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Supplementary Materials for

Designing high-performance hypergolic propellants based on materials genome

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This PDF file includes:

Supplementary Text

a. Toxicity assessment

The change of luminescence intensity of Vibrio bacterial are recorded after contact with the samples for 15 min. The EC_{50} values are determined by plotting log *Γ* against log *c*, where log *Γ* = log (inhibition (in %)/100 - inhibition (in %)) and c is the concentration of the test sample. A series aqueous solution of MMH, BmimMHT and BmimMHT/BmimDCA are prepared from 1000 ppm to 0.1 ppm.

b. Density prediction of ionic liquids

Density can be estimated reasonably well by the ratio of molar mass M to the molecular volume V_m. In this work, densities for the screened ionic liquids are estimated by following formula which introduces empirical parameters to reduce calculation errors.

$$\text{density} = \mathrm{a}\left[\alpha \frac{M}{V_m} + \beta\left(\frac{V_s^+}{A_s^+}\right) + \gamma\left(\frac{V_s^-}{A_s^-}\right) + \delta\right]$$

where V_s^+ is the volume of a cation's surface which shows positive electrostatic potential, V_s^- is the volume of a anion's surface which shows negative electrostatic potential, A_s^+ is the average value of that cation's potential and A_s^- is the average value of that anion's potential. The α, β, γ, δ and a are constants.

d. Comprehensive evaluation criteria of the propellants

Based on the existing literature, we choose 13 representative liquid propellant fuels that are widely used and studied. Their comprehensive behaviours are evaluated from the following aspects.

1.Toxicity: Doses leading to acute toxicity to human or aquatic organisms. This parameter is closely related to the fuels' production and transportation. The toxicity data is comes from literature and MSDS tables.

2.Stability: Temperatures of the decomposition of the fuels. The stability data is from NIST.

3.Volatility: The saturated vapor pressure of the fuels at 298 K, 0.1 MPa. Volatility is closely related to the safety of the fuels in case of combustion and explosion. The source of fuels' volatility is NIST.

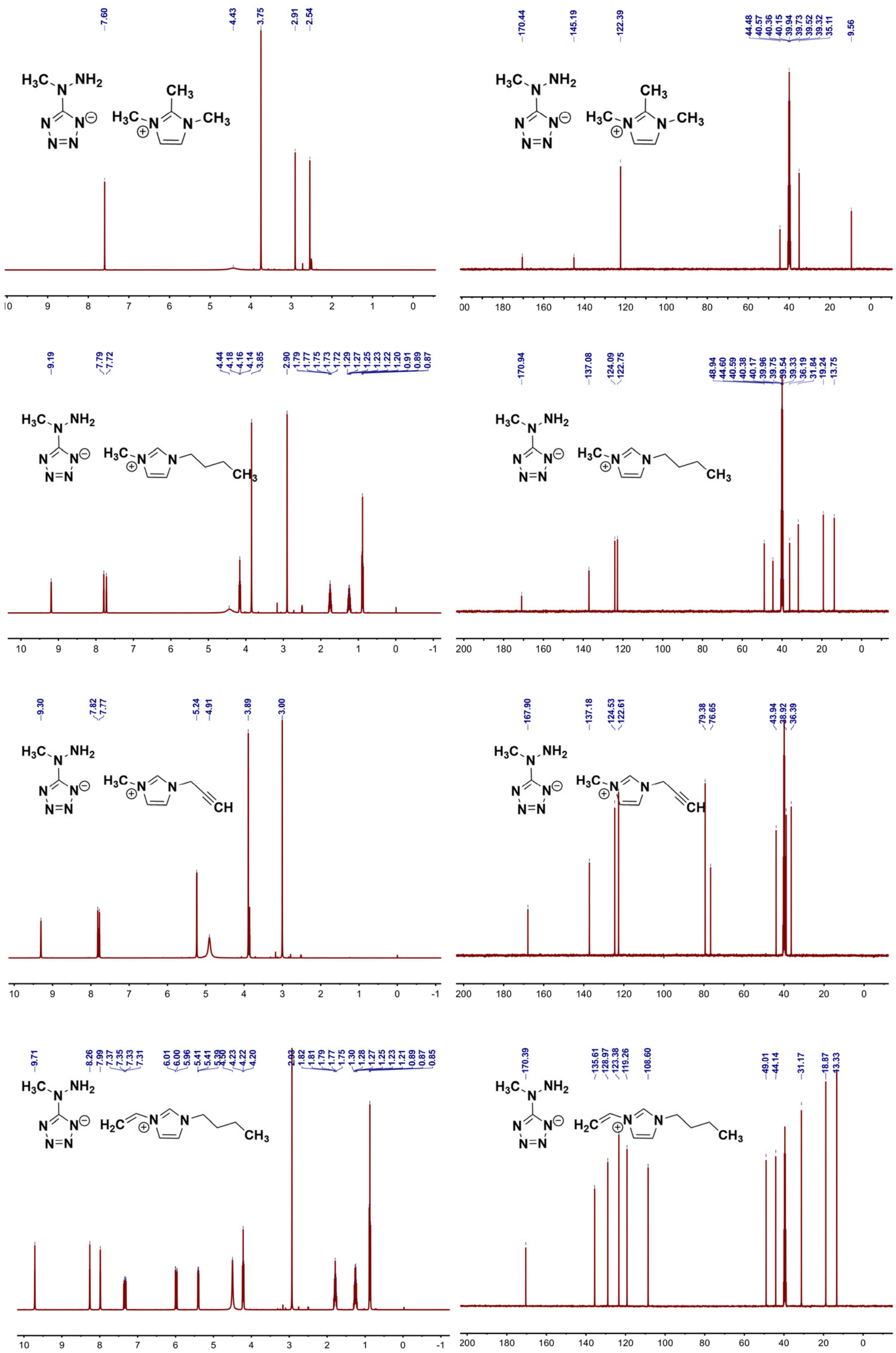
4.Ignition delay time: Hypergolic ability of the fuels which affects the structure and the cost of the rocket engine.

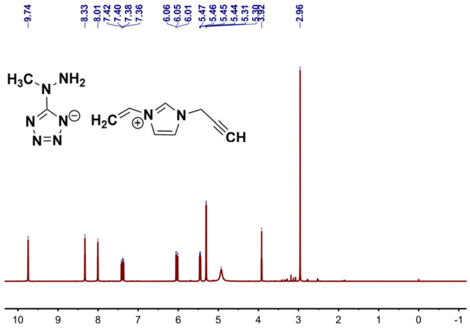
5.Energy density of the fuels: The total energy carried by rockets which determines the flight range of the rockets. The unit of energy density is kJ/kg.

e. Code for molecular screening program

Core code is uploaded on GitHub database https://github.com/whyx1993/smallmolecular for download.

Fig. S1. ^{1}H spectra (left) and ^{13}C spectra (right) of MHT ionic liquids.




9.74
8.33
8.01
7.42
7.40
7.38
7.36
6.06
6.05
6.01
5.47
5.46
5.45
5.44
5.31
5.30
3.92
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NH2
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N
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N
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CH
10 9 8 7 6 5 4 3 2 1 0 -1

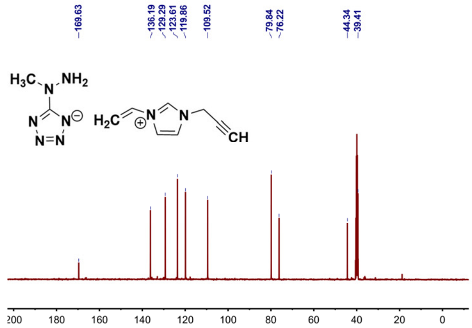

169.63
136.19
129.29
123.61
119.86
109.52
79.84
76.22
44.34
39.41
H3C
N
NH2
N
N
N
N
H2C
N
N
CH
200 180 160 140 120 100 80 60 40 20 0

Fig. S2. Spectra characterization of MHT ionic liquids. (A) IR spectra of MHT ionic liquids, (B, C) IR and Raman spectra of BmimMHT and BmimDCA ionic liquids with different ratios for homogeneity tests.

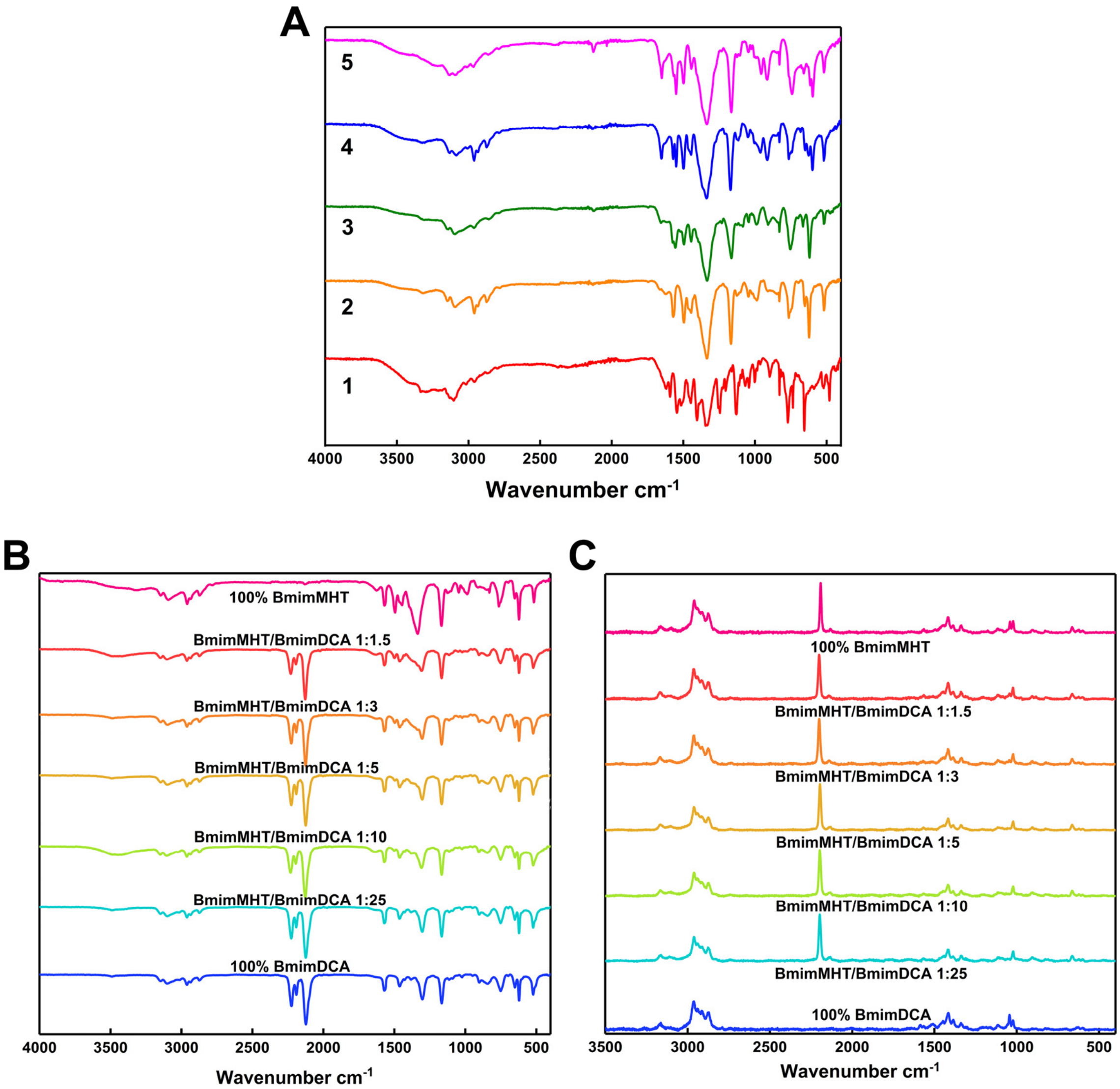


Fig. S3. Thermal evaluation of MHT ionic liquids by (A) DSC and (B) TGA analysis.

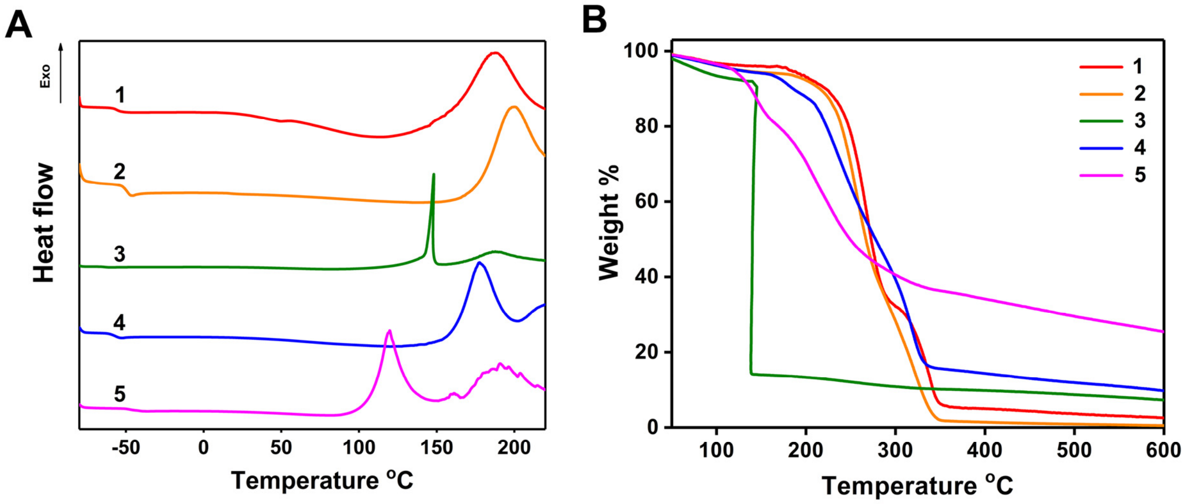


Fig. S4. Droplet test of BmimMHT/BmimDCA ionic liquids with a series of molar ratios.
Photo credit: Wen-Li Yuan, Sichuan University.

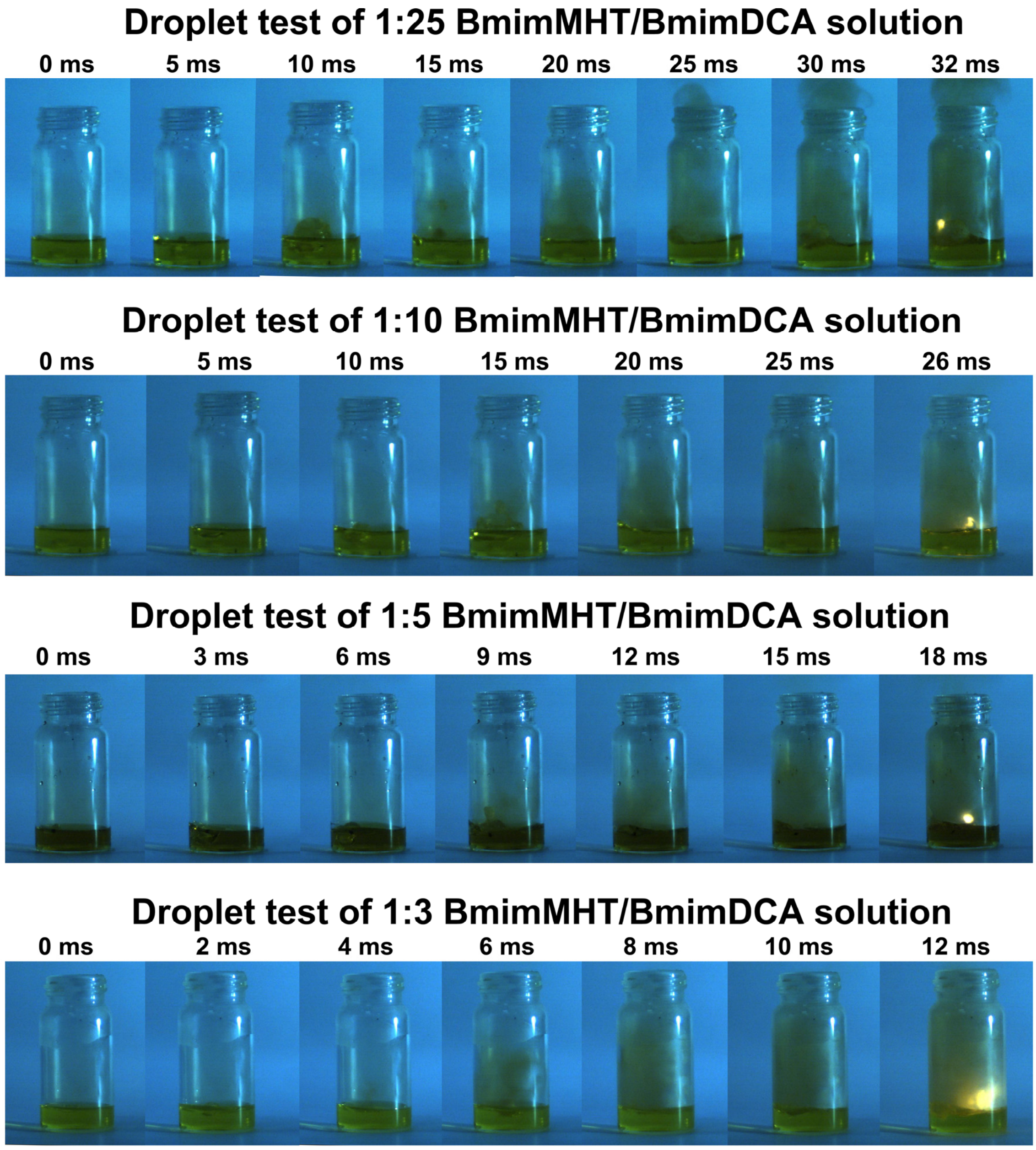
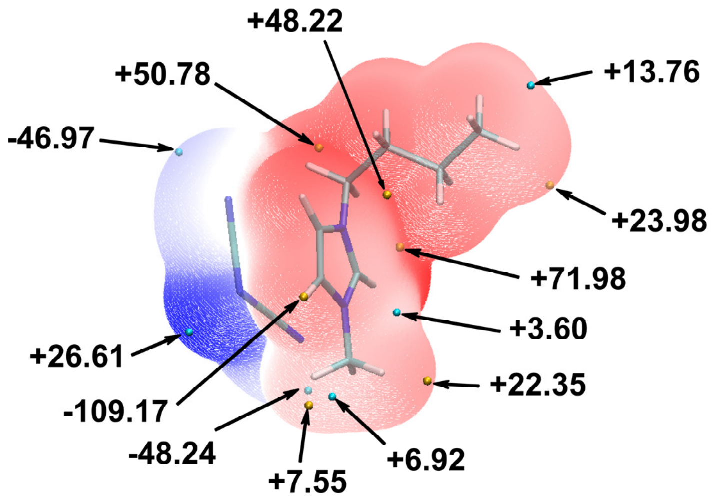
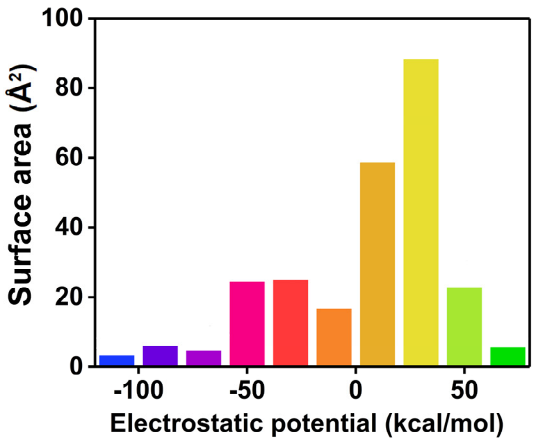


Fig. S5. Electrostatic potential of BmimDCA ionic liquid.





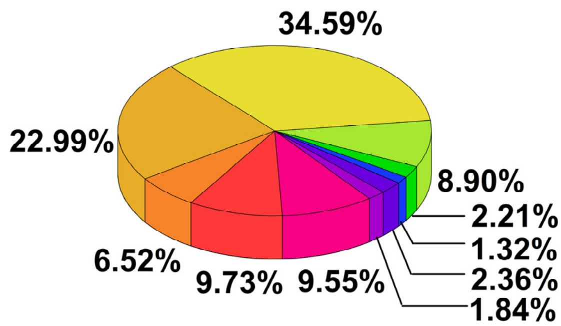


Table S1. Crystal data and structure refinement for the crystal 1.

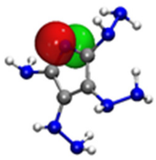
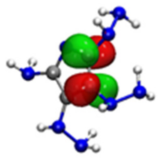
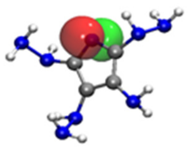
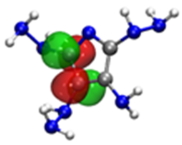
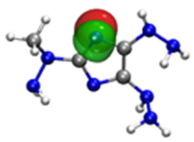
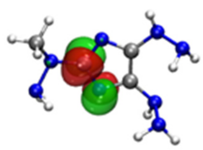
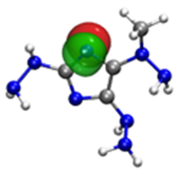
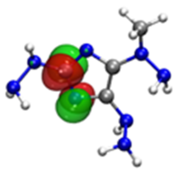
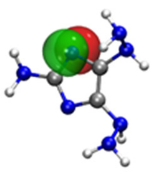
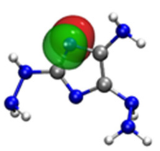
Crystal	C8H16N8
Formula weight/g mol^{-1}	224.29
T/K	293.28
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	7.70468(17)
b/Å	11.4875(2)
c/Å	12.9461(3)
α	90
β	96.4806(19)
γ	90
V/Å^3	1138.51(4)
Z	4
ρ/g cm^{-3}	1.309
μ/mm^{-1}	0.743
F(000)	480.0
$\lambda_{CuK\alpha}$/Å	1.54184
reflns	6122
R_{int} Independent reflections	0.0251
S on F^2	1.049
params	150
R_1 ($I > 2\sigma(I)$)^a	0.0544
wR_2 ($I > 2\sigma(I)$)^b	0.1538
R_1 (all data)^a	0.0597
wR_2 (all data)^b	0.1603
$\Delta\rho_{\text{min and max}}$/e Å^{-3}	-0.49

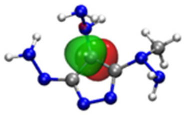
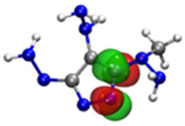
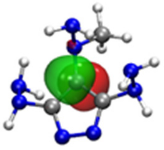
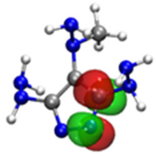
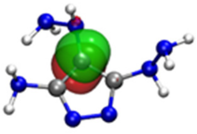
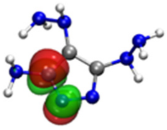
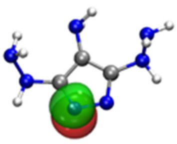
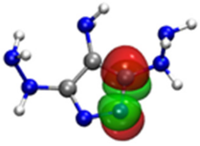
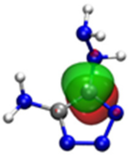
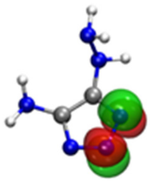
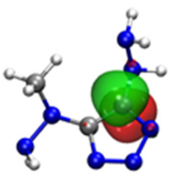
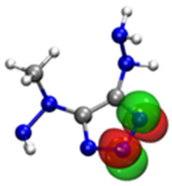
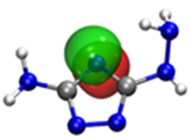
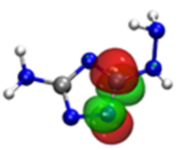
w=1/ [$\sigma^2(F_o^2) + (0.0460P)^2 + 0.23P$] P=(Max(F_o^2, 0) + 2F_c^2)/3

Table S2. Toxicity assessment of MMH, BmimMHT and BmimMHT/BmimDCA ionic liquids.

MMH		BmimMHT		BmimMHT/BmimDCA	
log C	Inhibition	log C	Inhibition	log C	Inhibition
0.82	-0.66	1.36	-1.29	2.04	-2.58
1.18	-0.51	1.64	-1.03	2.29	-1.84
1.55	-0.34	1.91	-0.65	2.54	-0.74
1.91	-0.05	2.18	0.14	2.73	-0.16
2.27	0.39	2.45	0.93	3.02	0.40
2.64	0.54	2.73	1.16	3.31	0.81
3.00	0.65	3.00	1.33	3.40	1.17

Table S3. Molecular orbitals, hypergolic reactivity and density prediction of screened anion molecules.

No.	HOMO	LUMO	Energy gap (eV)	Anion electrostatic potential	Anion Surface Area (Å^2)	Density (g/cm^3)
300	 **0.45 eV**	 **5.86 eV**	5.41/5.00	-83.44	209.22	1.19
301	 **0.51 eV**	 **5.99 eV**	5.48/5.06	-85.04	213.40	1.18
377	 **0.39 eV**	 **5.25 eV**	4.86/4.94	-85.24	210.15	1.20
378	 **0.39 eV**	 **5.30 eV**	4.91/4.94	-90.66	181.18	1.19
381	 **0.75 eV**	 **5.63 eV**	4.88/5.30	-85.51	209.53	1.20
382	 **0.76 eV**	 **5.64 eV**	4.88/5.31	-91.61	182.17	1.19

452	 **1.78 eV**	 **5.34 eV**	3.56/6.33	-85.95	206.11	1.20
453	 **1.84 eV**	 **5.42 eV**	3.58/6.39	-86.66	205.99	1.20
456	 **2.26 eV**	 **5.70 eV**	3.44/6.81	-93.85	179.39	1.19
457	 **0.86 eV**	 **5.71 eV**	4.85/5.41	-90.09	177.92	1.19
488	 **2.16 eV**	 **4.73 eV**	2.57/6.71	-101.36	146.00	1.22
490	 **1.84 eV**	 **4.33 eV**	2.49/6.39	-93.42	176.15	1.23
503	 **0.55 eV**	 **5.88 eV**	5.33/5.10	-99.67	146.39	1.23

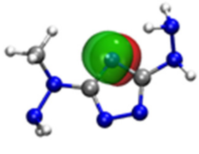
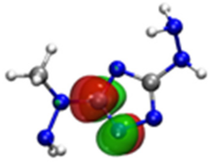
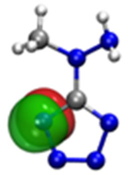
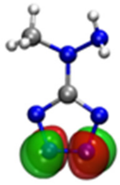
505	 **0.18 eV**	 **5.42 eV**	5.24/4.73	-91.13	179.24	1.23
510	 **0.15 eV**	 **4.46 eV**	4.31/4.70	-99.26	144.34	1.24

Table S4. Comprehensive evaluation criteria of the propellants.

Toxicity (mg/kg)		Stability (°C)	
Concentration	**Score**	**Temperature**	**Score**
5001-15000	5	> 201	5
501-5000	4	200-101	4
51-500	3	100-51	3
1-50	2	0-50	2
< 1	1	< 0	1
Volatility (kPa)		**Ignition delay time (ms)**	
Saturated vapor pressure	**Score**	**Time**	**Score**
Nonvolatile	5	< 5	5
< 10	4	5-10	4
11-200	3	10-50	3
201-1000	2	> 50	2
> 1001	1	Unhypergolic	1
Energy density (kJ/kg)			
Heat	**Score**		
>40000	5		
40000-30000	4		
30000-20000	3		
20000-10000	2		
<10000	1		

Table S5. Values of currently liquid propellants and MHT ionic liquids propellants.

	Toxicity	Stability	Volatility	ID time	Energy density
Kerosene	3	4	4	1	5
UDMH	2	2	3	5	3
Liquid H_2	5	1	1	1	2
Ethanol	5	2	4	1	3
Methanol	3	2	3	1	2
Liquid Methane	5	1	1	1	3
Hydrazine	1	2	4	5	2
Methyl hydrazine	2	2	4	5	3
Propane	5	1	1	1	3
Ethylene	5	1	1	1	2
Propylene	5	1	2	1	3
n-Butane	5	1	3	1	3
n-Pentane	5	2	3	1	4
BmimDCA	4	5	5	3	4
BmimDCA/BmimMHT	4	5	5	4	4