

## SUPPORTING INFORMATION

### Reversible Physisorption of SO<sub>2</sub> by Ionic Liquids

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#### Experimental details

##### General comments

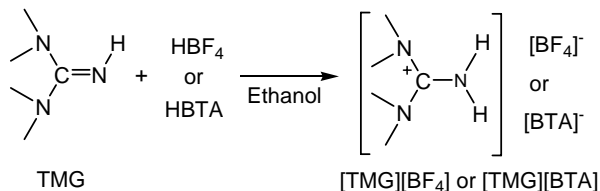
All reagents were used as received without any pretreatment. Lithium bis(trifluoromethanesulfonyl)amide (p.a.), fluoroboric acid (50 wt% solution in water), 1,1,3,3-Tetramethylguanidine (TMG, 99%) and *n*-iodobutane (99%) were purchased from Aldrich. SO<sub>2</sub> gas (99.95%) and N<sub>2</sub> gas (99.99%) were purchased from Air Liquide, Denmark. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM360 NMR spectrometer in CDCl<sub>3</sub> or *d*<sup>6</sup>-DMSO. Peak positions are reported relative to the solvent (CDCl<sub>3</sub>: δ<sub>H</sub> = 7.26 ppm; *d*<sup>6</sup>-DMSO: δ<sub>H</sub> = 2.50 ppm, δ<sub>C</sub> = 40.45 ppm). Melting points were determined by differential scanning calorimetry (TA-2620 DSC equipped with cryostat cooling, 5–20 mg samples, 5°C min<sup>-1</sup> heating and cooling rates). Thermal decomposition profiles were collected by thermogravimetric analysis (TA-2950 TGA, 10°C min<sup>-1</sup> heating rate under nitrogen gas). FT-IR spectra of ILs and SO<sub>2</sub> gas-saturated ILs were recorded using KBR tablets containing a drop of sample (Perkin Elmer FT-IR 1710 spectrophotometer).

##### Synthesis and characterization of ionic liquids [TMG][BF<sub>4</sub>] and [TMG][BTA]

The [TMG][BF<sub>4</sub>] and [TMG][BTA] ILs were prepared by direct neutralization of ethanolic TMG solution with aqueous fluoroboric acid (HBF<sub>4</sub>) or aqueous HBTA solution, respectively (Scheme 1).<sup>1</sup> The HBTA solution was prepared by cation exchange of LiBTA on Dowex 50X2 (H<sup>+</sup> form) resin. To a stirred solution of TMG (11.5 g, 0.10 mol) in ethanol (100 mL) cooled on an ice bath was carefully added concentrated 50% HBF<sub>4</sub> (17.6 g, 0.10 mol) or HBTA (for [TMG][BTA], 2.3 g TMG (0.02 mol) was used to react with 10 mL of 2.0 M HBTA). *Caution: Neutralization of base with a strong acid is highly exothermic.* After continuous stirring (25 °C, 24 h) the solvent was removed under reduced pressure (50 Pa) by heating to 70°C, followed by heating under higher vacuum (10 Pa), leaving the non-volatile ionic liquids [TMG][BF<sub>4</sub>] or [TMG][BTA] behind in near quantitative yield.

[TMG][BF<sub>4</sub>]: Mp. -32°C; δ<sub>H</sub>(300 MHz; *d*<sup>6</sup>-DMSO; 25°C) 2.29 (12 H, s, CH<sub>3</sub>), 5.59 (2 H, s, NH<sub>2</sub>); δ<sub>C</sub>(75.5 MHz; *d*<sup>6</sup>-DMSO; 25°C) 39.55 (N-CH<sub>3</sub>), 161.48 (N=C).

[TMG][BTA]: Mp. 35°C; δ<sub>H</sub>(300 MHz; CDCl<sub>3</sub>; 25°C) 3.01 (12 H, s, CH<sub>3</sub>), 6.20 (2 H, s, NH<sub>2</sub>); δ<sub>C</sub>(75.5 MHz; CDCl<sub>3</sub>; 25°C) 39.62 (N-CH<sub>3</sub>), 161.38 (N=C).



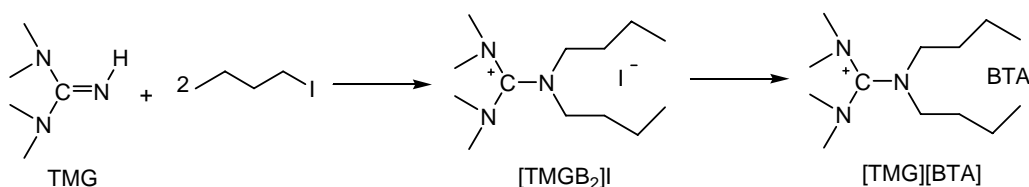
**Scheme 1:** Preparation of the ILs [TMG][BF<sub>4</sub>] and [TMG][BTA] by neutralization of TMG with HBF<sub>4</sub> or HBTA, respectively.

##### Synthesis and characterization of the ionic liquid [TMGB<sub>2</sub>][BTA]

The IL [TMGB<sub>2</sub>][BTA] were synthesized by alkylation of TMG with *n*-iodobutane (C<sub>4</sub>H<sub>9</sub>I)<sup>2</sup> followed by anion exchange (see Scheme 2). To a stirred solution of C<sub>4</sub>H<sub>9</sub>I (38.7 g, 0.21 mol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), TMG (11.5 g, 0.1 mol) was added dropwise with stirring while maintaining the temperature at 25°C. The reaction vessel was then sealed and stirred at room temperature for 24h. Afterwards, solid NaOH (6.0 g, 0.15 mol) was added to the solution, where after the vessel was sealed and stirred for another 24h. The

obtained solution of [TMGB<sub>2</sub>]I in CH<sub>2</sub>Cl<sub>2</sub> was then filtered and the solvent removed under reduced pressure (50 Pa, 70°C) to obtain a white solid of [TMGB<sub>2</sub>]I. The IL [TMGB<sub>2</sub>][BTA] was subsequently obtained as a separate phase after anion exchange of an equimolar solution of [TMGB<sub>2</sub>]I (7.12 g, 0.02 mol) in 30 mL water with LiBTA (5.74 g, 0.02 mol). The separated [TMGB<sub>2</sub>][BTA] IL was washed with additional 3 × 5 mL water and dried under reduced pressure (50 Pa) with heating at 70°C, followed by heating under higher vacuum (10 Pa), to yield a colourless liquid in near quantitative yield.

[TMGB<sub>2</sub>][BTA]: Mp. -42°C; δ<sub>H</sub>(300 MHz; CDCl<sub>3</sub>; 25°C) 0.95 (6 H, t, CH<sub>3</sub>), 1.32 (4 H, m, CH<sub>2</sub>), 1.65 (4 H, m, CH<sub>2</sub>), 2.98 (12 H, s, N-CH<sub>3</sub>), 3.20 (4 H, m, N-CH<sub>2</sub>); δ<sub>C</sub>(75.5 MHz; CDCl<sub>3</sub>; 25°C) 13.83 (CH<sub>3</sub>), 20.16 (CH<sub>2</sub>), 29.20 (CH<sub>2</sub>), 40.48 (N-CH<sub>3</sub>), 49.62 (N-CH<sub>2</sub>), 77.27 (CF<sub>3</sub>), 161.50 (N=C).



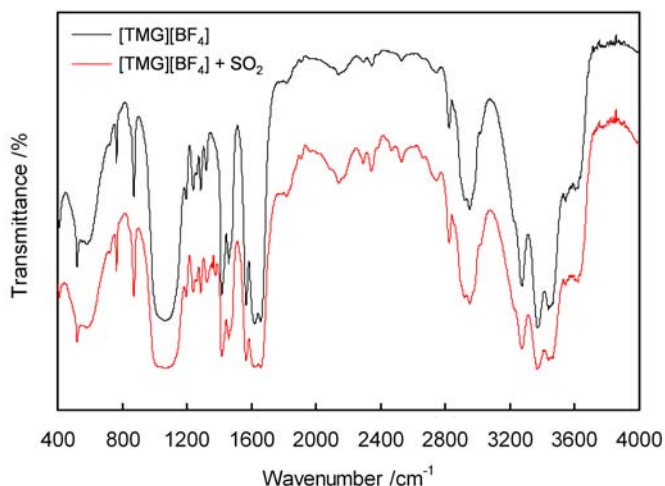
**Scheme 2:** Synthesis of [TMGB<sub>2</sub>][BTA] IL from TMG by alkylation and anion exchange.

#### SO<sub>2</sub> gas absorption/desorption experiments

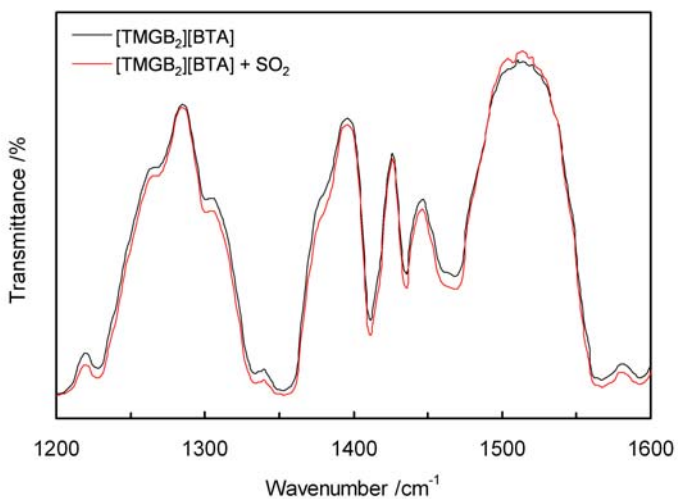
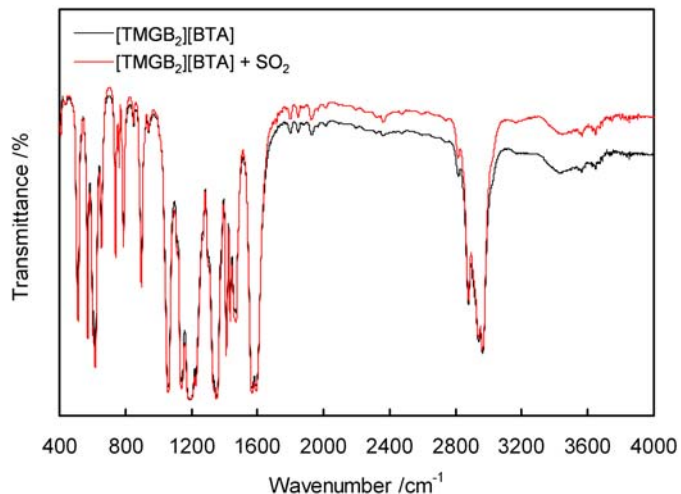
The absorption of SO<sub>2</sub> gas was carried out at ambient pressure of 1 bar (with pure SO<sub>2</sub>) and at room temperature (20°C). The gas stream was bubbled through about 3.5 g of IL loaded into a glass tube with an inner diameter of 12 mm with a flow rate adjusted to 50 mL min<sup>-1</sup>. The glass tube was partly immersed in an oil bath of which the temperature was carefully controlled. The weight of the IL solution was determined at regular intervals during absorption experiments until it remained constant between consecutive measurements.

Desorption of SO<sub>2</sub> gas from saturated IL solutions (as function of the temperature) was carried out and monitored in an analogous way as for the described absorption experiments. Hence, when gas evolution ceded at a given set-temperature (*i.e.* desorption completed), the solution was weighted (repeatedly) until constant weight. The described methods were also used for absorption/desorption experiments by the ILs using gas mixture containing 10% SO<sub>2</sub> gas in N<sub>2</sub>.

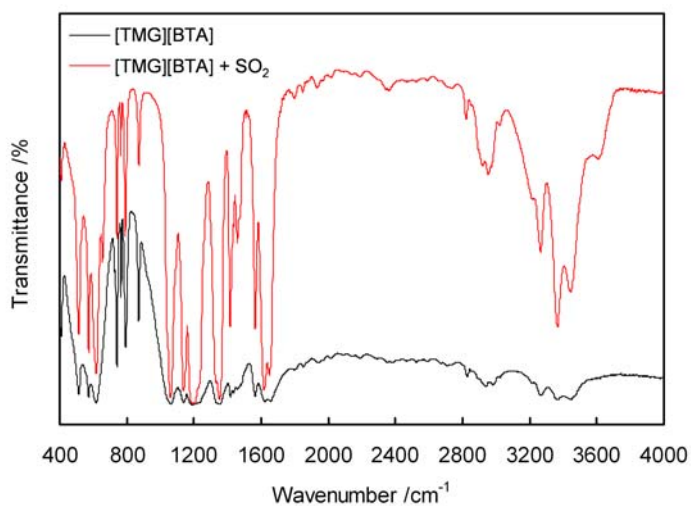
#### FT-IR and NMR spectra of ionic liquids and SO<sub>2</sub>-saturated ionic liquids



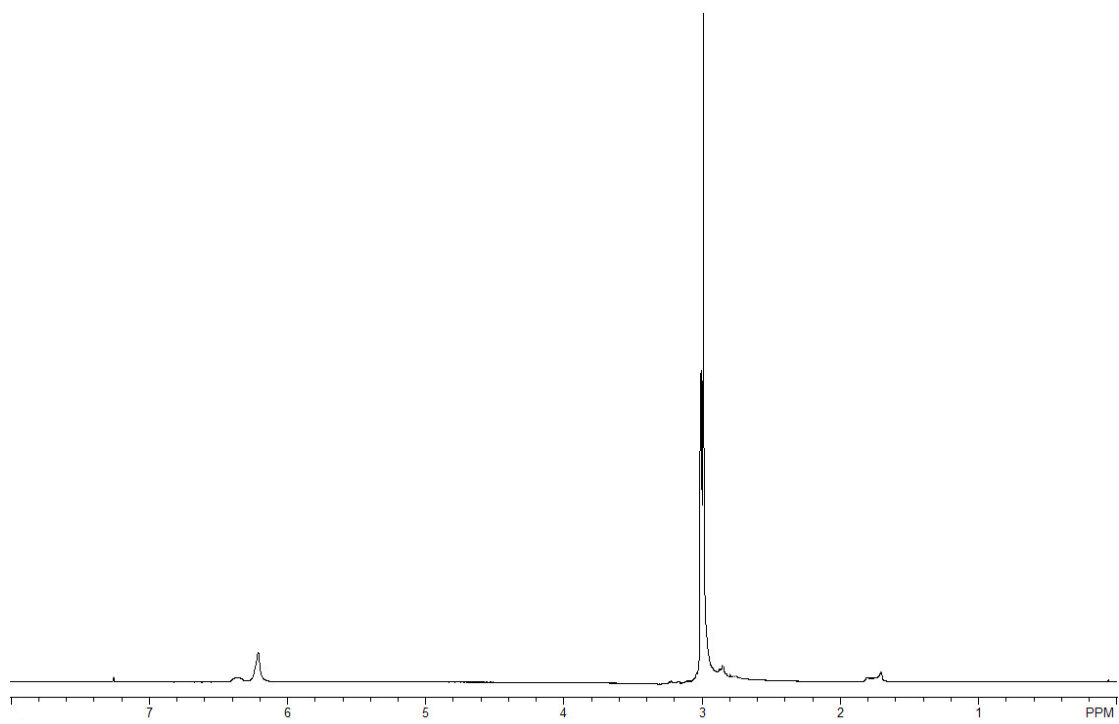
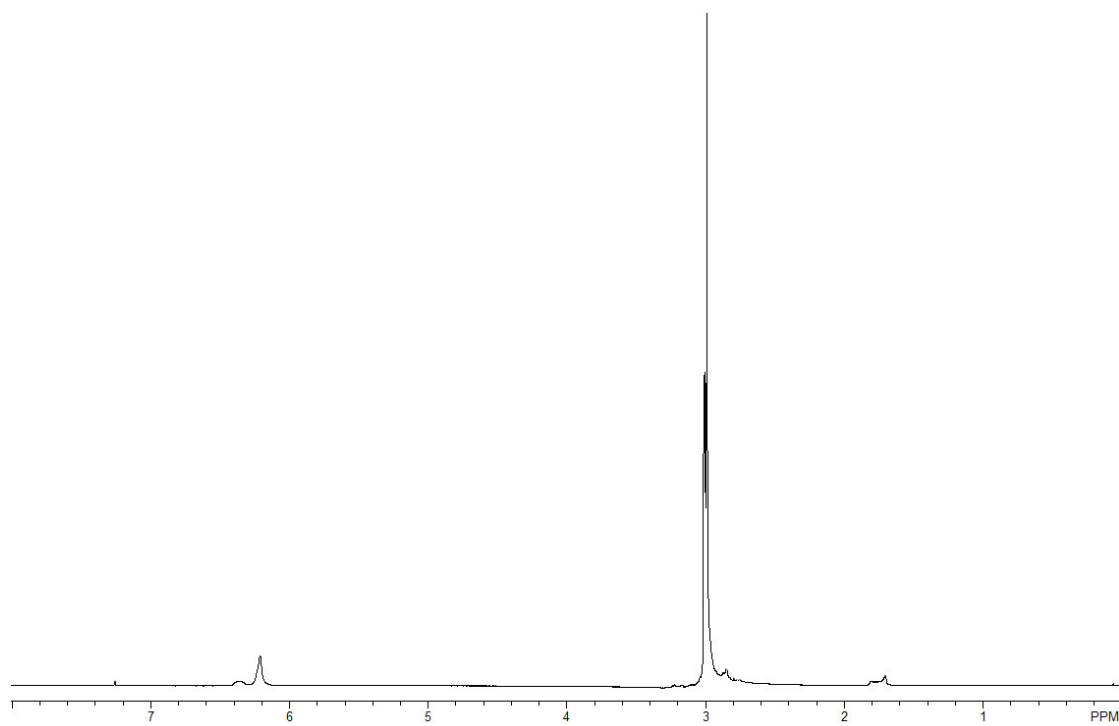
**Figure S1:** FT-IR spectra of ILs [TMG][BF<sub>4</sub>] and [TMG][BF<sub>4</sub>] saturated with SO<sub>2</sub> gas.



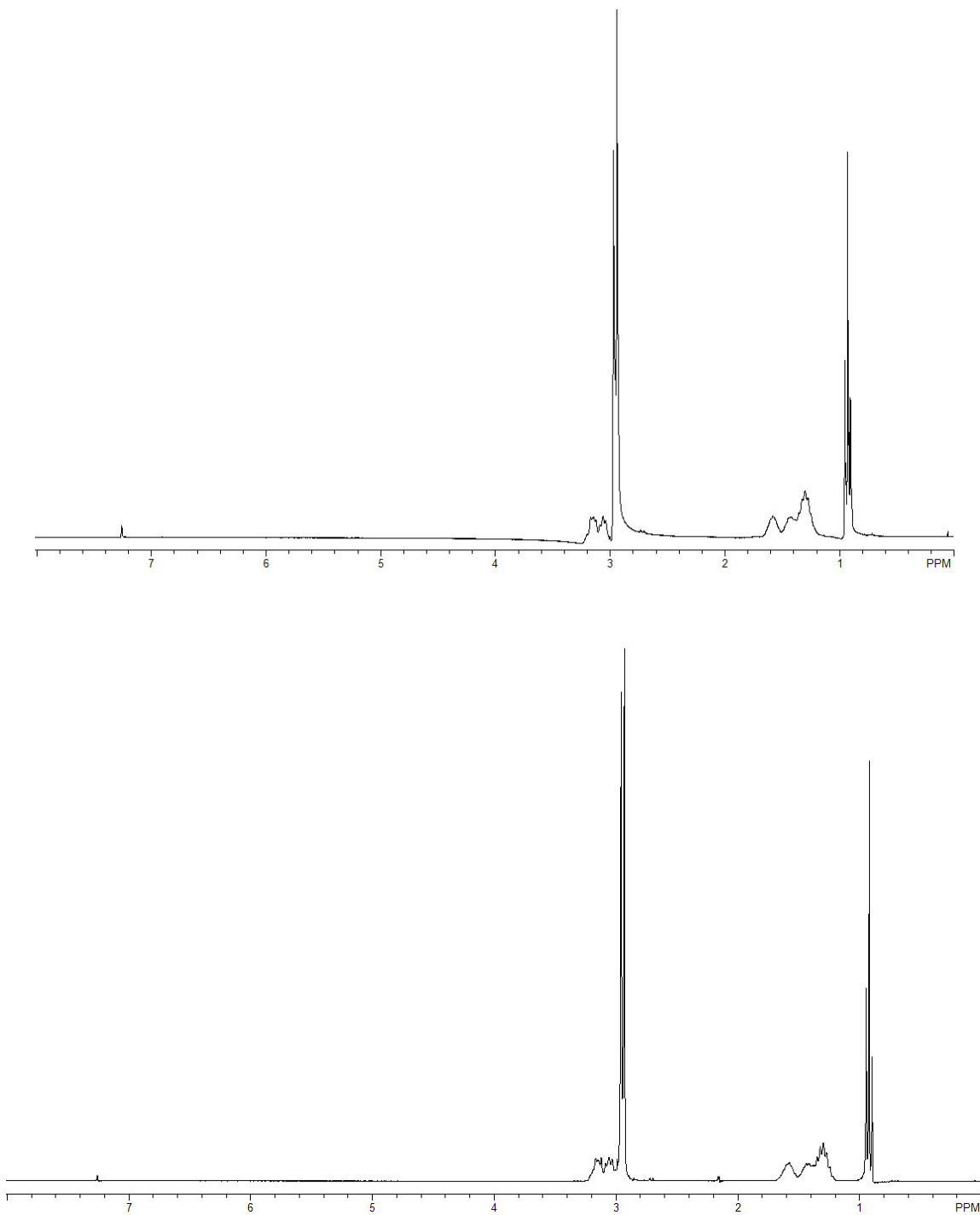
**Figure S2:** FT-IR spectra of ILs [TMGB<sub>2</sub>][BF<sub>4</sub>] and [TMGB<sub>2</sub>][BF<sub>4</sub>] saturated with SO<sub>2</sub> gas. The absorption from SO<sub>2</sub> (O-S-O asym. str.) can not be differentiated from the cation butyl group absorption (~1380 cm<sup>-1</sup>).



**Figure S3:** FT-IR spectra of ILs [TMG][BTA] and [TMG][BTA] saturated with SO<sub>2</sub> gas. [TMG][BTA] is a solid at room temperature (mp. 35°C) and is not translucent for IR light.



**Figure S4:** <sup>1</sup>H NMR spectra of ILs [TMG][BTA] (top) and [TMG][BTA] saturated with SO<sub>2</sub> gas (bottom).



**Figure S5:**  $^1\text{H}$  NMR spectra of ILs  $[\text{TMGB}_2][\text{BTA}]$  (top) and  $[\text{TMGB}_2][\text{BTA}]$  saturated with  $\text{SO}_2$  gas (bottom).

### References

- 1 J. Huang, T. Jiang, H. Gao, B. Han, Z. Liu, W. Wu, Y. Chang and G. Zhao, *Angew. Chem. Int. Ed.*, 2004, **43**, 1397.
- 2 a) A. V. Santoro and G. Mickevicius, *J. Org. Chem.*, 1979, **44**, 117; b) *US Pat.*, 5 082 968, 1992.