## **Supporting Information**

Title: Preparation, Reactivity and Controlled Release of SAMs of Calix[4,6] arenes and Calix[6]arene-based Rotaxanes and Pseudorotaxanes Formed on Polycristalline Cu, studied by XPS Author(s): Alice Boccia, Valeria Lanzilotto, Valeria Di Castro, Robertino Zanoni,\* Arturo Arduini, Luca Pescatori, and Andrea Secchi\*

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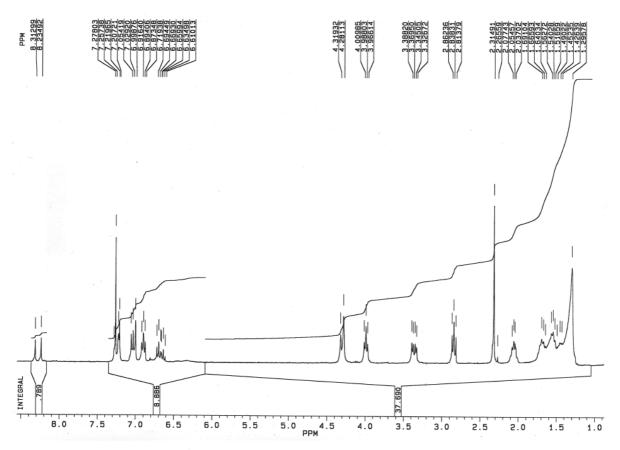


Figure S1. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz) of calix[4]arene 4.

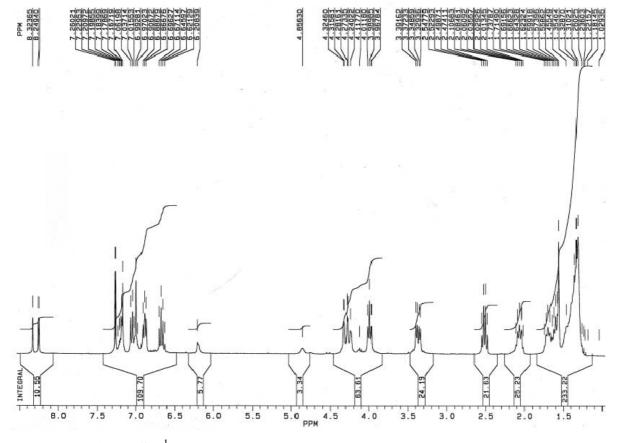


Figure S2.  $^{1}$ H NMR spectrum (CDCl<sub>3</sub>, 300 MHz) of calix[4]arene 5.

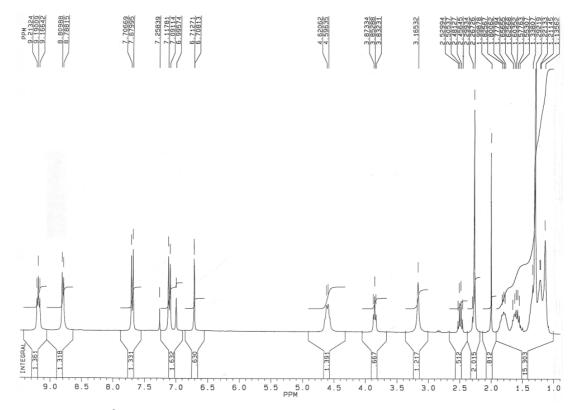


Figure S3. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz).of viologen-based "axle" 13

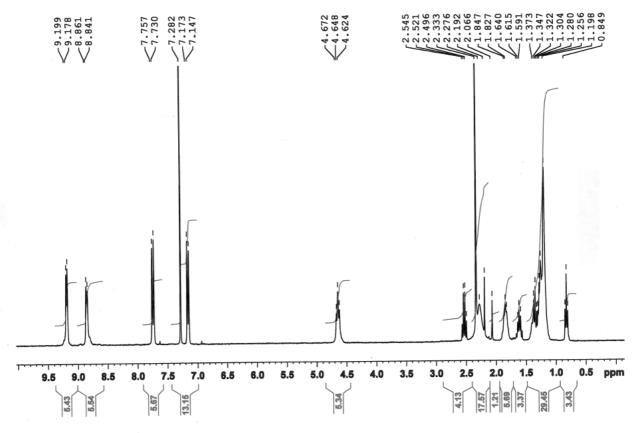
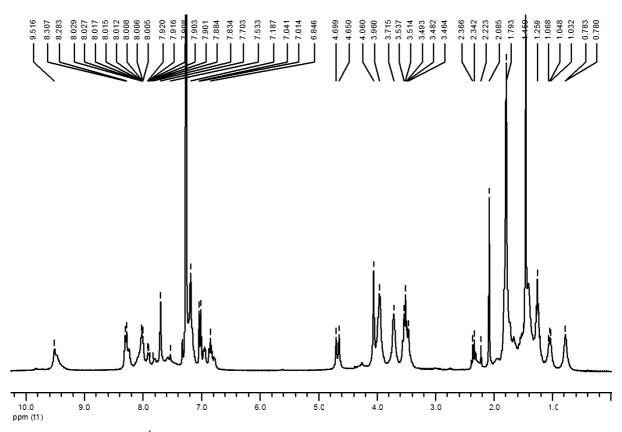
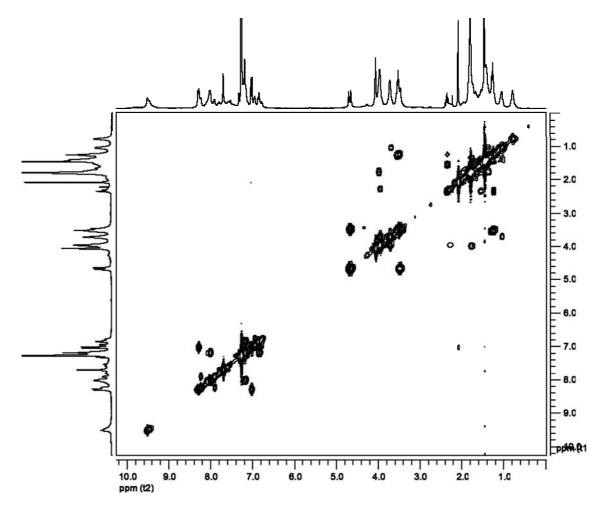
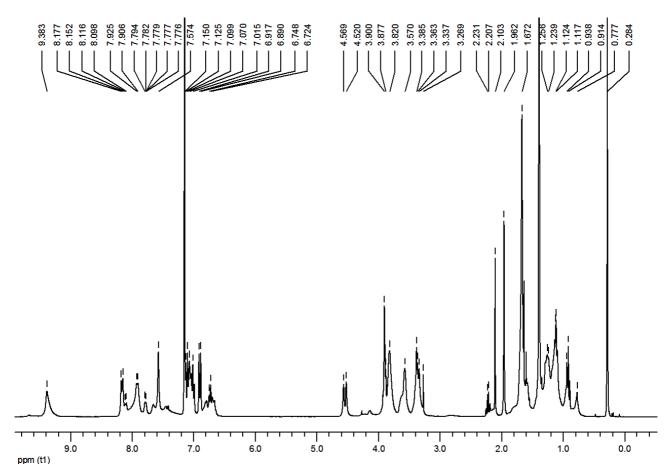


Figure S4.  $^{1}$ H NMR spectrum (CDCl<sub>3</sub>, 300 MHz) of viologen-based "axle" 15.



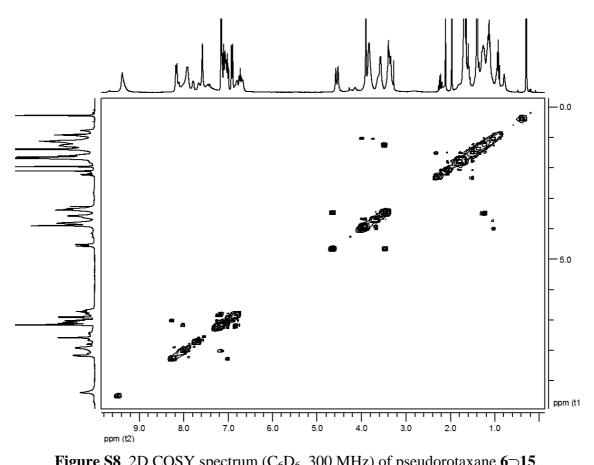
**Figure S5.** <sup>1</sup>H NMR spectrum ( $C_6D_6$ , 300 MHz) of pseudorotaxane  $6 \supset 13$ .





**Figure S6.** 2D COSY spectrum ( $C_6D_6$ , 300 MHz) of pseudorotaxane 6 $\supset$ 13.

**Figure S7.** <sup>1</sup>H NMR spectrum ( $C_6D_6$ , 300 MHz) of pseudorotaxane  $6 \supset 15$ .



**Figure S8**. 2D COSY spectrum ( $C_6D_6$ , 300 MHz) of pseudorotaxane 6 $\supset$ 15.

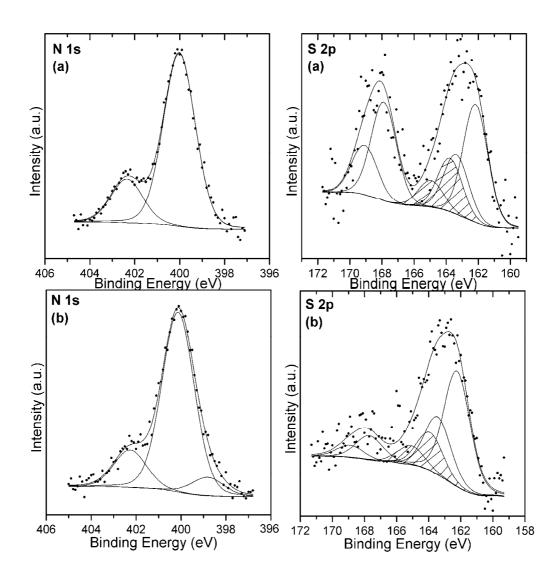
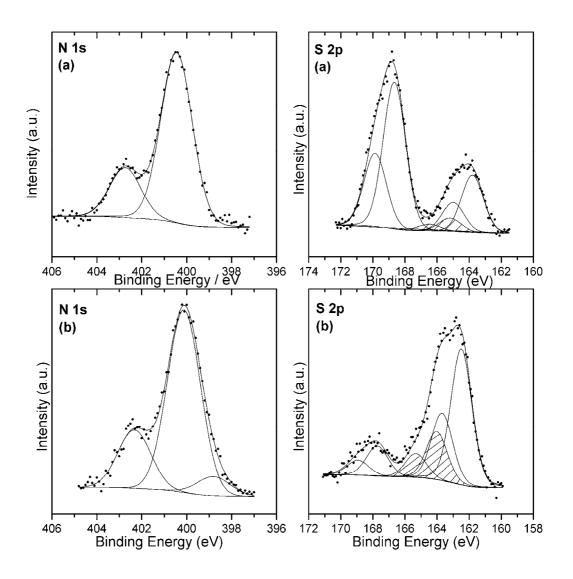
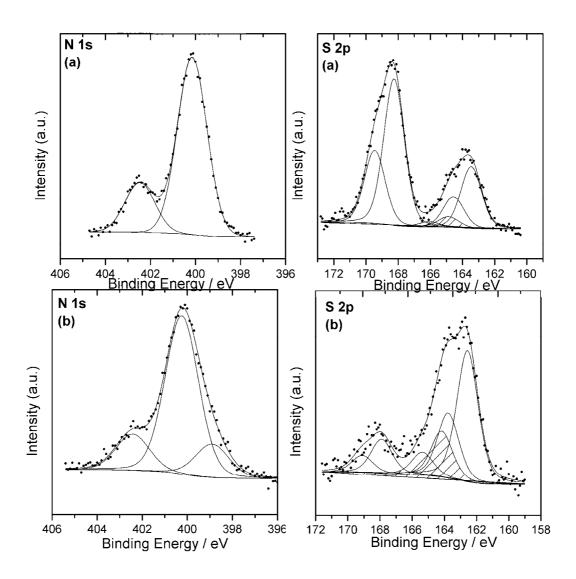


Figure S9. S 2p and N 1s XPS spectra of Cu/6 > 13 before (a) and after (b) 1 min biasing.



**Figure S10.** S 2p and N 1s XPS spectra of Cu/6⊃15 before (a) and after (b) 1 min biasing.



**Figure S11.** S 2p and N 1s XPS spectra of Cu/6⊃15 before (a) and after (b) 3 min biasing.