

Supplementary Information

Unlocking the Unrecognized Flammability of Deep Eutectic Solvents for Green Rocket Fuels

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1. Experimental details

Materials.

Choline chloride (ChCl, 99%), ethylene glycol (EG, 99.7%), cuprous chloride (CuCl, $\geq 99.95\%$), cupric chloride (CuCl₂, 99.99%), ferric chloride (FeCl₃, 99%), ferrous chloride (FeCl₂, 99.5%), zinc chloride (ZnCl₂, 99.95%), phenol (99.5%), methyltriphenylphosphonium bromide (Me(Ph)₃PBr, 98%), and 1-butyl-3-methylimidazolium chloride (BMIC, 98%) were purchased from Macklin. 3-Allyl-1-butylimidazolium chloride (ABIC) were synthesis according to the literature and dried under vacuum before use. ChCl and BMIC were recrystallized, filtered, and dried under vacuum before use. EG, CuCl, CuCl₂, FeCl₃, FeCl₂, ZnCl₂, and phenol were used as received.

Synthesis of new hybrid DESs.

As Choline chloride is hygroscopic, all DESs were prepared gravimetrically under nitrogen atmosphere to avoid the possible effect of moisture on the DESs' ignition performances. Conventional type I and type III DESs were synthesized following the previously reported procedure. Hybrid DESs were prepared by following two methods. Method 1: hybrid DESs could be simple prepared by mixing conventional type I DESs and type III DESs in a suitable molar ratio under nitrogen atmosphere, all DESs 1-8 were obtained for $\chi_{\text{type I DES}} = 0.10$ (i.e., 1 mole of type I DES per 9 mole of type III DES). Method 2: hybrid DESs can also be prepared by mixing four precursors of two types of DESs in corresponding molar ratio under nitrogen atmosphere and subsequent stirring under heating up 80 °C until a homogeneous liquid was formed. For example, DES 7 was obtained by mixing four solid compounds (ChCl, phenol, BMIC, and CuCl) in a more ratio of 9:27:1:1 under nitrogen at 80 °C (Supplementary Figure 2). The characterization of structure and properties show that hybrid DESs prepared by this method are the same with method 1.

Characterization of physical properties.

Thermal property measurements were performed on Netzsch DSC 214 Polyma at a heating rate of 10 °C·min⁻¹ from -150 °C to 25 °C for two cycles. Densities were measured on a Mettler Toledo Densito 30PX densimeter at 25 °C. Viscosity measurements were performed on a Brook field Rheometer DV3T at 25 °C.

Hypergolic drop tests.

The hypergolic properties were evaluated by a drop test, in which a single 5 μL liquid drop of 95% H₂O₂ was released from a fixed height of 3.5 cm using a 100 μL syringe into a vial containing about 0.3 mL of DESs. The hypergolic drop test was monitored using an Olympus i-speed 3 high-speed camera recording at 1000 frames/s. Each test was repeated three times and the ID time value was given as an average value of three times.

Synthesis of conventional Deep Eutectic Solvents (DESs). All DESs were prepared gravimetrically under nitrogen atmosphere. Metal contained type I DESs were synthesized following the previously reported procedure[1,2]. The general procedure including the mixing of imidazolium chloride salts (1-butyl-3-methylimidazolium chloride and 3-allyl-1-butylimidazolium chloride) and metal chloride (ZnCl₂, FeCl₃, FeCl₂, CuCl₂ and CuCl) with a suitable molar ratio and subsequent stirring at 80 °C

until a homogeneous liquid was formed. The composition details are summarized in Supplementary table 1.

Supplementary Table 1. Composition of used type I DESs

Entry	Type I DES	halide salt	metal chloride	halide salt: metal chloride ^a
1	BMIC-ZnCl ₂	1-butyl-3-methylimidazolium chloride	ZnCl ₂	1:1
2	BMIC-FeCl ₃	1-butyl-3-methylimidazolium chloride	FeCl ₃	1:1
3	BMIC-FeCl ₂	1-butyl-3-methylimidazolium chloride	FeCl ₂	3:2
4	BMIC-CuCl ₂	1-butyl-3-methylimidazolium chloride	CuCl ₂	1:1
5	BMIC-CuCl	1-butyl-3-methylimidazolium chloride	CuCl	1:1
6	ABIC-CuCl	3-allyl-1-butylimidazolium chloride	CuCl	1:1

[a] molar ratio

Type III DESs reline, ethaline, ChCl-phenol, and MeP(Ph)₃Br-EG were synthesized through a similar method of type I DESs by using quaternary ammonium salt (Choline chloride, recrystallization before use) and quaternary phosphate salt (methyltriphenylphosphonium bromide) to replace imidazolium chloride salts, and using hydrogen-bond donors (urea, ethylene glycol and phenol) to replace metal chloride. The composition details are summarized in Supplementary table 2.

Supplementary Table 2. Composition of used type III DESs.

Entry	Type III DES	halide salt	hydrogen-bond donor (HBD)	halide salt: HBD [a]
1	ethaline	Choline chloride	urea	1:2
2	reline	Choline chloride	ethylene glycol	1:2
3	ChCl-phenol	Choline chloride	phenol	1:3
4	MeP(Ph) ₃ Br-EG	methyltriphenylphosphonium bromide	ethylene glycol	1:4

[a] molar ratio

Synthesis of new hybrid DESs. Hybrid DESs were prepared by the following two methods (Supplementary figure 2). Method 1: hybrid DESs were prepared by mixing conventional type I DESs and type III DESs with a suitable molar ratio under nitrogen atmosphere, DESs **1-8** were obtained with $\chi_{\text{type I DES}} = 0.10$ (i.e., 1 mole of type I DES per 9 mole of type III DES). The composition details were summarized in Supplementary table 3, the chemical formula were shown in Supplementary figure 1. Method 2: hybrid DESs can also be prepared by mixing four precursors of two types

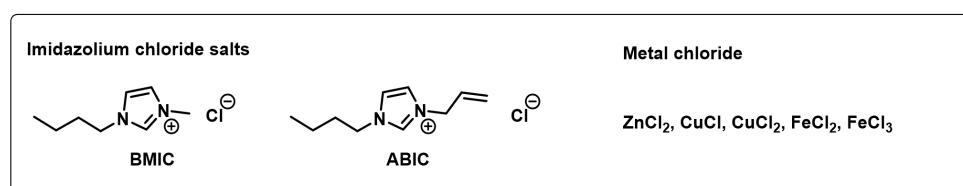
of DESs in corresponding molar ratio under nitrogen atmosphere and subsequent stirring at 80 °C until a homogeneous liquid was formed. In a typical experiment, DES 7 was obtained by mixing four solid compounds (ChCl, phenol, BMIC, and CuCl) in a molar ratio of 9:27:1:1 under nitrogen at 80 °C (Supplementary figure 2). The characterization of structure and properties revealed that hybrid DESs prepared by this method were the same with method 1.

Supplementary Table 3. Composition of prepared hybrid DESs.

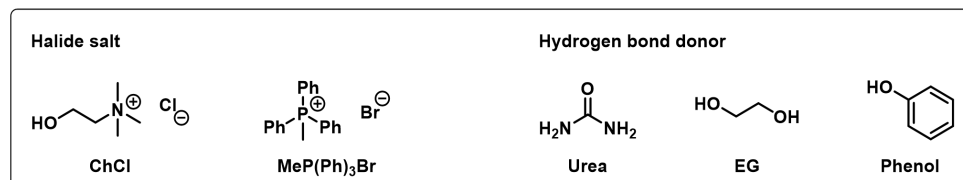
Entry	DESs	type I DES	type III DES	type I DES : type III DES ^[a]	$\chi_{\text{type I DES}}$ ^[b]
1	1	BMIC-ZnCl ₂	ethaline	1:9	0.1
2	2	BMIC-FeCl ₃	ethaline	1:9	0.1
3	3	BMIC-FeCl ₂	ethaline	1:9	0.1
4	4	BMIC-CuCl ₂	ethaline	1:9	0.1
5	5	BMIC-CuCl	ethaline	1:9	0.1
6	6	ABIC-CuCl	ethaline	1:9	0.1
7	7	BMIC-CuCl	ChCl-phenol-1:3	1:9	0.1
8	8	BMIC-CuCl	MeP(Ph) ₃ Br-EG-1:4	1:9	0.1

[a] Molar ratio; [b] $\chi_{\text{type I DES}} = (\text{the number of moles of type I DES}) / (\text{the total number of moles of type I DES and type III DES})$.

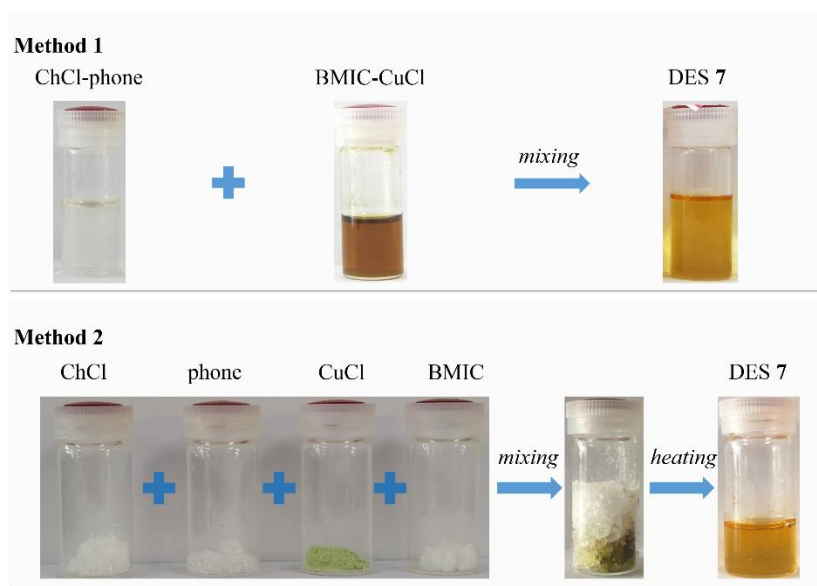
Type I DESs



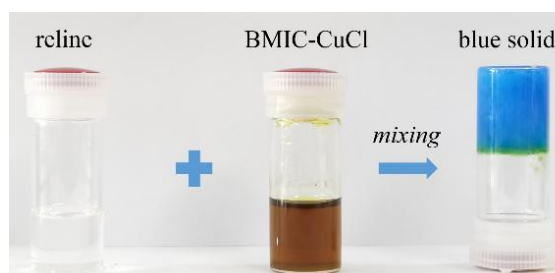
Type III DESs



Supplementary Figure 1. Chemical structures and abbreviations of raw materials forming DESs.



Supplementary Figure 2. Two method for the preparation of new hybrid DESs.

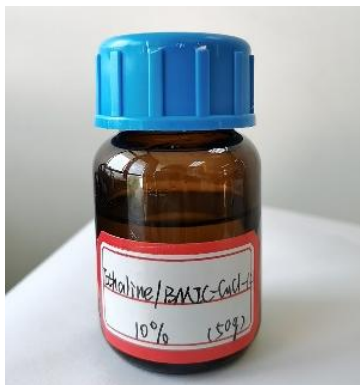


Supplementary Figure 3. Blue solid obtained by mix relinc and BMIC-CuCl.

In our initial attempt to prepare hybrid DESs, most popular type III DESs were investigated. When relinc, which was composed of Choline chloride and urea, was used prepare hybrid DESs by combination with BMIC-CuCl, the obtained material was liquid at 80 °C. However, when cooled to room temperature, the obtained material was blue solid. This is probably due to the presence of complexation between Cu(I) with urea.



Supplementary Figure 4. Digital photos of prepared hybrid DESs.



Supplementary Figure 5. 50 g scale-up hybrid DES **5** prepared by using method 2. This sample was prepared by mixing 23.73 g ChCl, 21.09 g EG, 3.29 g BMIC, and 1.87 g CuCl under nitrogen and stirred at 80 °C for 8 hours.

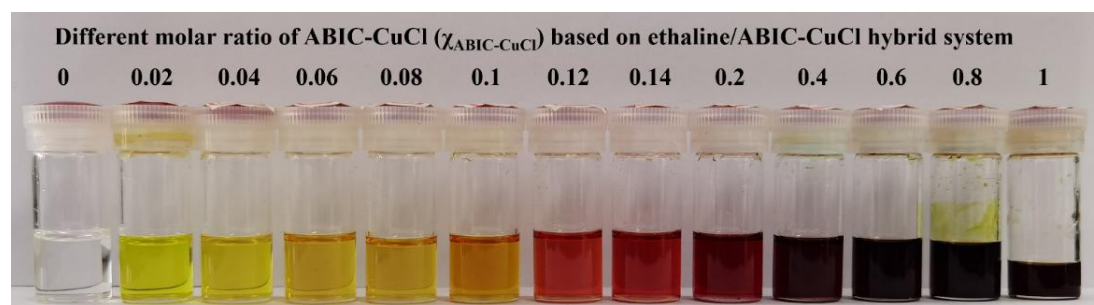
2. Ignition Details

Ignition experiments: The ignition delay (ID) times of new hybrid DESs were determined by using a standard drop tests, in which a droplet of 5 μL 95% H_2O_2 was released from a fixed height of 3.5 cm using a 100 μL syringe into a vial that containing 0.3 mL of hybrid DESs. The hypergolic droplet test was monitored using an Olympus i-speed 3 high-speed camera recording at 1000 frames/s. Each test was repeated three times and the ID time was given as an average value. The test results are summarized in Supplementary table 4.

Supplementary Table 4. The ignition details of new DESs.

Entry	DESs	Average ID time ^[a] (ms)	Drop test ^[b] (ms)		
			1 st	2 nd	3 rd
1	1	-	-	-	-
2	2	-	-	-	-
3	3	897	729	1054	908
4	4	188	198	177	190
5	5	41	38	40	45
6	6	36	39	37	33
7	7	76	74	77	78
8	8	156	168	145	154

[a] Ignition delay time of DESs with 95% H_2O_2 in drop test. [b] Each sample was test three times.



Supplementary Figure 6. The images of Hybrid DESs with different $\chi_{\text{ABIC-CuCl}}$ composed from ethaline and ABIC-CuCl.

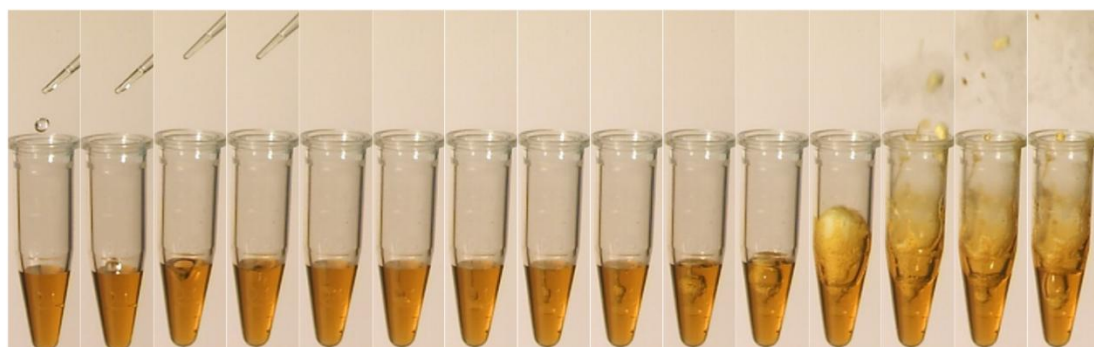
To investigate the effect of metal-containing components on the hypergolic performance of hybrid DESs with 95% H_2O_2 , a series of DESs with different $\chi_{\text{ABIC-CuCl}}$ based on ethaline/ABIC-CuCl hybrid system were prepared. The ignition test results are summarized in Supplementary table 5. The $\chi_{\text{ABIC-CuCl}}$ were ranged from 0 to 1, when $\chi_{\text{ABIC-CuCl}} \leq 0.02$, the hypergolic ignition did not happen. The lowest value of $\chi_{\text{ABIC-CuCl}}$ for effective auto-ignition is 0.04, the corresponding Cu content is 0.96% (wt) and ID time is 114 millisecond. The ignition can be realized effectively in the range of $\chi_{\text{ABIC-CuCl}} = 0.04$ to 0.6, an impressive average ID time of 9 ms was obtained at $\chi_{\text{ABIC-CuCl}} = 0.6$. When $\chi_{\text{ABIC-CuCl}}$ was further increased to ≥ 0.8 , only violent reactions occurred, but no hypergolic ignition was observed.

Supplementary Table 5. The effect of metal-containing components on hypergolic activity of hybrid DESs.

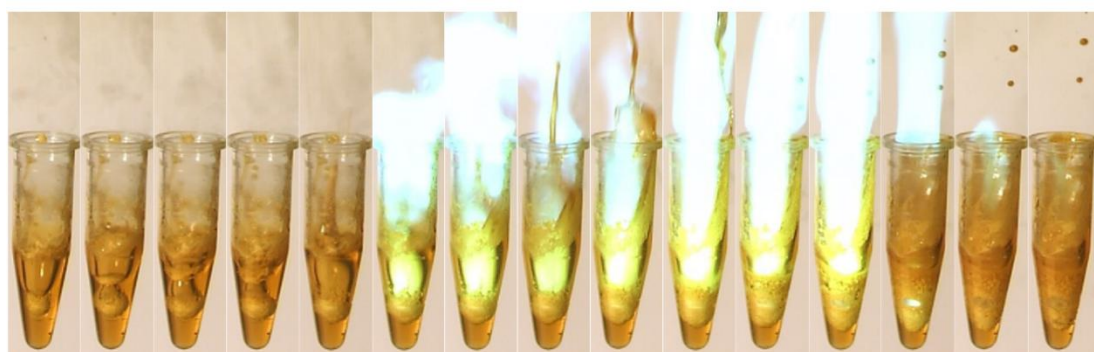
Entry	$\chi_{\text{ABIC-CuCl}}$ ^[a]	Cu wt (%) ^[b]	Average ID time ^[c] (ms)	Drop test ^[d] (ms)		
				1 st	2 nd	3 rd
1	0	0	-	-	-	-
2	0.02	0.48	-	-	-	-
3	0.04	0.96	114	113	118	110
4	0.06	1.43	75	90	63	73
5	0.08	1.91	50	49	50	52
6	0.10	2.38	36	39	37	33
7	0.12	2.84	27	27	25	28
8	0.14	3.31	24	25	24	24
9	0.2	4.69	18	20	16	17
10	0.4	9.14	13	14	12	13
11	0.6	13.36	9	10	8	9
12	0.8	17.38	-	-	-	-
13	1	21.2	-	-	-	-

[a] DESs of different $\chi_{\text{ABIC-CuCl}}$ based on ethaline/ABIC-CuCl hybrid system; [b] weight percent of Cu in DES; [c] ignition delay time of DES with 95% H₂O₂ in drop test; [d] each sample was test three times.

Auto-ignition process of drop tests. In order to show the difference in hypergolic behavior of prepared hybrid DESs more clearly, selected ignition process of hypergolic drop test are shown as follow:



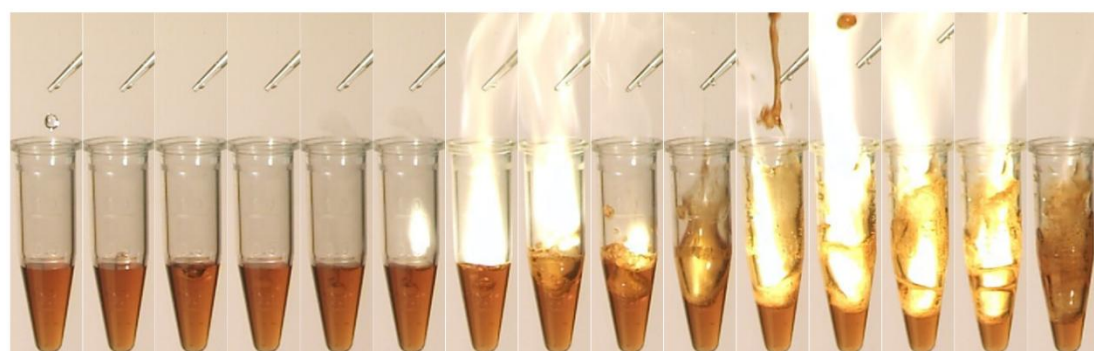
-50ms 0ms 10ms 20ms 200ms 400ms 500ms 600ms 620ms 633ms 640ms 650ms 660ms 670ms 680ms



690ms 700ms 710ms 720ms 728ms 729ms 731ms 733ms 740ms 750ms 760ms 770ms 775ms 780ms 790ms

Supplementary Figure 7. Details of drop test (1st test) for DES 3 (ethaline/BMIC-CuCl₂).

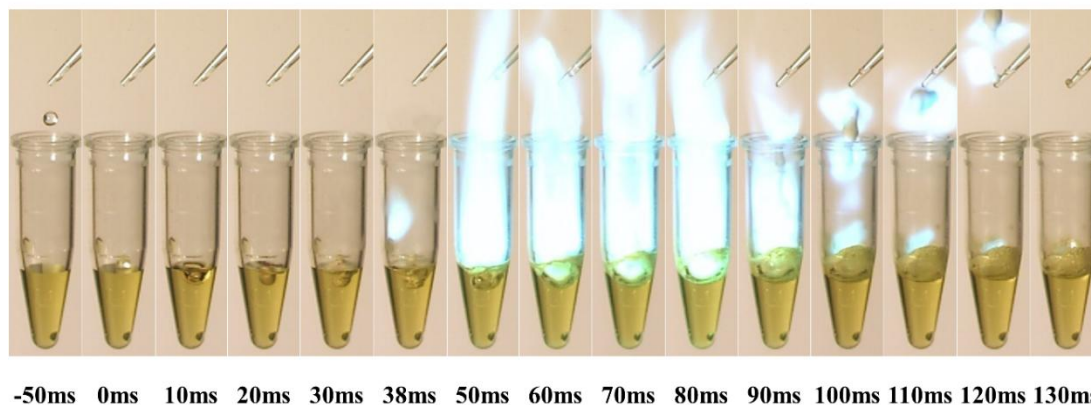
As shown in Supplementary figure 7, the H₂O₂ droplet contacted with DES 3 at 0 ms, and then sank into DES 3. At approximately 630 ms, visible bubbles and violent reaction was observed. Another 100 ms later, hypergolic ignition occurred (ID =729 ms) and the combustion sustained approximately 160 ms. The first observed flame is located near the bottom of vial.



-50ms 0ms 10ms 100ms 197ms 198ms 220ms 240ms 260ms 300ms 320ms 340ms 360ms 380ms 390ms

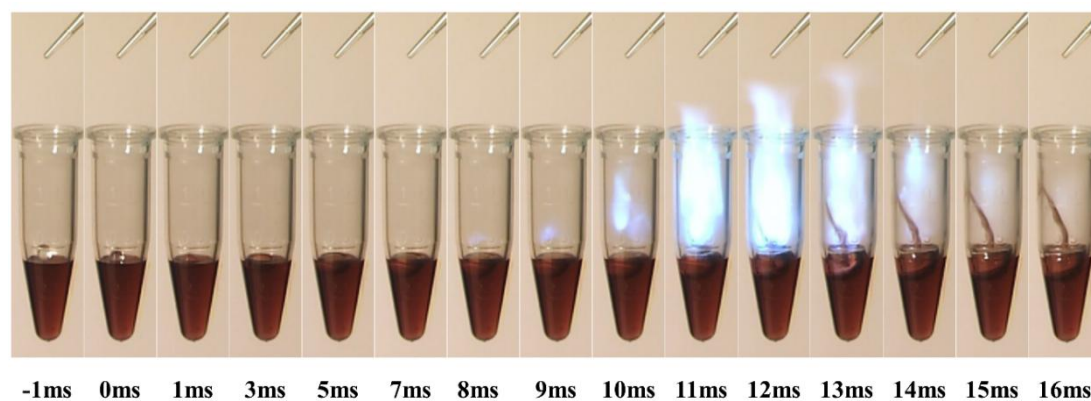
Supplementary Figure 8. Details of drop test (1st test) for DES 4 (ethaline/BMIC-FeCl₂).

In this drop test, the first flame was observed on the liquid surface and the ID time was 198 ms. At this time, the H₂O₂ droplet has sank into DES 4. Therefore, the combustion position was transferred from the surface of the fuel to the middle the fuel. The total combustion reaction sustained approximately 190 ms.



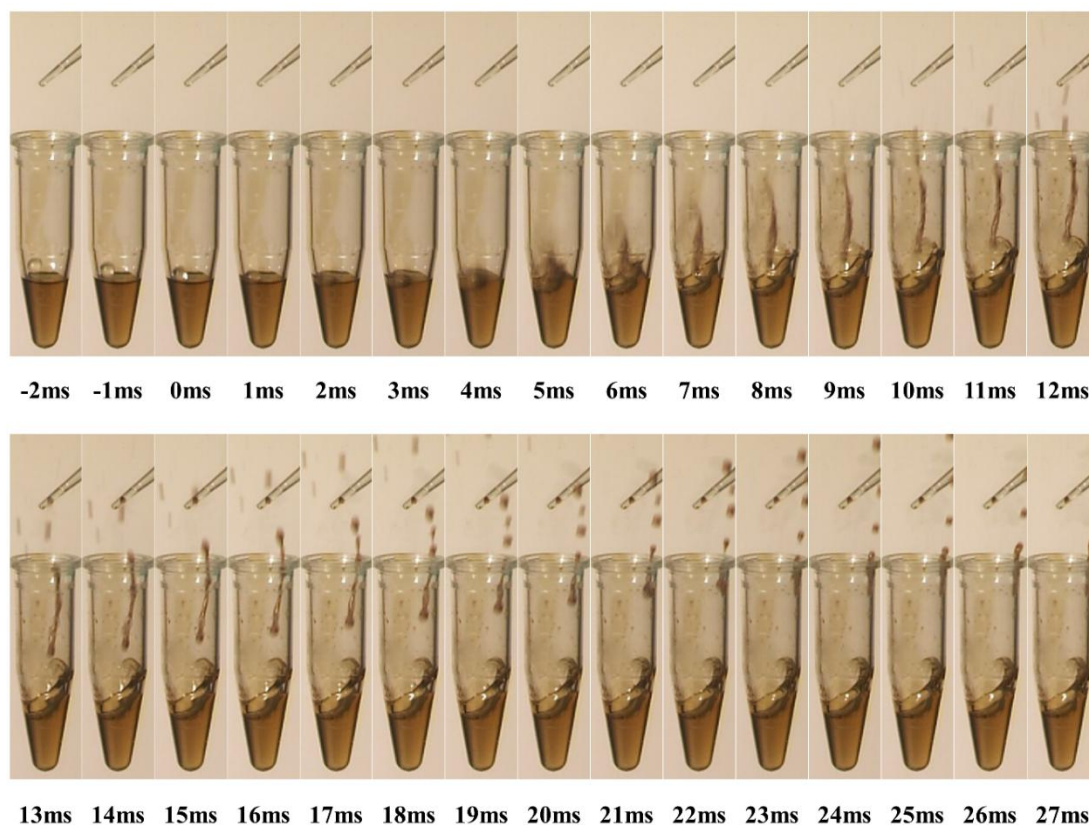
Supplementary Figure 9. Details of drop test (1st test) for DES 5 (ethaline/BMIC-CuCl).

The ID time of DES 5 with 95 % H₂O₂ is 38 ms. In this short time, the droplet of 95% H₂O₂ remained at the top of the fuel, and the formed flammable gasses were near the top surface of the fuel. Therefore, the combustion flame was observed at the surface of the fuel, and the total combustion time was about 90 ms.



Supplementary Figure 10. Details of drop test (2nd test) for hybrid DES ($\chi_{\text{ABIC-CuCl}} = 0.6$) based on ethaline/ABIC-CuCl.

This hybrid DES had ultrafast auto-ignition delay with 95% H₂O₂, the ID time was shorten to 9 ms. At this shorten time, the droplet of 95% H₂O₂ remained at the top of the fuel. Therefore, the combustion flame was observed on the surface of the fuel. The combustion flame sustained about 9 ms.

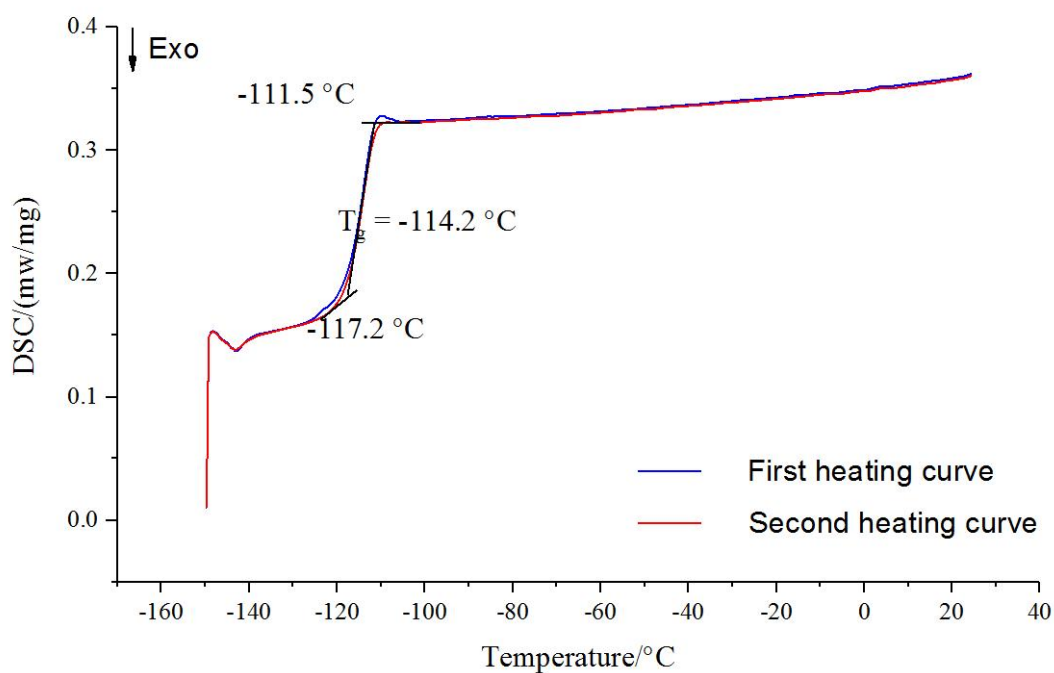


Supplementary Figure 11. Details of drop test for pure BMIC-CuCl.

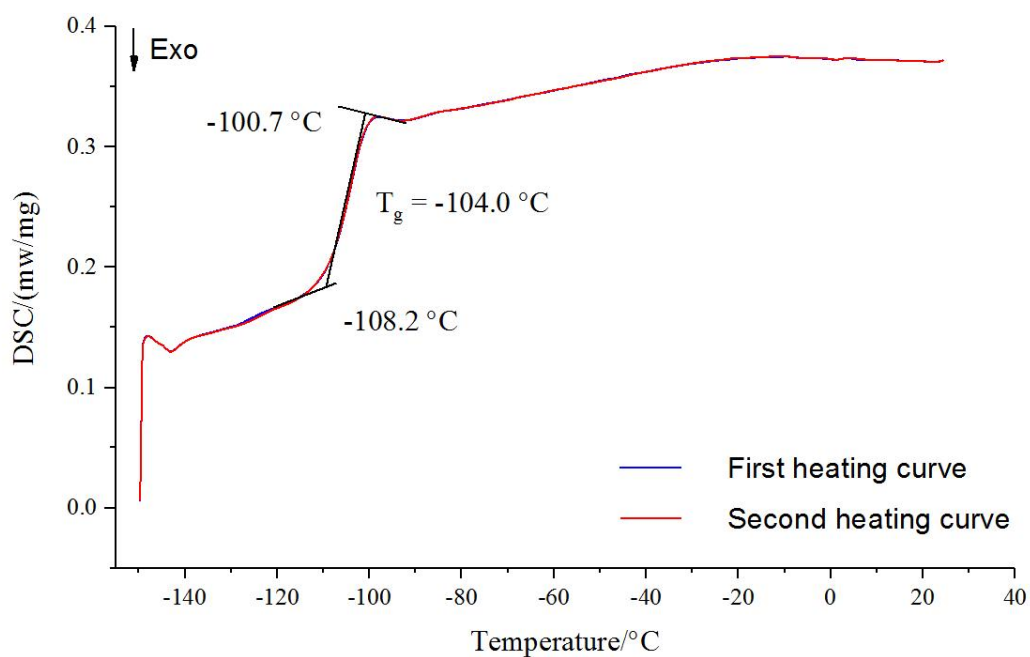
As shown in Supplementary figure 11, a violent reaction was observed as soon as the contact of BMIC-CuCl and 95% H_2O_2 . The droplet of 95% H_2O_2 cannot sink into the BMIC-CuCl fuel, instead the droplet was expelled and splash out by the gaseous products rapidly generated by the decomposition of H_2O_2 in a short time of less than 10 ms, thus leading to the separation of oxidizer and fuel. As a result, the hypergolic ignition behavior did not happen.

3. Differential Scanning Calorimetry (DSC)

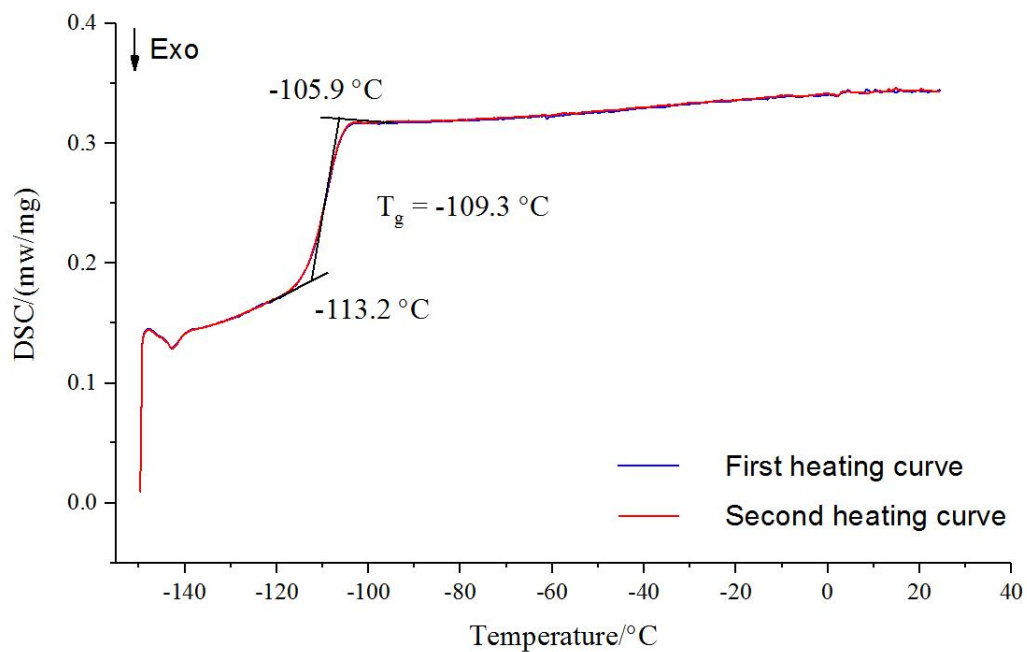
The DSC performed on Netzsch DSC 214 Polyma at a heating rate of $10^{\circ}\text{C min}^{-1}$ from -150°C to 25°C for two cycles.



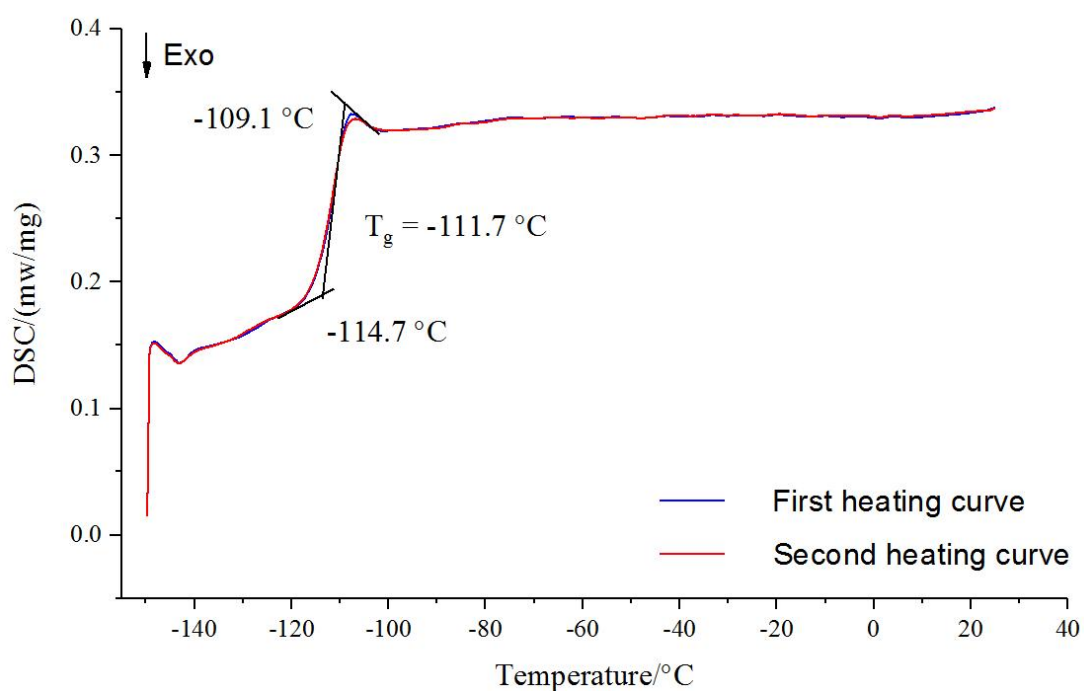
Supplementary Figure 12. DSC curve for DES 1.



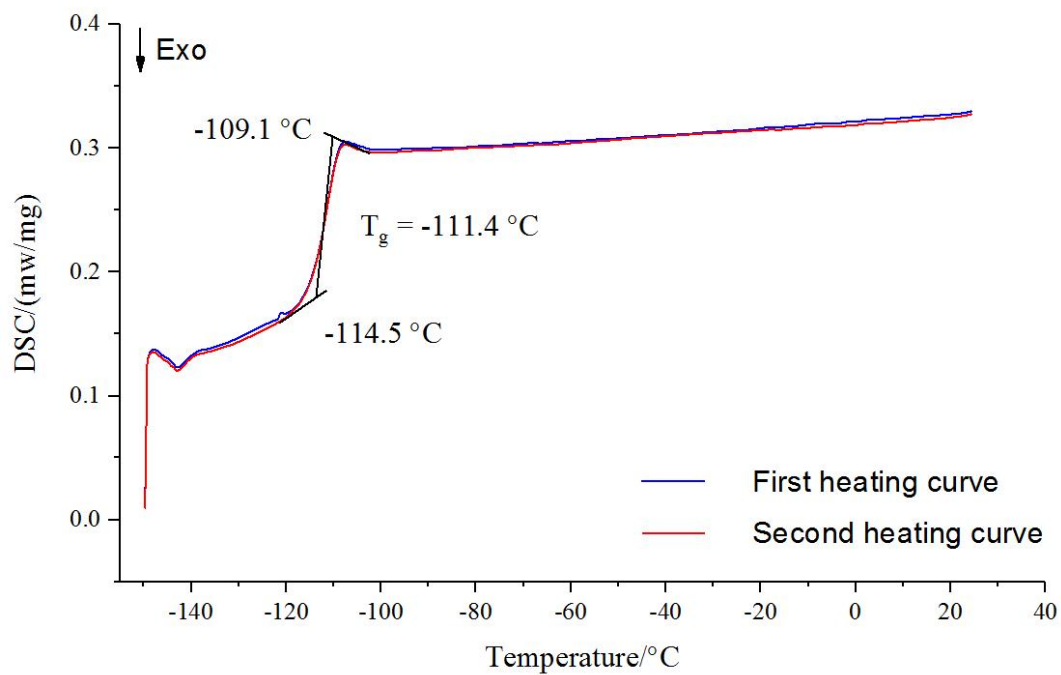
Supplementary Figure 13. DSC curve for DES 2.



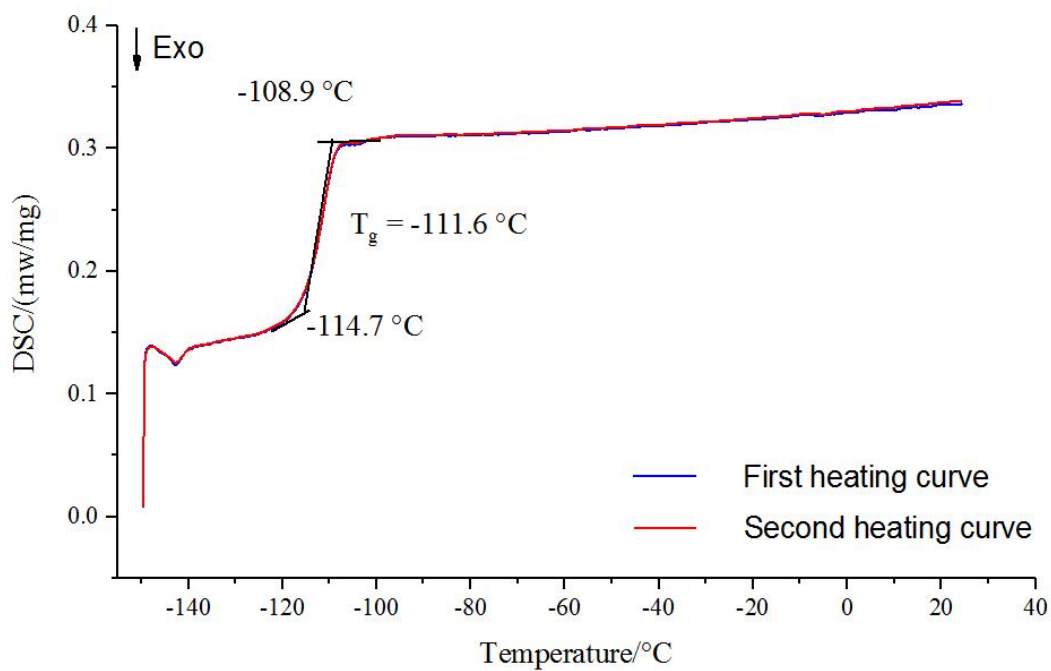
Supplementary Figure 14. DSC curve for DES 3.



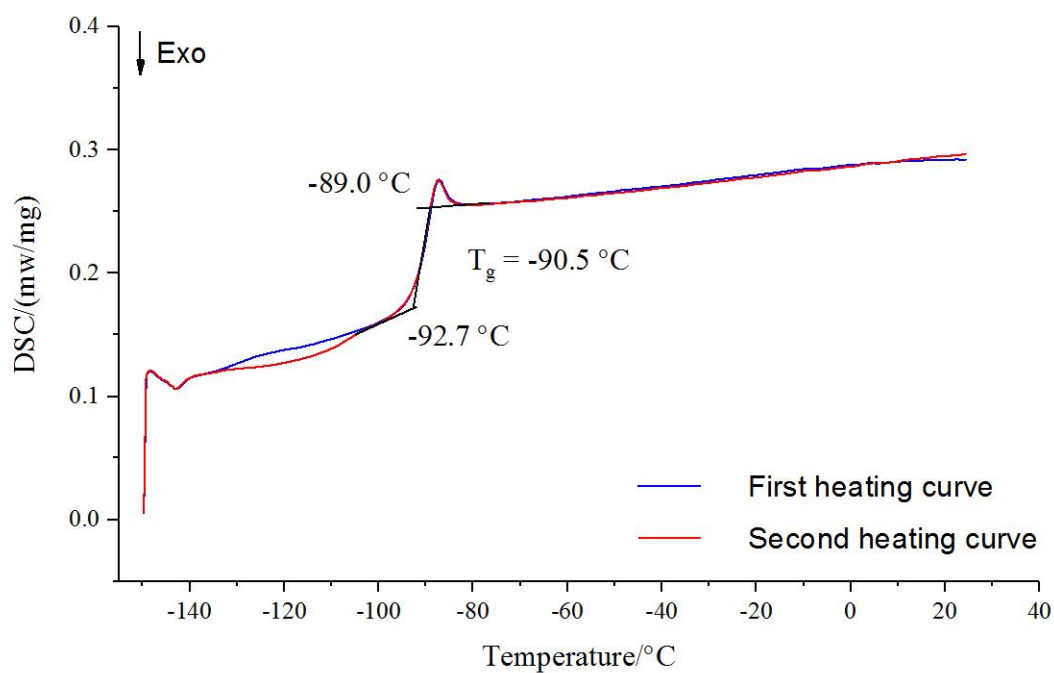
Supplementary Figure 15. DSC curve for DES 4.



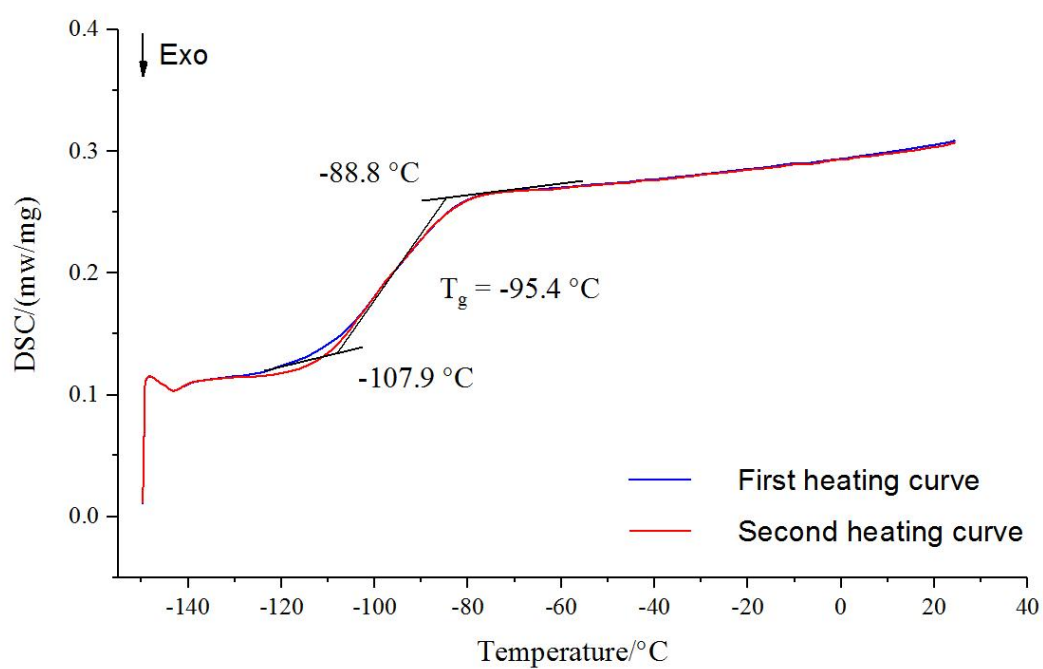
Supplementary Figure 16. DSC curve for DES 5.



Supplementary Figure 17. DSC curve for DES 6.



Supplementary Figure 18. DSC curve for DES 7.



Supplementary Figure 19. DSC curve for DES 8.

4. Abbreviations

ChCl: Choline chloride

EG: ethylene glycol

Me(Ph)₃PBr: methyltriphenylphosphonium bromide

BMIC: 1-butyl-3-methylimidazolium chloride

ABIC: 3-allyl-1-butylimidazolium chloride

Ethaline: a deep eutectic mixture of Choline chloride and ethylene glycol in a molar ratio of 1:2

Reline: a deep eutectic mixture of Choline chloride and urea in a molar ratio of 1:2

ChCl-phenol: a deep eutectic mixture of Choline chloride and phenol in a molar ratio of 1:3

MeP(Ph)₃Br-EG: a deep eutectic mixture of methyltriphenylphosphonium bromide and ethylene glycol in a molar ratio of 1:4

BMIC-ZnCl₂: a deep eutectic mixture of 1-butyl-3-methylimidazolium chloride and ZnCl₂ in a molar ratio of 1:1

BMIC-FeCl₃: a deep eutectic mixture of 1-butyl-3-methylimidazolium chloride and FeCl₃ in a molar ratio of 1:1

BMIC-FeCl₂: a deep eutectic mixture of 1-butyl-3-methylimidazolium chloride and FeCl₂ in a molar ratio of 3:2

BMIC-CuCl₂: a deep eutectic mixture of 1-butyl-3-methylimidazolium chloride and CuCl₂ in a molar ratio of 1:1

BMIC-CuCl: a deep eutectic mixture of 1-butyl-3-methylimidazolium chloride and CuCl in a molar ratio of 1:1

ABIC-CuCl: a deep eutectic mixture of 3-allyl-1-butylimidazolium chloride and CuCl in a molar ratio of 1:1

5. Supplementary References

- [1] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of Choline chloride/urea mixtures, *Chem. Commun.* (2003) 70–71. <https://doi.org/10.1039/B210714G>.
- [2] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids, *J. Am. Chem. Soc.* 126 (2004) 9142–9147. <https://doi.org/10.1021/ja048266j>.