Exploiting Cooperative Catalysis for the On-Surface Synthesis of Linear Heteroaromatic Polymers via Selective C–H Activation

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Experimental Procedures

**Chemicals.** Dipyrazino[2,3-f][2',3'-h]quinoxaline (HAT) was prepared according to literature procedures.\(^{[1,2]}\)

**STM/AFM Measurements.** Experiments were carried out with a low-temperature scanning tunneling and atomic force microscope (STM/AFM) equipped with a qPlus tuning fork\(^{[3]}\) (resonance frequency \(f_0 \approx 29.1\) kHz, spring constant \(k \approx 1.8\) kN m\(^{-1}\), quality factor \(Q \approx 3 \times 10^4\)) in ultra-high vacuum (\(p \approx 2 \times 10^{-10}\) mbar) and at a temperature of 7 K. Bias voltages are given as sample bias with respect to the tip. Positive constant-height offsets \(\Delta z\) correspond to a distance increase with respect to the STM/AFM set point above the substrate. After preparing a clean Ag(111) surface from cyclic Ne\(^+\) sputtering at 1 keV and annealing to 820 K, HAT molecules were deposited at a sample temperature below 10 K and annealed to high temperatures on the manipulator. NaCl islands (0.3-0.5 monolayers) were co-deposited together with the HAT. A small amount of CO was dosed onto the surface for tip functionalization.\(^{[4]}\) Additional NaCl islands were grown after the reaction, to facilitate the pick-up of CO molecules to the tip apex from these islands.

**XPS Measurements.** X-ray photoelectron spectra were recorded on a Leybold-Heraeus LHS 10 spectrometer using a non-monochromatized Al K\(_\alpha\) source (1486.7 eV). All XPS experiments were performed on a polycrystalline Ag foil (sputter cleaned by several cycles of 10 min Ar\(^+\) sputtering at 2 keV, followed by annealing up to 770 K). All spectra were recorded in an ultra-high vacuum chamber at a pressure below 5×10\(^{-8}\) mbar. The analyzer was operated at a constant pass energy of 100 eV leading to an energy resolution with a full width at half-maximum (fwhm) of \(\approx 1.1\) eV. Core level spectra were deconvoluted by using Voigt functions after linear (C 1s, N 1s, Na 1s and Cl 2p) or Shirley (Ag 3d) background subtraction.

*Figure S1.* Length distribution of linear polymers. The number of monomer constituting the chains (n) is defined as the number of coupled molecules having the same azimuthal orientation. The statistics is done over \(\approx 420\) molecules from several molecular resolved STM images acquired after annealing to 700 K.
Results and discussion

XPS results

Figure S2. a, XP spectra of the C 1s, N 1s, Na 1s and Cl 2p core levels after deposition of NaCl (black), HAT (blue) or both (green) on a polycrystalline Ag foil kept at 300 K and subsequent annealing to 550 K. b, Plot of the relative coverages of the C 1s, N 1s, Na 1s and Cl 2p core levels after deposition of NaCl (black), HAT (blue) or both (green) on a polycrystalline Ag foil kept at 300 K and subsequent annealing to 550 K.

The Na 1s and Cl 2p core levels observed after deposition of ~0.1 ML NaCl (black spectra in Figure S1) vanish entirely after annealing to 550 K (in Figure S2). The HAT molecules show a similar behavior: deposition at 300 K results in a C 1s core level with the main component at a binding energy of 286.5 eV and a N 1s core level at 400.1 eV. A significant decrease of the signal intensities after
Determination of the NaCl coverage was carried out by quantification of the Na 1s and Ag 3d core levels according to the following formula:

\[ \frac{N_{Na}}{N_{Ag}} = \frac{I_{Na\,1s}}{I_{Ag\,3d}} \frac{\sigma_{Ag\,3d}}{\sigma_{Na\,1s}} \frac{T(f_{\text{kin},Ag\,3d})}{T(f_{\text{kin},Na\,1s})} f(\lambda_{Ag\,3d}) f(\lambda_{Na\,1s}) \]

(1)

Here, \( N \) corresponds to the atomic number, \( I \) is the signal intensity, \( \sigma \) the photoemission cross section, \( T \) the transmission function of the analyzer, \( f(\lambda) \) the geometric factor and \( \lambda \) the signal attenuation length. As NaCl forms a layer on top of Ag, \( f(\lambda_{Na\,1s}) \) is approximately 1. \( \lambda_{Ag\,3d} \) is calculated as sum of the escape probabilities of photoelectrons originating from every layer.

\[ f(\lambda_{Ag\,3d}) = \sum_{n=0}^{\infty} e^{-nd} \frac{1}{\pi} = \frac{1}{1-e^{-d}} \approx 7 \]

(2)

The layer distance of the polycrystalline silver foil is approximated by the layer distance of an Ag(111) facet (\( d = 2.36 \, \text{Å} \)). \( \lambda_{Ag\,3d} \) is calculated following the TPP-2 model\(^{[5]}\) and amounts 15.4 Å at a kinetic energy of 1118 eV. We assume that NaCl appears as double layer on Ag with a lattice constant of 5.5 Å.\(^{[6]}\) Correcting the Na/Ag atomic ratio by a factor of \( 1/2 \) due to the double layer and a factor of 2.1 originating from the lattice mismatch between NaCl(100) and the Ag(111) substrate reveals the coverage of NaCl.

Bond dissociation energies

The DFT calculations of the bond dissociation energy (BDE) were performed by means of the Gaussian16 package\(^{[7]}\) using the ωB97XD functional\(^{[8]}\) with def2-SVP basis set \(^{[9]}\). In the case of free-standing HAT, it reaches 112.2 kcal/mol. This value is close to BDE of aromatic hydrocarbons and lowers the presence of Na adatom by ~20 kcal/mol, see Figure 4 in the main text.

The free-energy calculations using QM/MM-MD simulations

We employed QM/MM simulations to calculate the free energy profile of the dissociation of different hydrogen atoms (ortho, meta and para positions, see Figure 4c) in the monomer (HAT)\(_2\)-Na and dimer (HAT)\(_2\)-Na complexes using the umbrella sampling method. We employed \( \text{Sander}^{[10]} \) as the main program with Fireball\(^{[11]} \) as the code for QM calculations. The QM Fireball calculations and BLYP\(^{[12,13]} \) exchange correlation functional with D3 corrections,\(^{[14]} \) and an optimized numerical atomic-like orbitals\(^{[15]} \) as basis set with \( s \) orbital for H, \( sp^3 \) orbitals for C,N and \( sp^2 \) for Na and Ag. The accuracy of the QM/MM Fireball-Sander method was benchmarked with QM/MM Gaussian-Sander simulations using B3LYP\(^{[12,16,17]} \)(def2-SVP level of theory.

**Figure S3.** Calculated charge transfer between (HAT)\(_2\)-Na complex and the Ag(111) surface. To understand the interaction between the (HAT)\(_2\)-Na complex and the Ag(111) surface, we analyzed differential densities \( \Delta \rho = \rho_{\text{Ag}} - \rho_{\text{Na/Ag(111)}} \) obtained from the total energy DFT calculations, being \( \rho_{\text{Ag}}, \rho_{\text{HAT(111)}}, \) and \( \rho_{\text{Na/Ag(111)}} \) the electron densities of the relaxed complex on the surface, of two HAT molecules in gas phase, and of a Na adatom on the Ag(111) surface, respectively. Figure displays the differential electron density \( \Delta \rho \) isocontour 0.005 e/Å\(^2\) from top (upper) and side (lower) view, green and red color represent negative and positive value of \( \Delta \rho \), respectively. The differential density \( \Delta \rho \) shows that the Na adatom on the Ag(111) surface forms four coordination bonds with nitrogen atoms of HAT molecules (red density located between N and Na atoms in top view), which partially debilitates a strong interaction of the Na adatom with the Ag(111) surface (see green cloud in between Na and the Ag surface in panel b).
The reaction coordinate for umbrella sampling simulation was set along the C-H bond of interest for HAT complexes with Na adatoms. The whole protocol consists of four steps. First, the structure for each window was relaxed from the calculated TS with applied C-H restraint at temperature of 0 K. Second, only QM calculation to check the stability of wavefunction in the relaxed structure was submitted to assure a correct description of bond breaking in DFT. Then, MD tempering simulation was performed on the correct wavefunction to bring the system from 0 to 500 K. Finally, a production simulation was performed at final temperature with 0.5 fs steps for a total of 2.5 ps. The C-H bond length in each step was collected and WHAM applied to obtain the free energy profile.

The comparison of the free energy profiles obtained from both QM/MM methods is shown in Figure S4. The activation barrier is 4 kcal/mol higher than that obtained with Gaussian, validating the use of Fireball as a QM program for this system, allowing us to extend the simulations toward dimers.

Table S1. Calculated Hirshfeld and Mulliken charges of Ag or Na atom in the isolated states (adatom) and in the associated states ((HAT)_1,2-Ag/Na complex).

|                  | Ag (Hirshfeld) | Na (Hirshfeld) | Ag (Mulliken) | Na (Mulliken) |
|------------------|----------------|----------------|---------------|---------------|
| Adatom on Ag(111)| 0.04           | 0.35           | -0.01         | 0.38          |
| (HAT)_1-adatom on Ag(111)| 0.12 | 0.31           | 0.12          | 0.49          |
| (HAT)_2-adatom on Ag(111)| 0.16 | 0.24           | 0.27          | 0.56          |

Table S2. Binding energies ($E_{\text{bind}}$) of HAT monomer and dimer with Ag and Na adatoms on a Ag(111) surface, in kcal/mol.

|                | Ag  | Na  |
|----------------|-----|-----|
| monomer        | -12.3 | -48.8 |
| dimer          | -41.0 | -85.8 |

Total energy slab DFT calculations of infinite HAT chains

Density Functional Theory calculations have been carried out using the FHI-AIMS code\textsuperscript{[18]} to investigate the electronic properties and the energetic stability of the one-dimensional chain of the HAT molecule and of its complexes on a Ag(111) surface. The latter includes the single monomer and dimer formed by the molecule and with Ag and Na adatoms, respectively.

We performed the total energy DFT calculations of the (HAT)$_2$-Na chain on the Ag(111) surface at the GGA-PBE\textsuperscript{[19]} level taking into account the Tkatchenko-Scheffler treatment of the van der Waals interactions.\textsuperscript{[20]} We employed an 8x10 supercell of Ag(111) surface, made of three Ag layers. All atoms of the supercell structure were optimized, except for the bottom Ag layer. The calculations were converged when the remaining atomic forces and the total energy were found below 10$^{-2}$ eV/Å and 10$^{-5}$ eV respectively. We used a single gamma point to sample the Brillouin zone.
**SUPPORTING INFORMATION**

**AFM simulations**
The simulations of AFM images were based on the probe-particle model\(^2\) which includes the van der Waals (vdW) and electrostatic interactions between the CO tip and the surface. All the simulations were done with a charge scaling of -1e and a lateral stiffness of \((k)=0.25\) N/m. Note that the electrostatic forces were obtained based on the Hartree potential calculated from the total energy FHI-AIMS DFT calculations.

**TD-DFT**
The time-dependent density functional theory (TD-DFT) calculations were performed using Gaussian 16\(^7\) at the B3LYP/6-31G(d,p) level of theory. After structural relaxation in the gas phase, TD calculations for 40 singlet states were performed. The results were analyzed using GaussSum\(^22\) and molecular orbitals extracted using Avogadro\(^23\).

In the context of future studies of the interaction of light with molecular systems physisorbed on substrates by using surface plasmonics, the knowledge of their optical spectra is a prerequisite.\(^24,25\) Therefore, a computational approach is used to estimate the optical absorption behavior of a single HAT chain and to point to similarities to oligo-p-phenylene chains,\(^26\) as well as to the edge structure of a porous graphene nanoribbon.\(^27\) Essentially, the main electronic excitation of a HAT chain, which in a first approximation constitutes the principal chromophoric unit, is expected to lie at about 3.2 eV (see Figure S5, S6 and Table S3).

**Table S3. Calculated electronic excitations (energies and oscillator strengths) of a three monomer HAT chain using time-dependent DFT (TD-DFT) with Gaussian 16 package at the B3LYP/6-31G(d,p) level of theory.**

| \(\lambda\) (nm) | Oscillator strength | Molecular orbital contributions |
|-----------------|---------------------|--------------------------------|
| 404.6           | 0.0000              | \(H-4\) \(\rightarrow\) \(L\) 40%  |
|                 |                     | \(H-2\) \(\rightarrow\) \(L\) 27% |
|                 |                     | \(H-6\) \(\rightarrow\) \(L\) 21% |
| 390.6           | 0.0000              | \(H-5\) \(\rightarrow\) \(L\) 51%  |
|                 |                     | \(H-7\) \(\rightarrow\) \(L\) 27% |
|                 |                     | \(H-4\) \(\rightarrow\) \(L+1\) 11% |
| 390.0           | 0.0032              | \(H-1\) \(\rightarrow\) \(L\) 51%  |
|                 |                     | \(H-10\) \(\rightarrow\) \(L\) 26% |
| 383.2           | 1.9047              | \(H\) \(\rightarrow\) \(L\) 97% |
| 368.8           | 0.0000              | \(H-2\) \(\rightarrow\) \(L\) 38%  |
|                 |                     | \(H-6\) \(\rightarrow\) \(L\) 23% |
| 368.7           | 0.0029              | \(H-3\) \(\rightarrow\) \(L\) 54%  |
|                 |                     | \(H-7\) \(\rightarrow\) \(L\) 13% |

The optical absorption behavior of a single HAT chain is approximated through a trimeric unit. First, selected molecular orbitals and their energies were calculated in the gas phase (Figure S5). Interestingly, the frontier molecular orbitals HOMO and LUMO resemble approximately those of an oligo-p-phenylene (OPE) chain,\(^26\) as it was similarly observed along the edges of a porous graphene nanoribbon.\(^27\) The pending pyrazine moieties along the chain contribute only with small coefficients to the HOMO and insignificantly to the LUMO, whereas they share markedly with coefficients to HOMO-\(x\) (\(x = 1\) to 5), which all lie energetically close to the HOMO. Next, the electronic excitations of a trimeric HAT chain were calculated using the time-dependent DFT (TD-DFT) method (Table S3).
An intense absorption band based on an electronic transition dominated by a HOMO to LUMO excitation (97%) is calculated at 383 nm (3.2 eV), whereas further excitations are either symmetry forbidden or show negligible oscillator strengths (Figure S6). In the frame of a C2v point group symmetry, the HOMO to LUMO excitation is polarized along the chain axis. The calculated HOMO-LUMO gap amounts to 3.6 eV, in good agreement with the energy of the calculated strong absorption band.

**Figure S5.** Selected molecular orbitals of a trimeric unit of a single HAT chain with their respective energies, calculated in the gas phase at the B3LYP/6-31G(d,p) level of theory.

**Figure S6.** Computed absorption spectrum of a HAT chain consisting of three monomers with the corresponding HOMO and LUMO distributions.
