(4)	C(13B)–O(3B)	1.250(4)	C(13C)–O(3C)	1.255(4)	C(13D)–O(3D)	1.248(4)
C(15A)–O(5A)	1.252(4)	C(15B)–O(5B)	1.264(4)	C(15C)–O(5C)	1.254(4)	C(15D)–O(5D)	1.257(4)
C(16A)–O(6A)	1.229(4)	C(16B)–O(6B)	1.231(4)	C(16C)–O(6C)	1.216(4)	C(16D)–O(6D)	1.217(4)
C(11A)–C(12A)	1.349(5)	C(11B)–C(12B)	1.356(4)	C(11C)–C(12C)	1.351(5)	C(11D)–C(12D)	1.355(5)
C(11A)–C(16A)	1.456(5)	C(11B)–C(16B)	1.438(5)	C(11C)–C(16C)	1.461(5)	C(11D)–C(16D)	1.461(5)
C(12A)–C(13A)	1.516(5)	C(12B)–C(13B)	1.507(5)	C(12C)–C(13C)	1.516(5)	C(12D)–C(13D)	1.498(5)
C(13A)–C(14A)	1.402(5)	C(13B)–C(14B)	1.410(5)	C(13C)–C(14C)	1.406(5)	C(13D)–C(14D)	1.417(5)
C(14A)–C(15A)	1.401 (5)	C(14B)–C(15B)	1.392(5)	C(14C)–C(15C)	1.402(5)	C(14D)–C(15D)	1.395(5)
C(15A)–C(16A)	1.537 (5)	C(15B)–C(16B)	1.545(5)	C(15C)–C(16C)	1.541(5)	C(15D)–C(16D)	1.541(5)
C(12A)–C(11A)–Cl(1A)	122.1(3)	C(12B)–C(11B)–Cl(1B)	121.6(3)	C(12C)–C(11C)–Cl(1C)	121.9(3)	C(12D)–C(11D)–Cl(1D)	122.4(3)
C(12A)–C(11A)–C(16A)	120.3(3)	C(12B)–C(11B)–C(16B)	120.1(3)	C(12C)–C(11C)–C(16C)	120.2(3)	C(12D)–C(11D)–C(16D)	119.8(3)
C(16A)–C(11A)–Cl(1A)	117.6(2)	C(16B)–C(11B)–Cl(1B)	118.3(2)	C(16C)–C(11C)–Cl(1C)	117.8(2)	C(16D)–C(11D)–Cl(1D)	117.8(3)
O(2A)–C(12A)–C(11A)	121.8(3)	O(2B)–C(12B)–C(11B)	121.5(3)	O(2C)–C(12C)–C(11C)	121.9(3)	O(2D)–C(12D)–C(11D)	120.8(3)

O(2A)–C(12A)–C(13A)	116.9(3)	O(2B)–C(12B)–C(13B)	116.8(3)	O(2C)–C(12C)–C(13C)	116.5(3)	O(2D)–C(12D)–C(13D)	117.0(3)
C(11A)–C(12A)–C(13A)	121.3(3)	C(11B)–C(12B)–C(13B)	121.7(3)	C(11C)–C(12C)–C(13C)	121.6(3)	C(11D)–C(12D)–C(13D)	122.2(3)
O(3A)–C(13A)–C(12A)	115.7(3)	O(3B)–C(13B)–C(12B)	116.3(3)	O(3C)–C(13C)–C(12C)	116.5(3)	O(3D)–C(13D)–C(12D)	116.7(3)
O(3A)–C(13A)–C(14A)	125.4(3)	O(3B)–C(13B)–C(14B)	125.1(3)	O(3C)–C(13C)–C(14C)	125.5(3)	O(3D)–C(13D)–C(14D)	124.5(3)
C(14A)–C(13A)–C(12A)	118.8(3)	C(14B)–C(13B)–C(12B)	118.6(3)	C(14C)–C(13C)–C(12C)	118.6(3)	C(14D)–C(13D)–C(12D)	118.7(3)
C(13A)–C(14A)–Cl(2A)	118.4(2)	C(13B)–C(14B)–Cl(2B)	117.9(3)	C(13C)–C(14C)–Cl(2C)	118.2(2)	C(13D)–C(14D)–Cl(2D)	117.8(3)
C(15A)–C(14A)–Cl(2A)	118.9(3)	C(15B)–C(14B)–Cl(2B)	119.5(3)	C(15C)–C(14C)–Cl(2C)	118.9(3)	C(15D)–C(14D)–Cl(2D)	119.8(3)
C(15A)–C(14A)–C(13A)	122.7(3)	C(15B)–C(14B)–C(13B)	122.6(3)	C(15C)–C(14C)–C(13C)	122.8(3)	C(15D)–C(14D)–C(13D)	122.4(3)
O(5A)–C(15A)–C(14A)	125.8(3)	O(5B)–C(15B)–C(14B)	126.1(3)	O(5C)–C(15C)–C(14C)	126.1(3)	O(5D)–C(15D)–C(14D)	125.7(3)
O(5A)–C(15A)–C(16A)	116.7(3)	O(5B)–C(15B)–C(16B)	116.5(3)	O(5C)–C(15C)–C(16C)	116.4(3)	O(5D)–C(15D)–C(16D)	116.4(3)
C(14A)–C(15A)–C(16A)	117.5(3)	C(14B)–C(15B)–C(16B)	117.4(3)	C(14C)–C(15C)–C(16C)	117.5(3)	C(14D)–C(15D)–C(16D)	117.9(3)
O(6A)–C(16A)–C(11A)	122.8(3)	O(6B)–C(16B)–C(11B)	123.0(3)	O(6C)–C(16C)–C(11C)	122.5(3)	O(6D)–C(16D)–C(11D)	122.8(3)
O(6A)–C(16A)–C(15A)	118.0(3)	O(6B)–C(16B)–C(15B)	117.4(3)	O(6C)–C(16C)–C(15C)	118.5(3)	O(6D)–C(16D)–C(15D)	118.3(3)
C(11A)–C(16A)–C(15A)	119.2(3)	C(11B)–C(16B)–C(15B)	119.6(3)	C(11C)–C(16C)–C(15C)	119.0(3)	C(11D)–C(16D)–C(15D)	118.9(3)

Table S6. Experimental and calculated (on the DFT method level in the solid state) bond lengths (Å) and angles (°) TrMP·BRA (**4**) complex.

	Experimental	Calculated
TrMPH⁺		
N(1)–C(2)	1.345(3)	1.352
N(1)–C(6)	1.345(3)	1.347
N(2)—C(3)	1.337(3)	1.343
N(2)–C(5)	1.348(3)	1.349
C(5)–C(6)	1.378(3)	1.388
C(2)–C(3)	1.411(3)	1.412
C(2)–C(21)	1.494(3)	1.486
C(3)–C(31)	1.498(3)	1.490
C(5)–C(51)	1.499(3)	1.487
N1–C2–C3	117.1(2)	116.91
N1–C2–C21	119.3(2)	119.46
C2–N1–C6	122.1(2)	122.77
C3–N2–C5	119.2(2)	120.14
N2–C5–C6	120.8(2)	120.22
N2–C5–C51	117.7(2)	118.51
N2–C3–C2	121.6(2)	121.07
N2–C3–C31	117.9(2)	117.90
N1–C6–C5	119.2(2)	118.85
C6–C5–C51	121.5(2)	121.26
C3–C2–C21	123.6(2)	123.95
C2–C3–C31	120.5(2)	121.01
BRA⁻		
Br(1)–C(11)	1.876(2)	1.893
Br(2)–Cl(14)	1.888(2)	1.899
C(13)–O(3)	1.243(3)	1.261
C(12)–O(2)	1.330(3)	1.329
C(15)–O(5)	1.251(3)	1.265
C(16)–O(6)	1.222(3)	1.237
C(14)–C(15)	1.391(3)	1.398
C(14)–C(13)	1.413(3)	1.409
C(15)–C(16)	1.551(3)	1.551
C(16)–C(11)	1.454(3)	1.441
C(12)–C(11)	1.348(3)	1.363
C(12)–C(13)	1.517(3)	1.509
O2–C12–C11	122.3(2)	122.25
O2–C12–C13	115.48(19)	115.99
O3–C13–C14	126.1(2)	124.94
O3–C13–C12	115.8(2)	114.48
O5–C15–C14	126.3(2)	125.36
O5–C15–C16	116.1(2)	116.75
O6–C16–C15	117.66(19)	117.83
O6–C16–C11	123.2(2)	123.38
C11–C16–C15	118.95(19)	118.77
C11–C12–C13	122.2(2)	121.70
C12–C11–Br1	121.64(17)	121.45
C12–C11–C16	119.9(2)	120.38

Table S6. Experimental and calculated (on the DFT method level in the solid state) bond lengths and angles TrMP·BRA (**4**) complex. (Å, °) (continued).

C13–C14–Br2	117.25(17)	117.32
C14–C15–C16	117.66(19)	117.88
C14–C13–C12	118.1(2)	118.51
C15–C14–Br2	119.89(16)	120.09
C15–C14–C13	122.8(2)	122.55
C16–C11–Br1	118.43(17)	118.12

Table S7. Hydrogen bonds and short contacts for crystals **(1)** and **(2)**.

2MP·CLA (1)				
D–H···A (Å)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (°)**
O(2)–H(1)···N(1)	0.85(3)	1.85(3)	2.664(2)	159(3)
O(5)–H(2)···N(2)[2]	0.84(3)	1.91(3)	2.700(2)	155(3)
C(3)–H(3)···O(6)[1]	0.95	2.43	3.065(3)	124
C(6)–H(6)···O(3)	0.95	2.40	3.055(3)	125
C(21)–H(21)···O(2)	0.98	2.56	3.276(3)	130
C(21)–H(23)···O(5)[3]	0.98	2.64	3.414(3)	136
Symmetry codes: (1) *x*-1, *y*, *z*-1; (2) *x*+1, *y*, *z*+1; (3) -*x*+2, -*y*, -*z*+1.				
2MP·BRA (2)				
D–H···A (Å)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (°)**
O(2)–H(1)···N(1)	0.84	1.89	2.645(4)	149
C(3)–H(3)···O(3)	0.95	2.50	2.124(5)	123
C(21)–H(21C)···O(2)[3]	0.98	2.62	3.530(9)	155
Symmetry codes: (3) -*x*, *y*, -*z*+1/2.				

Table S8. Hydrogen bonds and short contacts for crystals **(3a)** at 200 K.

TrMP·CLA (3a) at 200 K				
D–H···A (Å)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A**
O(2)–H(2)···O(3)[1]	0.84	1.90	2.658(2)	150
N(1)–H(1)···O(5)	0.96	1.74(3)	2.681(2)	164(2)
C(6)–H(6)···O(6)	0.95	2.32	2.978(2)	126
C(21)–H(21)···O(5)	0.98	2.38	3.215(2)	143
C(31)– H(32)···Cl(2)[2]	0.98	2.93	3.560(2)	123
C(31)– H(33)···N(2)[4]	0.98	2.82	3.793(3)	1756
C(51)–H(53)···O(2)[3]	0.98	2.79	3.550(3)	135
symmetry codes: (1) -*x*+1, -*y*+1, -*z*; (2) -*x*, -*y*, -*z*+1; (3) *x*, *y*, *z*+1; (4) -*x*, -*y*+1, -*z*+2.				

Table S9. Hydrogen bonds and short contacts for crystals **(3b)** at 100 K.

TrMP·CLA (3b) at 100K				
D–H···A (Å)	**D–H**	**H···A (Å)**	**D···A (Å)**	**D–H···A**
ionic pair A				
N(1A)–H(1A)···O(5A)	0.88	1.84	2.702(4)	165
O(2A)–H(2A)···O(3B)[1]	0.84	1.92	2.668(3)	148
C(6A)–H(6A)···O(6A)	0.95	2.32	2.965(4)	125
C(21A)–H(21A)···O(5A)	0.98	2.37	3.215(5)	144
C(21A)–H(23A)···O(2D)[2]	0.98	2.67	3.312(4)	123
C(21A)–H(32A)···O(3D)[3]	0.98	2.70	3.268(4)	117
ionic pair B				
N(1B)–H(1B)···O(5B)	0.88	1.80	2.658(4)	165
O(2B)–H(2B)···O(3A)[1]	0.84	1.92	2.668(3)	148
C(6B)–H(6B)···O(6B)	0.95	2.29	2.945(4)	125
C(21B)–H(21B)···O(5B)	0.98	2.36	3.191(5)	142
C(21B)–H(22B)···Cl(1D)[4]	0.98	2.91	3.779(3)	149
C(31B)–H(32B)···Cl(2C)[4]	0.98	2.89	3.714(4)	143
C(51B)–H(53B)···Cl(1C)[4]	0.98	2.88	3.843(4)	168
C(51B)–H(51B)···Cl(2D)[2]	0.98	2.88	3.812(4)	159
ionic pair C				
N(1C)–H(1C)···O(5C)	0.88	1.81	2.668(4)	165
O(2C)–H(2C)···O(3C)[5]	0.84	1.97	2.715(3)	147
C(6C)–H(6C)···O(6C)	0.95	2.31	2.955(5)	125
C(21C)–H(21C)···O(5C)	0.98	2.36	3.190(5)	142
C(31C)–H(32C)···Cl(2A)[4]	0.98	2.92	3.796(3)	150
ionic pair D				
N(1D)–H(1D)···O(5D)	0.88	1.85	2.708(4)	165
O(2D)–H(2D)···O(3D)[7]	0.84	1.87	2.628(3)	149
C(6D)–H(6D)···O(6D)	0.95	2.33	2.972(5)	125
C(21D)–H(21D)···O(5D)	0.98	2.36	3.202(5)	144
C(21D)–H(23D)···O(2A)[2]	0.98	2.72	3.349(4)	123
C(21D)–H(22D)···O(6B)[2]	0.98	2.70	3.305(4)	121
C(31D)–H(33D)···Cl(1B)[2]	0.98	2.91	3.800(3)	151
Symmetry codes: (1) -*x*, -*y*, -*z*+1; (2) -*x*+1, -*y*+1, -*z*+1; (3) *x*+1, *y*, *z*+1; (4) *x*, *y*, *z*+1; (5) -*x*+1, -*y*, -*z*; (6) *x*+1, *y*, *z*; (7) -*x*, -*y*+1, -*z*.				

Table S10. Hydrogen bonds and short contacts for crystals **(4)**.

TrMP·BRA (4)				
D–H···A (Å)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (°)**
N1–H1···O5	0.92 (3)	1.79 (4)	2.682(3)	162 (3)
O2–H2···O3[1]	0.84	1.93	2.666(2)	146
C6–H6···O6	0.95	2.30	2.947(3)	125
C21–H21···O5	0.98	2.38	3.215(3)	143
C21–H22···O2[2]	0.98	2.74	3.356(3)	121
C21–H23···O6[3]	0.98	2.90	3.436(3)	115
C51–H52···O2[4]	0.98	2.80	3.526(3)	132
Symmetry codes: (1) -*x*, -*y*+1, -*z*; (2) -*x*, -*y*+1, -*z*+1; (3) -*x*+1, -*y*+1, -*z*+1; (4) *x*, *y*, *z*+1.				

Table S11. Calculated and experimental frequencies for the 2MP·CLA **(1)** complex.

IR FREQUENCIES [cm^{-1}]	RAMAN FREQUENCIES [cm^{-1}]	HARM. FREQUENCIES [cm^{-1}]	IR	RAMAN	ASSIGNMENTS
77 (vw)		75	A	I	
90 (vw)		89	A	I	
95 (w)		92	A	I	2MP: $\rho_{(r)}CH_3$
		96	A	I	
98 (w)		98	A	I	
100 (w)		102	A	I	2MP: $\rho_{(r)}CH_3$
112 (s)		107	A	I	2MP: $\rho_{(r)}CH_3$, $\delta_{(\pi)}$C-H
118 (s)		121	A	I	2MP: $\rho_{(r)}CH_3$, $\delta_{torsion}$ ring
131 (m)		129	A	I	2MP: r(r)CH3, CLA: d(p)C=O, r(r) ring
138 (m)		146	A	I	2MP: r(r)CH3, CLA: d(p)C-OH
141 (w)		148	A	I	2MP: $\rho_{(r)}CH_3$, $\delta_{(\pi)}$C-H, ring butter. (2MP+CLA)
156 (w)		161	A	I	CLA: dC-Cl, ring torsion (2MP+CLA)
	208 (vw)	207	I	A	ring butter. (2MP+CLA)
204 (s)		211	A	I	ring butter. (2MP+CLA)
213 (w)		213	A	I	ring butter. (2MP+CLA)
	218 (vw)	218	I	A	ring butter. (2MP+CLA)
216 (w)		219	A	I	ring butter. (2MP+CLA)
	221 (vw)	220	I	A	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, ring butter.
226 (vw)		224	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, $\delta_{(\pi)}$ C-CH_3
235 (vw)		224	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, $\delta_{(\pi)}$ C-CH_3
243 (vw)		250	A	I	CLA: $\rho_{(r)}$ ring
251 (vw)		251	A	I	CLA: $\rho_{(r)}$ ring
	246 (w)	252	I	A	CLA: $\rho_{(r)}$ ring
	266 (vw)	253	I	A	CLA: $\rho_{(r)}$ ring
322 (vw)		293	A	I	CLA: $\nu_{(ass)}$CCC, δC-OH, νC-Cl, νC=O
341 (vw)		347	A	I	2MP: $\rho_{(r)}CH_3$, δC-CH_3, $\nu_{(ass)}$)CNC, CLA: δC-OH, δC=O
352 (m)		352	A	I	2MP: $\rho_{(r)}CH_3$, δC-CH_3, $\nu_{(ass)}$)CNC, CLA: δC-OH, δC=O

Table S11. Calculated and experimental frequencies for the 2MP·CLA **(1)** complex (continued).

359 (s)		355	A	I	2MP: $\rho_{(r)}CH_3$, $\delta C\text{-}CH_3$, $\nu_{(ass)}CNC$, CLA: δC-OH, δC=O
371 (m)		378	A	I	CLA: $\delta_{(\pi)}CCC$, νC-Cl, δC-OH, δC=O
	385 (vw)	383	I	A	CLA: $\delta_{(\pi)}CCC$, νC-Cl, δC-OH, δC=O
386 (vw)		384	A	I	CLA: $\delta_{(\pi)}CCC$, νC-Cl, δC-OH, δC=O
398 (vw)		405	A	I	2MP: $\delta_{(\pi)}C\text{-}H$, $\delta_{(t,\pi)}CNC$
	395 (w)	405	I	A	2MP: $\delta_{(\pi)}C\text{-}H$, $\delta_{(t,\pi)}CNC$
411 (m)		406	A	I	2MP: δCNC, CLA: $\nu_{(ass)}CCC$, δC-OH, δC=O, δC-Cl
412 (m)		407	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}C\text{-}H$, CLA: δC-OH, δC=O
	412 (w)	407	I	A	CLA: $\nu_{(ass)}CCC$, δC-OH, δC=O
421 (vw)		421	A	I	2MP: $\nu_{(ass)}CNC$, νC-H, CLA: $\nu_{(ass)}CCC$, δC=O
430 (vw)		471	A	I	2MP: $\rho_{(w)}CH_3$, $\delta C\text{-}CH_3$, CLA: νC-Cl, ring butter.
	477 (vw)	471	I	A	2MP: $\rho_{(w)}CH_3$, $\delta C\text{-}CH_3$, CLA: νC-Cl, ring butter.
476 (vw)		472	A	I	2MP: $\rho_{(w)}CH_3$, $\delta C\text{-}CH_3$, CLA: νC-Cl, ring butter.
483 (vw)		488	A	I	CLA: $\rho_{(t)}CCC$, νC-OH
	490 (vw)	492	I	A	CLA: $\rho_{(t)}CCC$, $\delta_{(\pi)}C\text{-}OH$, $\delta_{(\pi)}C{=}O$, $\delta_{(\pi)}C\text{-}Cl$
492 (vw)		503	A	I	2MP: νCNC, $\nu_{(ass)}CH_3$, δC-H, CLA: δC-Cl
522 (vw)		508	A	I	2MP: $\rho_{(sc.)}CNC$, νC-H, CLA: δC-OH, $\nu_{(ass)}CCC$,
	526 (vs)	528	I	A	CLA: νCCC, νC-Cl, νC-OH, νC=O
535 (vw)		529	A	I	CLA: νCCC, νC-Cl, νC-OH, νC=O
553 (m)		547	A	I	CLA: νCCC, νC-Cl, νC-OH, νC=O
558 (s)		548	A	I	CLA: $\rho_{(t)}CCC$, $\delta_{(\pi)}C\text{-}OH$, $\delta_{(\pi)}C{=}O$
	568 (vw)	555	I	A	CLA: $\rho_{(t)}CCC$, $\delta_{(\pi)}C\text{-}OH$, $\delta_{(\pi)}C{=}O$
563 (vw)		573	A	I	2MP: νC-H, $\nu C\text{-}CH_3$, νCNC, CLA: νC-OH, νC=O, νCCC, νC-Cl
574 (vw)		573	A	I	2MP: νC-H, $\nu C\text{-}CH_3$, νCNC, CLA: νC-OH, νC=O, νCCC, νC-Cl
	575 (vw)	574	I	A	2MP: νC-H, $\nu C\text{-}CH_3$, νCNC, CLA: νC-OH, νC=O, νCCC, νC-Cl
617 (vw)		604	A	I	2MP: $\rho_{(sc.)}CNC$, $\nu C\text{-}CH_3$, νC-H, CLA: νC-OH
	661 (vw)	604	I	A	2MP: $\rho_{(sc.)}CNC$, $\nu C\text{-}CH_3$, νC-H, CLA: νC-OH
631 (vw)		604	A	I	2MP: $\rho_{(sc.)}CNC$, $\nu C\text{-}CH_3$, νC-H, CLA: νC-OH
697 (vw)		732	A	I	CLA: $\rho_{(t)}CCC$
719 (vw)		732	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}C\text{-}H$, $\rho_{(t)}CNC$, CLA: $\rho_{(t)}CCC$

Table S11. Calculated and experimental frequencies for the 2MP·CLA **(1)** complex (continued).

728 (vw)		733	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, $\rho_{(t)}$CNC, CLA: $\rho_{(t)}$CCC
	744 (vw)	736	I	A	CLA: $\rho_{(t)}$CCC
743 (vw)		736	A	I	2MP: $\delta_{(\pi)}$CH, CLA: $\delta_{(\pi)}$C=O, $\rho_{(t)}$CCC
768 (vw)		759	A	I	2MP: $\rho_{(sc.)}$CNC, CLA: δC-OH, δC=O, $\rho_{(r)}$ ring
	785 (vw)	800	I	A	CLA: $\rho_{(sc.)}$CCC, δC-OH, δC=O, νC-Cl
786 (vw)		804	A	I	CLA: $\rho_{(sc.)}$CCC, δC-OH, δC=O, νC-Cl
799 (w)		808	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H
811 (w)		812	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H
	818 (vw)	819	I	A	2MP: νC-CH_3, $\delta_{(\pi)}$C-H, $\rho_{(sc.)}$CNC
832 (m)		820	A	I	2MP: νC-CH_3, $\delta_{(\pi)}$C-H, νCNC
832 (m)		820	A	I	2MP: νC-CH_3, $\delta_{(\pi)}$C-H, νCNC
	833 (w)	821	I	A	2MP: νC-CH_3, $\delta_{(\pi)}$C-H, νCNC
848 (m)		852	A	I	CLA: νC-Cl, δOH, νC-Cl
885 (w)		886	A	I	2MP: $\rho_{(r)}CH_3$, δC-H, $\rho_{(sc.)}$CNC, CLA: νC-Cl
904 (w)		915	A	I	2MP: $\rho_{(w)}CH_3$, δC-H, CLA: δO-H
	910 (vw)	915	I	A	2MP: $\rho_{(w)}CH_3$, δC-H, CLA: δO-H
933 (w)		943	A	I	2MP: $\rho_{(w)}CH_3$, δC-H, $\rho_{(w)}$CNC
945 (w)		945	A	I	2MP: $\rho_{(w)}CH_3$, δC-H, $\rho_{(w)}$CNC
957 (w)		962	A	I	CLA: νC-Cl, $\nu_{(ass)}$CCC, δOH
975 (w)		964	A	I	CLA: νC-Cl, $\nu_{(ass)}$CCC, δOH
	975 (vw)	965	I	A	CLA: νC-Cl, $\nu_{(ass)}$CCC, δOH
985 (m)		993	A	I	2MP: $\rho_{(t)}CH_3$, CLA: $\delta_{(p)}$OH
991 (s)		994	A	I	2MP: $\rho_{(t)}CH_3$, CLA: $\delta_{(p)}$OH
	989 (vw)	995	I	A	2MP: $\rho_{(t)}CH_3$, CLA: $\delta_{(p)}$OH
1029 (m)		1025	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, CLA: $\delta_{(\pi)}$OH
1035 (m)		1026	A	I	2MP: $\rho_{(w)}CH_3$, $\rho_{(\tau)}$CCC, CLA: $\delta_{(\pi)}$OH
	1036 (w)	1027	I	A	2MP: $\rho_{(w)}CH_3$, $\rho_{(\tau)}$CCC, CLA: $\delta_{(\pi)}$OH
1054 (m)		1053	A	I	2MP: δC-H, νC-CH_3, νCNC, $\rho_{(w)}CH_3$
1067 (m)		1054	A	I	2MP: δC-H, νC-CH_3, νCNC, $\rho_{(w)}CH_3$
	1066 (w)	1054	I	A	2MP: δC-H, νC-CH_3, νCNC, $\rho_{(w)}CH_3$

Table S11. Calculated and experimental frequencies for the 2MP·CLA **(1)** complex (continued).

1130 (m)		1144	A	I	CLA: $\nu_{(ass)}$CCC, δOH
1144 (m)		1145	A	I	CLA: $\nu_{(ass)}$CCC, δOH
1163 (m)		1154	A	I	2MP: $\rho_{(t)}CH_3$, δC-H, $\nu_{(ass)}$CNC, CLA: δOH
1172 (m)		1156	A	I	2MP: $\rho_{(t)}CH_3$, δC-H, $\nu_{(ass)}$CNC, CLA: δOH
1187 (m)		1180	A	I	2MP: δC-H, νC-CH_3, CLA: νC-Cl, δOH
1196 (m)		1184	A	I	2MP: δC-H, νC-CH_3, CLA: νC-Cl, δOH
1211 (m)		1220	A	I	2MP: νC-CH_3, $\nu_{(ass)}$CNC, CLA: $\delta_{(\pi)}$C-H
1220 (m)		1221	A	I	2MP: νC-CH_3, $\nu_{(ass)}$CNC, CLA: $\delta_{(\pi)}$C-H
1235 (vs)		1235	A	I	2MP: δC-H, $\rho_{(w)}CH_3$, $\nu_{(ass)}$CNC, CLA: νC-OH, νC-Cl
1236 (vs)		1238	A	I	2MP: δC-H, $\rho_{(w)}CH_3$, $\nu_{(ass)}$CNC, CLA: νC-OH, νC-Cl
	1240 (w)	1243	I	A	2MP: δC-H, $\rho_{(w)}CH_3$, $\nu_{(ass)}$CNC, CLA: νC-OH, νC-Cl
	1243 (vw)	1244	I	A	2MP: δC-H, $\rho_{(w)}CH_3$, $\nu_{(ass)}$CNC, CLA: νC-OH, νC-Cl
1253 (m)		1249	A	I	CLA: $\nu_{(ass)}$CCC, νC-OH, νC=O
1261 (m)		1256	A	I	2MP: δC-H, δC-CH_3, $\nu_{(ass)}$CNC
1261 (m)		1257	A	I	2MP: δC-H, δC-CH_3, $\nu_{(ass)}$CNC
1299 (w)		1285	A	I	2MP: δC-H, CLA: δOH
	1299 (vw)	1294	I	A	2MP: δC-H, CLA: δOH
1310 (s)		1317	A	I	2MP: δC-H, CLA: $\rho_{(t)}$CCC
1312 (s)		1320	A	I	2MP: δC-H, CLA: $\rho_{(t)}$CCC
	1331 (vw)	1366	I	A	2MP: δC-H, CLA: $\rho_{(t)}$CCC
1354 (w)		1367	A	I	2MP: δC-H, $\nu_{(ass)}$CCC, $\nu_{(ass)}$CNC, CLA: $\nu_{(ass)}$CCC
1367 (w)		1369	A	I	2MP: δC-H, $\nu_{(ass)}$CCC, $\nu_{(ass)}$CNC, CLA: $\nu_{(ass)}$CCC
1384 (w)		1385	A	I	2MP: $\rho_{(w)}CH_3$, δC-H, νCC
	1392 (vw)	1396	I	A	2MP: δC-H, $\rho_{(sc.)}CH_3$, $\rho_{(t)}$CNC
1405 (w)		1401	A	I	2MP: δC-H, $\rho_{(sc.)}CH_3$, $\nu_{(ass)}$CNC
1414 (vw)		1415	A	I	2MP: δC-H, $\rho_{(sc.)}CH_3$, $\nu_{(ass)}$CNC
1446 (vw)		1443	A	I	2MP: δC-H, $\rho_{(sc.)}CH_3$
1464 (vw)		1464	A	I	2MP: δC-H, $\rho_{(t)}CH_3$, νCNC
1475 (vw)		1491	A	I	2MP: δC-H, $\rho_{(t)}CH_3$, $\nu_{(ass)}$CNC
1526 (vw)		1556	A	I	CLA: δC-OH, νC=O

Table S11. Calculated and experimental frequencies for the 2MP·CLA **(1)** complex (continued).

1548 (vw)		1560	A	I	CLA: δC-OH, νC=O
	1530 (vw)	1578	I	A	2MP: δC-H, $\rho_{(t)}$CCC, CLA: $\rho_{(t)}$CCC
1574 (w)		1579	A	I	2MP: $\rho_{(r)}CH_3$, δC-H, CLA: δC=O, δC-OH
	1599 (vs)	1602	I	A	2MP: δC-H, $\rho_{(r)}CH_3$, $\rho_{(t)}$CCC, CLA: δC-OH, δC=O
1606 (m)		1602	A	I	2MP: δC-H, $\nu_{(ass)}$CNC, CLA: δC-OH, δC=O
1615 (m)		1607	A	I	2MP: δC-H, $\nu_{(ass)}$CNC, CLA: δC-OH, δC=O
1625 (m)		1626	A	I	2MP: δC-H, $\nu_{(ass)}$CNC, CLA: δC-OH, δC=O
1626 (m)		1626	A	I	2MP: δC-H, $\nu_{(ass)}$CNC, CLA: δC-OH, δC=O
1655 (m)		1632	A	I	2MP: δC-H, $\rho_{(t)}$CCC, CLA: $\rho_{(t)}$CCC, δC=O
1667 (s)		1633	A	I	2MP: δC-H, $\rho_{(t)}$CCC, CLA: $\rho_{(t)}$CCC
	1637 (s)	1637	I	A	2MP: δC-H, $\rho_{(t)}$CCC, CLA: $\rho_{(t)}$CCC
1678 (m)		1644	A	I	2MP: δC-H, $\nu_{(ass)}$CNC
1684 (m)		1646	A	I	2MP: δC-H, $\nu_{(ass)}$CNC
	1672 (vw)	1647	I	A	2MP: δC-H, νC-C
2199 (vw)		2826	A	I	CLA: νO-H
2399 (w)		2827	A	I	CLA: νO-H
	2331 (vw)	2827	I	A	CLA: νO-H
2551 (w)		2831	I	A	2MP: $\nu_{(s)}CH_3$
2724 (w)		2955	A	I	2MP: $\nu_{(s)}CH_3$
	2931 (w)	2957	A	I	2MP: $\nu_{(s)}CH_3$
2932 (vw)		3039	A	I	2MP: $\nu_{(s)}CH_3$
3066 (vw)		3041	A	I	2MP: $\nu_{(s)}CH_3$
	3082 (vw)	3088	I	A	2MP: $\nu_{(ass)}CH_3$
3283 (vw)		3088	A	I	2MP: $\nu_{(ass)}CH_3$
3455 (vw)		3155	A	I	2MP: νC-H $_{(ring)}$

ν-streching, δ-deformation (bending), sc.-scissors, ρ_w-wagging, ρ_r-rocking, ρ_t-twisting, π-out of the plane, s-symmetric, ass-asymmetric, vs-very strong, s-strong, m-medium, w-weak, vw-very weak, A–active, I–inactive band

Table S12. Calculated and experimental frequencies for the 2MP·BRA **(2)** complex.

IR FREQUENCIES [cm^{-1}]	RAMAN FREQUENCIES [cm^{-1}]	HARM. FREQUENCIES [cm^{-1}]	IR	RAMAN	ASSIGNMENTS
62 (vw)		61	A	I	2MP: $\rho_{(r)}CH_3$
81 (vw)		80	A	I	BRA: $\delta_{(\pi)}$ C-OH, ring asym. torsion
94 (vw)		93	A	I	2MP: $\rho_{(r)}CH_3$
115 (w)		113	A	I	2MP: $\rho_{(r)}CH_3$
128 (w)		124	A	I	2MP: $\rho_{(r)}CH_3$
137 (w)		138	A	I	2MP: $\rho_{(r)}CH_3$
144 (w)		145	A	I	2MP: $\rho_{(r)}CH_3$
159 (w)		162	A	I	2MP: $\rho_{(r)}CH_3$
161 (w)		170	A	I	2MP: $\rho_{(r)}CH_3$, BRA: νO-H
193 (w)		172	A	A	2MP: $\rho_{(r)}CH_3$, BRA: νO-H
	194 (w)	194	I	A	BRA: δ ring, νC-Br, 2MP: $\delta_{(\pi)}$ $C\text{-}H_{(ring)}$
202 (m)		207	A	I	2MP: $\delta_{(\pi)}C\text{-}CH_3$, $\delta_{(\pi)}$C-H, ring butterfly BRA: ring butterfly
212 (w)		211	A	I	2MP: $\delta_{(\pi)}C\text{-}CH_3$, $\delta_{(\pi)}$C-H, ring butterfly BRA: ring butterfly
	222 (w)	215	I	A	2MP: $\delta_{(\pi)}C\text{-}CH_3$, $\delta_{(\pi)}$C-H, ring butterfly BRA: ring butterfly
233 (vw)		235	A	I	2MP: $\delta C\text{-}CH_3$, BRA: $\rho_{(r)}$ ring
240 (vw)		237	A	I	2MP: $\delta C\text{-}CH_3$, BRA: $\rho_{(r)}$ ring
	282 (vw)	274	I	A	BRA: $\rho_{(t,\pi)}$ ring
291 (w)		274	A	I	BRA: $\rho_{(t,\pi)}$ ring
294 (w)		305	A	I	2MP: $\nu_{(s)}CH_3$, BRA δ ring
302 (m)		306	A	I	2MP: $\nu_{(s)}CH_3$, BRA δ ring
348 (vw)		356	A	I	2MP: $\delta C\text{-}CH_3$, $\rho_{(w)}CH_3$, $\rho_{(r)}$ ring BRA: $\rho_{(r)}$ ring
365 (w)		357	A	I	2MP: $\delta C\text{-}CH_3$, $\rho_{(w)}CH_3$, $\rho_{(r)}$ ring BRA: $\rho_{(r)}$ ring
380 (w)		394	A	I	2MP: $\delta C\text{-}CH_3$, δ ring BRA: δ ring
	380 (w)	394	I	A	2MP: $\delta C\text{-}CH_3$, δ ring BRA: δ ring
406 (m)		408	A	I	2MP: $\delta C\text{-}CH_3$, $\delta_{(\pi)}$C-H, BRA: δC=O, δC-OH
	409 (w)	409	I	A	2MP: $\delta C\text{-}CH_3$, $\delta_{(\pi)}$C-H, BRA: δC=O, δC-OH
414 (m)		411	A	I	2MP: $\delta C\text{-}CH_3$, $\delta_{(\pi)}$C-H, $\rho_{(t,\pi)}$ ring

Table S12. Calculated and experimental frequencies for the 2MP·BRA **(2)** complex (continued).

460 (vw)		468	A	I	2MP: δC-CH_3, $δ_{(π)}$C-H, $ρ_{(t,π)}$ ring
465 (vw)		469	A	I	2MP: δC-CH_3, $δ_{(π)}$C-H, $ρ_{(t,π)}$ ring
	485 (w)	486	I	A	BRA: $ρ_{(t,p)}$ ring
474 (vw)		486	A	I	BRA: $ρ_{(t,p)}$ ring
484 (m)		494	A	I	BRA: νO-H, ν(C=O+C-OH), νC-Br, δ ring
493 (m)		495	A	I	BRA: νO-H, ν(C=O+C-OH), νC-Br, δ ring
511 (m)		516	A	I	BRA: νO-H, ν(C=O+C-OH), νC-Br, δ ring
	516 (vs)	516	I	A	BRA: νO-H, ν(C=O+C-OH), νC-Br, δ ring
547 (m)		549	A	I	BRA: $ρ_{(t)}$ ring
557 (s)		550	A	I	BRA: $ρ_{(t)}$ ring
568 (m)		564	A	I	2MP: νC-CH_3, νC-H, νCNC, BRA: νO-H
	570 (vw)	566	I	A	2MP: νC-CH_3, νC-H, νCNC, BRA: νO-H
598 (vw)		566	A	I	2MP: νC-CH_3, νC-H, νCNC, BRA: νO-H
	664 (vw)	670	I	A	2MP: δC-H, $ν_{(ass)}$CNC
733 (w)		733	A	I	BRA: $δ_{(t,π)}$ring, $δ_{(t,π)}$C=O
739 (w)		733	A	I	BRA: $δ_{(t,π)}$ring, $δ_{(t,π)}$C=O
	741 (vw)	744	I	A	BRA: $δ_{(t,π)}$ring, $δ_{(t,π)}$C=O
754 (w)		763	A	I	BRA: δO-H, δ(C=O+C-OH), $ρ_{(r)}$ring
781 (m)		774	A	I	BRA: δO-H, δ(C=O+C-OH), $ρ_{(r)}$ring
	771 (w)	779	I	A	BRA: δO-H, δ(C=O+C-OH), $ρ_{(r)}$ring
	785 (w)	808	I	A	2MP: $δ_{(π)}$C-CH_3, $δ_{(π)}$C-H
802 (m)		811	A	I	2MP: $δ_{(π)}$C-CH_3, $δ_{(π)}$C-H
804 (m)		814	A	I	BRA: δ ring
	823 (w)	814	I	A	2MP: νC-CH_3, νC-H, BRA: δ ring
824 (m)		829	A	I	2MP: νC-CH_3, νC-H, BRA: δ ring
	837 (w)	829	I	A	2MP: νC-CH_3, νC-H, BRA: δ ring
875 (w)		829	A	I	2MP: νC-CH_3, νC-H, BRA: δ ring
917 (w)		909	A	I	2MP: $ρ_{(w)}$$CH_3$, $δ_{(π)}$C-H
	934 (vw)	943	I	A	2MP: $δ_{(π)}$C-H
961 (m)		961	A	I	BRA: δO-H, δ ring
	972 (vw)	963	I	A	BRA: δO-H, δ ring

Table S12. Calculated and experimental frequencies for the 2MP·BRA **(2)** complex (continued).

974 (s)		980	A	I	2MP: $\rho_{(w)}CH_3$
998 (s)		982	A	I	2MP: $\rho_{(w)}CH_3$
1018 (s)		1030	A	I	2MP: $\rho_{(w)}CH_3$
1037 (m)		1030	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, δ ring
	1036 (w)	1036	I	A	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, δ ring
1043 (w)		1038	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, δ ring
1060 (w)		1059	A	I	2MP: $\rho_{(w)}CH_3$, $\delta_{(\pi)}$C-H, δ ring
	1067 (w)	1060	I	A	2MP: $\nu_{(ass)}$CNC, δC-H, BRA: δO-H
1088 (s)		1100	A	I	2MP: $\delta_{(\pi)}$C-H, BRA: $\delta_{(\pi)}$O-H
1110 (w)		1101	A	I	2MP: $\delta_{(\pi)}$C-H, BRA: $\delta_{(\pi)}$O-H
1123 (m)		1123	A	I	2MP: $\delta_{(\pi)}$C-H, BRA: δO-H
1145 (m)		1125	A	I	2MP: $\delta_{(\pi)}$C-H, BRA: δO-H
	1169 (w)	1151	I	A	2MP: $\delta_{(\pi)}$C-H, BRA: δO-H
1166 (s)		1151	A	I	BRA: δ O-H
1194 (m)		1191	A	I	2MP: $\nu_{(ass)}$CNC, BRA: δO-H
1222 (s)		1215	A	I	BRA: δO-H, νC-Br
	1230 (w)	1232	I	A	2MP: $\nu_{(ass)}$CNC, BRA: νCC
1241 (s)		1237	A	I	2MP: νC-CH_3, δC-H, $\nu_{(ass)}$CNC, BRA: δO-H
1255 (s)		1237	A	I	2MP: νC-CH_3, δC-H, $\nu_{(ass)}$CNC, BRA: δO-H
	1247 (vw)	1247	I	A	2MP: νC-CH_3, δC-H, $\nu_{(ass)}$CNC, BRA: δO-H
	1267 (vw)	1267	I	A	2MP: νC-H, BRA: δ O-H
1280 (m)		1283	A	I	2MP: δC-H, BRA: νC-OH, $\nu_{(ass)}$CCC
	1292 (vw)	1291	I	A	2MP: δC-H, $\nu_{(ass)}$CNC, BRA: δO-H
1302 (w)		1295	A	I	2MP: δC-H, $\nu_{(ass)}$CNC, BRA: δO-H
1309 (w)		1312	A	I	2MP: δC-H, $\nu_{(ass)}$CNC, BRA: δO-H, νC-Cl, νC-OH, νC=O
1350 (s)		1316	A	I	BRA: $\nu_{(ass)}$CCC, νC-OH, νC=O
	1380 (vw)	1385	I	A	BRA: $\nu_{(ass)}$CCC, νC-OH, νC=O
1353 (s)		1386	A	I	2MP: $\rho_{(w)}CH_3$, δC-H, BRA: νC-OH
1407 (vw)		1402	A	I	2MP: $\rho_{(w)}CH_3$, δC-H, BRA: νC-OH
1418 (vw)		1403	A	I	2MP: $\rho_{(w)}CH_3$, $\nu_{(ass)}$CNC, δC-H, BRA: δC-OH
1418 (vw)		1443	A	I	2MP: $\rho_{(sc.)}CH_3$, $\nu_{(ass)}$CNC, δC-H, BRA: δC-OH

Table S12. Calculated and experimental frequencies for the 2MP·BRA **(2)** complex (continued).

1450 (vw)		1445	A	A	2MP: $\rho_{(sc.)}CH_3$, $\nu_{(ass)}$CNC, δC-H
1476 (vw)		1446	A	I	2MP: $\rho_{(sc)}CH_3$, $\nu_{(ass)}$CNC, δC-H, BRA: δC-OH
	1530 (vw)	1532	I	A	2MP: $\nu_{(ass)}$CNC, δC-H, BRA: δC-OH
1533 (vw)		1535	A	I	2MP: $\nu_{(ass)}$CNC, δC-H, BRA: νC-Cl
1591 (w)		1574	A	I	BRA: δO-H, νC-C, νC-OH, νC=O
	1603 (m)	1602	I	A	2MP: $\rho_{(w)}CH_3$, δC-H, νC-C
1611 (s)		1602	A	I	BRA: νC-C, νC-OH, νC=O
	1627 (vs)	1608	I	A	BRA: νC=O, δ ring
1627 (s)		1609	A	I	BRA: νC=O, δ ring
1662 (vs)		1611	A	I	BRA: δ(π)O-H, δ ring
1665 (vs)		1612	A	I	BRA: δ(π)O-H
2158 (vw)		1987	A	I	BRA: νO-H
2369 (w)		1988	A	I	BRA: νO-H
2700 (vw)		2230	A	I	2MP: $\nu_{(s)}CH_3$
2920 (vw)		2246	A	I	2MP: $\nu_{(s)}CH_3$
	2929 (vw)	2961	A	I	2MP: $\nu_{(ass)}CH_3$
3099 (vw)		2962	A	I	2MP: $\nu_{(ass)}CH_3$
	3082 (vw)	3047	I	A	2MP: $\nu_{(ass)}CH_3$
3246 (vw)		3168	A	I	2MP: νC-H $_{(ring)}$
3480 (vw)		3168	A	I	2MP: νC-H $_{(ring)}$

ν-streching, δ-deformation (bending), sc.-scissors, ρ_w-wagging, ρ_r-rocking, ρ_t-twisting, π-out of the plane, s-symmetric, ass-asymmetric, vs-very strong, s-strong, m-medium, w-weak, vw-very weak, A–active, I–inactive band

Table S13. Calculated and experimental frequencies for the TrMP·CLA **(3a)** complex.

IR FREQUENCIES [cm^{-1}]	RAMAN FREQUENCIES [cm^{-1}]	HARM. FREQUENCIES [cm^{-1}]	IR	RAMAN	ASSIGNMENTS
69 (vw)		68	I	A	TrMP: $\rho_{(r)}CH_3$, ring asym. torsion
82 (vw)		80	A	I	TrMP+CLA: ring asym. torsion
110 (m)		111	A	I	TrMP+CLA: ring asym. torsion
116 (m)		115	A	I	TrMP+CLA: ring asym. torsion
199 (w)		199	A	I	CLA: ring butterfly(s), νCCl; TrMP: $\rho_{(r)}CH_3$
204 (w)		202	A	I	CLA: ring butterfly(s), νCCl; TrMP: $\delta_{(\pi)}CH$, $\rho_{(r)}CH_3$
	217 (vw)	213	I	A	CLA: δring, δC-OH
237 (vs)		232	A	I	TrMP: $\rho_{(r)}CH_3$, $\delta_{(\pi)}CNC$, $\delta_{(\pi)}$ C-H
	239 (s)	232	I	A	TrMP: $\rho_{(r)}CH_3$, $\delta_{(\pi)}CNC$, $\delta_{(\pi)}$ C-H
284 (w)		283	A	I	CLA: νCCl, δC-OH, δring
	288 (m)	285	I	A	CLA: νCCl, δC-OH, δring
	336 (vw)	328	I	A	TrMP: $\rho_{(r)}CH_3$, $\delta_{(\pi)ring}$, νC-CH_3
345 (s)		345	A	I	CLA: νCCl, δC-OH
	353 (vw)	351	I	A	CLA: δ(CO + OH), νCCl,
362 (m)		356	A	I	CLA: δ(CO + OH), νCCl,
	367 (w)	361	I	A	CLA: δ(CO + OH)
	389 (m)	384	I	A	CLA: δ ring
409		406	A	I	CLA: δ(CO + OH), νCCl,
	408 (w)	407	I	A	CLA: δCO
	458 (vw)	454	I	A	TrMP: $\rho_{(w,\pi)}CNC$, $\delta_{(\pi)}$ NH
459 (vw)		454	A	I	TrMP: $\rho_{(w,\pi)}CNC$, $\delta_{(\pi)}$ NH, $\rho_{(w,\pi)}CH_3$
		471	I	A	TrMP: $\rho_{(r)}$ring, δC-CH_3
472 (vw)		473	A	I	TrMP: $\rho_{(w,)}CH_3$, $\delta_{(\pi)}CH$, δring
484 (vw)		482	A	I	TrMP: $\rho_{(r)}$ring, νC-CH_3
	489 (w)	483	I	A	TrMP: $\rho_{(r)}$ring, νC-CH_3
	511 (vw)	499	I	A	CLA: δring
537 (vw)		532	A	I	CLA: δC-OH, νCCl, $\delta_{(sc.)}$CCC(ring)
	547 (vs)	536	I	A	CLA: δC-OH, νCCl, $\delta_{(sc.)}$CCC(ring)
	568 (w)	564	I	A	TrMP: νC-CH_3, δCNC

Table S13. Calculated and experimental frequencies for the TrMP·CLA **(3a)** complex (continued).

580 (s)		571	A	I	TrMP: νC-CH_3, δCNC; CLA: δ ring
694 (m)		708	A	I	TrMP: νNH, νC-CH_3, νCCC(ring)
	695 (w)	708	I	A	TrMP: νNH, νC-CH_3
748 (vw)		749	A	I	TrMP: νNH, νC-CH_3
	747 (vw)	751	I	A	TrMP: νNH, δC-$H_{(ring)}$, νC-CH_3
777 (vw)		759	A	I	CLA: $\rho_{(t, \pi)}CCC_{(ring)}$
	796 (vw)	797	I	A	CLA: δring, νCCl, δC-OH
800 (w)		802	A	I	CLA: ν(C=O + C-O^-), νCCl,
843 (m)		841	A	I	CLA: νCCring, νCCl,
	838 (vw)	844	I	A	TrMP:$\delta_{(\pi)}$C-$H_{(ring)}$, $\delta_{(w)}CH_3$
879 (w)		846	A	I	TrMP: $\delta_{(\pi)}$C-H
	877 (vw)	847	I	A	CLA: $\delta_{(\pi)}CH_{(ring)}$, νCCl, δring
	894 (vw)	852	I	A	CLA: $\delta_{(\pi)}$OH, νC-OH
885 (w)		892	A	I	CLA: $\delta_{(\pi)}$OH
	949 (vw)	948	I	A	TrMP: $\rho_{(w)}CH_3$, δNH, δring
947 (w)		948	A	I	TrMP: $\rho_{(t)}CH_3$, δNH, νCH, νC-CH_3
982 (m)		974	A	I	TrMP: δC-H, $\rho_{(t)}CH_3$, νCNC, νNH
		991	A	I	TrMP: $\delta_{(\pi)}$C-H, $\rho_{(w,\ ass)}CH_3$, $\delta_{(\pi)}$CNC
	988 (vw)	993	I	A	TrMP: $\delta_{(\pi)}$C-H, $\rho_{(w,\ ass)}CH_3$, $\delta_{(\pi)}$NH
1000 (w)		1001	A	I	TrMP: δC-H, $\rho_{(t)}CH_3$, νCNC, νNH
1033 (w)		1034	A	I	TrMP: δ(π)C-H, $\rho_{(t)}CH_3$, $\delta_{(\pi)}$C-CH_3
1136 (m)		1140	A	I	TrMP: δ(π)NH,
		1143	I	A	CLA: νOH, δOH; TrMP: δCH, $\delta_{(\pi)}$NH, νNH
		1146	I	A	CLA: νOH, δOH; TrMP: δCH, $\delta_{(\pi)}$NH, νNH
1167 (s)		1150	A	I	TrMP: δC-H, δC–CH_3, δNH
	1187 (vw)	1152	I	A	TrMP: νC-CH_3, δC-$H_{(ring)}$, δNH, $\rho_{(w)}CH_3$
1190 (vs)		1166	A	I	CLA: δOH
		1219	I	A	TrMP: νC-CH_3, δC-$H_{(ring)}$, νCN
1232 (vs)		1248	A	I	CLA: δOH + νCC + νC-OH + νCCl
	1255 (m)	1258	I	A	CLA: νCCl + νCC; TrMP: νC-CH3, δC-H(ring)
	1277 (s)	1264	I	A	TrMP: νC-CH_3, δC-$H_{(ring)}$, δCNC, $\rho_{(w)}CH_3$

Table S13. Calculated and experimental frequencies for the TrMP·CLA **(3a)** complex (continued).

1270 (vs)		1265	A	I	TrMP: νC-CH_3, δC-$H_{(ring)}$, $\nu_{(ass.)}$CNC, $\rho_{(w)}CH_3$
1286 (vs)		1289	A	I	TrMP: $\delta_{(\pi)}$C-CH_3, δC-$H_{(ring)}$, $\nu_{(ass.)}$CNC, $\rho_{(w)}CH_3$
		1289	I	A	TrMP: νC-$H_{(ring)}$, $\nu CC_{(ring)}$, νCN
	1346 (vs)	1330	I	A	TrMP: δC-CH_3, δNH, νCC
1346 (m)		1341	A	I	CLA: δring, δCCl
1377 (s)		1372	A	I	TrMP: $\rho_{(w)}CH_3$, νC-CH_3
	1371 (m)	1376	I	A	TrMP: $\rho_{(w)}CH_3$, δNH, $\delta CH_{(ring)}$
1386 (m)		1383	A	I	TrMP: $\rho_{(t)}CH_3$
	1390 (m)	1392	I	A	TrMP: $\rho_{(w)}CH_3$, δNH, $\delta CH_{(ring)}$
	1425 (vw)	1428	I	A	TrMP: $\rho_{(t)}CH_3$
		1447	I	A	TrMP: $\delta_{(sc.)}CH_3$, νC-CH_3, $\nu_{(ass)}$CN
1448 (m)		1448	A	I	TrMP: $\delta_{(sc.)}CH_3$, νC-CH_3, $\nu_{(ass)}$CN
		1451	I	A	TrMP: $\delta_{(w)}CH_3$, δNH, νCNC, νC-CH_3
	1496 (w)	1466	I	A	TrMP: $\rho_{(t)}CH_3$, δCH, νCN
	1518 (w)	1507	I	A	TrMP: $\delta_{(ass,\ sc.)}CH_3$, δNH, νCN, νCC
1502 (vs)		1509	A	I	TrMP: $\delta_{(t)}CH_3$, δNH, νCN, νCC
1530 (vs)		1527	A	I	CLA: $\nu_{(ass)}CC_{ring}$, δOH, δCCl
		1528	I	A	CLA: n(ass)CCl, δOH, νC-O-; TrMP: nCN
1616 (w)		1598	A	I	TrMP: δC-CH_3, $\delta CH_{(ring)}$, νCC_{ring}
	1602 (vs)	1602	I	A	TrMP: δNH, $\delta CH_{(ring)}$, δCC_{ring}, CLA: δCC_{ring},
	1633 (vs)	1622	I	A	TrMP: δNH, δCNC
1685 (m)		1642	A	I	CLA: νCC_{ring}, δOH, δ(C=O+C-O^-)
	1642 (m)	1642	I	A	TrMP: $\delta_{(\pi)}$NH; CLA: νC=O, δC-OH
	2740 (vw)	2607	I	A	TrMP: νNH
2447 (vw)		2616	A	I	TrMP: $\nu_{(s)}CH_3$
2931 (vw)		2968	A	I	TrMP: $\nu_{(s)}CH_3$
	2927 (w)	2968	I	A	TrMP: $\nu_{(s)}CH_3$
2950 (vw)		2972	A	I	TrMP: $\nu_{(s)}CH_3$
	2964 (vw)	2973	I	A	TrMP: $\nu_{(s)}CH_3$
	2994 (vw)	2976	I	A	TrMP: $\nu_{(s)}CH_3$
		3041	I	A	TrMP: $\nu_{(s)}CH_3$

Table S13. Calculated and experimental frequencies for the TrMP·CLA **(3a)** complex (continued)

3166 (w)		3093	A	I	CLA: νOH
3155 (w)		3094	A	I	TrMP: $\nu_{(ass)}CH_3$
	3113 (vw)	3113	I	A	CLA: νOH
3160 (w)		3194	A	I	TrMP: $\nu CH_{(ring)}$
	3166 (vw)	3194	I	A	TrMP: $\nu CH_{(ring)}$

ν-streching, δ-deformation (bending), sc.-scissors, ρ_w-wagging, ρ_r-rocking, ρ_t-twisting, π-out of the plane, s-symmetric, ass-asymmetric, vs-very strong, s-strong, m-medium, w-weak, vw-very weak, A–active, I–inactive band

Table S14. Calculated and experimental frequencies for the TrMP·BRA **(4)** complex.

IR FREQUENCIES [cm^{-1}]	RAMAN FREQUENCIES [cm^{-1}]	HARM. FREQUENCIES [cm^{-1}]	IR	RAMAN	ASSIGNMENTS
82 (vw)		79	A	I	
95 (vw)		97	A	I	
112 (vw)		105	A	I	BRA: ring asym. torsion
		108	I	A	BRA: ring asym. torsion
160 (vw)		156	A	I	TrMP: $\rho_{(w)}CH_3$
	160 (vw)	171	I	A	TrMP: $\rho_{(r)}CH_3$, $\nu CH_{(methyl)}$
	178 (vw)	176	I	A	TrMP: $\rho_{(r)}CH_3$, $\nu CH_{(methyl)}$
193 (w)		185	A	I	TrMP: $\rho_{(r)}CH_3$
	195 (w)	189	I	A	TrMP: $\rho_{(r)}CH_3$, $\nu CH_{(methyl)}$
198 (vw)		198	A	I	TrMP: $\rho_{(r)}CH_3$, BRA: δring, νC-Br
	201 (w)	205	I	A	BRA: δring, νC-Br
	209 (m)	207	I	A	TrMP: $\rho_{(r)}CH_3$, BRA: ring butterfly
211 (w)		211	A	I	TrMP: $\rho_{(r)}CH_3$, BRA: ring butterfly
		221	A	I	BRA: δC-Br
		224	I	A	BRA: δC-Br
	271 (vw)	287	I	A	BRA: $\delta_{(t,\pi)}$ring
	297 (vw)	300	I	A	TrMP: $\delta C\text{-}CH_3$
293 (vw)		302	A	I	BRA: νC-Br, $\delta_{(s,r)}$ (C-O+C=O)
350 (m)		340	A	I	TrMP: $\delta_{(\pi)}C\text{-}CH_3$, $\delta_{(\pi)}CH_{(ring)}$
	337 (vw)	340	I	A	TrMP: $\delta_{(\pi)}C\text{-}CH_3$, $\delta_{(\pi)}CH_{(ring)}$
350 (m)		357	A	I	BRA: δ(CO + OH)
	362 (w)	369	I	A	BRA: δ(CO + OH)
	388 (m)	390	I	A	BRA: δring
405 (m)		406	A	I	BRA: δCO
	406 (w)	407	I	A	BRA: δCO
	458 (vw)	447	I	A	TrMP: $\rho_{(w,\pi)}$CNC, $\delta_{(\pi)}$ NH
455 (vw)		448	A	I	TrMP: $\rho_{(w,\pi)}$CNC, $\delta_{(\pi)}$ NH
471 (vw)		474	A	I	TrMP: $\rho_{(r)}$ring

Table S14. Calculated and experimental frequencies for the TrMP·BRA **(4)** complex (continued).

491 (vw)		491	A	I	TrMP: $\nu_{(s)}$C-CH_3
	493 (w)	491	I	A	TrMP: $\nu_{(s)}$C-CH_3
	510 (vw)	511	I	A	BRA: δ ring, νC-Br
519 (vw)		519	A	I	BRA: δ ring, νC-Br
	540 (vw)	549	I	A	TrMP: $\rho_{(\pi)}$ring, $\delta_{(\pi)}CH_{(ring)}$
561 (w)		553	A	I	BRA: ring butterfly$_{(s)}$
	557 (s)	556	I	A	TrMP+BRA: ring butterfly
	570 (w)	570	I	A	TrMP: νC-CH_3, δCNC
570 (w)		570	A	I	TrMP: νC-CH_3, δCNC
	698 (w)	713	I	A	TrMP: δ ring, νNH, νC-CH_3
693 (m)		713	A	I	TrMP: δ ring, νNH, νC-CH_3
	746 (vw)	732	I	A	BRA: $\rho_{(t,\pi)}CC_{(ring)}$, $\delta_{(\pi)}$OH
744 (vw)		735	A	I	BRA: $\rho_{(t,\pi)}CC_{(ring)}$, $\delta_{(\pi)}$OH
763 (vw)		761	A	I	BRA: $\rho_{(t,\pi)}CC_{(ring)}$
	793 (vw)	781	I	A	BRA: δ ring, νC-Br
804 (m)		813	A	I	BRA: δ ring
	801 (vw)	813	I	A	BRA: $\delta_{(\pi)}$OH
	832 (vw)	816	I	A	BRA: $\delta_{(\pi)}$OH, νC-Br, νC-C
877 (vw)		862	A	I	TrMP:$\delta_{(\pi)}$C-H, $\delta_{(\pi)}$N-H, $\delta_{(\pi)}$C-CH_3
	882 (vw)	863	I	A	TrMP: $\delta_{(\pi)}C\text{-}H_{(ring)}$
	956 (vw)	971	I	A	TrMP: δC-CH_3, $\rho_{(w,ass)}CH_3$, δCNC
968 (m)		975	A	I	TrMP: δC-CH_3, $\rho_{(w,ass)}CH_3$, δCNC
	968 (vw)	996	I	A	TrMP: $\rho_{(w,ass)}CH_3$, $\delta_{(\pi)}$NH
1008 (vw)		1004	A	I	TrMP: δC-CH_3, $\rho_{(w,ass)}CH_3$, $\delta_{(\pi)}$CH (ring), νCC
1035 (vw)		1033	A	I	TrMP: νC-CH_3, $\rho_{(w,ass)}CH_3$, $\delta_{(\pi)}$CH (ring), $\delta_{(t)}$CC
1124 (w)		1140	A	I	TrMP: δCH, $\delta_{(\pi)}$NH, $\delta_{(\pi)}$CNC
	1171(vw)	1155	I	A	TrMP: δCH, $\delta_{(\pi)}$NH, νNH
1178 (s)		1164	A	I	BRA: δOH, νCC
1193 (m)		1226	A	I	TrMP: νC-CH_3, δC-$H_{(ring)}$, νCN
	1258(s)	1257	I	A	BRA: νCC, νCO
1264 (vs)		1261	A	I	BRA: δOH + νCC

Table S14. Calculated and experimental frequencies for the TrMP·BRA **(4)** complex (continued).

1270 (vs)		1272	A	I	TrMP: νC-$H_{(ring)}$, ν$CC_{(ring)}$
1323 (m)		1301	A	I	BRA: νCC, νCO
1323 (m)		1330	A	I	TrMP: δC-CH_3, δNH, νCC
	1337 (m)	1332	I	A	TrMP: δC-CH_3, δNH, νCC
1342 (s)		1346	A	I	BRA: νCC, νC=O
1369 (m)		1362	A	I	TrMP: $\delta_{(w)}CH_3$, δNH, δ$CH_{(ring)}$
	1370 (m)	1371	I	A	TrMP: $\delta_{(w)}CH_3$, δNH, δ$CH_{(ring)}$
1371 (m)		1374	A	I	TrMP: $\delta_{(ass,\ w)}CH_3$, δNH, νC-CH_3
1382 (w)		1383	A	I	TrMP: $\delta_{(ass,\ w)}CH_3$, δNH, νC-CH_3
1397 (vw)		1395	A	I	TrMP: $\delta_{(w)}CH_3$, νC-CH_3, δNH, νCN
	1393 (w)	1395	I	A	TrMP: $\delta_{(w)}CH_3$, νC-CH_3, δNH, νCN
1425 (w)		1428	I	A	TrMP: $\delta_{(sc.)}CH_3$, νC-CH_3, νCN
1439 (vw)		1435	A	I	TrMP: $\delta_{(ass,\ sc.)}CH_3$, νC-CH_3, νCN
	1433 (vw)	1437	I	A	TrMP: $\delta_{(ass,\ sc.)}CH_3$, νC-CH_3, νCN
1442 (w)		1442	A	I	TrMP: $\delta_{(ass,\ sc.)}CH_3$, νCN
1470 (vw)		1456	A	I	TrMP: $\delta_{(ass,sc.)}CH_3$, δNH
1489 (vw)		1463	A	I	TrMP: $\delta_{(ass,\ sc.)}CH_3$ + δ$CH_{(ring)}$, νCN
	1516 (vw)	1513	I	A	TrMP: $\delta_{(ass,\ sc.)}CH_3$, δNH, νCN, νCC
1517 (vs)		1513	A	I	TrMP: $\delta_{(ass,\ sc.)}CH_3$, νC-CH_3, νCN
1520 (s)		1528	A	I	BRA: νCC, δOH, νC=O
1544 (w)		1585	A	I	BRA: νCC, νC=O
1595 (w)		1594	A	I	BRA: δOH, νC=O, ν$CC_{(ring)}$, TrMP: δNH
1601 (vw)		1600	A	I	TRMP: ν$CC_{(ring),}$ δ$CH_{(ring),}$ δNH
	1621 (s)	1622	I	A	TrMP: δNH, BRA: δC=C, δOH
1620 (w)		1626	A	I	TrMP: δNH, νCN, BRA: δC=C, δOH
	1680 (m)	1639	I	A	TrMP: δNH, νCN, BRA: δC=C, δOH
1637 (w)		1640	A	I	TrMP: δNH, BRA: νCC, νCO
	2740 (vw)	2579	I	A	TrMP: νNH
2495 (vw)		2598	A	I	TrMP: νNH
2927 (vw)		2957	A	I	TrMP: $\nu_{(s)}CH_3$
	2958 (vw)	2958	I	A	TrMP: $\nu_{(s)}CH_3$

Table S14. Calculated and experimental frequencies for the TrMP·BRA **(4)** complex (continued).

2964 (vw)		2983	A	I	TrMP: $\nu_{(s)}CH_3$
2997 (vw)		2987	A	I	TrMP: $\nu_{(s)}CH_3$
	2994 (vw)	2987	I	A	TrMP: $\nu_{(s)}CH_3$
	3000 (vw)	3029	I	A	TrMP: $\nu_{(ass)}CH_3$
3083 (vw)		3082	A	I	TrMP: $\nu_{(ass)}CH_3$
3109 (w)		3106	A	I	BRA: νOH, TrMP: $\nu_{(ass)}CH_3$
	3105 (vw)	3106	I	A	BRA: νOH, TrMP: $\nu_{(ass)}CH_3$
3167 (m)		3109	A	I	BRA: νOH, TrMP: $\nu_{(ass)}CH_3$
	3120 (vw)	3129	I	A	BRA: νOH
	3183 (vw)	3207	I	A	TrMP: $\nu CH_{(ring)}$
3215 (vw)		3208	A	I	TrMP: $\nu CH_{(ring)}$

ν-streching, δ-deformation (bending), sc.-scissors, ρ_w-wagging, ρ_r-rocking, ρ_t-twisting, π-out of the plane, s-symmetric, ass-asymmetric, vs-very strong, s-strong, m-medium, w-weak, vw-very weak, A–active, I–inactive band

Table S15. Comparison of the hydrogen bonds geometry with tunnelling frequencies and tunnelling activation energies for known supramolecular complexes of methyl derivatives of pyrazine. PT-the proton transfer, HB- the hydrogen bond without proton transfer, a,b- the number of protonated nitrogen atoms in pyrazine ring.

Compounds	Type of HB	Type of structure	Numbering of methyl groups	Tunneling frequencies	Activation energy	Literature
TMP·CLA (1:1)	$HB_{a,b}$ O−H···N O−H···N	infinite chain	C(14) C(15) C(14)' C(15)'	±2.2 μeV ±3.7 μeV ±22 μeV ±31 μeV	14.5meV	[1-4]
TMP·H_2SQ (1:1)	HB_a, PT_b O−H···N O^-−H···N^+	dimeric unit	C(121) C(131) C(151) C(161)	±1.55 μeV ±4.20 μeV	15.0 meV 13.2 meV	[5,6]
TMP·PIC (1:2)	$PT_{a,b}$ O^-−H···N^+ O^-−H···N^+	trimeric unit	C(22) C(23) C(22)' C(23)'	±3.16 μeV ±4.24 μeV	6.9 meV 6.3 meV	[7]
TMP·BrA	HB_a, PT_b O−H···N O^-−H···N^+	dimeric unit	C(21) C(31) C(51) C(61)	only elastic peak	----------	[1]
TrMP·CLA	HB_a, PT_b O−H···N O^-−H···N^+	dimeric unit	C(21) C(31) C(51)	±4. μeV	10.4 meV	present work
TrMP·BRA	HB_a, PT_b O−H···N O^-−H···N^+	dimeric unit	C(21) C(31) C(51)	only elastic peak	----------	present work
2MP·CLA	$HB_{a,b}$ O−H···N O−H···N	infinite chain	C(21)	only elastic peak	----------	present work
2MP·BRA	$HB_{a,b}$ O−H···N O−H···N	infinite chain	C(21)	±13.9 μeV	7.3 meV	present work