Supporting Information:

Single Molecule Magnets: A New Approach to Investigate the Electronic Structure of Mn_{12} Molecules by Scanning Tunneling Spectroscopy

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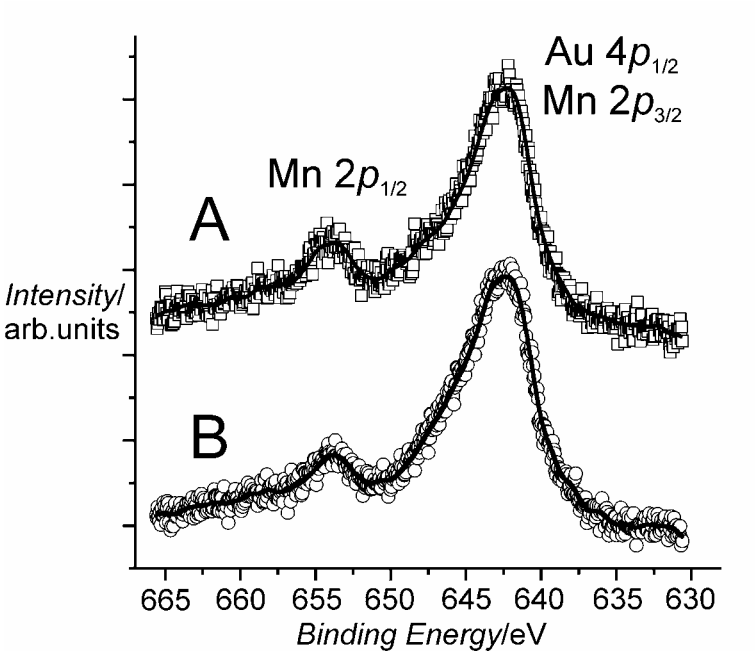
Synthesis of 4-Mercapto-2, 2',3, 3', 5, 5',6 ,6'-octafluorobiphenyl:

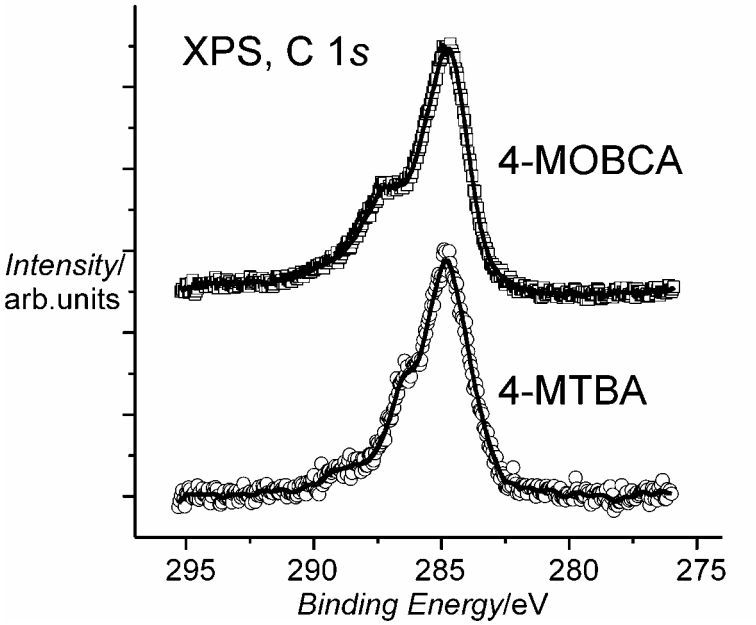
n-Butyllithium (10.1ml, 1.6M in hexane) was added dropwise to a precooled solution (-75°C) of 2, 2',3, 3',5, 5',6,6'-octafluorobihpenyl (4.5g, 15mmol) in 100 ml of anhydrous THF. The reaction mixture was allowed to warm to -50°C and was cooled down to -80°C afterwards. A solution of sulphur in THF (0.49g, 15mmol, 70ml) was added dropwise and after completeness of addition the mixture was allowed to warm to room temperature. After addition of 70ml of ethyl acetate (technical grade) the mixture was hydrolyzed with 100ml of 3 N HCl and phase separated. The organic layer was dried over magnesium sulfate. The crude product was sublimated at 0.1mbar and 50°C to give pure 4-Mercapto-2, 2',3, 3', 5, 5',6, 6'-octafluorobiphenyl (4.6g, 93%).
M.p. = 121.6°C; Elemental analysis calc. for $C_{12}H_2F_8S$ (%): C 43.65 H 0.61 found: C 43.66 H 0.62; IR (KBr): ν = 3075.8 (w), 2614.7 (w), 1653.7 (w), 1611.8(w), 1505.4 (s), 1476.3 (s), 1441.5 (s), 1378.8 (w), 1308.8 (w), 1231.5 (m), 1180.6 (m), 1134.8 (w), 1041.7 (w), 1010.6 (m), 960.7 (w), 946.6 (m), 906.4 (s), 882.7 (w), 859.6 (m), 760.8 (w), 739.7 (m), 721.8 (w), 707.4 (s), 612.9 (w) $cm^{-1;}$ ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.27 (m, 1H, 4-C*H*), 3.92 (s, 1H, S*H*); ^{13}C-NMR (CDCl3, 100 MHz): δ = 146.1, 143.8, 143.2, 115.4, 107.9; ^{19}F-NMR (CDCl3, 376 MHz): δ = -138.75 (m, 4F, 2,2',6,6'-C*F*), -138.33 (m, 2F, 3',5'-C*F*), -137.31 (m, 2F, 3,5-C*F*); GC-MS: (*m/z*) = 330 (100%, M^+), 311 (11%), 298 (12%), 285 (8%), 267 (7%), 247 (8%), 216 (5%), 193 (5%), 165 (5%).

Synthesis of 4'-Mercapto-2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-carboxylic acid

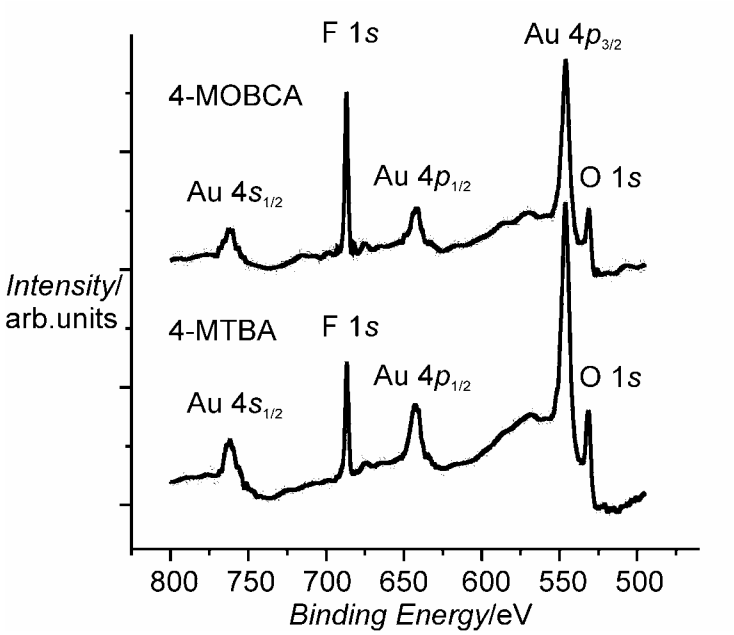
n-Butyllithium (7.9ml, 1,6 in hexane) was given slowly to a precooled solution (-80°C) of 4-Mercapto-2, 2',3, 3', 5, 5',6 ,6'-octafluorobiphenyl (2.0g, 6.1mmol) in 50ml of anhydrous THF while temperature was kept under -70°C. After completion of addition temperature was allowed to rise to -50°C and CO_2 was bubbled through the mixture for 1h. After this the reaction mixture was quenched with 6M HCl and 50ml of ethyl acetate were added. The phases were separated and the aqueous layer was extracted three times with 40ml of ethyl acetate. The organic layer was dried over magnesium sulphate and the solvent was removed. Recrystallization from $CHCl_3$/EtOH yielded 1.9g (83%) of pure 4'-Mercapto-2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-carboxylic acid.
Elemental analysis calc. for $C_{13}H_2F_8SO2$ (%): C 41.73 H 0.54 found: C 41.76 H 0.53; IR (KBr): ν = 3000 (br), 1728.9 (s), 1653.5 (m), 1471.1 (s), 1418.2 (s), 1314.6 (w), 1278.3 (m), 1227.6 (w), 993.2 (s), 917.3(m), 864.6 (m), 704.5 (s)$cm^{-1;}$ ^{13}C-NMR (DMSO, 100 MHz): δ = 159.8, 146.2, 143.4, 118.2, 116.3, 108.5, 107.6; ^{19}F-NMR (CDCl3, 376 MHz): δ = 139.51 (m, 2F, 3,5-C*F*), 138.69 (m, 2F, 2',6'-C*F*), 137.83 (m, 2F, 2,6-C*F*), 137.26 (m, 2F, 3',5'-C*F*); EI-MS: (*m/z*) = 374 (100%, M^+), 357 (10%), 330 (8%), 310 (9%), 298 (7%), 279 (8%), 265 (15%), 247 (13%).



Supporting Figure. Mn 2*p* core level XPS spectra of Mn_{12}-pfb on 4-MTBA/Au(111) (A) and on 4-MOBCA/Au(111) (B).



Supporting Figure. C 1*s* core level XPS spectra of 4-MTBA/Au and on 4-MOBCA/Au.



Supporting Figure. XPS overview spectra of 4-MTBA/Au(111) and on 4-MOBCA/Au(111) including F 1*s* peak at 686.8 eV.