SUPPORTING INFORMATION

High water soluble agrichemicals by engineered organic salts for reducing adverse environmental impacts

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Table S1. Crystal data and refinement parameters of AMT and AMT salts

Compound	**AMT**	**AMT FUM**	**AMT MAL-I**	**AMT MAL-II**	**(AMTMAL) ·2H$_2$O**
Empirical formula	$C_{18}H_{34}N_{10}S_2$	$C_{13}H_{21}N_5O_4S$	$C_{39}H_{63}N_{15}O_{12}S_3$	$C_{13}H_{21}N_5O_4S$	$C_{13}H_{25}N_5O_6S$
Formula weight	454.67	342.95	343.41	343.41	379.44
Temperature/K	120	120.0	120.0	298	298
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P21/c	$P\bar{1}$
a/Å	12.018(4)	18.132(3)	13.495(3)	8.5300(3)	8.8250(4)
b/Å	22.054(6)	11.105(2)	16.262(3)	9.8310(3)	9.7640(5)
c/Å	9.300(3)	16.920(3)	23.781(5)	22.6570(8)	12.0800(6)
α/°	90	90	90	90	107.075(4)
β/°	101.617(5)	95.693(3)	99.226(4)	111.5740(10)	100.749(3)
γ/°	90	90	90	90	96.427(3)
Volume/Å^3	2414.5(12)	3390.1(10)	5151.4(17)	1766.87(10)	962.04(8)
Z, Z'	4, 2	4, 2	4,3	4, 1	2, 1
ρ_{calc}g/cm^3	1.251	1.344	1.328	1.291	1.310
μ/mm^{-1}	0.247	0.218	0.215	0.209	0.206
F(000)	976.0	1452.0	2184.0	728.0	404.0
Crystal size/mm^3	0.253 x 0.076 x 0.021	0.277 x 0.12 x 0.121	0.218 x 0.096 x 0.04	0.36 x 0.30 x 0.19	0.170 x 0.160 x 0.10
2Θ range for data collection/°	5.8 to 52.744	4.516 to 52.044	4.98 to 51.358	7.13 to 50.786	5.912 to 52.41
Index ranges	$-15 \le h \le 15$ $-27 \le k \le 27$ $-11 \le l \le 11$	$-22 \le h \le 22$ $-13 \le k \le 13$ $-20 \le l \le 20$	$-16 \le h \le 16$, $-19 \le k \le 19$, $-28 \le l \le 28$	$-10 \le h \le 10$ $-11 \le k \le 11$ $-27 \le l \le 27$	$-10 \le h \le 10$ $-12 \le k \le 11$ $-15 \le l \le 14$

Reflections collected	50224	67624	101144	6249	6996
Independent reflections	4917 [R_{int} = 0.1074, R_{sigma} = 0.0515]	6669 [R_{int} = 0.0414, R_{sigma} = 0.0267]	9760 [R_{int} = 0.0436, R_{sigma} = 0.0210]	3227 [R_{int} = 0.0182, R_{sigma} = 0.0279]	3806 [R_{int} = 0.0776, R_{sigma} = 0.0876]
Data/restraints/parameters	4917/17/292	6669/128/472	9760/26/651	3227/0/213	3806/0/249
Goodness-of-fit on F^2	1.030	1.089	1.028	1.011	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1369	R_1 = 0.0955, wR2 = 0.2342	R_1 = 0.0545, wR_2 = 0.1436	R_1 = 0.0590, wR2 = 0.1761	R_1 = 0.0651, wR_2 = 0.1754
Final R indexes [all data]	R_1 = 0.0944, wR_2 = 0.1595	R_1 = 0.1009, wR2 = 0.2379	R_1 = 0.0671, wR_2 = 0.1531	R_1 = 0.0789, wR2 = 0.1934	R_1 = 0.1077, wR_2 = 0.2094
Largest diff. peak/hole / e $Å^{-3}$	0.64/-0.52	1.51/-0.66	1.38/-1.15	0.75/-0.28	0.24/-0.35

Table S2. The pK_a differences between AMT and the conformer (carboxylic acids). Following this approach, the salt formation is expected for both cases, even to HFUM that ΔpK_a is less than 2-3 pK_a units[1].

Compound	pK_{a1}	$\Delta pK_a = pK_a(AMT) - pK_{a1}(acid)$
Ametryn (AMT)	4.10	-
Fumaric acid (HFUM)	3.03	1.07
Maleic acid (HMAL)	1.83	2.27

Table S3. Geometric parameters of the H-bonds in the AMT and AMT salts.

Interaction	D···A(Å)	H···A(Å)	D−H···A(°)	Symmetry Code
		AMT		
N2B–H2B···N3A	3.077(3)	2.249(2)	161.38(17)	x+1,+y,+z
N4A–H4A···N1B	3.033(3)	2.182(2)	170.44(18)	x-1,+y,+z
N4B–H4B···N1A	3.007(4)	2.155(3)	170.79(17)	x,y,z
N2A–H2A···N3B	3.126(4)	2.269(3)	174.92(19)	x,y,z
C9A–H9AB···N2B	3.487(5)	2.730(3)	136.28(25)	x-1,+y,+z
C9A–H9AA···N4A	3.613(5)	2.673(3)	166.40(26)	x,-y+1/2,+z-1/2
		AMT FUM		
N5–H5···O1A	2.687(4)	1.810(3)	173.66(22)	x,y,z
N4A–H4A···O2A	2.771(4)	1.903(3)	168.36(22)	x,y,z
N5B–H5B···O1B	2.783(11)	1.910(10)	171.04(36)	x,y,z
N2B–H2B···O2B	2.522(18)	1.654(15)	167.84(69)	x,y,z
O4A–H4AE···O1A	2.534(4)	1.696(3)	176.20(22)	-x+1,+y-1/2,-z+1/2+1
N2A–H2A···O3A	2.833(5)	2.025(4)	152.22(25)	-x+1,+y+1/2,-z+1/2+1
N4B–H4B···O3B	2.842(5)	2.059(4)	147.80(26)	-x+2,+y-1/2,-z+1/2
O4B–H4BE···O1B	2.748(11)	1.914(15)	171.90(55)	-x+2,+y+1/2,-z+1/2
C8B–H8BC···O3B	3.419(7)	2.677(4)	132.71(33)	-x+2,+y-1/2,-z+1/2
C11A–H11A···O4A	3.125(5)	2.496(3)	123.75(24)	-x+1,+y+1/2,-z+1/2+1
C4B–H4BD···S1A	3.856(21)	2.920(1)	140.28(50)	x,-y+1/2+1,+z+1/2
		AMT MAL-I		
N3C–H3C···O2C	2.660(3)	1.810(2)	161.66(15)	x,y,z
N1B–H1B···O2B	2.687(3)	1.830(2)	163.94(15)	x,y,z
N4C–H1C··· O1C	2.928(3)	2.053(2)	172.72(15)	x,y,z
N2B–H2B···O1B	2.841(3)	1.963(2)	174.92(16)	x,y,z
N4A–H4A···O1A	2.875(3)	1.999(2)	173.54(16)	-x,-y+1/2,-z+1/2
N3A–H3A···O2A	2.666(3)	1.797(2)	168.69(16)	-x,-y+1/2,-z+1/2
N2C–H2C···O4C	2.830(3)	1.952(2)	175.29(16)	x-1,+y,+z
N4B–H4B···O4B	2.921(3)	2.050(2)	170.08(16)	x+1,+y,+z
N2A–H2A···O4A	2.886(3)	2.015(2)	169.82(16)	-x+1,+y+1/2,-z+1/2

C7A–H7AB···O4B	3.346(4)	2.546(2)	138.83(23)	x,y,z
C5A–H5AE···O2B	3.447(9)	2.629(2)	141.11(49)	x,y,z
C9C–H9CB···O2B	3.341(3)	2.516(2)	141.75(17)	-x+1,-y+1,-z+1
C9C–H9CC···O2C	3.441(3)	2.497(2)	161.73(16)	-x+1,-y+1,-z+1
C9A–H9AA···O2B	3.413(3)	2.441(2)	171.24(16)	-x+1,+y-1/2,-z+1/2
C9A–H9AC···O2C	3.346(3)	2.5382)	139.70(17)	-x+1,+y-1/2,-z+1/2
C9B–H9BA···O2A	3.453(3)	2.525(2)	158.04(17)	x+1,+y+1,+z
C7B–H7BB···O3A	3.553(12)	2.603(2)	161.42(50)	x+1,-y-1/2,+z+1/2
C7B–H7BC···O3C	3.312(9)	2.682(2)	122.42(50)	-x+2,-y+1,-z+1
C9A–H9AC···S1C	3.736(3)	2.941(1)	138.91(16)	-x+1,+y-1/2,-z+1/2
		AMT MAL-II		
N1–H1···O2	2.696(3)	1.842(2)	171.87(15)	x,y,z
N2–H2···O1	2.855(4)	1.999(3)	173.49(17)	x,y,z
N4–H4··· O3	3.008(3)	2.196(3)	159.29(17)	x,-y+1/2+1,+z+1/2
C9–H9A···O4	3.424(4)	2.488(2)	164.90(20)	-x+2,-y+2-1,-z+1
C9–H9B···O1	3.381(4)	2.589(2)	139.99(21)	-x+2,-y+1,-z+1
C11–H11···O3	3.490(6)	2.759(4)	136.22(22)	-x+2,-y+1,-z+1
		(AMTMAL)-2H_2O		
N3–H3···O2	2.701(2)	1.846(2)	172.27(13)	x,y,z
N4–H4···O1	2.870(3)	2.011(2)	176.67(16)	x,y,z
N2–H2···OW1	3.011(4)	2.187(3)	160.47(18)	-x,-y+1,-z
OW1–HW1B···OW2B	2.687(19)	1.965(19)	142.20(57)	x,y,z
OW2B–HW2A···O1	2.756(26)	2.003(2)	147.16(80)	-x+1,-y+1,-z+1
C12–H12···O3	3.417(4)	2.489(2)	175.39(20)	-x+2,-y+2,-z+2
C8–H8B···O3	3.594(3)	2.709(3)	153.42(13)	x-1,+y-1,+z
C9–H9B···O4	3.372(5)	2.552(3)	143.44(25)	-x+1,-y+2,-z+1

COMPLEMENTARY FIGURES AND TABLES

FIG. S1. ASYMMETRIC UNIT OF (A) AMT ($P2_1/c$, Z' = 2), (B) AMT-FUM ($P2_1/c$, Z' = 2), (C) AMT-MAL-I ($P2_1/c$, Z' = 3), (D) AMT-MAL-II ($P2_1/c$, Z' = 1) AND (E) (AMT-MAL)·H_2O ($P\bar{1}$, Z' = 1) WITH LABELLING THE SYMMETRY-INDEPENDENT MOLECULES. THE ELLIPSOID PLOT ARE DRAWN AT 50% PROBABILITY LEVEL. THE LOWEST OCCUPANCY PARTS OF DISORDERED FRAGMENTS ARE SHOWN WITH 50% TRANSPARENCY FOR CLARITY.

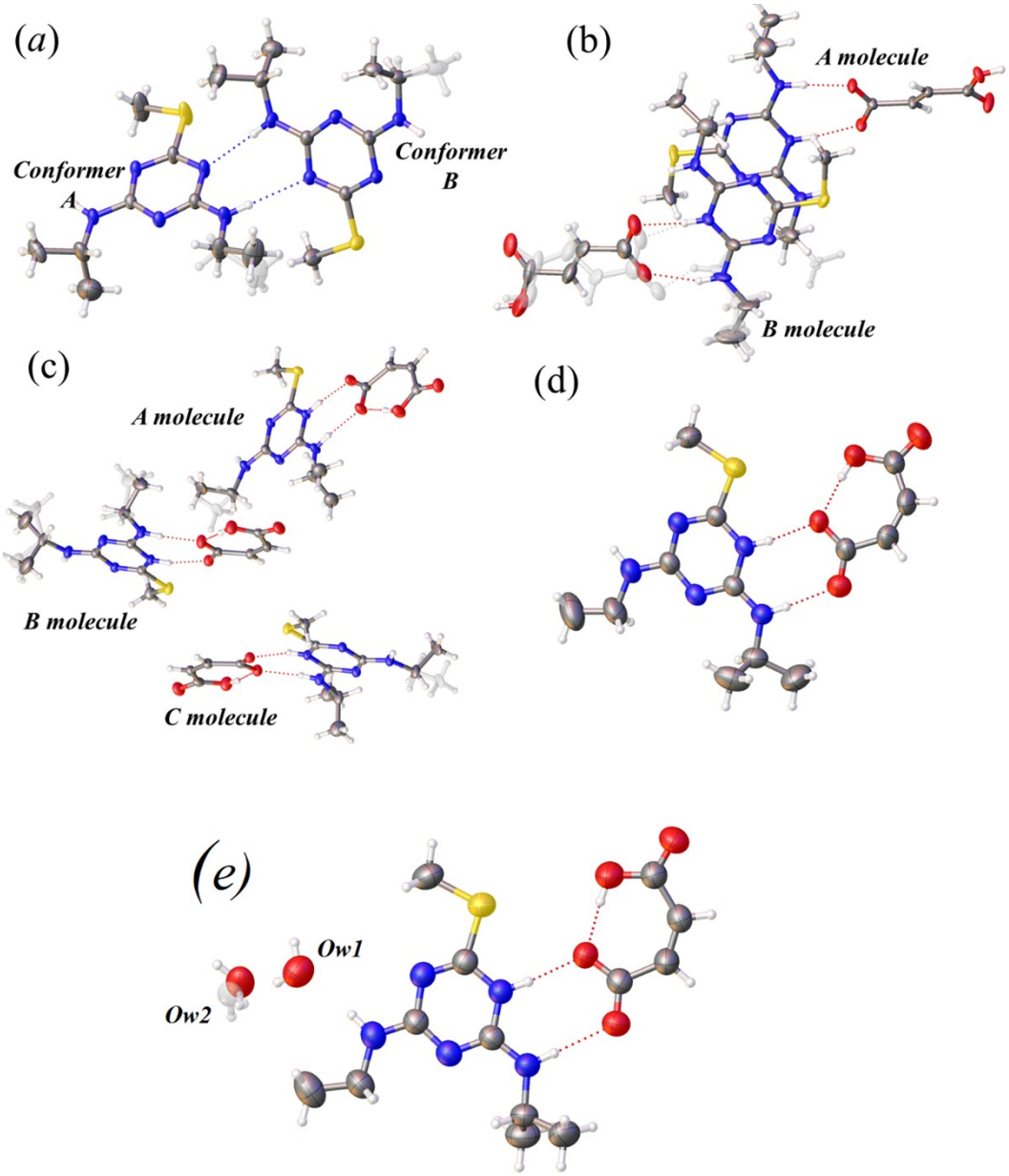

FIG. S2: ALONG THE [100] DIRECTION, ADJACENT AMT CHAINS STACKS PARALLEL TO EACH OTHER VIA CH•••Π (LIGHT GREEN DASH LINE) AND S•••Π (ORANGE DASH LINE) INTERACTIONS RESULTING IN DOMAINS OF LAYERED STRUCTURE.

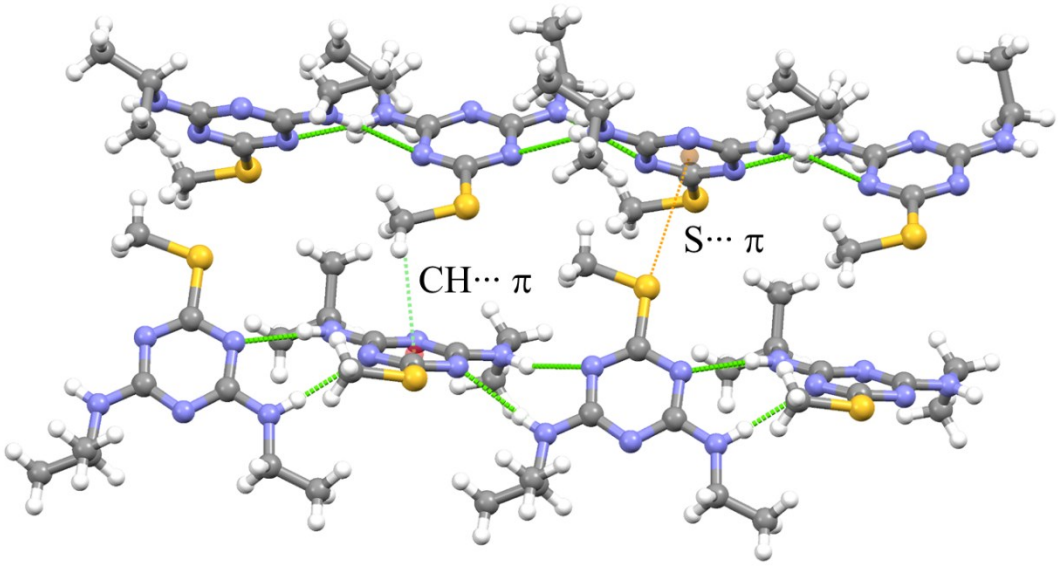

Fig. S3. In the unit cell of AMT (Z' = 2), the A and B conformers are alternately arranged along the [100] direction, such that, the independent molecules are offset each other by 55.34º. In this figure, the red plane defines to that formed by the main plane of conformer A while the blue one is define by conformer B. The molecular overlay of highest occupancy parts of A and B conformers from AMT superimposed through s-triazine groups.

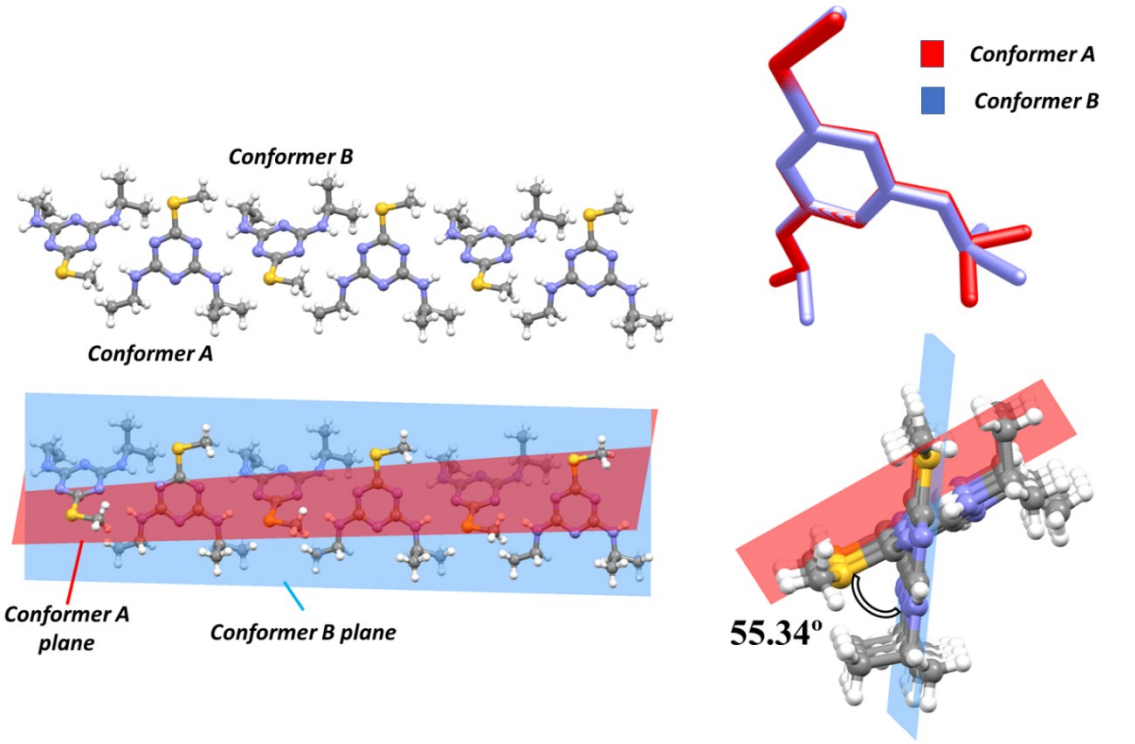

FIG. S4: FOURIER DIFFERENCE MAP FOR THE (*A*) MOLECULE A AND B FROM AMT-FUM SALT. IT SEEN THE PROTONATION OF AMT MOLECULE ON THE N5-ATOM FOR BOTH CASES. (B) MOLECULAR CONFORMATIONS OF AMT CATIONS (A AND B MOLECULES) IN AMT-FUM SALT. HIGHEST OCCUPANCY PARTS CONSIDERED IN THE PRESENTATION.

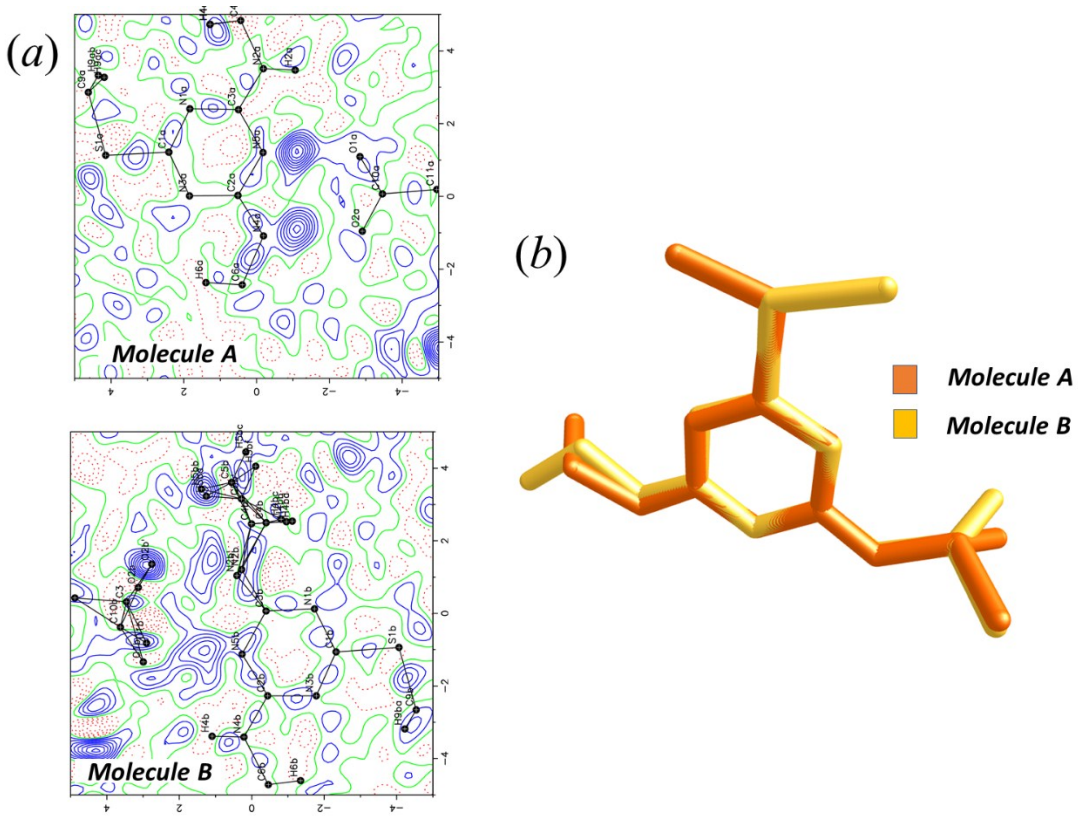

Fig. S5 - (a) Fourier difference maps of both A and B molecules of AMT-MAL-I showing the presence of an H-atom attached to N5 atom ones for both cases. (b) Overlay of the AMT^{+} conformers of AMT-MAL-I using the s-triazine groups as the common reference.

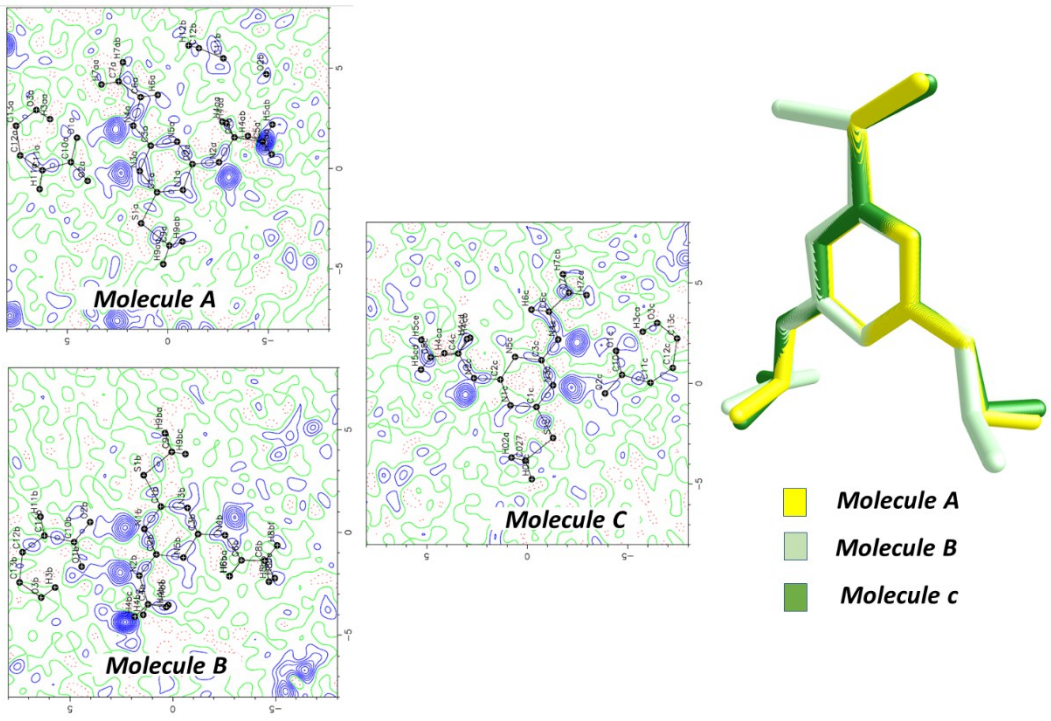

Fig. S6 - Beside the conformational and ionization multiplicity of AMT^+, the polymorphism of ametryn maleate is also associated to diversity of cation-anion assemblies. (a) The ionic pair in AMT-MAL-I interact that way carboxylic of acid and the sulfur-methyl groups of AMT are cis-oriented. Opposite situation are found in AMT-MAL-II. (c) π···π interaction between AMT^+ molecules in AMT-MAL-I.

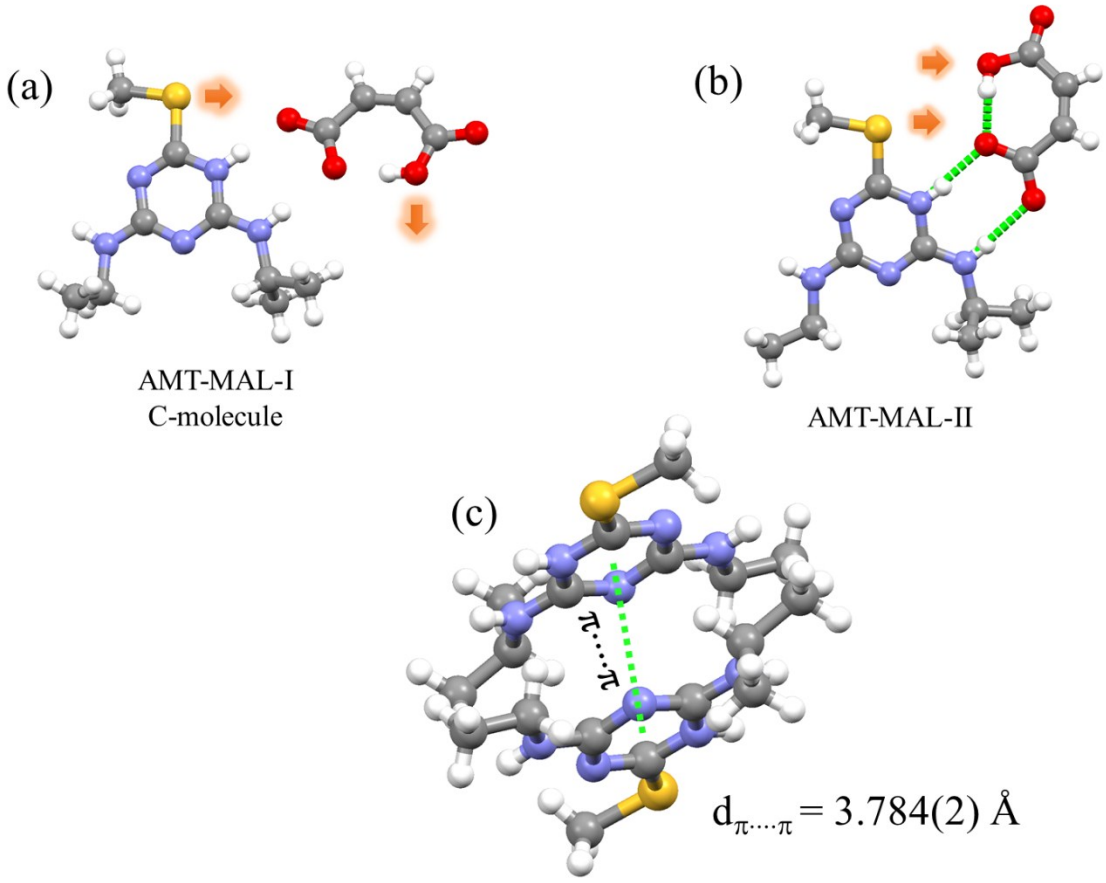

Fig. S7 - (a) The packing of (AMT-MAL)·2H_2O illustrating the water channels (blue circles - viewed along [100] direction). (b) The $(H_2O)_2$ clusters featuring in the crystal structure (water channel core). (c) π···π Interactions between AMT^+···H_2O assemblies.

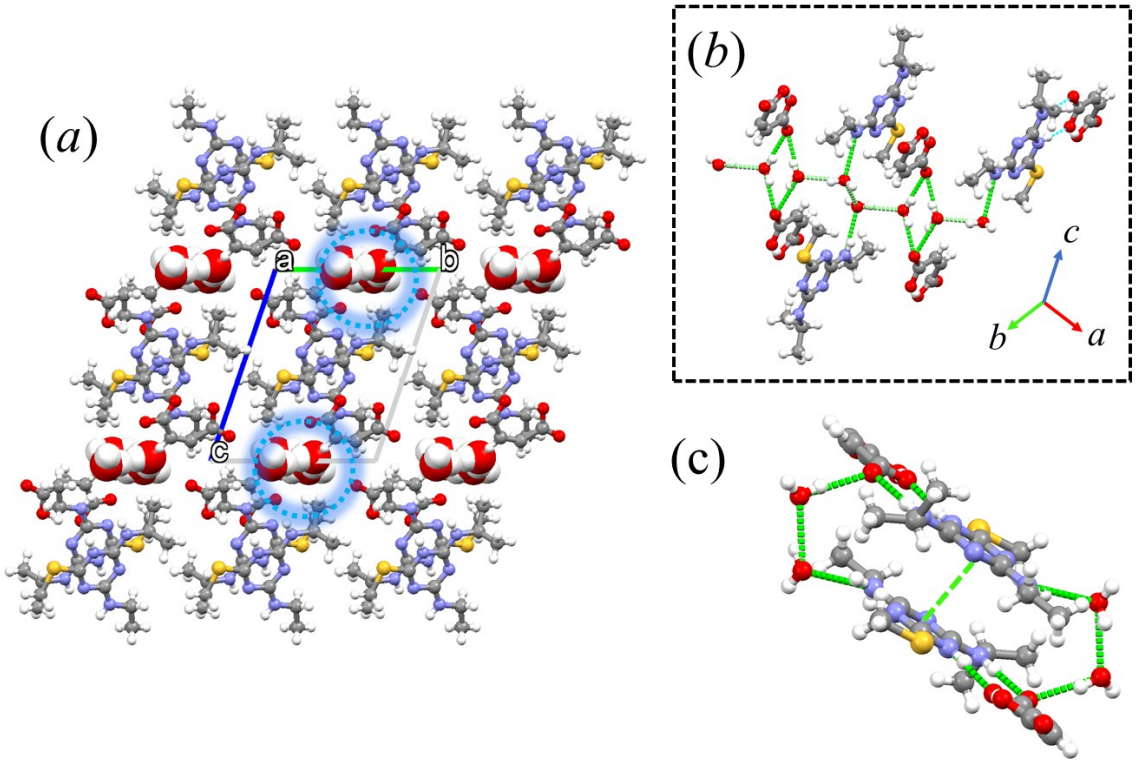

Figure S8 - Diffractograms of AMT and its salts. For all compounds, the experimental and calculated PXRD patterns show an excellent agreement which indicates the purity (unique phase) of the samples.

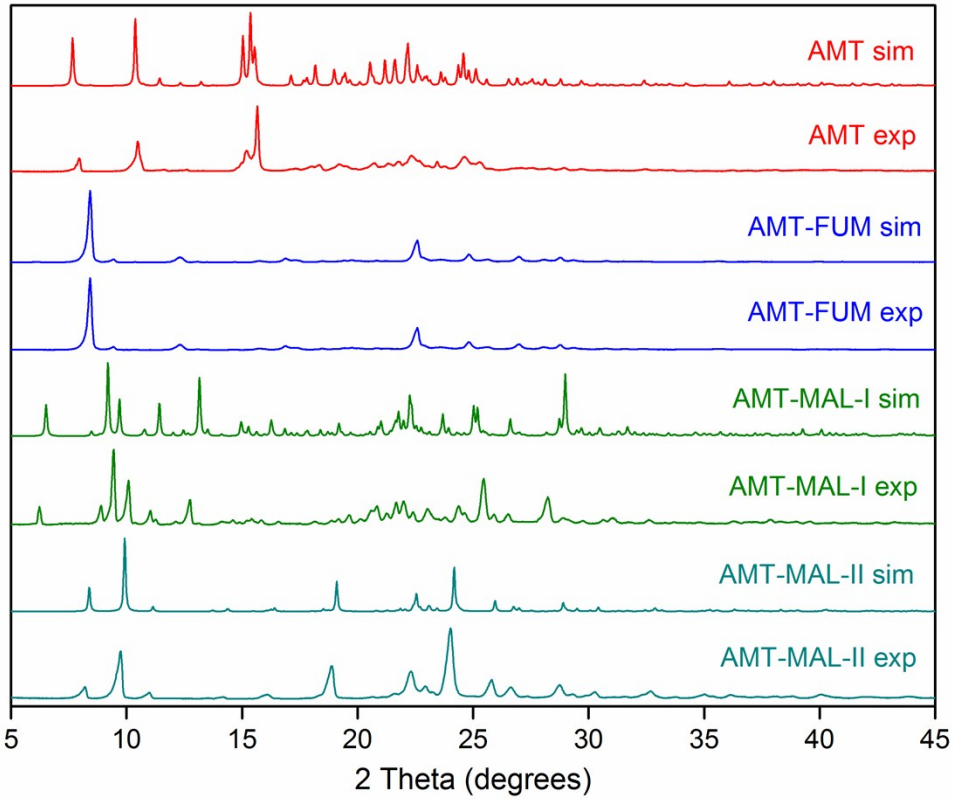

Figure S10 - Aqueous solubility (blue bars) and melting point (line) of AMT and its salts.

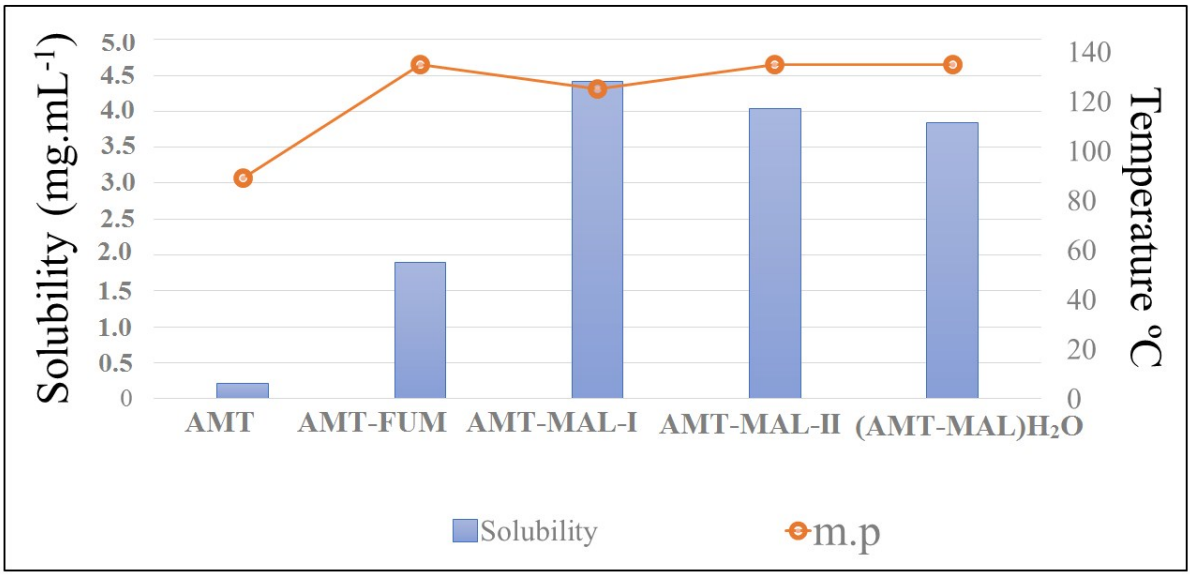

Table S3 - Energy differences between the AMT conformer from AMT and AMT-FUM

Ametryn	
	E + E_{ZPVE}, kcal. mol^{-1}
A	-643115,0062
B	-643118,0213
Ametryn fumarate	
A*	-643424,1252
B*	-643426,9791
Ametryn Fumarate Deprotonated	
A†	-643108,0278
B†	-643108,8987
$[E(A†) + E(A†)_{ZPVE}] - [E(A) + E(A)_{ZPVE}]$	-6,9784275
$[E(B†) + E(B†)_{ZPVE}] - [E(B) + E(B)_{ZPVE}]$	-9,122595

Figure S11. Herbicide 4.98 to 51.358 application system

Similarly, applications of AMT salts were tested. These application solutions prepared dissolving an amounts of AMT-FUM and AMT-MAL-I salts equivalent to the to 1.0 kg ha^{-1} dose in water in order to simulate the field application of 400 L ha^{-1}. After stirring, 150 rpm during 5 min, an aliquot of the solution was collected to determine the soluble concentration of AMT in solution before spraying. The GIW of these systems were compared with the control treatment, the 0 dose of AMT. All experiments were carried out in triplicate.

After 14 days of herbicide application, the plants were cut and dried in a forced-air oven at 70 ºC for 72h to determine the dry matter content (DM). The herbicidal efficacy of AMT (at different doses), AMT-FUM and AMT-MAL-I were estimated through of the growth inhibition of *Brachiaria decumbens* after herbicide application. The Growth Inhibition index (ν) was calculated using the equation:

$$\nu = 100 - [(DM_x - DM_i)/(DM_{control} - DM_i)] \times 100 \qquad \text{Equation 1}$$

where DM_x is the dry matter content of each sample, DM_i is the dry matter average content before AMT application, and $DM_{control}$ is the dry matter content of control treatment (0 dose of AMT).

REFERENCES

[1] S. L. Childs, G. P. Stahly, A. Park, *Mol. Pharm.* **2007**, *4*.

[2] a) A. D. Burrows, in *Supramolecular Assembly via Hydrogen Bonds I* (Ed.: D. M. P. Mingos), Springer Berlin Heidelberg, Berlin, Heidelberg, **2004**; b) V. R. Aldilla, M. Bhadbhade, S. Bhattacharyya, N. Kumar, A. M. Rich, C. E. Marjo, *CrystEngComm* **2017**, *19*; c) T. Le, M. Bhadbhade, J. Gao, J. M. Hook, C. E. Marjo, *CrystEngComm* **2016**, *18*; d) G. J. Perpétuo, J. Janczak, *J Mol Struct* **2018**, *1152*.

[3] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr B* **2016**, *72*.

[4] J. Bernstein, R. J. Davey, J.-O. Henck, *Angew Chem Int Ed Engl* **1999**, *38*.

[5] Bruker, in *Bruker AXS Inc*, Madison, Wisconsin, USA., **2001**.

[6] R. W. W. Hooft, (Ed.: N. BV), Delft, The Netherlands, **1998**.

[7] Z. Otwinowski, W. Minor, in *Methods in Enzymology, 276* (Ed.: Charles W. Carter, Jr.), Academic Press, **1997**.

[8] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J Appl Crystallogr* **2009**, *42*.

[9] G. Sheldrick, *Acta Crystallogr C* **2015**, *71*.

[10] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J Appl Crystallogr* **2008**, *41*.

[11] W. I. F. David, *Structure Determination from Powder Diffraction Data*, Oxford University Press, **2002**.

[12] P. Hohenberg, W. Kohn, *Physical Review* **1964**, *136*, B864-B871; bW. Kohn, L. J. Sham, *Physical Review* **1965**, *140*, A1133-A1138.

[13] 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, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, 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, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Wallingford CT, **2009**.

[14] Y. Zhao, D. Truhlar, *Theor Chem Account* **2008**, *120*.

[15] C. o. Europe, *European Pharmacopoeia 5th Ed. Main Volume 5.0, 2005 with Supplements 5.1 and 5.2*, Renouf Publishing Company Limited, **2004**; bH. M. Eirkson C, Osbourne CM, Sayre PG, Zeeman M in *Environmental assessment technical assistance handbook, Vol. 31* (Ed.: U. S. F. a. D. Administration), Washington DC, **1987**.

[16] a) V. J. Kilmer, l. T. Alexander, *Soil Science* **1949**, *68*; b) V. V. H. Alvarez, R. Novais, L. Dias, J. A. Oliveira, *Pesq. agropec. bras.* **2000, 52**; c) EMBRAPA, 3th ed. (Ed.: E. B. d. P. Agropecuária), Embrapa-SEA, Brasília, **2017**; d) D. W. Nelson, L. E. Sommers, in *Methods of Soil Anlysis. Part 3 Chemical Methods, 5* (Ed.: D. L. Sparks, et. al.), SSSA and ASA, Madison, WI, **1996**.

[17] R. F. Novais, J. C. L. Neves, N. F. Barros, in *Métodos de pesquisa em fertilidade do solo* (Eds.: W. E. Garrido, J. D. Araújo, S. Lourenço), Embrapa-SEA, Brasília, **1991**.