

## Abstract

$\pi$ -Conjugated organic semiconductors have been explored in several optoelectronic devices, yet their use in molecular detection as surface-enhanced Raman spectroscopy (SERS)-active platforms is unknown. Herein, we demonstrate that SERS-active, superhydrophobic and ivy-like nanostructured films of a molecular semiconductor,  $\alpha,\omega$ -diperfluorohexylquaterthiophene (DFH-4T), can be easily fabricated by vapour deposition. DFH-4T films without any additional plasmonic layer exhibit unprecedented Raman signal enhancements up to  $3.4 \times 10^3$  for the probe molecule methylene blue. The combination of quantum mechanical computations, comparative experiments with a fluorocarbon-free  $\alpha,\omega$ -dihexylquaterthiophene (DH-4T), and thin-film microstructural analysis demonstrates the fundamental roles of the  $\pi$ -conjugated core fluorocarbon substitution and the unique DFH-4T film morphology governing the SERS response. Furthermore, Raman signal enhancements up to  $\sim 10^{10}$  and subzeptomole ( $< 10^{-21}$  mole) analyte detection were accomplished by coating the DFH-4T films with a thin gold layer. Our results offer important guidance for the molecular design of SERS-active organic semiconductors and easily fabricable SERS platforms for ultrasensitive trace analysis.