Fig. 1 Bias dependence of (a–c) experimental and (d–e) simulated constant current STM images of the porous network of TAPP on Cu(111). All images were obtained at the same region with the area 4×4 nm². Tunnelling parameters were (a) -1V/20pA, (b) 2.7V/1pA, (c) 3V/1pA. The LDOS behind the simulated images was integrated from the Fermi level, \(E_F\), to (d) \(E_F - 1.0\) eV, (e) \(E_F + 3.2\) eV. (f) Schematics of the TAPP molecule. Ball and stick models of the molecular structure of TAPP including the Cu adatoms (red balls) were over-layered in (a–e).

Fig. 2 Calculated local density of states at 6 Å above the Cu surface, laterally positioned above the crossing between four TAPP molecules corresponding to the position of the bright protrusion in Fig. 1e).

Fig. 3 Visualisation of the molecular band density of the isolated Cu-TAPP overlayer which gives rise to a bright protrusion in Fig. 1e). (a) Contour plot of density at 5 Å above the overlayer (b) Three dimensional surface contour plot of the electronic charge density at a value of -0.005 e/Å³.

Fig. 4 Projected density of states onto the molecular orbitals of the isolated TAPP molecular layer for Cu-TAPP overlayers being (a) isolated and structurally optimized, (b) adsorbed on Cu(111), and (c) adsorbed on Cu(111) without adatoms. The legend refers to the orbitals of the isolated TAPP molecule. In (a) the energy is given relative to the vacuum level, and the Fermi level is set to the middle of the band gap of this system. In (b) and (c) the energy is given relative to the Fermi level and the vacuum levels of (a) and (b) are aligned. For an isolated TAPP molecule the four lone-pair orbitals appear at two distinct energy levels (solid and dashed green lines).

Fig. 5 Energy as a function of unit cell area of isolated, structurally optimised, Cu-TAPP coordination networks. The solid line is the result of a cell with \(D_{4h}\) symmetry. The areas and energies of the observed unit cell (□) and an alternative unit cell (○), both being commensurate with the Cu(111) surface, are included.