

Supporting Information for:

Determination of Energetic Positions of

Electronic States and the Exciton Dynamics in a

π -Expanded N-Heterotriangulene Derivative

Adsorbed on Au(111)

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1 Experimental methods

2PPE measurements were conducted in an ultra-high vacuum chamber. A clean Au(111) substrate was prepared by a standard procedure including Ar⁺ sputtering and subsequent annealing to 800 K under ultra-high vacuum conditions. The N-HTA-557-P molecules were synthesized according to Ref.[Michalsky *et al.*, Chem. Eur. J. 2022, 28, e202200326], purified by column chromatography and degassed in vacuum at 400 K for several hours. They were deposited from an effusion cell held at a temperature of 453 K while the surface was kept at 100 K. The experiments were performed at a sample temperature of around 90 K. In 2PPE, a femtosecond pump laser pulse induces electronic transitions from occupied electronic states of the substrate or the adsorbate into unoccupied electronic or virtual states. These excited states are then probed with a second laser pulse by lifting the excited electron above the vacuum level. The kinetic energy of the emitted electrons is measured with a time-of-flight spectrometer. Photoelectron signals may arise from the occupied or unoccupied electronic states; therefore, photon energy-dependent measurements are needed for the assignment. A temporal delay between pump and probe pulse was introduced to obtain population dynamics of excited states on a femtosecond time scale.

2 Two-photon photoemission data

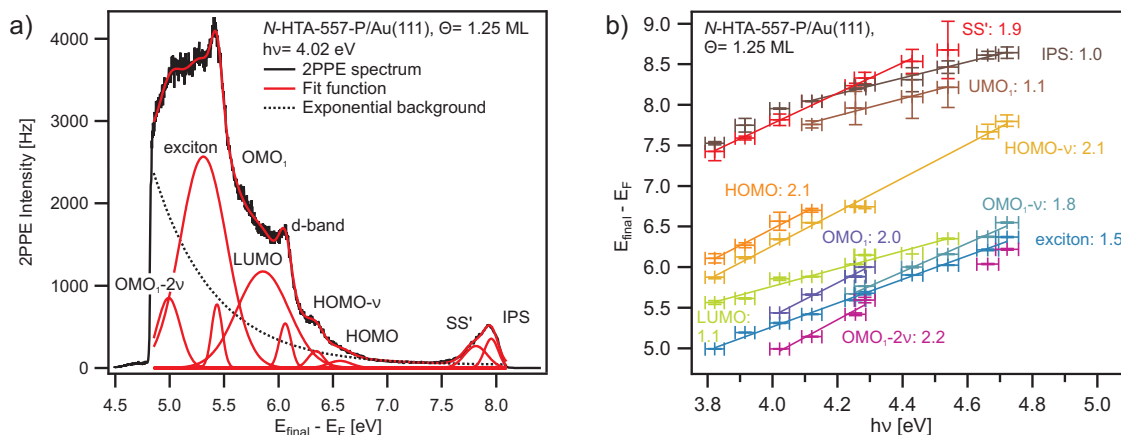


Figure S1: a) 2PPE spectrum of 1.25 monolayer (ML) N-HTA-557-P adsorbed on Au(111). The data are fitted with an exponential background and Gaussian-shaped peaks (red curves). The energy axis reveals the final state (E_{Final}) of photoemitted electrons with respect to the Fermi energy E_F ($E_{Final} - E_F = E_{kin} + \Phi$); thus, the low-energy cutoff corresponds to the work function (Φ) of the adsorbate/substrate system (UMO: unoccupied molecular orbital; OMO: occupied molecular orbital, IPS: image potential state, SS: surface state). b) Photon-energy-dependent peak position extracted to assign peaks observed in the 2PPE spectrum to occupied, unoccupied intermediate or final electronic states. A slope of 1 suggests that a peak originates from an unoccupied intermediate state, a slope of zero from an unoccupied final state (located above the vacuum level), while a slope of 2 is related to peaks originating from occupied states. The slopes from the fits are given next to the respective data.

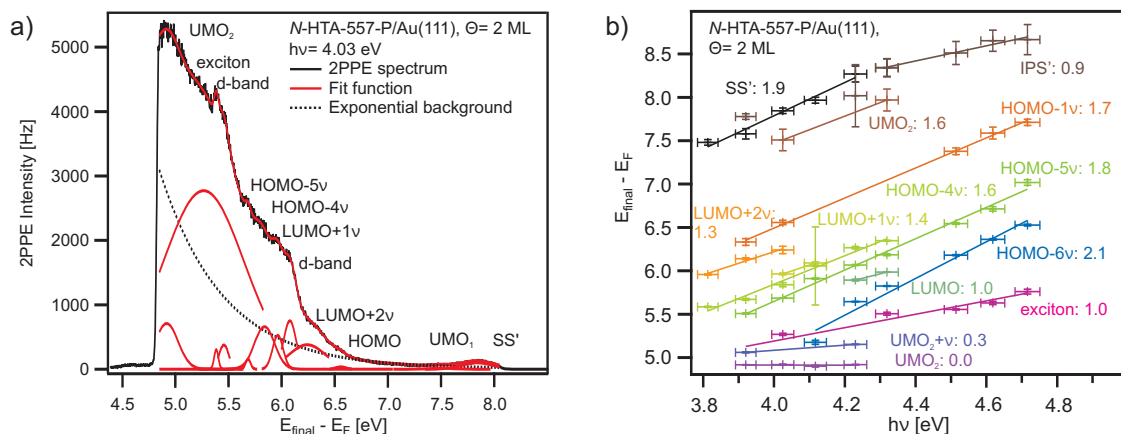
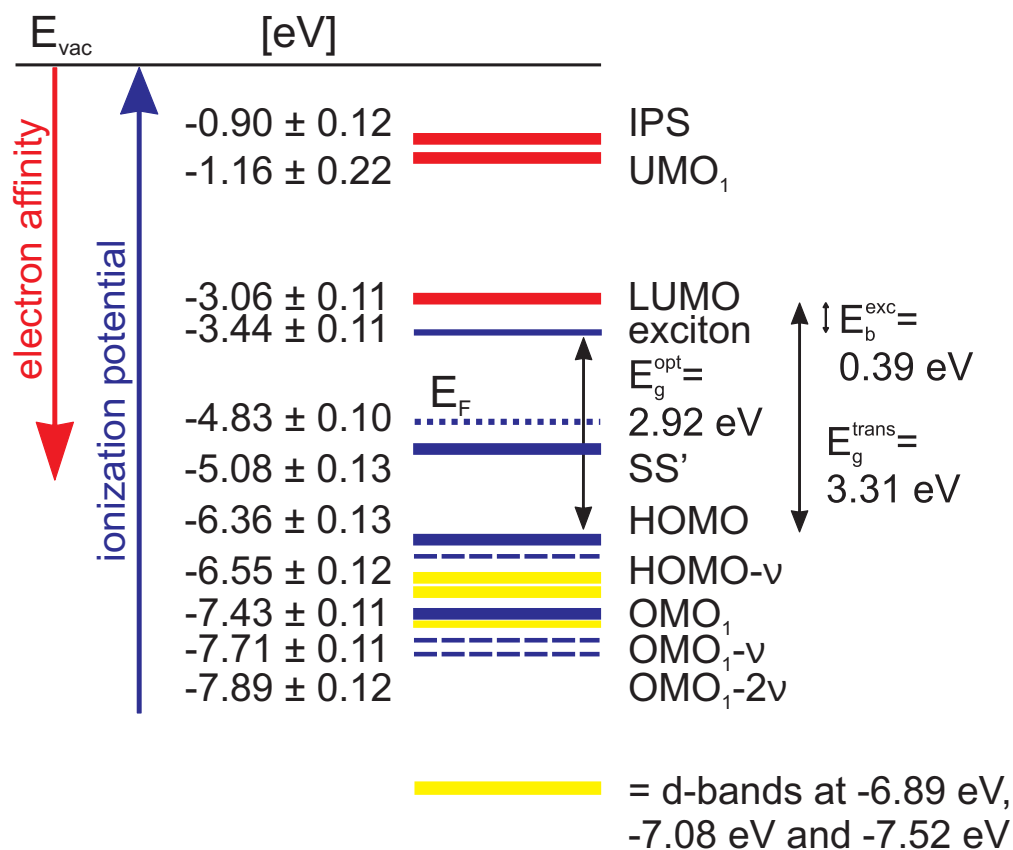


Figure S2: a) 2PPE spectrum of 2 ML N-HTA-557-P adsorbed on Au(111). The data are fitted with an exponential background and Gaussian-shaped peaks (red curves). b) Photon-energy-dependent peak position extracted to assign peaks observed in the 2PPE spectrum to occupied, unoccupied intermediate or final electronic states. The slopes from the fits are given next to the respective data.



N-HTA-557-P/Au(111), $\Theta \sim 1\text{ML}$

Figure S3: Energy level diagram of N-HTA-557-P adsorbed on Au(111) for N-HTA-557-P coverages around 1 ML with respect to the vacuum level. The blue levels are the ionization potentials and the red ones are the electron affinities, which are in the molecular orbital picture represented by the energies of the HOMOs, LUMO, UMOs (unoccupied molecular orbital) or OMO (occupied molecular orbital), respectively. In addition the Au(111) d-bands, the shifted surface state (SS) and the first image potential state (IPS) are observed. The dashed lines indicate vibronic transition. E_F is the Au(111) Fermi level.

3 UV/vis absorption and emission

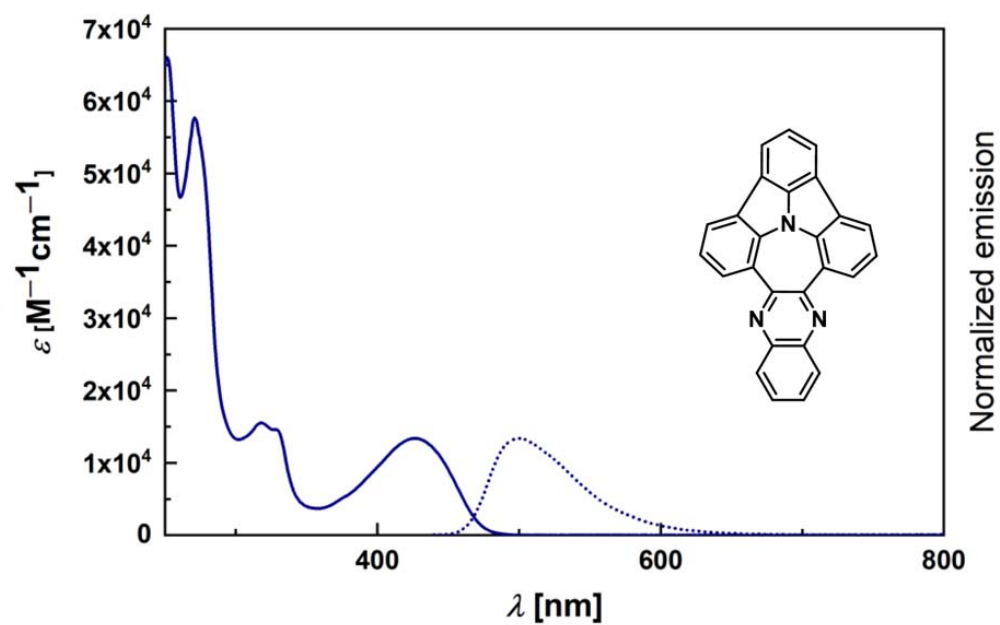


Figure S4: UV-vis absorption and emission spectra (normalized) of N-HTA-557-P in CH₂Cl₂ solution. The optical gap (2.61 eV) was determined from the absorption edge ($\lambda = 475$ nm) via $E_{opt.} = h \cdot c / \lambda$ (with h the Planck constant and c the speed of light).

4 Infrared spectroscopic data

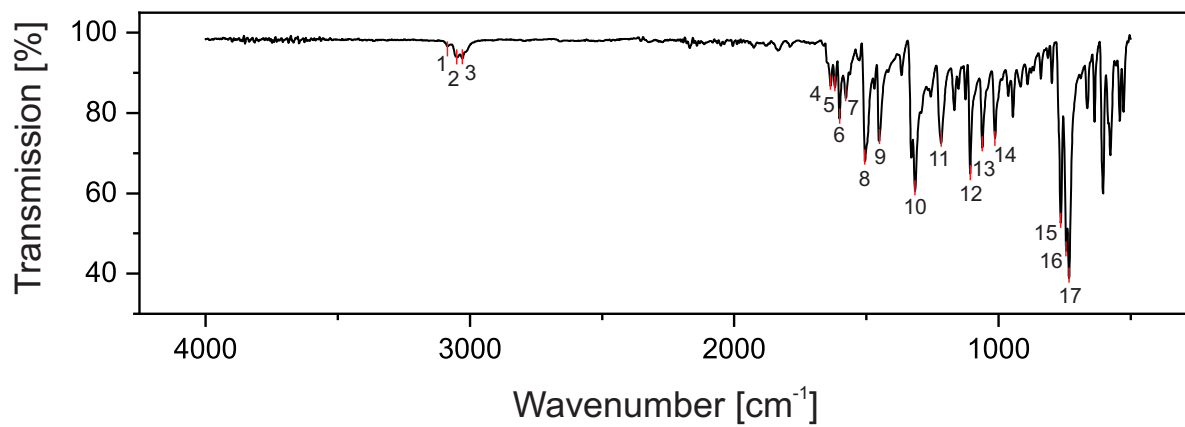


Figure S5: Infrared spectrum of N-HTA-557-P in a KBr-pellet.

Table S1: Assigned vibrations (in cm^{-1}) of N-HTA-557-P and the corresponding DFT calculated frequencies of the molecule in the gas-phase at the B3LYP level and the 6-311G basis set. The identified modes for each vibration are described with the following abbreviations; γ – out-of-plane; ρ – rocking; δ – scissoring; ν – stretching; ω – wagging. Representation (Repr.) of the associated point groups and the orientation of the calculated dipole derivative vector with respect to the molecular geometry, x, perpendicular to the molecular plane; y, short axis and z, long axis of molecular backbone for each mode are listed.

#	IR	DFT	Mode	Repr.
1	3084	3230	ν (C-H)	B ₂ (y)
2	3048	3209	ν (C-H)	A ₁ (z)
3	3029	3192	ν (C-H)	B ₂ (y)
4	1636	1674	ν (C-C), δ (C-H)	A ₁ (z)
5	1618	1655	ρ (C-H), δ (C-H)	B ₂ (y)
6	1601	1643	ρ (C-H), δ (C-H)	B ₂ (y)
7	1577	1619	δ (C-H)	A ₁ (z)
8	1504	1535	ρ (C-H)	B ₂ (y)
9	1452	1496	ρ (C-H)	A ₁ (z)
10	1316	1342	ρ (C-H)	A ₁ (z)
11	1217	1235	δ (C-H)	A ₁ (z)
12	1108	1137	ρ (C-H), δ (C-H)	A ₁ (z)
13	1062	1091	δ (C-H)	A ₁ (z)
14	1011	1028	ρ (C-H)	B ₂ (y)
15	766	820	γ_{ω} (C-H)	B ₁ (x)
16	743	797	γ_{ω} (C-H)	B ₁ (x)
17	733	794	γ_{ω} (C-H)	B ₁ (x)