Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2017

## 1. Experimental Section



**General procedure for the synthesis of anion-functionalized ILs:** A solution of  $[P_{66614}][OH]$  in ethanol was prepared by  $[P_{66614}][Br]$  using an anion-exchange resin. The anion-functionalized fluorescent ILs could be easily prepared by the neutralization of 2-(2'-hydroxyphenyl) benzoxazole [HBO] with the solution of  $[P_{66614}][OH]$  according to a literature method. <sup>1</sup> Equimolar [HBO] was added to the  $[P_{66614}][OH]$  solution in ethanol. The mixture was then stirred at 60 °C for 12 h. Subsequently, the sample was dried under vacuum at 60 °C for 24 h. The ionic liquid was treated with N<sub>2</sub> bubbling at 80 °C to reduce the possible trace amount of water or ethanol. The structure of the anion-functionalized fluorescent ILs was confirmed by NMR and IR spectroscopy; no impurities were found by NMR. The water content of the ILs was determined with a Karl Fisher titration and found to be less than 0.1 wt%.

**Absorption and desorption of SO<sub>2</sub>:** In the typical absorption of SO<sub>2</sub>, SO<sub>2</sub> of atmospheric pressure (1.00 bar) was bubbled through about 1.0g ILs in a glass container with an inner diameter of 10mm, and the flow rate was about 60 ml/min. The glass container was partly immersed in a circulation water bath of desirable temperature. The amount of SO<sub>2</sub> absorbed was determined at regular intervals by the electronic balance with an accuracy of 0.1 mg. During the absorption of SO<sub>2</sub> under reduced pressure, SO<sub>2</sub> was diluted with N<sub>2</sub> in order to reduce the partial pressure of SO<sub>2</sub> passing through the system. The SO<sub>2</sub> partial pressure was controlled by changing the flow of SO<sub>2</sub> and N<sub>2</sub>. Finally, the SO<sub>2</sub> absorption capacities were determined on the basis of the gravimetric difference.

Desorption of SO<sub>2</sub> from saturated IL was carried out and monitored in an analogous way to the described absorption method. The ILs was regenerated by heating and bubbling nitrogen through the IL. In a typical desorption of SO<sub>2</sub>, N<sub>2</sub> at atmospheric pressure was bubbled through about 1.0 g captured IL in a glass container, which was partly immersed in a circulation oil bath at the desired temperature, and the flow rate was about 100 ml/min under 90 °C. The release of SO<sub>2</sub> was determined at regular intervals using an electronic balance.

In the reversibility experiments, SO<sub>2</sub> absorption and desorption by pure [P<sub>66614</sub>][HBO] were carried out for 5 cycles. Absorption was carried out at 30  $^{\circ}$ C and 1 bar under SO<sub>2</sub> (60 ml/min) for 15min in each cycle, and desorption was performed at 90  $^{\circ}$ C and 1 bar under N<sub>2</sub> (100 ml/min) for 60 min in each cycle.

## 2. General procedures:

All chemicals used in this work were purchased from commercial and used without further purification unless otherwise stated. 2-(2'-hydroxyphenyl) benzoxazole [HBO] were purchased

from Energy Chemical. Trihexyl (tetradecyl) phosphoniumbromide ([P<sub>66614</sub>][Br]) was obtained from J&K Chemicals. An anion-exchange resin -711(Cl) was obtained from Aladdin Reagents. SO<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> gas (purity: 99.999%) were obtained from Hangzhou Jingong Special Gas Co. Ltd., China. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance DMX-400 spectrometer in DMSO-d6 with tetramethylsilane as the standard. FT-IR spectra were obtained using a Nicolet 470 FT-IR spectrometer. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Fluorescence spectras were obtained on Edinburgh Instruments FLS920 spectrometer.

## 3. <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and ESI-MS data of ILs

**[P<sub>66614</sub>][HBO]:** <sup>1</sup>H NMR (DMSO-d6) δ (ppm): 7.63 (s, 1H), 7.50 (d, J=8.8Hz, 2H), 7.17 (d, J=36.7Hz, 2H), 6.83 (s, 1H), 6.19 (d, J=8.6Hz, 1H), 5.89 (ddd, J=7.8,6.7,1.1Hz, 1H), 2.26-2.04 (m, 8H), 1.63-1.03 (m, 48H), 0.93-0.81 (m, 12H); <sup>13</sup>C NMR (DMSO-d6) δ (ppm): 172.33, 167.68, 149.78, 142.57, 131.74, 130.96, 124.19, 123.14, 122.05, 117.38, 112.30, 109.42, 106.09, 31.30, 30.40, 29.83, 29.68, 29.07, 29.05, 29.02, 28.96, 28.72, 28.64, 28.10, 22.10, 21.81, 20.57, 20.53, 20.48, 17.70, 17.23, 13.94, 13.85. FT-IR σ(cm-1): 2924, 2854, 1612, 1594, 1544, 1519, 1477, 1454, 1356, 1267, 1234, 1177, 1146, 1109, 1009, 895, 843, 796, 738. ESI-MS: m/z 483.9[M]+ (100%), 210.1 [M]-(100%).

The FT-IR	peaks	could	be	assigned	as	follows:
THC FF IN	peaks	coura	ыc	ussigneu	us	10110103.

2924 cm <sup>-1</sup> ,	2854 cm <sup>-1</sup>	v	CH2
1594 cm <sup>-1</sup> ,	1454 cm <sup>-1</sup>	v	benzene
1612 cm <sup>-1</sup> ,	1544 cm <sup>-1</sup> , 1519 cm <sup>-1</sup>	v	heterocycle
1477 cm <sup>-1</sup> ,	738 cm <sup>-1</sup>	γ	CH2
1356 cm <sup>-1</sup>		γ	СНЗ
1234 cm <sup>-1</sup>		v	C-N
1234 cm <sup>-1</sup>		v	phenol
1146 cm <sup>-1</sup> , 1009 cm <sup>-1</sup>			ether
895 cm <sup>-1</sup> , 8	343 cm <sup>-1</sup> , 796 cm <sup>-1</sup>	γ	benzene





## 4. DFT calculations

All the calculations were performed with Gaussian 09 package. Geometry Optimizations and frequency calculations were carried out at the M062x/6-31+G (d,p) level . Each stationary point was confirmed by insuring there is no imaginary frequency. The NMR data was calculated at the B3LYP/ 6-311+g(2d,p) level with the optimized structures.

	НОМО	LUMO	energy gap/eV	absorption wavelength/nm				
[HBO] <sup>-</sup>	-0.08263	0.10506	5.1	243				
[HBO-SO <sub>2</sub> ] <sup>-</sup>	-0.12979	0.07855	5.6	221				
[HBO-SO <sub>2</sub> ] <sup>-</sup> -SO <sub>2</sub>	-0.14573	0.05542	5.5	225				

Table S1. The calculated HOMOs and LUMOs of [HBO, [HBO-SO<sub>2</sub>], [HBO-SO<sub>2</sub>]-SO<sub>2</sub>.



**Figure S1.** The assignment of <sup>13</sup>C NMR peaks for anion[HBO]<sup>-</sup>. The rest of the NMR peaks, which appear from 40 ppm to 10ppm, are assigned to the carbon chains in cation  $[P_{66614}]^+$ .



Scheme S1. Possible SO<sub>2</sub> chemical and physical absorption mechanism by [P<sub>66614</sub>][HBO].



**Figure S2.** The corresponding fluorescence spectra of  $[P_{66614}][HBO]$  upon the exposure to different concentrations of SO<sub>2</sub>. (a) Fresh ionic liquid exposed to 0.01 bar SO<sub>2</sub> (60 ml/min) for 60min at 30°C; (b) followed by exposure to 1.00 bar SO<sub>2</sub> (60 ml/min) for 15min at 30°C.



**Figure S3.** 1H NMR spectra of  $[P_{66614}][HBO]$  (black),  $[P_{66614}][HBO]$  after SO<sub>2</sub> chemical absorption stage (red) and  $[P_{66614}][HBO]$  after SO<sub>2</sub> physical absorption stage (blue)



**Figure S4.** UV-vis spectra of  $[P_{66614}][HBO]$  (black),  $[P_{66614}][HBO]$  after SO<sub>2</sub> chemical absorption stage (red line, 30 °C, 0.01 bar under SO<sub>2</sub>, 60 ml/min, 60min) and  $[P_{66614}][HBO]$  after SO<sub>2</sub> physical absorption stage (blue line, 30 °C, 1.00 bar under SO<sub>2</sub>, 60 ml/min, 15min).



**Figure S5.** The corresponding fluorescence spectra of benzoxazole ( $1*10^{-6}M$  benzoxazole in hexane) (black) and benzoxazole ( $1*10^{-6}M$  benzoxazole in hexane) exposed to 1.00 bar SO<sub>2</sub> (red line,  $30^{\circ}C$ , 60 ml/min, 0.5min).



**Figure S6.** Selective fluorescence responses of  $[P_{66614}][HBO-SO_2]$  sensor to different gas under a 400nm UV lamp. The pressures of all gases are 1.00 bar (60 ml/min).

 C. M. Wang, X. Y. Luo, H. M. Luo, D. E. Jiang, H. R. Li and S. Dai, *Angew. Chem. Int. Ed.*, 2011, 50, 4918-4922.