

## Supplementary Information

### Bicyclic ammonium ionic liquids as dense hypergolic fuels

Yutao Yuan,<sup>a,b</sup> Yanqiang Zhang,<sup>a\*</sup> Long Liu, Nianming Jiao,<sup>a,b</sup> Kun Dong,<sup>a</sup> Suojian Zhang<sup>a\*</sup>

<sup>a</sup> Division of Ionic Liquids and Green Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China. E-mail:  
yqzhang@ipe.ac.cn, sjzhang@ipe.ac.cn; FAX: +86-10-82544875

<sup>b</sup> School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

### Contents

**Table S1.** Bond lengths [Å] for **15b**

**Table S2.** Bond angles [°] for **15b**

**Table S3.** Torsion angles [°] for **15b**

**Scheme S1.** Isodesmic reactions for calculating the heat of ABCO-based cations

**Scheme S2.** Isodesmic reactions for calculating the heat of DABCO-based cations

**Figure S1.** DSC curves of **12b** and **15a**

**Figure S2.** Ignition delay times recorded by a high-speed camera (1000 frames s<sup>-1</sup>) of DABCO-based ionic liquids

**Figure S3.** Ignition delay times recorded by a high-speed camera (1000 frames s<sup>-1</sup>) of ABCO-based ionic liquids

**Table S1.** Bond lengths [ $\text{\AA}$ ] for **15b**

N (2) – C (7)	1.500(2)
N (2) – C (5)	1.512(2)
N (2) – C (3)	1.514(2)
N (2) – C (1)	1.514(2)
C (7) – C (8)	1.468(3)
C (4) – C (3)	1.535(3)
C (5) – C (6)	1.542(3)
N (3) – C (8)	1.144(3)
C (1) – C (2)	1.540(3)
C (10) – N (6)	1.160(3)
C (10) – N (4)	1.320(3)
C (9) – N (5)	1.160(3)
C (9) – N (4)	1.309(3)

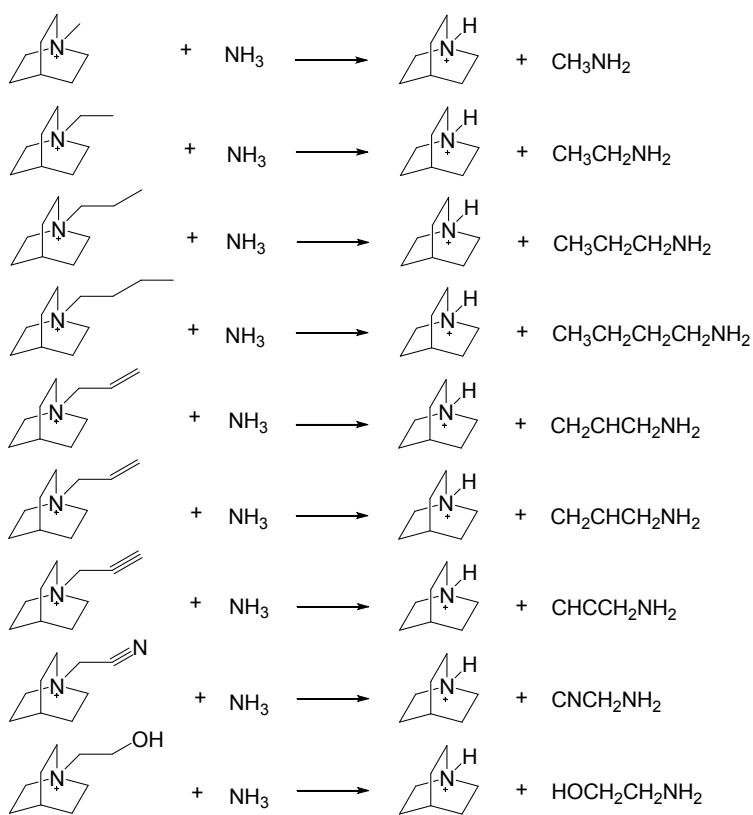
**Table S2.** Bond angles [ $^\circ$ ] for **15b**<sup>a</sup>

N (1) – C (4) – C (3)	111.72(15)
N (2) – C (5) – C (6)	107.92(15)
N (2) – C (3) – C (4)	108.36(15)
N (1) – C (6) – C (5)	111.90(15)
N (2) – C (1) – C (2)	108.36(14)
N (3) – C (8) – C (7)	179.8(2)
N (1) – C (2) – C (1)	111.46(15)
N (6) – C (10) – N (4)	173.5(2)
N (5) – C (9) – N (4)	173.3(2)
C (9) – N (4) – C (10)	119.94(17)
C (6) – N (1) – C (4)	108.68(15)
C (2) – N (1) – C (4)	109.14(15)
C (2) – N (1) – C (6)	108.25(15)
C (7) – N (2) – C (5)	110.71(14)
C (7) – N (2) – C (3)	111.09(14)
C (7) – N (2) – C (1)	108.49(14)
C (3) – N (2) – C (5)	108.90(14)
C (3) – N (2) – C (1)	109.16(15)
C (1) – N (2) – C (5)	108.43(15)
C (8) – C (7) – N (2)	111.44(15)

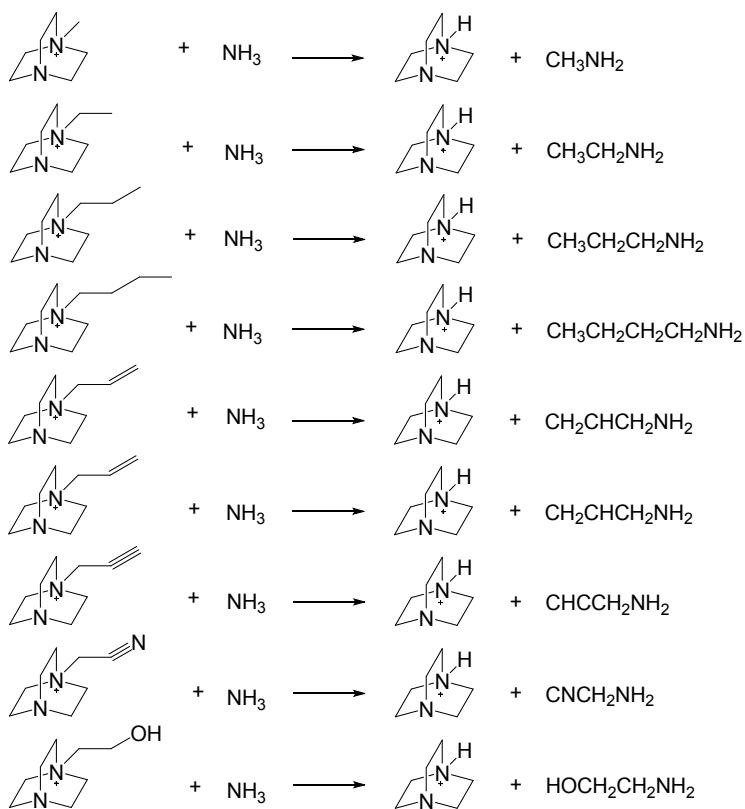
<sup>a</sup> Symmetry transformations used to generate equivalent atoms

**Table S3.** Torsion angles [°] for **15b**

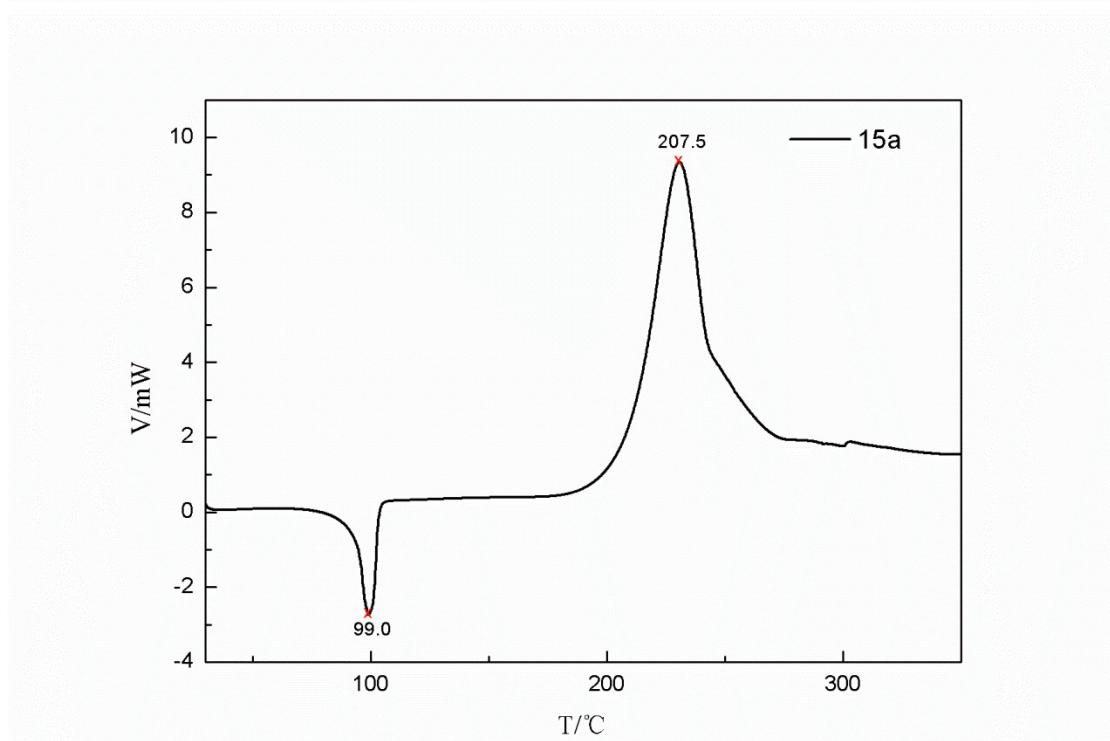
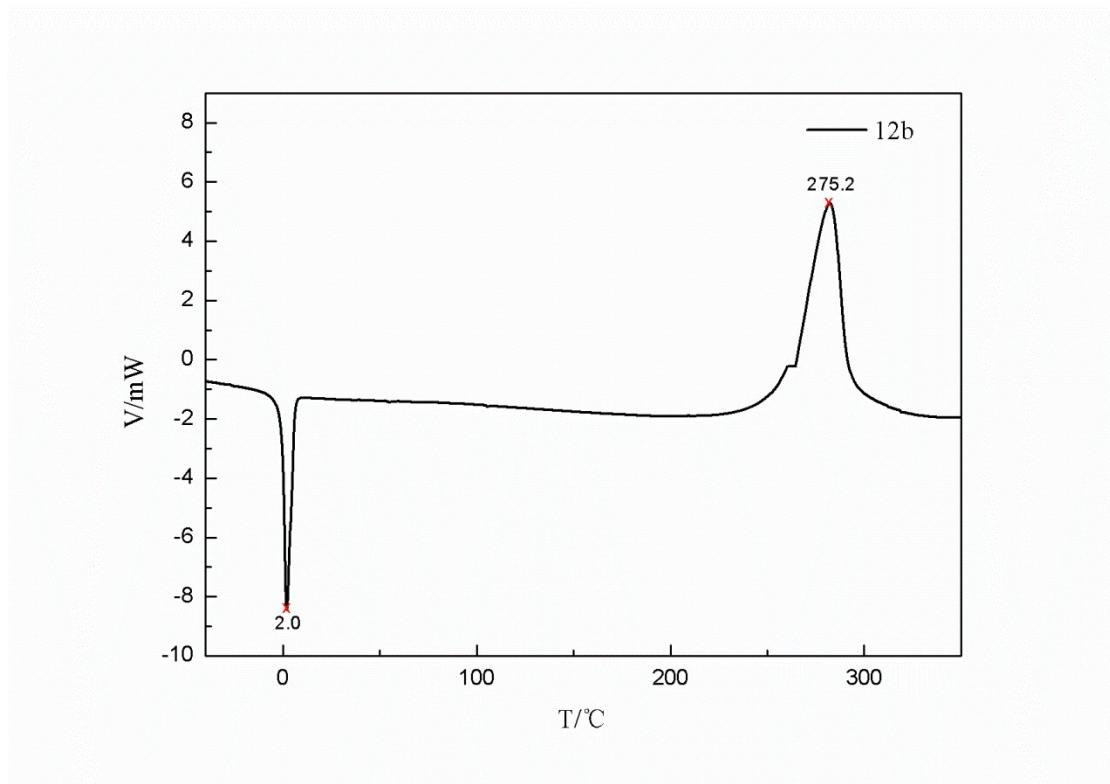
C (5) – N (2) – C (7) - C (8)	-65.5(2)
C (3) – N (2) – C (7) – C (8)	55.7(2)
C (1) – N (2) – C (7) – C (8)	175.58(17)
C (2) – N (1) – C (4) – C (3)	-54.8(2)
C (6) – N (1) – C (4) – C (3)	63.7(2)
C (7) – N (2) – C (5) – C (6)	-173.94(15)
C (3) – N (2) – C (5) – C (6)	63.6(2)
C (1) - N (2) - C (5) - C (6)	-55.0(2)
C (7) – N (2) – C (3) – C (4)	-177.35(16)
C (5) – N (2) – C (3) – C (4)	-55.1(2)
C (1) – N (2) – C (3) – C (4)	63.1(2)
N (1) – C (4) – C (3) – N (2)	-7.5(2)
C (2) – N (1) – C (6) – C (5)	64.4(2)
C (4) – N (1) – C (6) – C (5)	-54.6(2)
N (2) – C (5) – C (6) – N (1)	-7.7(2)
C (7) – N (2) – C (1) – C (2)	-175.79(17)
C (5) – N (2) – C (1) – C (2)	63.8(2)
C (3) – N (2) – C (1) – C (2)	-54.6(2)
N (2) – C (7) – C (8) – N (3)	-151(100)
C (6) – N (1) – C (2) – C (1)	-55.2(2)
C (4) – N (1) – C (2) – C (1)	63.6(2)
N (2) – C (1) – C (2) – N (1)	-7.5(2)
N (5) –C (9) – N (4) – C (10)	161.5(19)
N (6) – C (10) – N (4) – C (9)	-176(2)



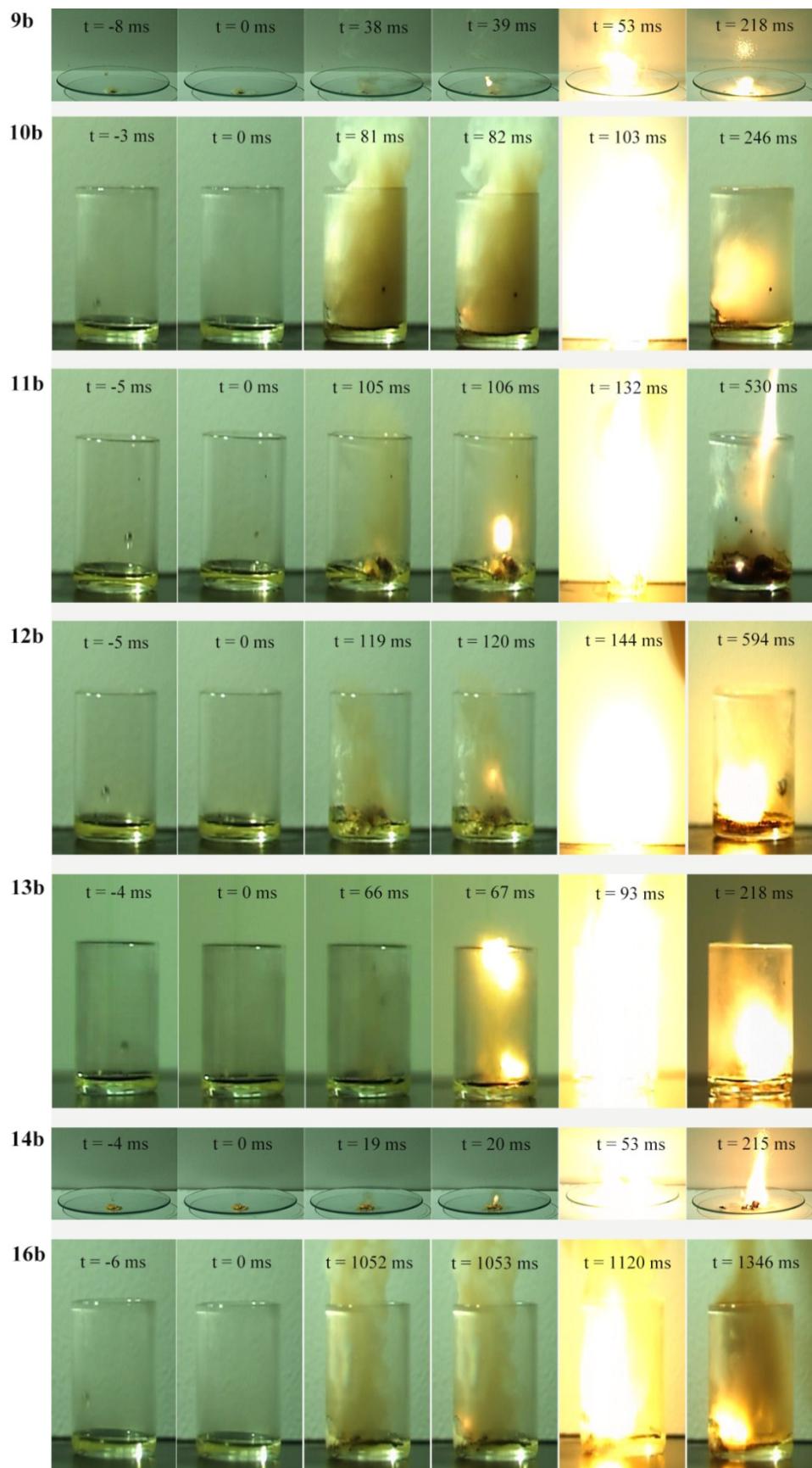
**Scheme S1.** Isodesmic reactions for calculating the heat of ABCO-based cations



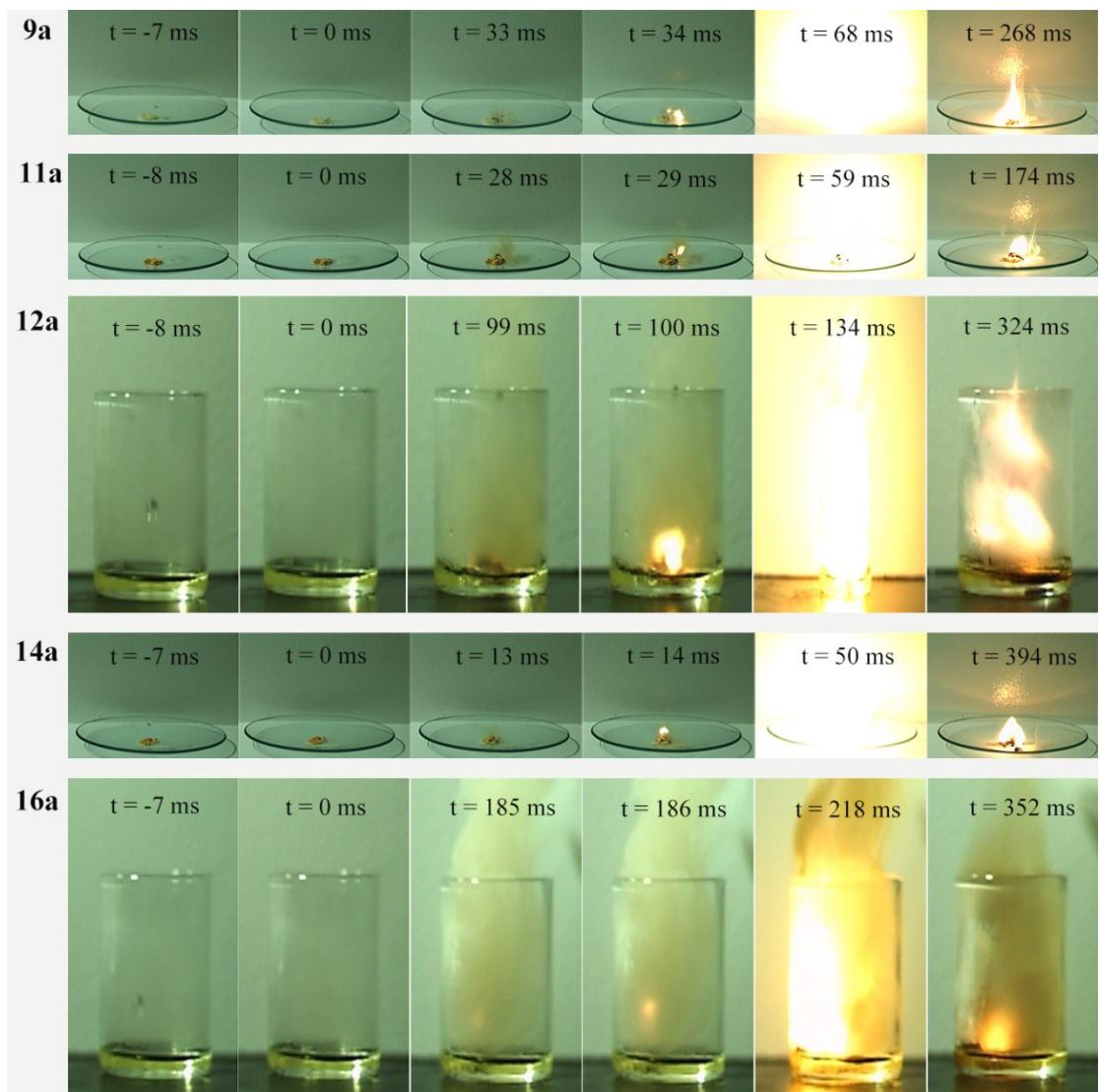
**Scheme S2.** Isodesmic reactions for calculating the heat of DABCO-based cations



**Figure S1.** DSC curves of **12b** and **15a**



**Figure S2.** Ignition delay times recorded by a high-speed camera ( $1000 \text{ frames s}^{-1}$ ) of DABCO-based ionic liquids



**Figure S3.** Ignition delay times recorded by a high-speed camera ( $1000 \text{ frames s}^{-1}$ ) of ABCO-based ionic liquids