

**NHC-Based Self-Assembled Monolayers on Solid Gold Substrates**

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**Accessory Publication**

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*Materials*

A mixture of BIET and its dimer was obtained by deprotonation of 1,3-diethylbenzimidazolium bromide<sup>[S1]</sup> with KO<sup>t</sup>Bu in THF in analogy to the procedure described for BI<sup>i</sup>Pr,<sup>[S2]</sup> and the monomer–dimer equilibrium investigated by a VT-NMR study essentially identical to that described by Lemal and coworkers;<sup>[S3]</sup> however, THF-*d*<sub>8</sub> instead of diglyme-*d*<sub>14</sub> was used as solvent (temperature range 20–60 °C, Varian Inova-400 spectrometer operating at 400 MHz for <sup>1</sup>H).

*X-ray Crystallography*

For the X-ray structure analysis of (BIET)<sub>2</sub>, a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. The data set was corrected for absorption and for Lorentz and polarisation effects. The structure was solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against  $F^2$  (SHELXL97).<sup>[S4]</sup> All non H atoms were found in

difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameter. The ellipsoid plot with the atomic numbering scheme (Fig. 1) was made using ORTEP-3 win.<sup>[S5]</sup> CCDC reference number 823497.

Crystallographic data for (BIET)<sub>2</sub>: chemical formula C<sub>22</sub>H<sub>28</sub>N<sub>4</sub>, formula mass 348.48, yellow needle, dimensions 0.28 mm × 0.18 mm × 0.10 mm,  $T = 100(2)$  K,  $a = 13.1993(10)$ ,  $b = 19.9863(14)$ ,  $c = 30.210(2)$  Å, orthorhombic, space group  $Fddd$  (no. 70),  $V = 7969.7(10)$  Å<sup>3</sup>,  $Z = 16$ ,  $F(000) = 3008$ ,  $d_{\text{calc}} = 1.162$  g cm<sup>-3</sup>,  $\mu = 0.070$  mm<sup>-1</sup>,  $T_{\text{max}}/T_{\text{min}} = 0.995/0.982$ . Within the  $\theta$  range of 1.97 and 25.00° 9297 reflections were collected, 1754 unique [ $R_{\text{int}}: 0.0717$ ], of which 1067 were observed [ $I > 2 \sigma(I)$ ]. At final convergence:  $S = 0.824$ ,  $R_1 = 0.0376$ ,  $wR_2 = 0.0566$  [ $I > 2 \sigma(I)$ ] and  $R_1 = 0.0819$ ,  $wR_2 = 0.0648$  (all data), for 121 parameters and 0 restraints.

### *Film Fabrication*

The gold substrates for film fabrication were prepared by thermal evaporation of 100 nm gold (99.99% purity) onto polished single-crystal silicon (111) wafers (Silicon Sense) primed with a 5 nm Ti adhesion layer. The resulting films were polycrystalline with a grain size of 20–50 nm with predominately (111) orientation.<sup>[S6]</sup> Films were formed by immersion of 1×1 cm<sup>2</sup> gold substrates in ca. 10 μM solutions of the adsorbate species in THF at room temperature for 24 h. After immersion the samples were sonicated and carefully rinsed with copious amounts of THF, blown dry with nitrogen, and kept in plastic containers filled with nitrogen until they were characterised.

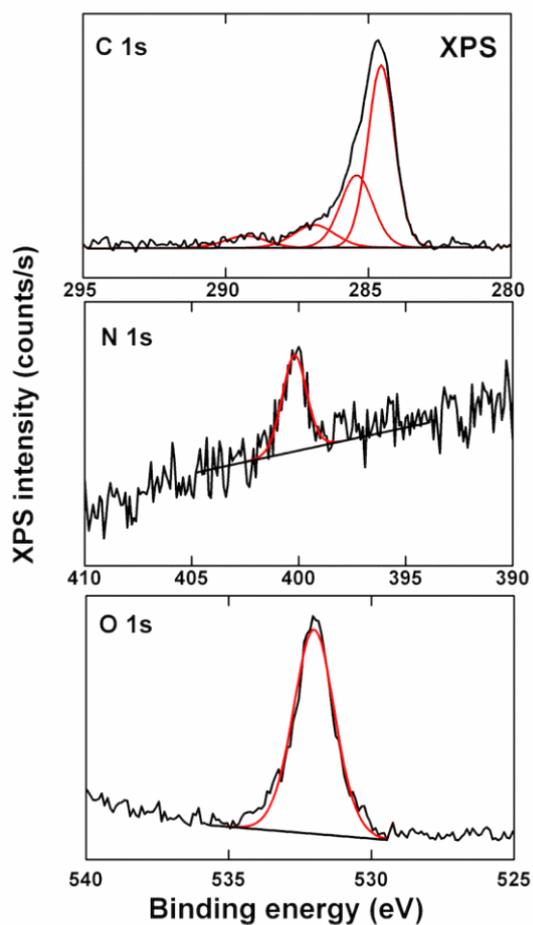
### *Surface Characterisation*

The films were characterised by XPS using a Kratos AXIS Ultra DLD instrument (Kratos, Manchester, England) in the hybrid mode equipped with a monochromatic Al-K<sub>α</sub> X-ray source (photon energy = 1486.6 eV). The photoelectron take-off angle normal was normal to the substrate; the effective take-off angle for hybrid mode was 40°. The photoelectron energy scale was calibrated to the Au 4f<sub>7/2</sub> emission (84.0 eV) of the underlying gold substrate. The XPS

determined compositions were an average from three spots per sample. Atomic compositions were calculated from peak areas obtained from 0 to 1100 eV survey scans (C 1s, Au 4f) and selected region scans (524–544 eV for O 1s; 390–410 eV for N 1s; 155–173 eV for S 2p) acquired at an analyser pass energy of 80 eV. Molecular environments of the samples were probed by collecting high-resolution (analyser pass energy = 20 eV) spectra from the O 1s, N 1s, and C 1s regions. A linear background was subtracted for all peak quantifications. The peak areas were normalised by the manufacturer-supplied sensitivity factors and surface concentrations were calculated using Casa XPS software. NEXAFS spectra were collected at the U7A beamline at the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, Upton, NY) using an elliptically ~85% p-polarised beam. The beamline is equipped with a monochromator and a 600 l/mm grating that provides a full-width at half maximum resolution of ~0.15 eV at the carbon *K*-edge (285 eV). The monochromator energy scales at the C and N *K*-edges were calibrated using graphite and titanium nitride transmission grids with characteristic resonances at 285.35 eV<sup>[S7]</sup> and 401.6 eV, respectively. A channeltron detector with bias voltages of 150 V and 300 V monitored partial electron yields for the C and N *K*-edge. Beam intensity fluctuations and monochromator absorption artefacts were suppressed by normalising the spectra using a drain current reference spectrum collected from an Au-coated mesh. All samples were mounted to allow rotation about the vertical axis, thus allowing the NEXAFS angle, i. e. the angle between the incident X-ray beam and the sample surface, to change.

**Table S1. Summary of XPS determined elemental compositions.** Values are given in at.% with standard deviations in parentheses.

	Au	C	N	O
Unmodified Au substrate	67.8 (0.9)	30.5 (1)	n.d.	1.7 (0.3)
Unmodified Au substrate without Au		94.6 (1)	n.d.	5.4 (0.9)
NHC film	36.8 (1.4)	49.5 (2.1)	11.4 (0.2)	3.1 (0.5)
NHC film without Au		79.2 (1.6)	16.5 (0.7)	4.3 (0.9)
Expected NHC film composition		84.6	16.4	0



**Fig. S1.** High-resolution XP spectra of the BIET-based film on gold. Top: C 1s spectrum, fitted with four peaks at 284.6 eV (C=C), 285 eV (C-C), 286.6 eV (C-N) and 289.3 eV (C=O); middle: N 1s spectrum, fitted with a single peak at 400.2 eV (CN); bottom: O 1s spectrum, fitted with a single peak at 532 eV.

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