

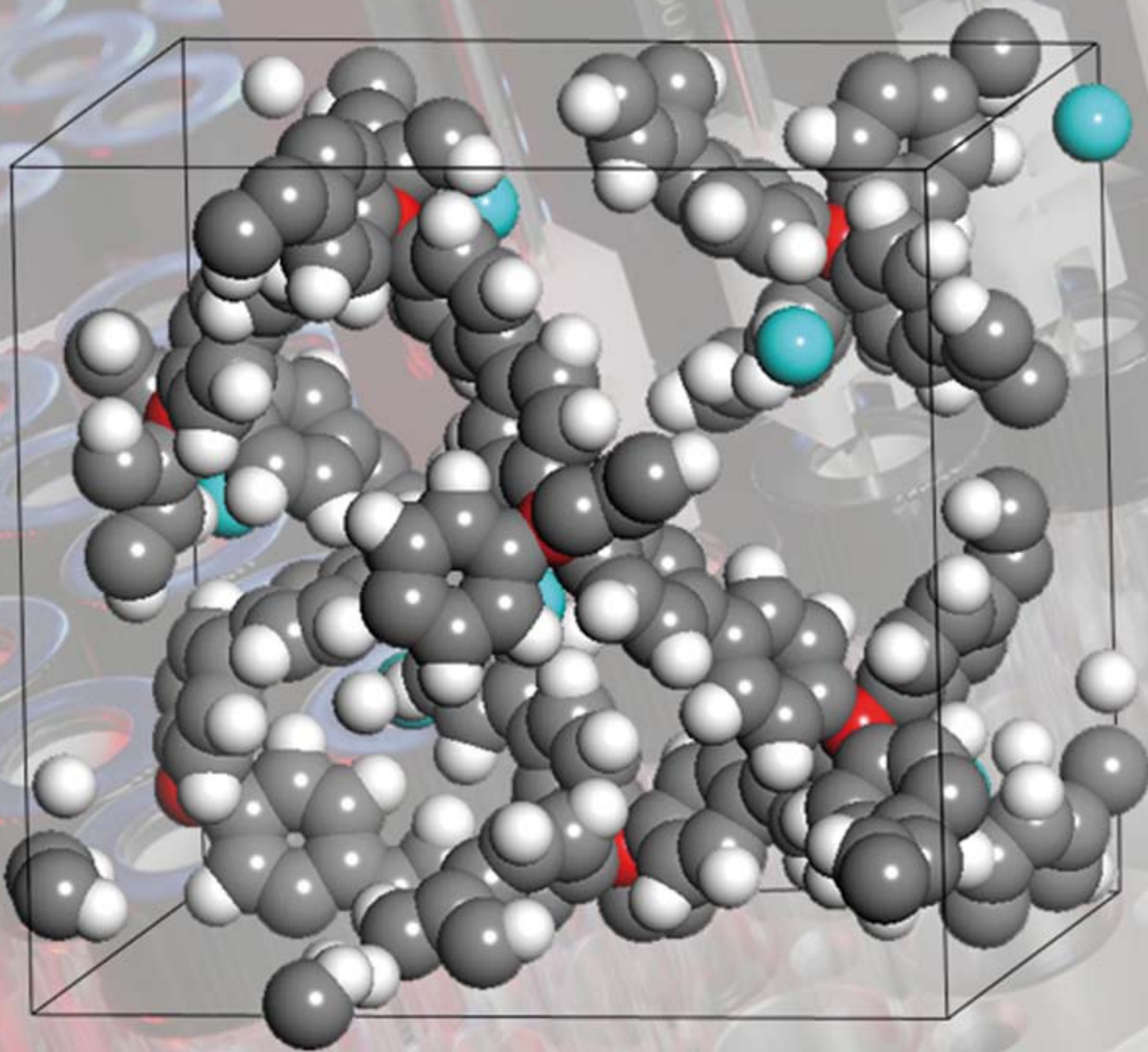
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## LETTER

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# “Naked” fluoride binding sites for physisorptive hydrogen storage

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**Charge separated ammonium fluorides are calculated to have enhanced binding affinities with molecular hydrogen; a model is proposed for a hypothetical porous polymer where “naked” fluoride moieties are site isolated and available for H<sub>2</sub> physisorption.**

The widespread use of hydrogen as a fuel is limited by the lack of a convenient method of H<sub>2</sub> storage.<sup>1</sup> Molecular H<sub>2</sub> storage by physisorption is appealing because it is reversible, cyclable, and sorbents exist that are tolerant to minor impurities such as water. Many porous sorbents have been investigated including carbon,<sup>2</sup> metal–organic frameworks (MOFs) and zeolites,<sup>3</sup> and organic polymers.<sup>4</sup> A significant drawback to H<sub>2</sub> physisorption, however, is the low temperature required and the associated thermodynamic and system weight implications. To date, most H<sub>2</sub> physisorption experiments have been conducted at 77.3 K because of the low average isosteric heat of sorption (4–7 kJ mol<sup>−1</sup>) of H<sub>2</sub> with most porous materials.<sup>5</sup> Hence, there is a need to consider new H<sub>2</sub> sorbents with substantially higher average isosteric heats which might store H<sub>2</sub> at more practicable temperatures—for example, metallation of porous frameworks has been suggested and attempted.<sup>6,7</sup>

Molecular H<sub>2</sub> can interact with a porous substrate *via* weak dispersive interactions, electrostatic interactions, orbital interactions, or in non-classical dihydrogen complexes.<sup>8–10</sup> Dispersive forces dominate in substrates such as carbon<sup>2</sup> and porous organic polymers.<sup>4</sup> Electrostatic interactions between H<sub>2</sub> and charged sites are typically stronger; for example, a recent report refers to a maximum isosteric heat range of sorption (at low H<sub>2</sub> coverage) of 10.1 kJ mol<sup>−1</sup> for exposed Mn<sup>2+</sup> coordination sites in a microporous MOF.<sup>11</sup> Lochan and Head-Gordon<sup>8</sup> have calculated much higher H<sub>2</sub> binding affinities in the broad range 10–350 kJ mol<sup>−1</sup> for charged metals (*e.g.*, Li<sup>+</sup>, Al<sup>3+</sup>), ligands (*e.g.*, SO<sub>4</sub><sup>2−</sup>, F<sup>−</sup>), and metal complexes (*e.g.*, M[(CO)<sub>x</sub>]<sup>p+</sup>). Other studies have calculated the interaction energies for F<sup>−</sup>–(H<sub>2</sub>)<sub>n</sub> (*n* = 1–8) anion complexes using quantum chemical calculations at the MP2/aug-cc-pVTZ level.<sup>12</sup> It is, however, impossible to achieve isolated “bare” ions such as Al<sup>3+</sup> or F<sup>−</sup> in real physical materials.<sup>8</sup>

Our broad aim is to design and evaluate synthetically-viable high-energy “binding sites” for hydrogen physisorption which can be incorporated into real materials. In this study we have

drawn on the concept of “naked” fluoride ions, as used quite widely as strong nucleophiles and bases in organic synthesis.<sup>13</sup> Truly naked anions, not interacting with any other chemical species, will exist only in the gas phase. However, small “naked” anions such as fluoride can be prepared and used in chemical reactions by pairing F<sup>−</sup> with a larger and delocalized cation (*e.g.*, tetraalkylammonium, phosphazenes) such that the coulombic interaction between cation and anion is greatly decreased.<sup>13</sup> In principle, such species, if “site isolated”, could also act as highly polarizing, charged binding sites for H<sub>2</sub> physisorption.

*Ab initio* calculations employing the GAMESS-UK code<sup>14</sup> were used to investigate the binding interactions between molecular H<sub>2</sub> and a range of simple molecules with increasing levels of localized charge density. All systems were geometry optimized at the MP2 level. First, we calculated the binding energy between H<sub>2</sub> and benzene using a range of different basis sets (Table 1).

We obtained a maximum benzene–H<sub>2</sub> binding energy (for TZVPP) of 3.86 kJ mol<sup>−1</sup>, in agreement with a previous study,<sup>15</sup> but somewhat lower than the 4.5–5 kJ mol<sup>−1</sup> reported by others.<sup>8,16</sup> At the other extreme of charge localization, we computed binding energies for a range of basis sets (with BSSE-corrected values found using the Boys–Bernardi scheme<sup>17</sup> in parentheses) for H<sub>2</sub> to a fluoride ion.<sup>18</sup> The largest basis set employed was a combination of cc-pV5Z for the H<sub>2</sub> molecule and the F<sup>−</sup> ion to which it bonds, with the remainder of the molecule represented by the DZP basis set. In this mixed basis, the binding energy of H<sub>2</sub> to F<sup>−</sup> is in the range 18.37 to 23.58 kJ mol<sup>−1</sup>, which compares favourably with other literature values (24.1 kJ mol<sup>−1</sup>,<sup>12a</sup> 26.1 kJ mol<sup>−1</sup><sup>12b</sup>).

Table 1 shows a general increase in H<sub>2</sub> binding energy for molecules with more localized charge density for all basis sets used. Significantly higher binding energies were calculated for simple aliphatic amines (Et<sub>2</sub>NH and Et<sub>3</sub>N) compared to benzene. The H<sub>2</sub> molecule interacted preferentially with the lone pair of the nitrogen atom in both cases. The binding energy of H<sub>2</sub> with the fluoride in tetraethylammonium fluoride (TEAF) was found to be the highest of all the molecules we have considered—in the range of 9–13 kJ mol<sup>−1</sup> for the largest basis set. This is significantly higher than energies calculated for a close ion-pair such as Li<sup>+</sup>F<sup>−</sup>. A similar trend was recently reported for the binding energies of H<sub>2</sub> and Li<sup>+</sup> in which the binding energy of H<sub>2</sub> to Li<sup>+</sup> was twice that of H<sub>2</sub> to the close ion-pair Li<sup>+</sup>OH<sup>−</sup>.<sup>19</sup> Binding of H<sub>2</sub> to TEAF led to notable shortening of the L–H bond distance (with respect to benzene) and lengthening of the H–H bond.

Binding energies of the order of 9–13 kJ mol<sup>−1</sup> would facilitate physisorption at unprecedented temperatures, if

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**Table 1** Calculated binding energies and bond lengths for molecular H<sub>2</sub> with a series of organic molecules using basis sets TZVP 6-311G\*, DZP, and cc-pV5Z + DZP

Organic molecule	–Binding energy/kJ mol <sup>–1</sup>			Distance/Å <sup>b</sup>	
	TZVP 6-311G*	DZP	cc-pV5Z + DZP	L–H <sup>c</sup>	H–H
Benzene <sup>a</sup>	3.24 (1.71)	2.90 (1.38)	—	3.202	0.739
Et <sub>2</sub> NH	7.42 (2.25)	5.74 (1.98)	—	2.418	0.743
Et <sub>3</sub> N	7.21 (2.60)	9.45 (5.35)	—	2.572	0.743
LiF	9.03 (0.77)	6.66 (3.60)	—	2.539	0.741
Et <sub>4</sub> NF	18.16 (6.58)	14.49 (6.51)	13.08 (9.23)	2.257	0.746
Et <sub>4</sub> NF · H <sub>2</sub> O	10.71 (0.71)	10.04 (1.78)	8.27 (2.49)	1.972	0.746
F <sup>–</sup>	83.65 (51.31)	49.95 (28.75)	23.58 (18.37)	1.050	1.179

<sup>a</sup> Calculated interaction energies of H<sub>2</sub> with benzene for basis sets TZVP-dTZVP, 6-311G\* and TZVPP were 3.10, 3.25 and 3.86 kJ mol<sup>–1</sup>, respectively. <sup>b</sup> Bond lengths calculated using TZVP 6-311G\*. <sup>c</sup> Shortest distance between H<sub>2</sub> molecule and binding species.

reflected in an average isosteric heat of sorption.<sup>20</sup> One practical difficulty is that tetraalkylammonium fluorides are often unstable in the anhydrous form due to Hofmann elimination reactions, unless prepared under special conditions.<sup>21</sup> Tetraethylammonium fluoride monohydrate (TEAF · H<sub>2</sub>O), by contrast, is readily prepared by heating higher hydrates of TEAF at 65 °C under vacuum. The binding energy of H<sub>2</sub> with TEAF · H<sub>2</sub>O was calculated to be 10.04 kJ mol<sup>–1</sup> and 10.71 kJ mol<sup>–1</sup> using the DZP and TZVP 6-311G\* basis sets, respectively, and 8.27 kJ mol<sup>–1</sup> using cc-pV5Z + DZP. The BSSE corrected values are somewhat lower; however, it has been noted that for similar systems the BSSE over-corrects for relatively small basis sets,<sup>22,23</sup> and that the uncorrected results for the DZP level are fortuitously accurate due to a cancellation of errors. More detailed calculations are required but we contend that the binding energy for the TEAF monohydrate is significant in comparison with the other molecules studied here. The reduction in H<sub>2</sub> binding energy for the monohydrate with respect to anhydrous TEAF is consistent with increased delocalization of the negative fluoride charge upon introduction of the hydrogen-bonded water molecule. The close proximity of the water molecule (the distance between the bonding water hydrogen and H<sub>2</sub> is 2.85 Å) perturbs the bonding interaction between the H<sub>2</sub> and the F<sup>–</sup>, resulting in a shortening of the bond H<sub>2</sub>–F<sup>–</sup> distance in comparison to anhydrous TEAF.

Table 1 shows that the qualitative trends in binding energy are broadly similar for TZVP 6-311G\*, DZP, and cc-pV5Z + DZP basis sets, allowing us to explore the qualitative variance in binding energies for larger assemblies using the less computationally expensive DZP basis set. The incremental binding energies for seven successive additions of H<sub>2</sub> to TEAF were calculated (Table 2).

Table 2 shows that it is energetically favorable to bind up to six H<sub>2</sub> molecules to the hypothetical anhydrous TEAF species. This suggests that a suitably isolated TEAF moiety might physisorb up to six H<sub>2</sub> molecules at low temperatures (*e.g.*, 77.3 K). The successive BE depends strongly on the number of dihydrogens coordinated, as found for models of isolated F<sup>–</sup>.<sup>12a</sup> Even allowing for the significant overestimation of the H<sub>2</sub> binding energy using DZP, comparison with the larger basis sets (Tables 1 and 2) suggests that the first three (or possibly more) H<sub>2</sub> molecules could bind strongly enough to

display persistent physisorption up to higher temperatures (Fig. 1).<sup>20</sup>

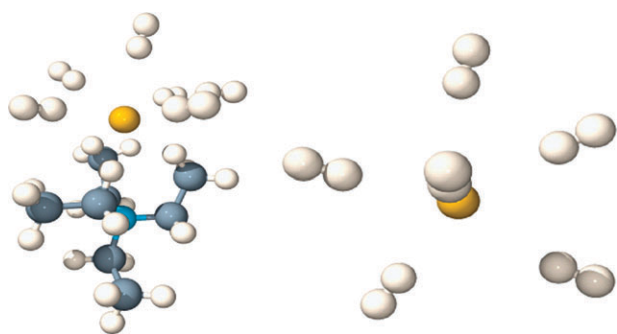
The calculations above refer to isolated TEAF molecules. Clearly, TEAF and its hydrate are non-porous solids and the scope for interaction with H<sub>2</sub> is limited. Even if one could increase the surface area of TEAF—for example, by the production of very small nanoparticles—the “naked” F<sup>–</sup> character discussed above would tend to be dissipated by multiple intermolecular cation–anion interactions which occur in the extended solid. Likewise, TEAF or its hydrate could in principle be supported on a high surface area porous substrate—such as activated carbon<sup>2</sup>—but this may also lead to TEAF–TEAF interactions, especially at significant TEAF loadings, or substantial interactions between the fluoride ion and the porous support. In all of these cases one might expect the strength of these idealized TEAF–H<sub>2</sub> interactions to be greatly diminished, even if the coordination sphere around the fluoride ion remains somewhat accessible to H<sub>2</sub>. It is possible however to conceive of extended porous solids where the fluoride anion is fixed in space in such a way that intermolecular self-interactions are minimized and that the coordination sphere of the anion is left partially vacant to facilitate H<sub>2</sub> coordination. A hypothetical extended structure consisting of a biphenyl-linked tetrabiphenylammonium fluoride subunit is shown in Scheme 1.

To assess the viability of a structure composed of such units, a model was constructed using the Materials Studio Modeling 4.0 package (Accelrys Inc., San Diego, CA, 2005) and fully optimized (both cell parameters and the atomic positions) using the density functional theory code VASP<sup>24</sup> (with the standard ultrasoft pseudopotentials) treating exchange and

**Table 2** Binding energies for multiple binding of molecular H<sub>2</sub> to Et<sub>4</sub>N<sup>+</sup>F<sup>–</sup> calculated at the MP2 level using the DZP basis set

<i>n</i>	–Binding energy/kJ mol <sup>–1</sup>	
	Et <sub>4</sub> N <sup>+</sup> F <sup>–</sup> · (H <sub>2</sub> ) <sub><i>n</i></sub> successive	Et <sub>4</sub> N <sup>+</sup> F <sup>–</sup> · (H <sub>2</sub> ) <sub><i>n</i></sub> average
1	13.91	13.91 (5.00)
2	13.56	13.74 (4.39)
3	13.20	13.56 (4.95)
4	9.93	11.54 (4.20)
5	2.85	10.69 (2.43)
6	1.78	9.21 (3.24)

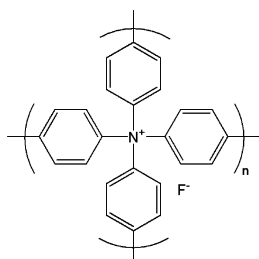




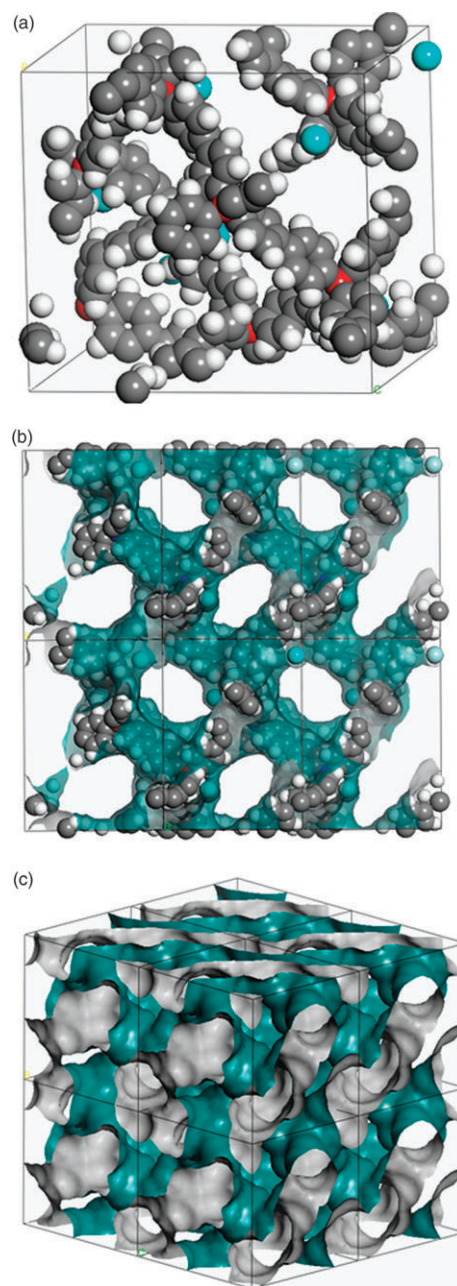
**Fig. 1** Left: Side view of molecular model showing six  $\text{H}_2$  molecules binding to  $\text{Et}_4\text{N}^+\text{F}^-$ . Right: Top view showing distribution of  $\text{H}_2$  molecules around the fluoride anion (tetraethylammonium cation removed for clarity).

correlation with the PW91 generalized gradient approximation,<sup>25</sup> using a 450 eV cutoff for the plane wave basis set sampled at the  $\Gamma$ -point of the Brillouin zone (Fig. 2).

After minimization, this hypothetical structure has a relatively low calculated bulk density of  $0.40 \text{ g cm}^{-3}$ . The micropore structure in the model is fully interconnected and the network has a distorted diamondoid structure. The fluoride ions are situated adjacent to micropore cavities; as such, each “naked” fluoride has a substantial vacant coordination space. The fluoride ions are well separated with an average  $\text{F}^--\text{F}^-$  distance of  $11.03 \text{ \AA}$ . This separation is a function of the specific polymer structure and will not necessarily be realized in other porous materials incorporating fluorine.<sup>3b</sup> The calculated surface area for this modelled structure was  $4464 \text{ m}^2 \text{ g}^{-1}$  with a calculated pore volume of  $1.89 \text{ cm}^3 \text{ g}^{-1}$ . These values were obtained by creating a Connolly surface using the Atom, Volumes and Surface module in Materials Studio using a coarse grid resolution and a Connolly radius set to  $1.82 \text{ \AA}$  (the kinetic radius of  $\text{N}_2$ ).<sup>4d</sup> While this is a hypothetical structure and we have no synthetic route to this hypothetical tetraphenyl-onium polymer, real materials do exist that have micropore properties similar to those calculated here. For example, IRMOF-20 was reported to have a Langmuir surface area of  $4346 \text{ m}^2 \text{ g}^{-1}$  (calculated Connolly surface area =  $3275 \text{ m}^2 \text{ g}^{-1}$ ) and a measured pore volume of  $1.53 \text{ cm}^3 \text{ g}^{-1}$ .<sup>26</sup> We are currently exploring the synthetic potential of *amorphous* conjugated microporous polymers as substrates to incorporate “site isolated” fluoride groups for gas sorption applications.<sup>27</sup> We also believe that this general strategy might be applicable to other microporous materials such as MOFs<sup>3</sup> and polymers of intrinsic microporosity.<sup>4a</sup>



**Scheme 1** Repeat unit structure for hypothetical biphenyl-linked tetraphenylammonium fluoride network.



**Fig. 2** Molecular simulation of biphenyl-linked tetraphenylammonium fluoride (a) unit cell with dimensions  $2.2 \times 2.2 \times 2.4 \text{ nm}$ , nitrogen atoms are shown as red spheres, and fluorine as blue. (b)  $3 \times 2$  lattice with a Connolly surface shown in green/grey. (c) A  $2 \times 2$  lattice showing only the Connolly surface, omitting atoms for clarity.

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