



**Figure 1.** (i) UPS spectra of the valence band region, (ii) LEED patterns of mixed  $M_1$ TPP+ $M_2$ TPP organic monolayers sequential deposition on Fe(001)- $p(1 \times 1)$ O substrate, (iii) LEED pattern of mixed  $M_1$ TPP+ $M_2$ TPP organic monolayer co-deposition on Fe(001)- $p(1 \times 1)$ O substrate.

In (i), the red dotted lines indicate the O 2p peak position which is a contribution from the underlying Fe(001)- $p(1 \times 1)$ O substrate. Here, the absence of sharp peaks in such positions indicate complete monolayer coverages. In (ii), top row: 0.25 ML CoTPP is deposited first ( $M_1$ TPP), followed by 0.75 ML ZnTPP ( $M_2$ TPP); bottom row: 0.25 ML ZnTPP is deposited first ( $M_1$ TPP), followed by 0.75 ML CoTPP ( $M_2$ TPP). Results from 1ML pure ZnTPP on Fe(001)- $p(1 \times 1)$ O (top row) and 1 ML pure CoTPP on Fe(001)- $p(1 \times 1)$ O (bottom row) are presented for comparison. In (ii) and (iii), patterns highlighted by yellow circles exhibit  $(5 \times 5)$  ordering and patterns highlighted by pink circles exhibit  $(5 \times 5)R37^\circ$  ordering.

**References:** [1] N. Xin, J. Guan, C. Zhou, X. Chen, C. Gu, Y. Li, M. A. Ratner, A. Nitzan, J. F. Stoddart, X. Guo, Concepts in the design and engineering of single-molecule electronic devices, Nature Reviews Physics, 2019, 1: p. 211-230.

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