Supporting Information

Full reference 8

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Experimental section.

Sample preparation. The synthesis of the BP4 and BP6 molecules has been described elsewhere[1]. Commercially available Au/mica substrates from Georg Albert PVD, consisting of 150 nm Au evaporated on mica (rate 2 nm/s, temp. 340 ^{o}C) were flame-annealed in a butane/oxygen flame and subsequently immersed into a 100 μM solution of BP4 or BP6 in ethanol at room temperature for 24h. After immersion, samples were rinsed with pure ethanol and blown dry with nitrogen. Annealing of the SAMs was done in a sealed container which was purged with nitrogen prior to temperature treatment.

STM measurements. All STM measurements were carried out in air at room temperature using a Molecular Imaging Picoscan STM instrument. In all cases tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Goodfellow) wire. The data were collected in constant current mode using tunneling currents between 400 pA and 700 pA and a sample bias between 800 mV and 1.0 V (tip positive). No tip-induced changes were observed.

HRXPS measurements. The HRXPS experiments were performed at the bending magnet beamline D1011 at the MAX II storage ring of the MAX-lab synchrotron radiation facility in Lund, Sweden. The HRXPS spectra were acquired in normal emission geometry at photon energies of 350 and 580 eV for the C 1s range and 350 eV for the S 2p region, respectively. In parallel, the Au 4f spectra were acquired and the O 1s range was monitored. The binding energy (BE) scale of every spectrum was individually calibrated using the Au $4f_{7/2}$ emission line of AT-covered Au substrate at 83.95 eV. The latter value is the latest ISO standard.[2] It is very close to a value of 83.93 eV, which has been obtained by us for Au $4f_{7/2}$ using a separate calibration to the Fermi edge of a clean Pt-foil.[3] The energy resolution was better than 100 meV, which is noticeably smaller than the full widths at half maximum (FWHM) of the photoemission peaks addressed in this study. Thus, these FWHMs are representative for the natural widths of the respective lines. HRXPS spectra were fitted by symmetric Voigt functions and a Shirley-type background. To fit the S $2p_{3/2,1/2}$ doublet we used two peaks with the same FWHM, the standard[4] spin-orbit splitting of ≈ 1.18 eV (verified by a fit), and a

branching ratio of 2 ($S2p_{3/2}/S2p_{1/2}$). The fits were performed self-consistently: the same fit parameters were used for identical spectral regions.

NEXAFS measurements. The NEXAFS spectroscopy measurements were performed at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin, Germany. The spectra acquisition was carried out at the C K-edge in the partial electron yield mode with a retarding voltage of –150 V. Linear polarized synchrotron light with a polarization factor P of ≈ 82% was used. The energy resolution was ≈ 0.40 eV. The incidence angle of the light was varied from 90° (***E***-vector in surface plane) to 30° (***E***-vector near surface normal). The raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. The energy scale was referenced to the pronounced π* resonance of highly oriented pyrolytic graphite at 285.38 eV.

Contact angle measurements: Advancing contact angles of distilled water were measured with a Krüss goniometer, model G10. The experiments were performed under ambient conditions with the needle tip in contact with the drop. Averaged values of at least 10 measurements at different locations on each sample are reported here. Deviations from the average were less than ±1°.

(1) Rong, H. T.; Frey, S.; Yang, Y. J.; Zharnikov, M.; Buck, M.; Wühn, M.; Wöll, C.; Helmchen, G. *Langmuir* **2001**, *17*, 1582-1593.

(2) *Surface chemical analysis - X-ray photoelectron spectrometers - Calibration of the energy scales, ISO 15472:2001*.

(3) Heister, K.; Rong, H. T.; Buck, M.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O. *J. Phys. Chem. B* **2001**, *105*, 6888-6894.

(4) Moulder, J. F.; Stickle, W. E.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photo-electron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN., 1992.