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Supplementary Information for

Understanding Unique Interaction of Amine-Containing Ionic Compounds with SO_2 for High Absorption Capacity

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Synthesis of [Bztmeda][$MeSO_3$] ionic liquids

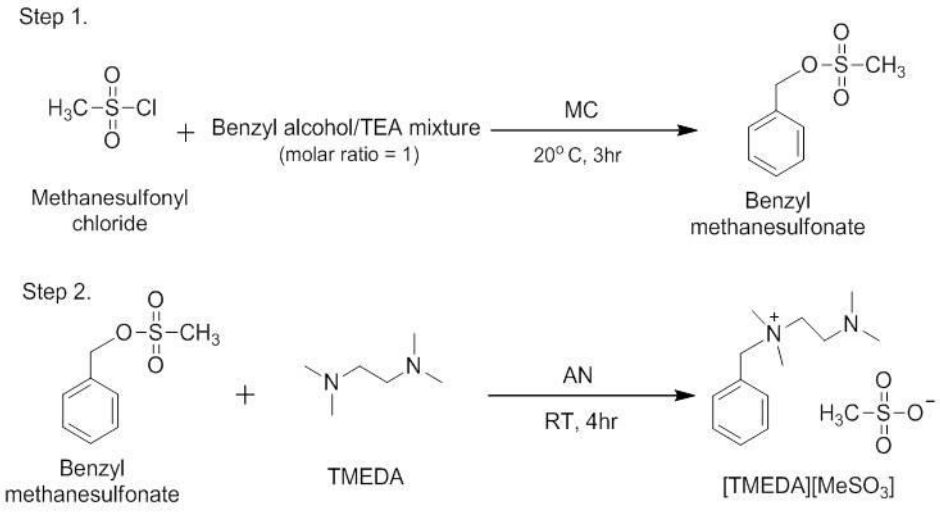
Synthesis of Benzyl Methanesulfonate

To the methanesulfonyl chloride (0.065 mol) was added benzyl alcohol (0.065 mol) and triethylamine (0.065 mol) in methylene chloride. The reaction temperature was kept about 20 ℃ using the water bath. After stirring the solution for 3 hours at room temperature, the organic layer was washed with water. Product layer was isolated using $MgSO_4$ and removed from water. Then, $MgSO_4$ was filtered and washed with methylene chloride. The methylene chloride was removed with a rotary evaporator. A colorless benzyl methanesulfonate liquid was produced.

Synthesis of [Bztmeda][$MeSO_3$]

The prepared equimolar amounts of benzyl methanesulfonate and tetramethylethylenediamine were mixed in acetonitrile at room temperature. After mixing for 4 hours, the reaction mixture was dried at RT under vacuum to remove solvent and unreacted reactant. The product was washed using excess of ethyl acetate for 30 minutes. The [Bztmeda][$MeSO_3$] was separated and washed with acetone and then vacuum dried for 6 hours at room temperature. Finally, white solid [Bztmeda][$MeSO_3$] was produced.

The synthetic procedures of [Bztmeda][$MeSO_3$] are shown in the following schematic illustration



Principal component analysis (PCA)

PCA decomposes the original data matrix into the product of scores and loadings matrices. Score matrix contains information on how samples are related to each other. The loading vectors are usually separated into two categories: significant loadings representing the linear combinations of spectral contributions of actual components and the noise or insignificant vectors. The two matrices are linearly combined with the original data; hence in most discussions of PCA results, the two matrices are explored in parallel. The fundamental idea of PCA is that the significant part of the data matrix (**A**) can be expressed as the product of score (**W**) and loading (**V**) matricies

$$\mathbf{A} = \mathbf{W}\,\mathbf{V}' + \mathbf{E} \qquad (1)$$

where **E** is the residual matrix often associated with pure noise. Here V' stands for the transpose of **V**.

Two-dimensional infrared correlation spectroscopy (2D IR COS)

The synchronous and asynchronous 2D correlation spectra were obtained by using the same software as that described previously. In light of recent publications concerning the normalization procedure in 2D correlation analyses, we tested various methods and found that the best results were obtained by using non-normalized data. The notable features of 2D COS correspond to the deconvolution of complicated, overlapped spectra, the enhancement of the spectral resolution by spreading the peaks along the second dimension, the establishment of unambiguous assignments through the correlation of selectively coupled bands, and the determination of the sequence of spectral peak emergence. Hence, 2D COS is thought to be suitable to elucidate complex chemical reactions such as acid-base chemistry.

In generalized 2DCOS, a set of spectraobserved as a function of the perturbation variable *t* (e.g., time, temperature, or concentration) during the interval between T_{min} and T_{max} is then transformed into a set of 2D correlation spectra by a form of cross correlation analysis. The *dynamic spectrum* $\tilde{y}(\nu,t)$ of a system induced by the application of an external perturbation is formally defined as

$$\tilde{y}(\nu,t) = \begin{cases} y(\nu,t) - \bar{y}(\nu) & \text{for } T_{\min} \le t \le T_{\max} \\ 0 & \text{otherwise} \end{cases} \qquad (2)$$

where $\bar{y}(\nu)$ is the *reference spectrum* of the system which is chosen as the *averaged* spectrum. The intensity of 2D correlation spectrum X(ν_1, ν_2) represents the quantitative measure of a comparative similarity or dissimilarity of spectral intensity variations $\tilde{y}(\nu,t)$ measured at two different spectral variables, ν_1 and ν_2, during a fixed interval. The generalized 2D correlation function given below

$$\mathrm{X}(\nu_1,\nu_2)=\Phi(\nu_1,\nu_2)+i\Psi(\nu_1,\nu_2)$$
$$=\frac{1}{\pi(T_{\max}-T_{\min})}\int_0^{\infty}\tilde{Y}_1(\omega)\cdot\tilde{Y}_2^{*}(\omega)d\omega \qquad (3)$$

formally defines the synchronous and asynchronous correlation intensity, $\Phi(\nu_1,\nu_2)$ and $\Psi(\nu_1,\nu_2)$. The term $\tilde{Y}_1(\omega)$ is the forward Fourier transform of the spectral intensity variations $\tilde{y}(\nu_1,t)$ observed at a given spectral variable ν_1 with respect to the external variable *t*. The conjugate of the Fourier transform $\tilde{Y}_2^{*}(\omega)$ of the spectral intensity variation $\tilde{y}(\nu_2,t)$ observed at another spectral variable ν_2.

The intensity of a synchronous 2D correlation spectrum represents the simultaneous or coincidental changes of two separate spectral intensity variations measured at ν_1 and ν_2 during the interval between T_{min} and T_{max} of the externally defined variable *t*. The intensity of peaks located at diagonal positions mathematically corresponds to the autocorrelation function of spectral intensity variations observed during an interval between T_{min} and T_{max}. The diagonal peaks are therefore referred to as *autopeaks*, and the slice trace of a synchronous 2D spectrum along the diagonal is called the *autopower spectrum*. The magnitude of an autopeak intensity, which is always positive, represents the overall extent of spectral intensity variation observed at the specific spectral variable ν during the observation interval between T_{min} and T_{max}. Thus, an autopeak represents the overall susceptibility of the corresponding spectral region to change in spectral intensity as an external perturbation is applied to the system. *Cross peaks* located at the off-diagonal positions of a synchronous 2D spectrum represent simultaneous or coincidental changes of spectral intensities observed at two different spectral variables ν_1 and ν_2. Such a synchronized change, in turn, suggests the possible existence of a coupled or related origin of the spectral intensity variations. The sign of synchronous cross peaks becomes positive if the spectral intensities at the two spectral variables corresponding to the coordinates of the cross peak are either increasing or decreasing together as functions of the external variable *t* during the observation interval. However, the negative sign of cross peaks indicates that one to the spectral intensities is increasing while the other is decreasing.

The intensity of an asynchronous 2D correlation spectrum represents sequential or successive, but not coincidental, changes of spectral intensities measured separately at ν_1 and ν_2. Cross peaks develop only if the intensity varies out of phase with each other for some Fourier frequency components of signal fluctuations. The sign of asynchronous cross peak provides useful information on sequential order of events observed by the spectroscopic technique along the external variable. If the signs of synchronous and asynchronous cross peaks are the same, the intensity change at ν_1 occurs before ν_2. If the signs of synchronous and asynchronous cross peaks are different, the intensity change at ν_1 occurs after ν_2.

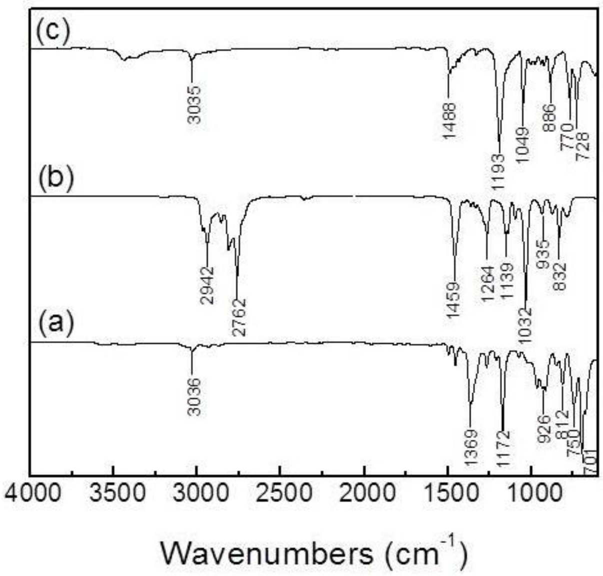


Fig. S1 (a) Benzyl methanesulfonate, (b) N,N,N′,N′-Tetramethylethylenediamine, and (c) [Bztmeda][$MeSO_3$] of FT-IR spectra.

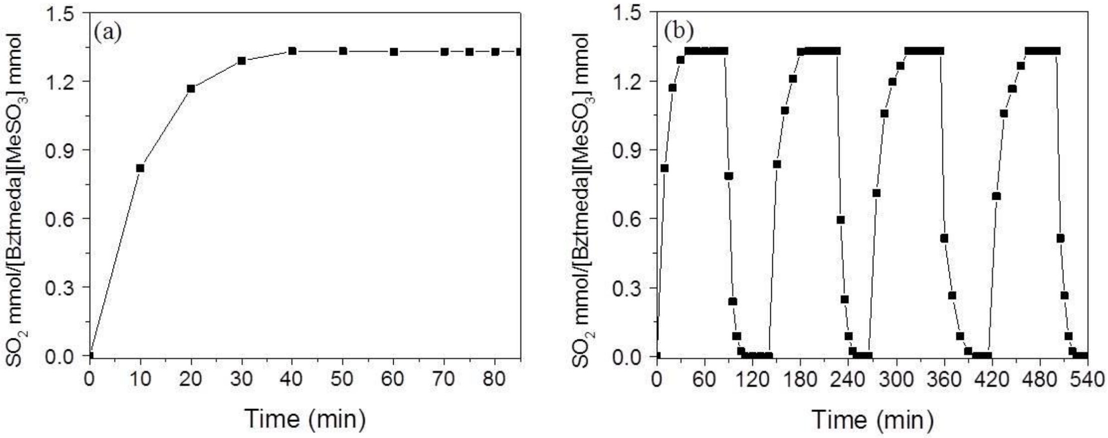


Fig. S2 (a) Time-dependent SO_2 absorption behavior of and (b) SO_2 absorption–desorption cycles of [Bztmeda][$MeSO_3$] on a basis of molar ratio.

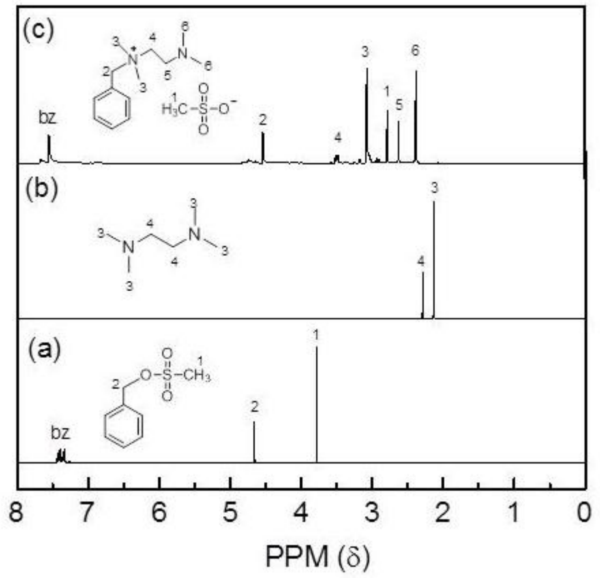


Fig. S3 (a) Benzyl methanesulfonate, (b) N,N,N′,N′-Tetramethylethylenediamine, and (c) [Bztmeda][$MeSO_3$] of 400 MHz ^{1}H NMR spectra.

Benzyl methanesulfonate (a). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.26 (m, 1H), 4.66 (s, 2H), 3.78(s, 3H).

N,N,N′,N′-Tetramethylethylenediamine (b). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.29 (s, 2H), 2.13 (s, 3H).

[TMEDA][$MeSO_3$] (c). ^{1}H NMR (400 MHz, D_2O): δ = 7.47 (m, 1H), 4.54 (s, 2H), 3.52-3.50 (t, *J* = 8.0 Hz, 2H), 3.08 (m, 3H), 2.78 (s, 3H), 2.62 (s, 2H) 2.38 (s, 3H).

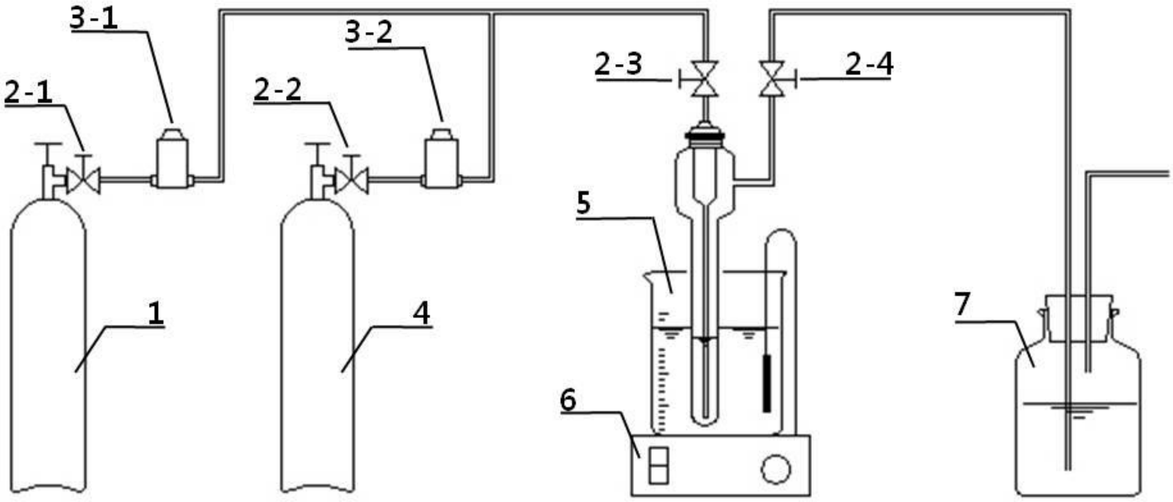


Fig. S4 Experimental apparatus for SO_2 absorption and desorption : 1, N_2 Gas Cylinder; 2-1 to 2-4, Valves; 3-1 to 3-2, Mass Flow Controller; 4, SO_2 Gas Cylinder; 5, Silicon Oil Bath; 6, Heater; 7, Gas Outlet (Absorbed by NaOH Solution before Venting).

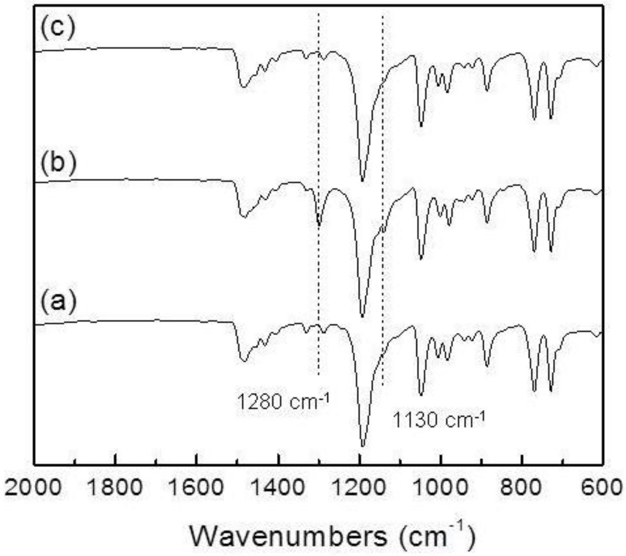


Fig. S5 FT-IR spectra of (a) [Bztmeda][$MeSO_3$], (b) SO_2-adsorbed [Bztmeda][$MeSO_3$] and (c) SO_2 desorbed [Bztmeda][$MeSO_3$].