# **Supplementary Information**

## Preorganized dual H-bond donor promotes benzoic acid active

### in polymerization of $\delta$ -valerolactone

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<sup>1</sup>H NMR and <sup>13</sup>C NMR of the 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD)



Figure S1. <sup>1</sup>H NMR spectrum of the 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) (400 MHz, DMSO).



Figure S2. <sup>13</sup>C NMR spectrum of the 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) (400 MHz, DMSO).

The first-order kinetics plots for poly-  $\delta$  -valerolactones (PVL) catalyzed by the ABTD with different carboxylic acid



Fig S3. The first-order kinetics plots for poly-  $\delta$  -valerolactones (PVL) catalyzed by ABTD/benzoic acid(BA)([ $\delta$ -VL]<sub>0</sub>/[ABTD]<sub>0</sub>/[ carboxulic acid]<sub>0</sub>/[BnOH]<sub>0</sub> =30:1:1:1, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) (red line), and by BA ([VL]<sub>0</sub>/[carboxulic acid]<sub>0</sub>/ [BnOH]<sub>0</sub> = 30:1:1, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) (black line).



Fig S4. The first-order kinetics plots for PVL catalyzed by ABTD/ p-Toluic acid(CH<sub>3</sub>-BA)( $[\delta$ -VL]<sub>0</sub>/[ABTD]<sub>0</sub>/[carboxulic acid]<sub>0</sub>/[BnOH]<sub>0</sub> = 30:1:1:1, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) (red line), and by CH3-BA ([VL]<sub>0</sub>/[carboxulic acid]<sub>0</sub>/ [BnOH]<sub>0</sub> = 30:1:1, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) (black line).



Fig S5. The first-order kinetics plots for PVL catalyzed by ABTD/4-fluorobenzoic acid (F-BA) ([VL]<sub>0</sub>/[ABTD]<sub>0</sub>/[carboxulic acid]<sub>0</sub>/[BnOH]<sub>0</sub> = 30:1:1:1, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) (red line), and by F-BA ([VL]<sub>0</sub>/[carboxulic acid]<sub>0</sub>/ [BnOH]<sub>0</sub> = 30:1:1, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) (black line).

#### Chemical shifts of carbonyl carbon of the VL in the <sup>13</sup>C NMR spectra



Fig S6. Chemical shifts of carbonyl carbon of the VL in the <sup>13</sup>C NMR spectra observed by the titration of BA in DMSO.



Fig S7. Chemical shifts of carbonyl carbon of the VL in the  $^{13}$ C NMR spectra observed by the titration of CH<sub>3</sub>-BA in DMSO.



Fig S8. Chemical shifts of carbonyl carbon of the VL in the  $^{13}$ C NMR spectra observed by the titration of F-BA in DMSO.

<sup>1</sup>H NMR of the PVL



Figure S9. <sup>1</sup>H NMR spectrum of the obtained PVL prepared at room temperature (400 MHz,  $CDCl_3$ ).