Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

Probing Surface Mediated Configurations of Nonplanar Regioisomeric Adsorbates using Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy

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S1. Chemical structure and UV-Vis absorption spectra of *trans*- and *cis*-H_2F_{20}TPPDL:

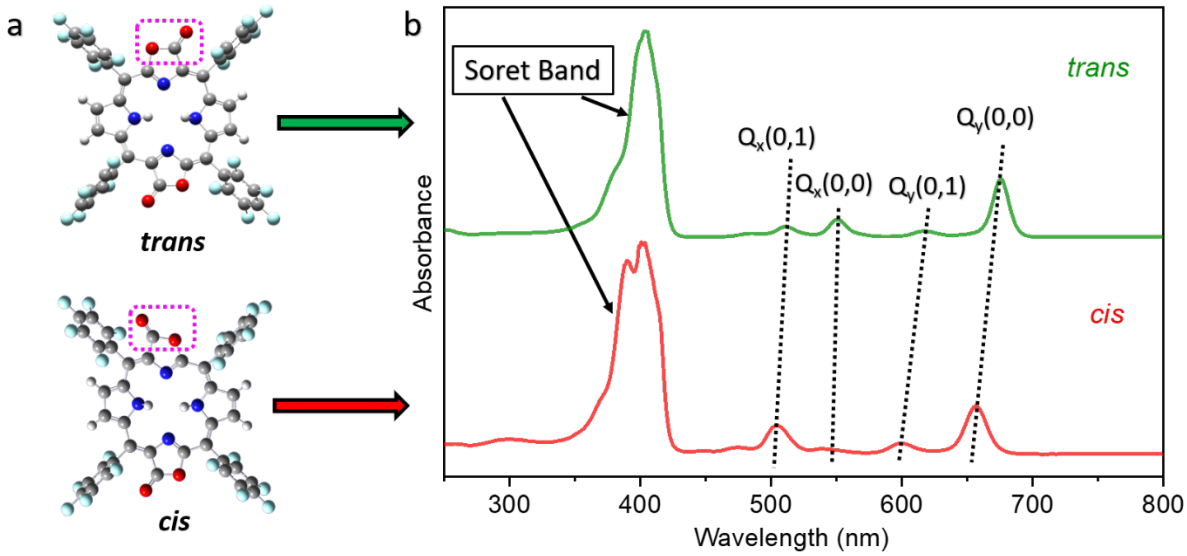


Figure S1. (a) Chemical structure of *trans*- and *cis*-H_2F_{20}TPPDL. The pink dotted rectangle suggests the structural change in the central porphodilactone (PDL) core. (b) UV-Vis absorption spectra of *trans*-(green) and *cis*-(red) isomers in dichloromethane (DCM) at 298 K. The Soret band and other four Q bands are highlighted.

S2. TERS spectra (tip-engaged and tip-retracted) of *trans*-H_2F_{20}TPPDL on Ag(100):

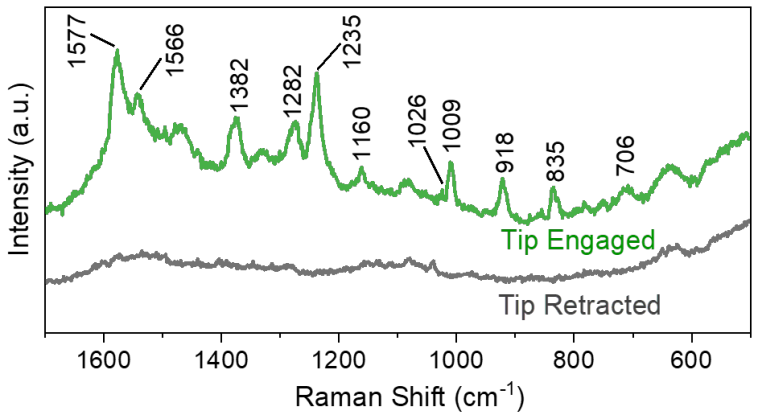


Figure S2. UHV-TERS spectra of *trans*-H_2F_{20}TPPDL on Ag(100) collected using 561 nm laser source. Tip-engaged (green) and tip-retracted (dark grey) signals are highlighted.

S3. TERS spectra (tip-engaged and tip-retracted) of *trans*-H_2F_{20}TPPDL on Cu(100):

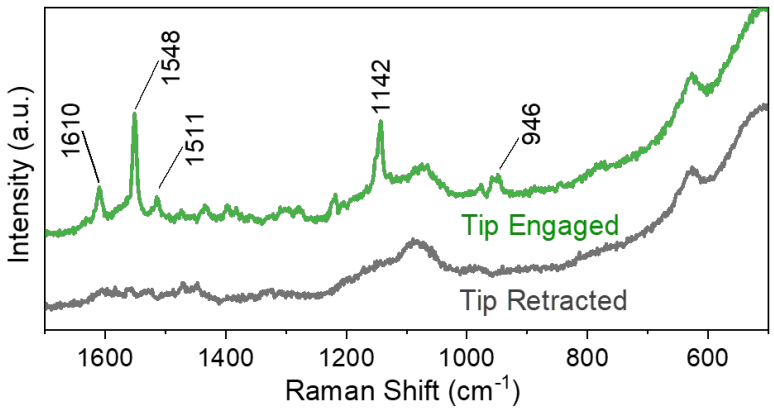


Figure S3. TERS spectra of *trans*-H_2F_{20}TPPDL on Cu(100) obtained using 561 nm laser source. Tip-engaged (green) and tip-retracted (dark grey) signals are highlighted.

S4. Proposed model for *trans*-H_2F_{20}TPPDL on Cu(100):

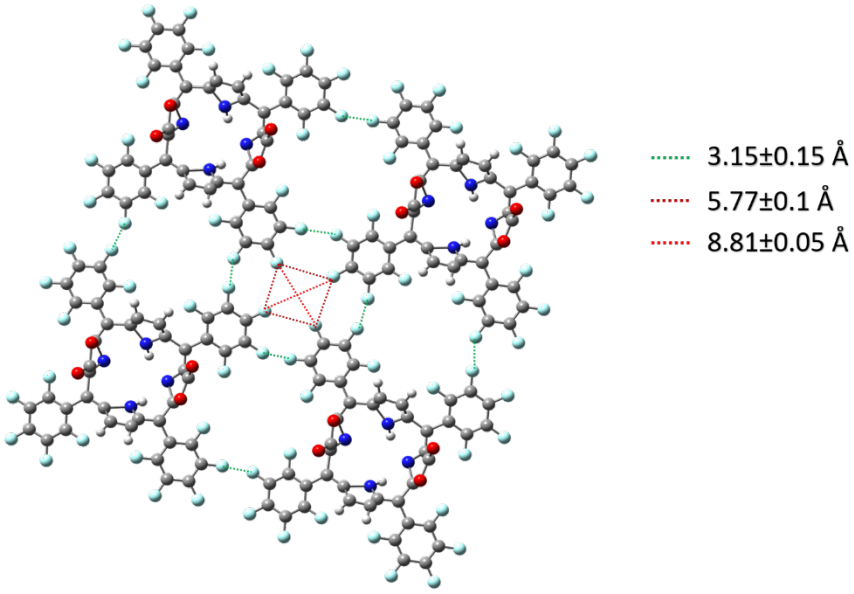


Figure S4. Proposed model for *trans*-H_2F_{20}TPPDL on Cu(100). The green, brown and red dotted lines represent C-F…F attractive intermolecular interactions with the length 3.15±0.15 Å, 5.77±0.1 Å and 8.81±0.05 Å respectively. The green dotted lines are within the range of fluorine-fluorine interactions, according to previous literature (~3.1 Å),[1] while the other two lengths are out of the concerned range.

S5. TERS spectra (tip-engaged and tip-retracted) of *cis*-H_2F_{20}TPPDL on Ag(100) and Cu(100):

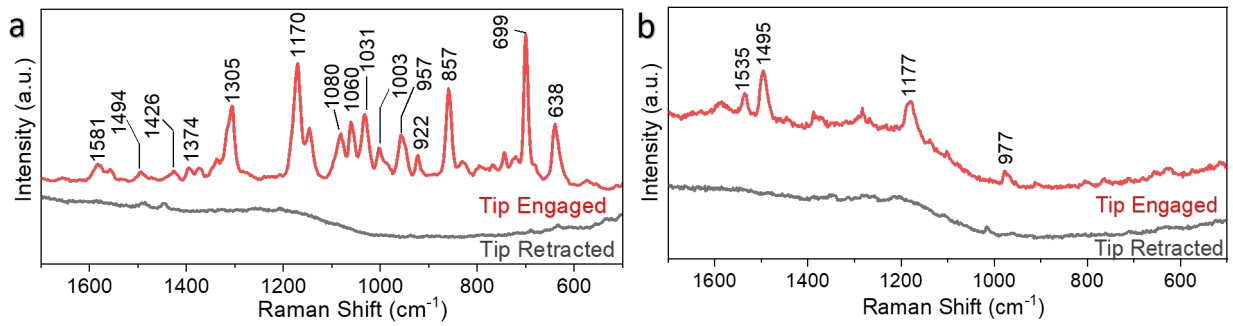


Figure S5. (a) UHV-TERS spectra of *cis*-H_2F_{20}TPPDL on Ag(100) collected using 633 nm laser source. Tip-engaged (red) and tip-retracted (dark grey) signals are highlighted. (b) UHV-TERS spectra of *cis*-H_2F_{20}TPPDL on Cu(100) acquired by 633 nm laser source. Tip-engaged (red) and tip-retracted (dark grey) signals are highlighted.

S6. Proposed model for *cis*-H_2F_{20}TPPDL molecules on Ag(100) and Cu(100):

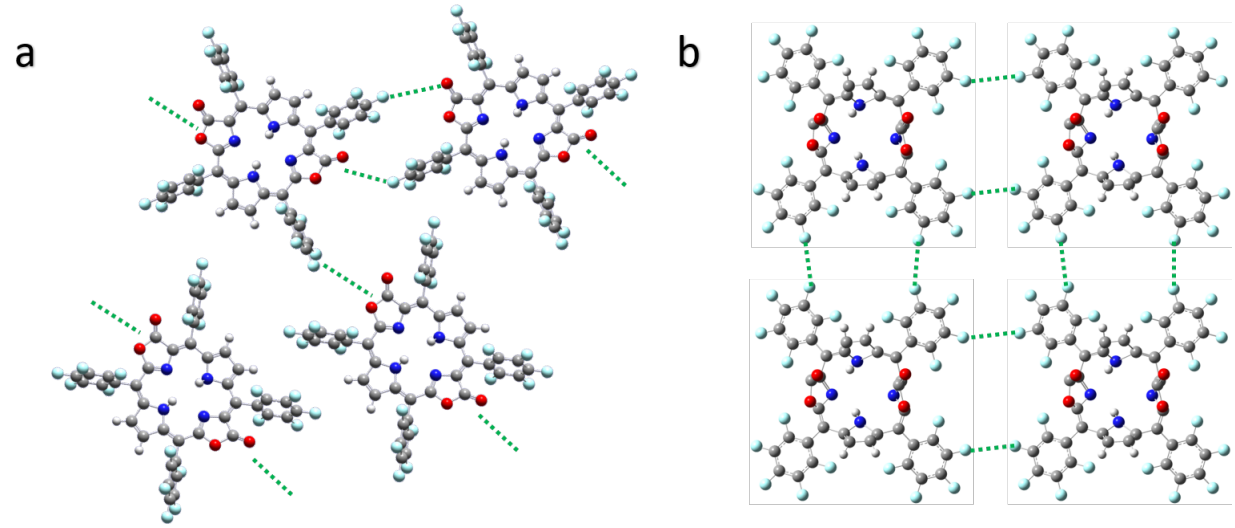


Figure S6. (a) Proposed model for *cis*-H_2F_{20}TPPDL on Ag(100). Interactions involving lactone moieties and phenyl (-C_6F_5) rings are marked using green dotted line. (b) Proposed model for *cis*-H_2F_{20}TPPDL on Cu(100). C-F···F interactions are highlighted.

S7. TERS spectra (tip-engaged and tip-retracted) of *trans*- and *cis*-H_2F_{20}TPPDL on Au(100):

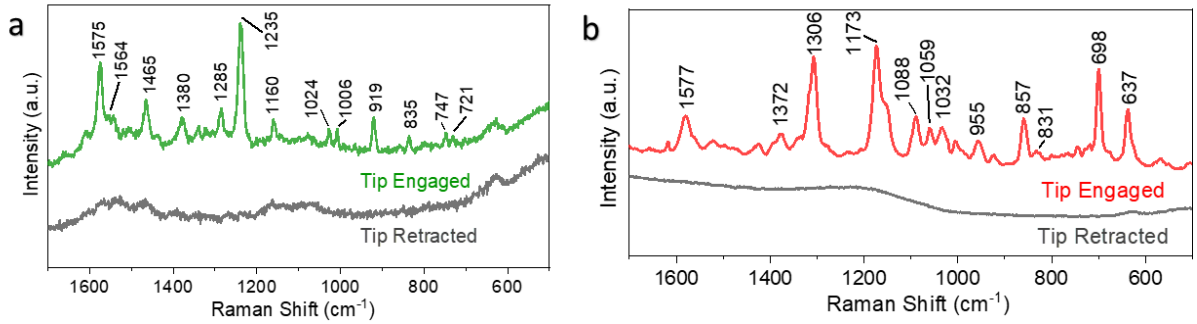


Figure S7. (a) TERS spectra of *trans*-H_2F_{20}TPPDL on Au(100) obtained by 561 nm laser source. Tip-engaged (green) and tip-retracted (dark grey) signals are highlighted. (b) TERS spectra of *cis*-H_2F_{20}TPPDL obtained using 633 nm laser source. Tip-engaged (red) and tip-retracted (dark grey) signals are highlighted.

S8. Comparison of TERS of *trans*- and *cis*-H_2F_{20}TPPDL on Cu(100), Ag(100) and Au(100):

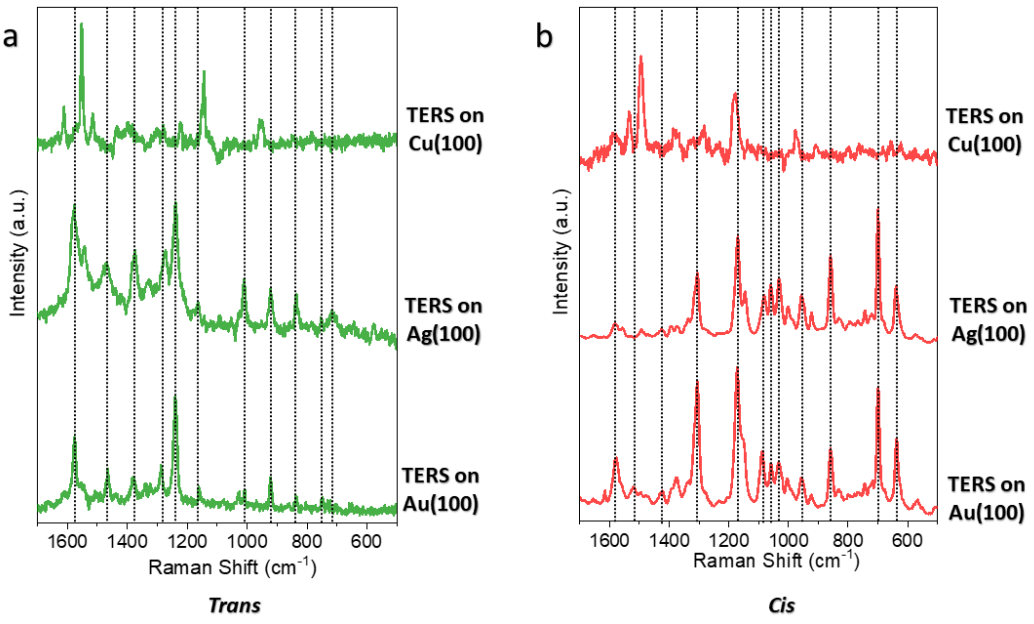
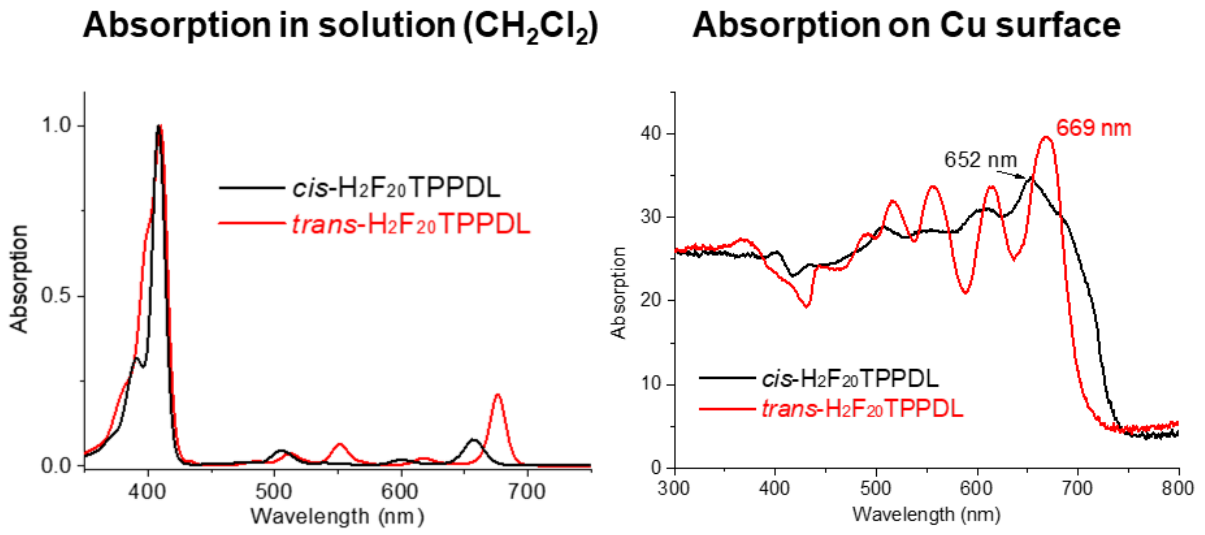


Figure S8. (a) Comparison of TERS spectra of *trans*-H_2F_{20}TPPDL on Cu(100), Ag(100) and Au(100) obtained by 561 nm laser source. (b) Comparison of TERS spectra of *cis*-H_2F_{20}TPPDL on Cu(100), Ag(100) and Au(100) recorded with 633 nm laser source. The black dotted lines represent the peak positions of these two molecules recorded on Ag(100).

S9. Comparison of absorption spectra of *trans*- and *cis*-H_2F_{20}TPPDL in solution and surface:



Compound	Absorption (nm) in solution (CH_2Cl_2)	Absorption (nm) on Cu surface
***trans*-H_2F_{20}TPPDL**	512, 552, 618, 676	517, 556, 614, 669
***cis*-H_2F_{20}TPPDL**	505, 539, 600, 657	507, 550, 605, 652

Figure S9. Comparison of absorption spectra of *trans*- and *cis*-H_2F_{20}TPPDL in solution and on Cu surface. The four Q bands show very slight difference in peak positions on surface compared to the solution.

References:

1. Kawai, S.; Sadeghi, A.; Xu, F.; Peng, L.; Orita, A.; Otera, J.; Goedecker, S.; Meyer, E. Extended Halogen Bonding between Fully Fluorinated Aromatic Molecules. *ACS Nano* **2015,** *9* (3), 2574-2583.