## Supplementary Data

Thermochemical properties are given as differences  $(\Delta E)$  in calculated DFT-BP86 absolute electronic energies  $(E_{abs})$ . No vertical energy differences are quoted: all  $\Delta E$  are 'adiabatic' in the sense that they are calculated from optimised geometry to optimised geometry. The sign convention is that a positive  $\Delta E(X)$  corresponds to an endothermic reaction  $X \rightarrow Y$ ; X is then stable with respect to Y. As an example, Na<sub>4</sub>O is stable with respect to loss of one sodium atom:

$$Na_4O \rightarrow Na_3O + Na, \Delta E = +149 \text{ kJ/mol}$$

Therefore the sodium abstraction energy of Na<sub>4</sub>O is  $\Delta E_{\text{Na}} = +149 \text{ kJ/mol}$ .  $\Delta E_{\text{Na}}^{i}$  and  $\Delta E_{\text{Na}}$  refer to abstraction energies for inner and outer shell sodium respectively.  $\Delta E_{\text{Na}}^{io}$  is the inner  $\rightarrow$  outer isomerisation energy.  $\Delta E_{ox}$  is the energy gained on oxidation, that is, the binding energy relative to an isolated neutral sodium cluster and neutral O<sub>2</sub>.

## **Basis Sets**

**Sodium**: Single Valence Polarisation (SVP): (10s6p) / [4s2p]

**Oxygen**: Single Valence Polarisation (SVP): (7s4p1d) / [3s2p1d]

**Oxygen:** Single Valence Polarisation with diffuse p on oxygen (SVP+): (7s5p1d) / [3s3p1d] from SVP plus  $\eta_p=0.06$ 

For SVP basis sets see: A.Schäfer, H.Horn & R.Ahlrichs, J. Chem. Phys., 1992, 97, 2571.