Supporting Information for:

CO_2-Responsive deep eutectic solvents for reversible emulsion phase separation

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Experimental Section

Materials: Imidazole (Im, ≥ 99%) and *n*-dodecane (99%) were purchased from J&K. Ethylene glycol (EG, >99%), glycerol (Gly, >99%), 1,4-butanediol (BDO, >99%), and polyethylene glycol 200 (PEG-200, >99%) were provided by Sinopharm Chemical Reagent Co., Ltd. Olive oil and peanut oil were purchased from the supermarket. Decyl ether (95%, GC) was supplied by TCI. N_2 (99.999%) and CO_2 (99.995%) were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd. All chemicals were used directly without further purification.

Instruments and Analytical methods: The IR spectra were obtained by coupling of the attenuated total reflection (ATR) equipment with the FT-IR spectrometer (Prestige 21, Shimadzu) in the range of 400 to 4000 cm^{-1}. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments, USA) system at a heating rate of 10 °C min^{-1}. All DESs were run in aluminium pans in a sealed furnace and were cooled to -120 ^oC before heating up to room temperature. The viscosity (η) of DESs was measured using an Anton Paar DMA 5000 M three times and the average value was reported. ^{13}C NMR spectra were analysed by Bruker Fourier 300 NMR spectrometer (300 MHz) with dimethyl

sulfoxide-D6 as the external standard because an internal reference may change the interaction between imidazole and HBDs. The data of ^{13}C NMR after CO_2 bubbling and removal was later processed by the MestReNova Program. The changes of electrical conductivities were measured by using a conductivity meter (DDS-307A, Shanghai INESA Scientific Instrument Co., Ltd, China) three times at 298.15 K. The emulsion morphologies prepared and phase separation were observed by laser scanning confocal microscopy. The water content in the synthesized DESs was determined by Karl Fisher (Coulometric KF Titrator C30).

The preparation of the imidazole-based DESs: The desired imidazole-based DESs were prepared by simply mixing imidazole and four HBDs in different molar ratio under room temperature. The ratio of imidazole and ethylene glycol/glycerol/ butanediol was 1:1, while the ratio was 2:1 for the DES formed between imidazole and polyethylene glycol 200. After being stirred at room temperature for 6 h, clear and transparent homogenous liquids could be observed. Finally, the obtained DESs were dried under vacuum at 50 ^oC with a time of 48 h to ensure low moisture content. All these DESs are stable at room temperature and reaction conditions. The obtained DESs were stored in a vacuum dryer.

The bubbling of CO_2 through the developed DESs: In a typical experiment, 2 mL imidazole-based DESs was loaded in the centrifuge tube (4 mL). First, CO_2 was used as the atmosphere at approximately 2-3 bubbles per second at room temperature for half an hour. Then, the sample was purged with N_2 again to release CO_2 at approximately 2-3 bubbles at room temperature. The samples were analysed by ATR FT-IR spectra and ^{13}C NMR spectra.

Phase separation of olive oil/DESs emulsion: The imidazole/EG DES (3 mL) and olive oil (1 mL) were loaded in 10 mL centrifuge tube, and oscillated the liquid mixture to form a homogeneous emulsion system, and the formed emulsion could be observed in the images of laser scanning confocal microscopy. Then, CO_2 was bubbled into the emulsion, and an obvious phase separation was observed by the bubbling of CO_2 for 30 minutes. Finally, the

emulsion would be re-formed after the removal of CO_2 by the bubbling of N_2 for 2 h.

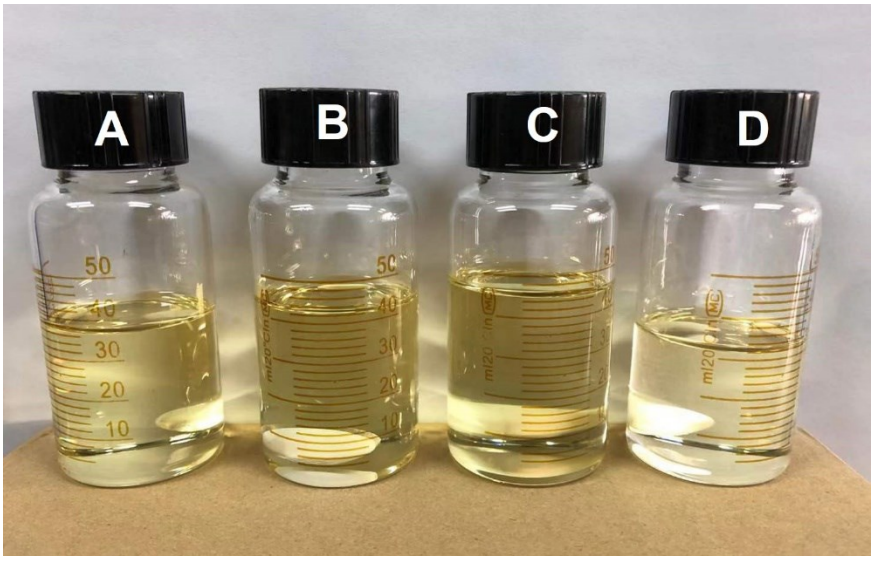

Fig. S1. Photo of the synthesized DESs. (A) imidazole/EG, (B) imidazole/Gly, (C) imidazole/BDO, and (D) imidazole/PEG-200.

Table S1. The moisture content in the synthesized DESs.

DES	Moisture content (mg/g)
imidazole/EG	2.635
imidazole/Gly	2.588
imidazole/BDO	2.403
imidazole/PEG-200	2.452

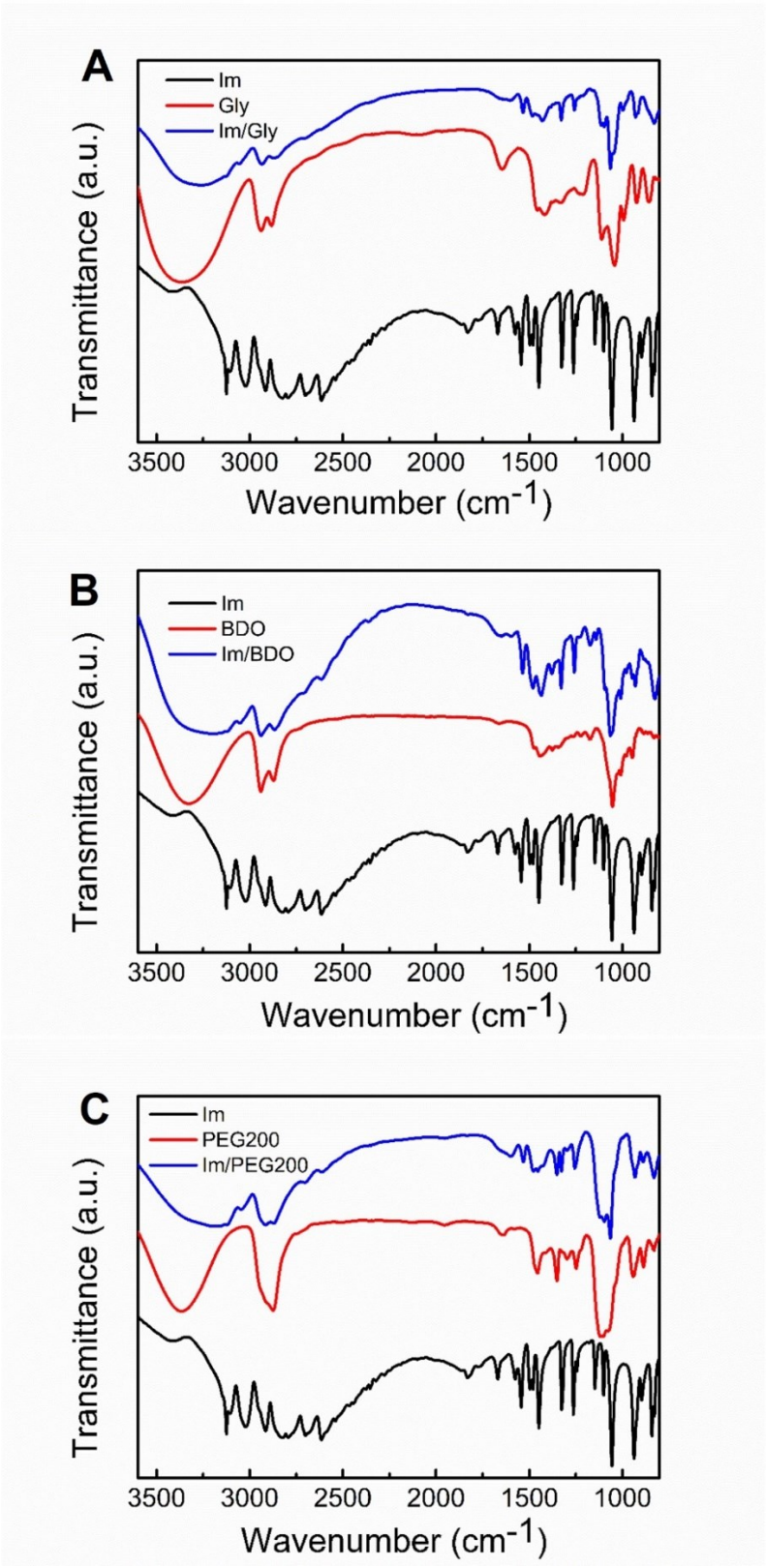

Fig S2. FT-IR spectra of imidazole and different HBDs. (A) imidazole/Gly, (B) imidazole/BDO, and (C) imidazole/PEG-200.

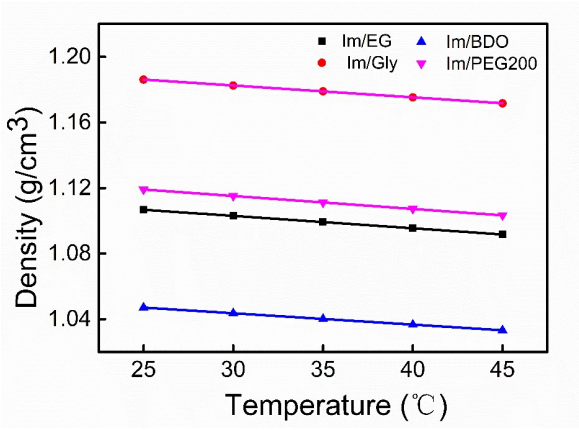

Fig. S3. The densities of all the prepared imidazole-based DESs.

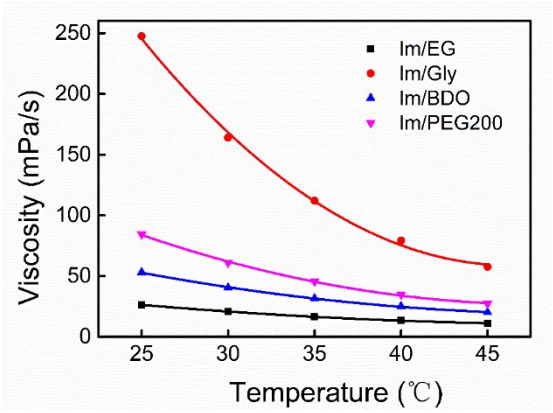

Fig. S4. The viscosities of all the prepared imidazole-based DESs.

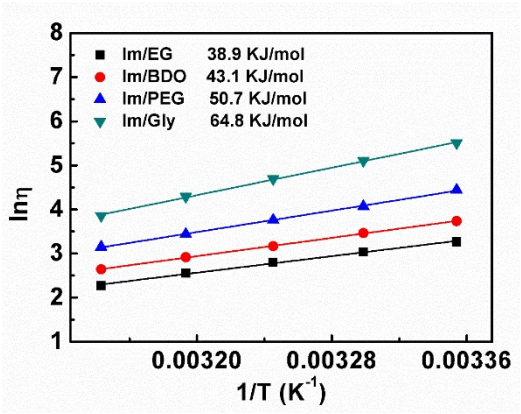

Fig. S5. The viscous flow activation energy of all the prepared imidazole-based DESs.

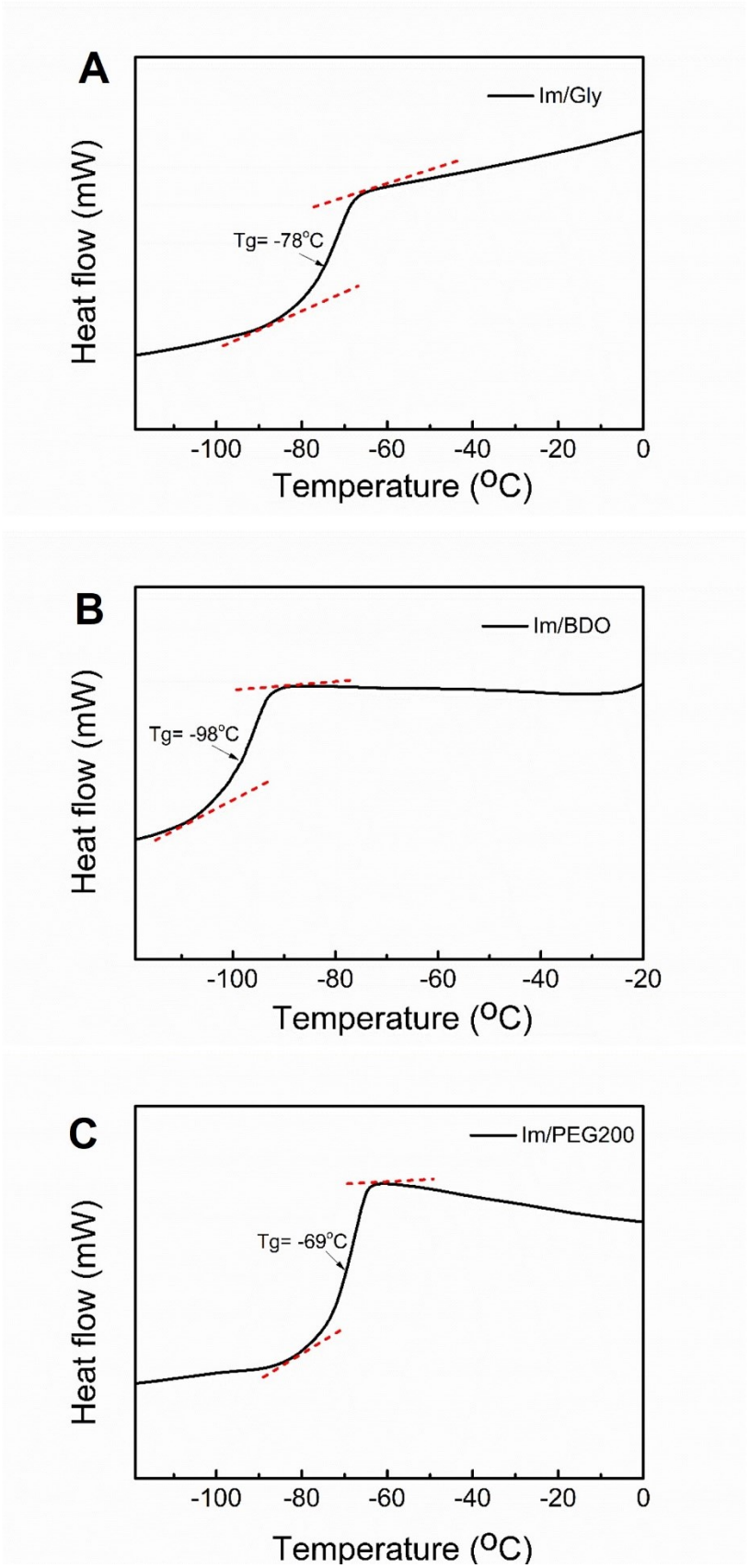

Fig. S6. Glass transition temperature (T_g) of imidazole/Gly (A), imidazole/BDO (B), imidazole/PEG-200 (C) analyzed by differential scanning calorimetry (DSC).

Table S2. Glass transitions temperature (T_g) of the synthesized DES and the corresponding components.

DES or the component	T_g (°C)
imidazole/EG	-96
imidazole/Gly	-78
imidazole/BDO	-98
imidazole/PEG-200	-69
imidazole	90[a]
EG	-13[a]
Gly	18[a]
BDO	20[a]
PEG-200	-58[b]

[a]The temperature was the melting point of the chemical. bThe data was obtained from our previous work (*Green Chem., 2017, 19, 3023*).

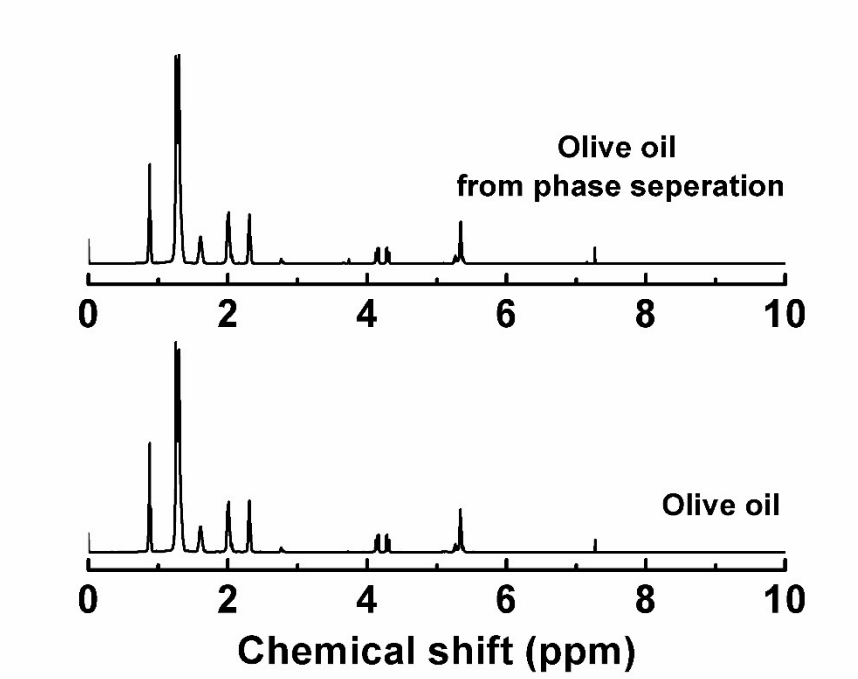

Fig. S7. ^{1}H NMR spectra of pure olive oil and the olive oil from the phase separation.

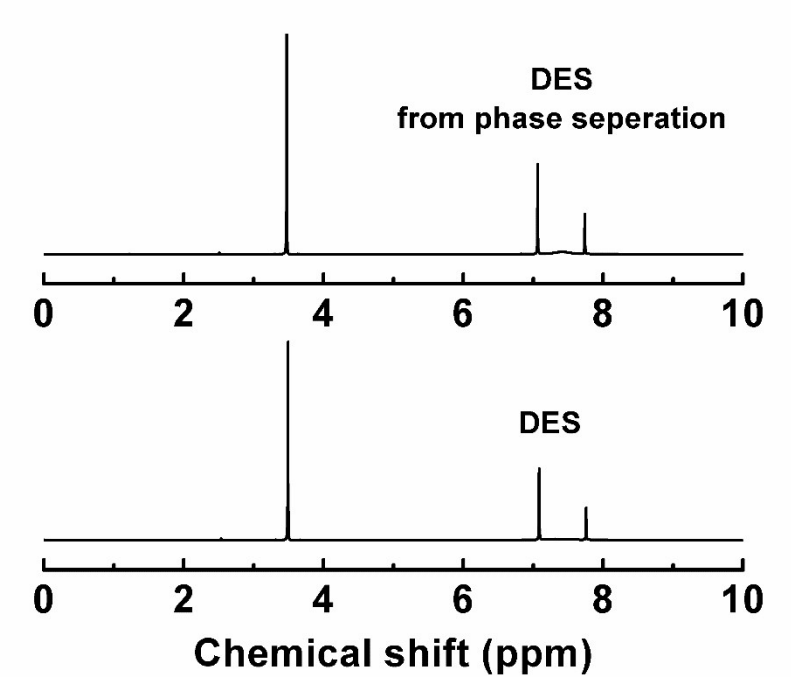

Fig. S8. ^{1}H NMR spectra of pure imidazole/EG DES and the DES from the phase separation.

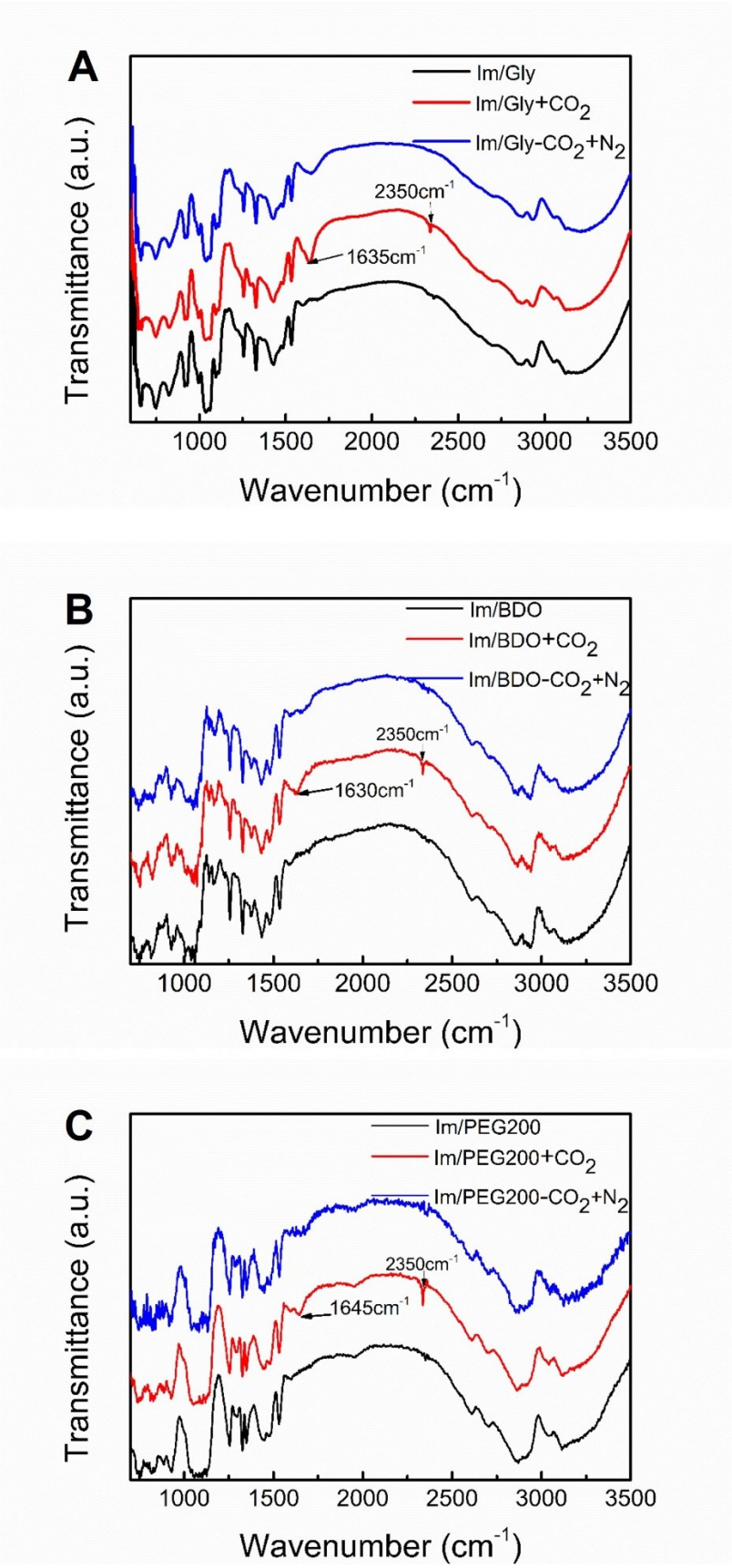

Fig. S9. ATR FT-IR spectra of imidazole/Gly (A), imidazole/BDO (B), imidazole/PEG-200 (C) before and after CO_2 bubbling.

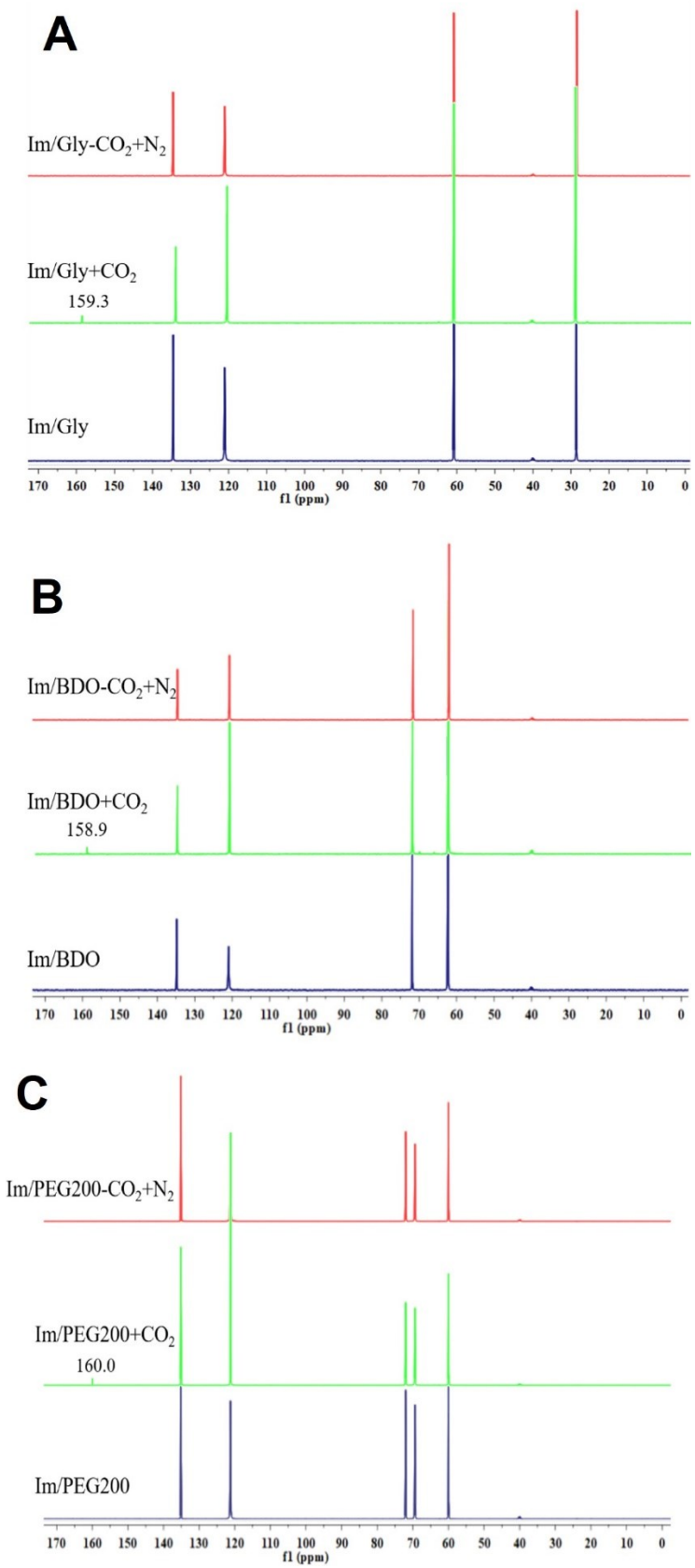

Fig. S10. ^{13}C NMR spectra of imidazole/Gly (A), imidazole/BDO (B), imidazole/PEG-200 (C) before and after CO_2 bubbling.