Supporting Information

A Trapezoidal Octacyanoquinoid Acceptor Forms Solution and Surface Products by Antiparallel Shape Fitting with Conformational Dipole Momentum Switch

Samara Medina Rivero, Javier Urieta-Mora, Agustín Molina-Ontoria, Cristina Martín-Fuentes, José I. Urgel, Maria Zubiria-Ulacia, Vega Lloveras, David Casanova, José I. Martínez, Jaume Veciana,* David Écija, Nazario Martín,* and Juan Casado*

anie_202104294_sm_miscellaneous_information.pdf
General Methods. Chemicals and reagents were purchased from commercial suppliers and used as received. All solvents were dried according to standard procedures. Air-sensitive reactions were carried out under argon atmosphere. The device preparation was done in a glovebox under nitrogen atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Advance 300 (\(^1\)H: 700 MHz; \(^{13}\)C: 176 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (\(\delta\)) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. FT-IR spectra were recorded on a VERTEX 70 FT-IR spectrometer. UV-Vis spectra were recorded in a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Mass spectra Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively. Cyclic voltammetry (CV) experiments were conducted in 0.1 M solution of NBu\(_4\)PF\(_6\) in DCM and THF. Glassy carbon electrode was used as a working electrode and platinum wires were used as a counter and reference electrode. Before each measurement, the solution was deoxygenated with N\(_2\).

Quantum Chemistry Calculations. Molecular geometries of all studied species (neutral ground and excited singlet, anion, and dianion) of 1 have been optimized at the CAM-B3LYP level. All structures showed positive force constants for all normal modes of vibration. Relative Gibbs free energies between the twisted and folded conformers of neutral 1, and the transition state structure have been obtained from the geometries and vibrational frequencies computed at the CAM-B3LYP/6-31+G(d) level, while electronic energies have been refined by single point calculations with the larger 6-311++G(2df,2p) basis set. Computed vibrational frequencies have been scaled by a 0.93 factor in order to correct the systematic slight overestimation obtained at the density functional theory (DFT) level. Electronic transitions have been obtained within the time-dependent DFT (TDDFT) using the 6-31+G(d) basis and with different exchange-correlation functionals: B3LYP, CAM-B3LYP, \(\omega\)B97X and M06-2X. Solvent effects have been introduced by means of the conductor-like polarized continuum model (C-PCM) [Chem. Phys. Lett., 1995, 240, 253–260; J. Phys. Chem. A, 1998, 102, 1995–2001; J. Comput. Chem., 2003, 24, 669–681]. Transition energies in solution have been computed with the linear response (LR) approach [J. Chem. Phys., 1999, 110, 9877–9886; J. Chem. Phys., 2001, 115, 4708–4717]. The relative energy of the different
electronic isomers of the dianion have been estimated with constrain DFT (C-DFT) [Phys. Rev. A, 2001, 72, 024502] at the CAM-B3LYP level. Reduction potentials have been computed with B3LYP, CAM-B3LYP and ωB97X-D at the CAM-B3LYP optimized geometries, and with the IEF-PCM solvent model as indicated in [Chem. Eur. J. 2013, 19, 5050–5060]. Magnetic hyperfine couplings between unpaired electrons and nuclear spins for the anion species of 1 were computed at the CAM-B3LYP level in DCM solution. The basis 6-31+G(d) was used in all calculations, unless indicated. Frequency calculations have been done with the Gaussian16, revison B.01 program. All other calculations have been performed with the Q-Chem package [Mol. Phys., 2015, 113, 184–215].

In order to theoretically characterize the structure and STM-imaging properties of a molecule on the Au(111) surface in a dilute phase we have used two complementary DFT-based atomistic simulation packages: (i) the accurate plane-wave code QUANTUM ESPRESSO [J. Phys.: Condens. Matter, 2009, 21, 395502] that we used for determination of the complex interfacial atomic geometries and (ii) the efficient local-orbital code FIREBALL [Phys. Status Solidi Basic Res., 2011, 248, 1989–2007] used to simulate of the theoretical STM images. Exchange and Correlation (XC) effects have accounted by a GGA-PBESol functional [Phys. Rev. B, 2009, 79, 075126], and KJPAW pseudopotentials [Phys. Rev. B, 1999, 59, 1758] have been adopted to model the ion–electron interaction for all the involved atoms (H, C, N, S and Au). Brillouin zone (BZ) has been sampled using optimal Monkhorst-Pack grids [Phys. Rev. B, 1977, 16, 1748–1749], guaranteeing a full convergence in energy and electronic density. A perturbative van der Waals (vdW) (DFT+D3) [J. Chem. Phys., 2010, 132, 154104] correction was used to add dispersive forces to conventional density functionals. Spin-polarized fashion has been considered in all the calculations, and atomic relaxations were carried out using a conjugate gradient minimization scheme until the maximum force on any atom was lower than 0.02 eV Å⁻¹.

On the other hand, in the FIREBALL code [Phys. Status Solidi Basic Res., 2011, 248, 1989–2007] we use a local-orbital formulation in such a way that self-consistency is implemented on the orbital occupation numbers (for further details revise Refs. [Condens. Matter Mater. Phys., 1995, 52, 1618–1630; Comput. Mater. Sci., 2007, 39, 759–766] and references therein). This local-orbital formulation has been adopted for the STM-imaging simulations, where tunnelling currents for the STM images have been computed by using the Keldysh-Green function formalism, together with the first-principles tight-binding Hamiltonian obtained from the FIREBALL code, as explained in full detail elsewhere [Prog. Surf. Sci., 2006, 81, 403–443; Phys. Rev. B - Condens. Matter]
Mater. Phys., 2004, 70, 1–9]. Our STM theoretical simulation approach includes a detailed description of the electronic properties of both the W-tip and the sample simultaneously.

To construct all the dilute interfacial models we have considered, to achieve the ground-state structure, (varying on-surface adsorption site and molecular orientation): i) a slab of 4 physical Au(111) layers, with a minimum distance of ~20 Å of vacuum between neighboring cells along the axis perpendicular to the surface, and ii) full periodic boundary conditions representing an infinite Au(111) surface. For the structural optimization calculations the 2 bottommost Au(111) physical layers were kept fixed.

**Spectroelectrochemical Measurements.** In situ IR and UV-Vis-NIR spectroelectrochemical studies were conducted on a VERTEX 70 FT-IR spectrometer and on a Varian Cary 5000 UV-Vis-NIR spectrophotometer, respectively. A C3 epsilon potentiostat from BASi was used for the electrolysis using a thin layer cell from a demountable omni cell from Specac. In this cell a three electrodes system was coupled to conduct in situ spectroelectrochemistry. A Pt gauze was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag wire was used as the pseudo-reference electrode. The spectra were collected at constant potential electrolysis and the potentials were changed in intervals of 10 mV. The electrochemical medium used was 0.1 M tetrabutyl ammonium hexafluorophosphate, Bu₄NPF₆, in fresh distilled dichloromethane, at room temperature with sample concentrations of 10⁻³ M.

Commercial 7,7,8,8-tetracyanoquinodimethane (TCNQ) from Sigma-Aldrich (CAS Number 1518-16-7, 98%) was employed in the electrochemical studies as reference molecule.

**Electron Paramagnetic Resonance (EPR) Measurements.** Electron Paramagnetic Resonance spectroscopy (EPR). Spectra were obtained with an X-Band (9.4 GHz) Bruker ELEXSYS E-500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit, a field frequency lock system Bruker ER 033 M and an NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation. All samples were previously degassed with Ar.

The neutral 1 compound was EPR silent in solution at room temperature. Chronoamperometry reduction experiments of 1 were performed in a 3-electrode cell
using a Pt mesh electrode as the working electrode, in a 0.1 M solution of TBAHFP in anhydrous DCM, well degassed with argon. Fixed redox potentials were applied for ca. 300 sec to reduce the full solution and the samples were monitored by UV-Vis and EPR. The EPR spectra obtained from solutions reduced either at fixed -0.1 V, -0.2 V or -0.4 V redox potentials (vs Ag/AgCl) gave rise to the same 9-line EPR spectrum, indicating: i) the quick formation of the radical anion species $1^{*-}$ and ii) the formation of only one radical species, the same at each assayed redox potential. When we further decreased to lower redox potentials the EPR spectral intensity of such a radical anion species decreased until completely disappear at potentials below -0.6 V (vs Ag/AgCl) obtaining the UV-Vis-NIR of the second reduced species, the dianion, which was found to be EPR silent.

The 9-line EPR spectrum at $g = 2.0020$ of the radical anion was simulated reasonably well with a line width of 0.15 G and hyperfine coupling constants with a few nuclei of the BQ moiety: $a_N(2N) = 0.79$ G and $a_H(2H) = 1.58$ G. In addition, the weak satellite lines observed experimentally at the extreme wings of the main lines, due to the coupling with $^{33}$S nuclei with a natural isotope abundance of 0.75%, was simulated with the following coupling constants with the nuclei located at the MQ and BQ moieties: $a_{S,MQ}(1S) = 1.33$ G; $a_{S,BQ}(2S) = 1.05$ G. Such results confirmed that in the radical anion the unpaired electron is mainly delocalized on the BQ moiety, but also partially spreads over the MQ fragment. These results are in a qualitative agreement with theoretical calculations (see Quantum Chemistry Calculations).

**Scanning Tunneling Microscopy (STM) Measurements.** Experiments were performed in a custom-designed ultra-high vacuum system (base pressure below $4 \times 10^{-10}$ mbar) hosting a commercial low-temperature microscope with STM/AFM capabilities from Scienta Omicron and located at IMDEA Nanoscience.

The Au(111) substrate was prepared by repeated cycles of Ar$^+$ sputtering ($E = 1$ keV, SPECS IQE 11/35) and subsequent annealing to 740 K for 10 minutes. All STM images shown were taken in constant current mode, unless otherwise noted, with electrochemically etched tungsten tips, at a sample temperature of 4.3 K (LakeShore). Scanning parameters are specified in each figure caption. $1$ was thermally deposited (Kentax TCE-BSC) onto the clean Au(111) surface held at room temperature with a typical deposition rate of 0.4 Å/min (sublimation temperature of 182 °C), controlled by a quartz micro balance (LewVac). The STM images were analyzed using WSxM. (ref: *Rev. Sci. Instrum.*, 2007, **78**, 013705).
Synthesis

Compounds 2, 3, and 4 were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

Synthesis of compound 1

A mixture of 2,4,6,8-tetrabromobenzo[1,2-b:6,5-b':3,4-c’]trithiophene (4) (85 mg 0.15 mmol), tetracyanoethylene oxide (TCNEO) (84 mg, 0.61 mmol) and copper (96 mg, 1.51 mmol) was refluxed in 1,2-dibromoethane (6 mL) during 3 days under nitrogen atmosphere. Then, additional TCNEO (39 mg, 0.07 mmol) and copper (48 mg, 0.76 mmol) were added and the reaction was refluxed for another 2 days. The resulting mixture was filtered to remove the insoluble materials and, the filtrate was concentrated under vacuum. The crude product was purified through flash column chromatography (eluent; CH₂Cl₂) to afford compound 1 (14 mg, 0.03 mmol) as a dark red solid, yield 18%.

\(^1\)H NMR (700 MHz, CDCl₃) δ/ppm 8.10 (s, 2H); \(^{13}\)C NMR (176 MHz, CDCl₃) δ/ppm 165.2, 142.3, 131.2, 129.1, 128.1, 120.0, 112.4, 112.1, 78.3; FTIR (neat): 2924, 2854, 2218, 1526, 1500, 1236, 946, 730 cm⁻¹; MS calcd. for C₂₄H₂₂N₈S₃ [M⁺] 498.52; found 498.98; elemental analysis calcd. for C₂₄H₂₂N₈S₃, C: 57.82, H: 0.40, N: 22.48, S: 19.29; found C: 57.69, H: 0.38, N: 22.54, S: 19.38.
Figure S1. $^1$H NMR (700 MHz, CDCl$_3$, 298 K) of compound 1.

Figure S2. $^{13}$C NMR (176 MHz, CDCl$_3$, 298 K) of compound 1.
Figure S3. MALDI-TOF mass spectrum of 1.
Table S1. Main optical vertical transitions of neutral species of 1 computed at the TDDFT level with different energy functionals and the 6-31+G(d) basis set in DCM solution. Main orbital contributions in %. H = HOMO, L = LUMO.

| State | $\Delta E_{\text{abs}}$ | $f$ | $\%$ | $\Delta E_{\text{abs}}$ | $f$ | $\%$ |
|-------|------------------------|-----|------|------------------------|-----|------|
| $S_1$ | 1.8143                 | 0.5699 | 97 H-L | 1.3734                 | 0.1764 | 95 H-L |
| $S_2$ | 2.4448                 | 0.1227 | 76 H-1-L | 2.0432                 | 0.0234 | 80 H-1-L |
| $S_3$ | 2.7218                 | 0.4959 | 70 H-2-L | 2.2171                 | 0.1950 | 80 H-2-L |
| $S_4$ | 2.9110                 | 0.6641 | 82 H-L+1 | 2.4900                 | 1.0262 | 76 H-L |
| $S_5$ | 3.3353                 | 0.0343 | 93 H-3-L | 2.6295                 | 0.0233 | 97 H-3-L |
| $S_6$ | 3.5525                 | 0.4593 | 80 H-1-L+1 | 2.9991                 | 0.2752 | 77 H-1-L+1 |
| $S_7$ | 3.6818                 | 0.2465 | 94 H-4-L | 3.0854                 | 0.1099 | 94 H-4-L |
| $S_8$ | 3.8833                 | 0.1299 | 96 H-L+3 | 3.1926                 | 0.4600 | 79 H-2-L+1 |

| State | $\Delta E_{\text{abs}}$ | $f$ | $\%$ | $\Delta E_{\text{abs}}$ | $f$ | $\%$ |
|-------|------------------------|-----|------|------------------------|-----|------|
| $S_1$ | 1.7962                 | 0.5087 | 98 H-L | 2.0109                 | 0.8779 | 96 H-L |
| $S_2$ | 2.4603                 | 0.1076 | 77 H-1-L | 2.6557                 | 0.2693 | 78 H-1-L |
| $S_3$ | 2.7054                 | 0.4671 | 70 H-2-L | 2.9688                 | 0.4737 | 72 H-2-L |
| $S_4$ | 2.9003                 | 0.7041 | 80 H-L+1 | 3.2466                 | 0.4848 | 84 H-L+1 |
| $S_5$ | 3.3068                 | 0.0367 | 95 H-3-L | 3.6908                 | 0.0489 | 85 H-3-L |
| $S_6$ | 3.5511                 | 0.4605 | 83 H-1-L+1 | 3.9039                 | 0.4366 | 97 H-1-L+1 |
| $S_7$ | 3.6964                 | 0.2150 | 95 H-4-L | 3.9839                 | 0.3959 | 86 H-4-L |
| $S_8$ | 3.8463                 | 0.2261 | 78 H-2-L+2 | 4.2340                 | 0.0099 | 87 H-L+2 |
**Figure S4.** Frontier molecular orbitals involved in the main optical transitions of neutral species of 1 computed at the B3LYP/6-31+G(d) level in DCM solution, as indicated in Table S3.

**Figure S5.** Different views for the molecular geometry of 1 optimized at CAM-B3LYP/6-31+G(d) computational level. The moderate relative torsion between the two moieties can be seen in side representation (right).
Comparison between twisted and folded conformers

In the following we show computational results regarding the comparison between the two structural conformers of 1 (twisted and folded) computed at the CAM-B3LYP/6-31+G(d) in vacuum (unless indicated).

![Figure S6](image.png)

Figure S6. Optimized structures of twisted (a) and folded (b) conformers of neutral 1 computed at CAM-B3LYP/6-31+G(d) level in vacuum.

Table S2. Relative Gibbs free energies (ΔG in kcal/mol) between the twisted and folded conformers of neutral, anion and dianion 1 computed at the CAM-B3LYP/6-31+G(d) level. ΔG = G(folded) – G(twisted).

| form    | ΔG  |
|---------|-----|
| neutral | 1.4 |
| anion   | 1.8 |
| dianion | 1.3 |

Table S3. Atomic charges (in atomic units) calculated from natural population analysis (NPA) for the MQ and BQ moieties (C-C shared atoms included in the MQ fragment) for the neutral, anion, and dianion species of twisted and folded forms of 1 computed at the CAM-B3LYP/6-31+G(d) level in vacuum.

|          | neutral        | anion          | dianion        |
|----------|----------------|----------------|----------------|
|          | twisted | folded | twisted | folded | twisted | folded |
| MQ       | -0.046   | -0.108  | -0.512   | -0.538  | -0.957   | -0.939  |
| BQ       | 0.046    | 0.108   | -0.488   | -0.462  | -1.043   | -1.061  |
**Table S4.** Atomic spins (in atomic units) calculated from natural population analysis (NPA) for the MQ and BQ moieties (C-C shared atoms included in the MQ fragment) for the neutral, anion, and dianion species of twisted and folded forms of 1 computed at the CAM-B3LYP/6-31+G(d) level in vacuum.

|       | MQ  | MQ    | BQ  | BQ    |
|-------|-----|-------|-----|-------|
|       | 0.490 | 0.434 | -0.322 | -0.307 |
|       | 0.510 | 0.564 | 0.322  | 0.307  |

**Figure S7.** Simulated infrared spectroelectrochemical spectra for the neutral (black), anion (red), and dianion (blue) twisted (a) and folded (b) species of 1 computed at CAM-B3LYP/6-31+G(d) in vacuum. Vibrational frequency modes have been scaled by a 0.93 factor.

**Figure S8.** Simulated UV-vis absorption spectra for the neutral (black), anion (red), and dianion (blue) twisted (a) and folded (b) species of 1 computed at CAM-B3LYP/6-31+G(d) in vacuum.
Figure S9. Full range cyclic voltammogram of 1 in CH$_2$Cl$_2$ 0.1 M PF$_6$NBu$_4$ at room temperature.

Table S5. Atomic charges (in atomic units) calculated from natural population analysis (NPA) for the MQ and BQ moieties (C-C corresponds to the shared fragment) for the neutral, anion, and dianion species of 1 computed at the CAM-B3LYP/6-31+G(d) level in DCM solution.

| NPA  | neutral | anion  | dianion |
|------|---------|--------|---------|
| MQ   | -0.130  | -0.380 | -0.749  |
| C-C  | 0.122   | -0.144 | -0.179  |
| BQ   | 0.009   | -0.476 | -1.072  |
**Figure S10.** Electrostatic potential (isovalue of 0.02 a.u.) for the anion species of 1 computed at CAM-B3LYP-6-31+G(d) level in DCM solution.

**Figure S11.** Permanent electric dipole moment of the neutral (left), anion (middle) and dianion (right) species of 1 computed at CAM-B3LYP-6-31+G(d) level in DCM solution. The modulus of the dipole moment is 1.519 D, 1.792 D, 1.761 D for the neutral, anion and dianion, respectively.
**Figure S12.** UV-Vis-NIR spectroelectrochemical measurements of 1 in the cathodic wave carried out in CH$_2$Cl$_2$ 0.1 M PF$_6$NBu$_4$ at room temperature. Black line corresponds to the electronic absorption spectrum of the neutral species; blue lines correspond to the completely formed radical anion species; and orange line corresponds to the completely formed dianion species. Light color lines correspond to the intermediate spectra of the completely formed reduced species.
Table S6. Main optical vertical transitions of anion species of 1 computed at the TDDFT level with different energy functionals and the 6-31+G(d) basis set in DCM solution. Main orbital contributions in %. H = HOMO, L = LUMO, S = SOMO.

| State | \(\Delta E_{\text{abs}}\) | f | S² | % | \(\Delta E_{\text{abs}}\) | f | S² | % |
|-------|-----------------|---|----|---|-----------------|---|----|---|
| \(S_1\) | 0.7405 | 0.3081 | 1.0208 | | \(\alpha\) 34 H-1-L | | \(\beta\) 94 H-S1 |
|       | 1.2081 | 0.1881 | 0.8446 | | \(\alpha\) 98 S1-L | | \(\beta\) - |
|       | 1.4775 | 0.0476 | 1.4539 | | \(\alpha\) 39 H-2-L | | \(\beta\) 76 H-1-S1 |
|       | 2.0078 | 0.0051 | 2.1427 | | \(\alpha\) 38 H-1-L | | \(\beta\) 65 H-L+1 |
|       | 2.2428 | 0.0024 | 1.4210 | | \(\alpha\) 25 H-2-L | | \(\beta\) 56 H-2-S1 |
|       | 2.5431 | 0.1910 | 1.8494 | | \(\alpha\) 45 H-1-L | | \(\beta\) 40 H-2-S1 |
|       | 2.6206 | 0.0841 | 0.8740 | | \(\alpha\) 27 H-4-L | | \(\beta\) 66 H-3-S1 |
|       | 2.7251 | 0.6497 | 1.7641 | | \(\alpha\) 58 H-1-L | | \(\beta\) 46 H-L+1 |
|       | 2.9982 | 0.0921 | 1.4064 | | \(\alpha\) 30 H-5-L | | \(\beta\) 54 H-4-S1 |
|       | 3.0049 | 0.0569 | 1.3839 | | \(\alpha\) 56 S1-L+1 | | \(\beta\) 45 H-1-L+1 |

| State | \(\Delta E_{\text{abs}}\) | f | S² | % | \(\Delta E_{\text{abs}}\) | f | S² | % |
|-------|-----------------|---|----|---|-----------------|---|----|---|
| \(S_1\) | 0.9617 | 0.2446 | 0.9712 | | \(\alpha\) 30 H-1-L | | \(\beta\) 93 H-S1 |
|       | 1.1901 | 0.1840 | 0.8198 | | \(\alpha\) 98 S1-L | | \(\beta\) - |
|       | 1.6747 | 0.0609 | 1.3323 | | \(\alpha\) 36 H-2-L | | \(\beta\) 80 H-1-L+1 |
|       | 2.0810 | 0.0065 | 2.2478 | | \(\alpha\) 45 H-1-L | | \(\beta\) 70 H-L+1 |
|       | 2.2436 | 0.0142 | 1.3121 | | \(\alpha\) 33 S1-L+1 | | \(\beta\) 50 H-2-S1 |
|       | 2.5792 | 0.5290 | 1.5691 | | \(\alpha\) 69 H-1-L | | \(\beta\) 34 H-L+1 |
|       | 2.5945 | 0.3566 | 0.8252 | | \(\alpha\) 61 S1-L+1 | | \(\beta\) 46 H-L+1 |
|       | 2.7312 | 0.0719 | 1.5780 | | \(\alpha\) 28 H-1-L+1 | | \(\beta\) 74 H-3-S1 |
|       | 2.9307 | 0.0000 | 1.6249 | | \(\alpha\) 58 S1-L+1 | | \(\beta\) 40 H-1-L+1 |
|       | 3.0611 | 0.0070 | 1.4958 | | \(\alpha\) 82 H-3-L | | \(\beta\) 32 H-2-S1 |

| State | \(\Delta E_{\text{abs}}\) | f | S² | % | \(\Delta E_{\text{abs}}\) | f | S² | % |
|-------|-----------------|---|----|---|-----------------|---|----|---|
| \(S_1\) | 0.5920 | 0.4273 | 1.0125 | | \(\alpha\) 31 H-1-L | | \(\beta\) 99 H-S1 |
|       | 1.2401 | 0.2131 | 0.8878 | | \(\alpha\) 97 S1-L | | \(\beta\) - |
|       | 1.4509 | 0.0330 | 1.6616 | | \(\alpha\) 41 H-2-L | | \(\beta\) 71 H-1-S1 |
|       | 2.1853 | 0.0072 | 1.9447 | | \(\alpha\) 29 H-1-L | | \(\beta\) 54 H-2-S1 |
|       | 2.5394 | 0.0241 | 1.5355 | | \(\alpha\) 41 S1-L+1 | | \(\beta\) 52 H-1-S1 |
|       | 2.6684 | 0.0348 | 1.4464 | | \(\alpha\) 47 S1-L+1 | | \(\beta\) 45 H-2-S1 |
|       | 2.7092 | 0.1012 | 1.8908 | | \(\alpha\) 25 H-1-L+1 | | \(\beta\) 59 H-3-S1 |
|       | 2.8244 | 0.7617 | 1.5237 | | \(\alpha\) 65 H-1-L | | \(\beta\) 41 H-L+1 |
|       | 3.0577 | 0.0839 | 2.1385 | | \(\alpha\) 30 H-5-L | | \(\beta\) 43 H-4-S1 |
|       | 3.3333 | 0.4055 | 1.4779 | | \(\alpha\) 77 H-3-L | | \(\beta\) 33 H-2-S1 |
Table S7. Main optical vertical transitions of dianion species of 1 computed at the TDDFT level with different energy functionals and the 6-31+G(d) basis set in DCM solution. Main orbital contributions in %. H = HOMO, L = LUMO.

| State | \( \Delta E_{\text{abs}} \) | \( f \) | % | \( \Delta E_{\text{abs}} \) | \( f \) | % |
|-------|-----------------|-----------------|---|-----------------|-----------------|---|
| \( S_1 \) | 0.4017 | 0.0034 | \( \alpha \) 76 H-L | \( \beta \) 85 H-L | 1.4248 | 0.3362 | 99 H-L |
| \( S_2 \) | 1.5615 | 0.4473 | \( \alpha \) 74 H-L | \( \beta \) 66 H-L | 2.0098 | 0.4244 | 97 H-1-L |
| \( S_3 \) | 1.5916 | 0.0948 | \( \alpha \) 41 H-1-L | \( \beta \) 80 H-L | 2.3993 | 0.1520 | 87 H-2-L |
| \( S_4 \) | 1.7963 | 0.0038 | \( \alpha \) 68 H-2-L | \( \beta \) 50 H-2-L | 2.5151 | 0.3227 | 92 H-L+1 |
| \( S_5 \) | 2.4891 | 0.4234 | \( \alpha \) 61 H-1-L | \( \beta \) 39 H-2-L | 2.7697 | 0.1093 | 82 H-3-L |
| \( S_6 \) | 2.5607 | 0.3161 | \( \alpha \) 42 H-2-L | \( \beta \) 54 H-3-L | 3.1794 | 0.0176 | 75 H-1-L+1 |
| \( S_7 \) | 2.6932 | 0.1978 | \( \alpha \) 63 H-3-L | \( \beta \) 27 H-L+1 | 3.3280 | 0.0902 | 67 H-5-L |
| \( S_8 \) | 2.7574 | 0.0040 | \( \alpha \) 53 H-L+1 | \( \beta \) 46 H-L+1 | 3.4283 | 0.0025 | 98 H-L+2 |
| \( S_9 \) | 2.8998 | 0.0004 | \( \alpha \) 34 H-1-L+1 | \( \beta \) 47 H-4-L | 3.4433 | 0.0320 | 88 H-L+3 |
| \( S_{10} \) | 2.9578 | 0.1246 | \( \alpha \) 51 H-L+1 | \( \beta \) 59 H-L+1 | 3.5174 | 0.0593 | 64 H-5-L |
| \( S_{11} \) | 3.2533 | 0.2500 | \( \alpha \) 45 H-3-L | \( \beta \) 71 H-3-L | 3.6564 | 0.8514 | 88 H-L+4 |

| State | \( \Delta E_{\text{abs}} \) | \( f \) | % | \( \Delta E_{\text{abs}} \) | \( f \) | % |
|-------|-----------------|-----------------|---|-----------------|-----------------|---|
| \( S_1 \) | 1.5139 | 0.4445 | 98 H-L | 1.7598 | 0.7047 | 97 H-L |
| \( S_2 \) | 2.3886 | 0.6702 | 93 H-1-L | 2.6472 | 0.3568 | 56 H-1-L |
| \( S_3 \) | 2.6137 | 0.1869 | 69 H-2-L | 2.9504 | 1.0642 | 76 H-1-L |
| \( S_4 \) | 2.9091 | 0.2374 | 83 H-L+1 | 3.3518 | 0.0772 | 79 H-L++1 |
| \( S_5 \) | 3.1607 | 0.2621 | 87 H-3-L | 3.5705 | 0.4634 | 77 H-3-L |
| \( S_6 \) | 3.8307 | 0.0679 | 83 H-1-L+1 | 4.2311 | 0.0079 | 85 H-5-L |
| \( S_7 \) | 3.8945 | 0.0738 | 75 H-5-L | 4.3614 | 0.1777 | 86 H-1-L+1 |
| \( S_8 \) | 3.9561 | 0.0108 | 70 H-L+3 | 4.4091 | 0.1108 | 67 H-L+4 |
| \( S_9 \) | 4.0381 | 0.4371 | 93 H-L+2 | 4.4638 | 0.8073 | 87 H-L+2 |
| \( S_{10} \) | 4.0679 | 0.0550 | 78 H-4-L | 4.4924 | 0.0312 | 63 H-L+4 |
| \( S_{11} \) | 4.0887 | 0.3433 | 91 H-L+5 | 4.6068 | 0.1969 | 60 H-4-L |
Figure S13. Infrared spectroelectrochemical measurements of 1 in the cathodic wave carried out in CH$_2$Cl$_2$ 0.1 M PF$_6$NBu$_4$ at room temperature. Black line corresponds to the IR spectrum of the neutral species; blue lines correspond to the completely formed radical anion species; and orange line corresponds to the completely formed dianion species. Light color lines correspond to the intermediate spectra of the completely formed reduced species.
Figure S14. Representation of the CAM-B3LYP/6-31+G(d) computed two (antisymmetric) $\nu$(C=N) IR active modes of neutral 1 responsible for the IR band computed at 2217 cm$^{-1}$.

Figure S15. Simulated infrared spectroelectrochemical spectra for the neutral (black), anion (red), and dianion (blue) species of 1 computed at CAM-B3LYP/6-31+G(d) in DCM solution. Vibrational frequency modes have been scaled by a 0.93 factor.
**Figure S16.** UV-Vis-NIR spectroelectrochemical measurements of TCNQ in the cathodic wave carried out in CH$_2$Cl$_2$ 0.1 M PF$_6$NBu$_4$ at room temperature. Black line corresponds to the electronic absorption spectrum of the neutral species; blue lines correspond to the completely formed radical anion species; and orange line corresponds to the completely formed dianion species. Light color lines correspond to the intermediate spectra of the completely formed reduced species.
Figure S17. Infrared spectroelectrochemical measurements of TCNQ in the cathodic wave carried out in CH$_2$Cl$_2$ 0.1 M PF$_6$NBu$_4$ at room temperature. Black line corresponds to the IR spectrum of the neutral species; blue lines correspond to the completely formed radical anion species; and orange line corresponds to the completely formed dianion species. Light color lines correspond to the intermediate spectra of the completely formed reduced species.
Table S8. Relative energies ($\Delta E$ in kcal/mol) between the ground state of dianion 1 (D1) in the singlet and triplet state, and the charge constrained forms D1a/D1b compute at the B3LYP/6-31+G(d) level in DCM solution. Optimized geometries and energies for the D1a/D1b forms have been obtained with C-DFT.

| form | $\Delta E$(singlet) | $\Delta E$(triplet) |
|------|---------------------|---------------------|
| D1   | 0.0                 | 0.0                 |
| D1a  | 14.8                | 30.9                |
| D1b  | 31.9                | 33.8                |

Table S9. Singlet-triplet adiabatic energy gap ($E(T_1) - E(S_0)$, in kcal/mol) computed with B3LYP and wB97X-D functionals and the 6-31+G(d) and 6-311+G(d,p) basis sets for the neutral and dianion species of 1 in DCM solution.

|                  | neutral | dianion |
|------------------|---------|---------|
| B3LYP/6-31+G(d)  | 6.52    | 12.58   |
| B3LYP/6-311+G(d,p) | 7.03   | 12.87   |
| $\omega$B97X-D/6-31+G(d) | 1.44   | 11.55   |
| $\omega$B97X-D/6-311+G(d,p) | 2.28   | 11.82   |
**Table S10.** Bond distances (Å) for each specie of the different conformers computed at CAM-B3LYP/6-31+G* level.

|   | twisted conformer |   | folded conformer |   |
|---|------------------|---|-----------------|---|
|   | neutral         | dianion | neutral | dianion |
| 1 | 1.758           | 1.760 | 1.766 | 1.762 |
| 2 | 1.758           | 1.760 | 1.766 | 1.762 |
| 3 | 1.462           | 1.418 | 1.466 | 1.418 |
| 4 | 1.462           | 1.418 | 1.466 | 1.418 |
| 5 | 1.375           | 1.446 | 1.375 | 1.454 |
| 6 | 1.453           | 1.418 | 1.454 | 1.422 |
| 7 | 1.453           | 1.418 | 1.454 | 1.422 |
| 8 | 1.545           | 1.422 | 1.455 | 1.442 |
| 9 | 1.545           | 1.422 | 1.455 | 1.442 |
| 10| 1.349           | 1.364 | 1.350 | 1.362 |
| 11| 1.359           | 1.405 | 1.360 | 1.406 |
| 12| 1.440           | 1.391 | 1.440 | 1.395 |
| 13| 1.750           | 1.762 | 1.756 | 1.764 |
| 14| 1.440           | 1.748 | 1.755 | 1.750 |
| 15| 1.359           | 1.405 | 1.360 | 1.406 |
| 16| 1.440           | 1.391 | 1.440 | 1.395 |
| 17| 1.750           | 1.762 | 1.756 | 1.764 |
| 18| 1.440           | 1.748 | 1.755 | 1.750 |
Table S11. NICS values (ppm) for each specie of the different conformers computed at CAM-B3LYP/6-31+G* level.

| # ring | twisted conformer | folded conformer |
|--------|-------------------|------------------|
|        | neutral | dianion | neutral | dianion |
| 1      | -0.37    | -4.28   | -1.15   | -5.38   |
| 2      | -4.94    | -6.43   | -4.51   | -6.04   |
| 3      | -4.99    | -6.49   | -4.91   | -5.89   |
| 4      | -4.77    | -5.09   | -4.52   | -3.90   |
Table S12. Top) Atomic labelling of 1 employed for the hyperfine calculations. Bottom) Magnetic hyperfine couplings between unpaired electrons and nuclear spins for the anion specie of 1 computed at the CAM-B3LYP/6-31+G(d) level in DCM solution. FC: Fermi contact contribution. All values are given in MHz.

|           | FC     | spin-dipole | Total  |
|-----------|--------|-------------|--------|
| MQ(N1)1.427 | 1.291  | 1.736       | 3.027  | 0.136 | 0.309 | 4.455 |
| MQ(N2)1.415 | 1.012  | 1.391       | 2.403  | 0.024 | 0.403 | 3.818 |
| MQ(N3)1.427 | 1.291  | 1.736       | 3.027  | 0.136 | 0.309 | 4.455 |
| MQ(N4)1.415 | 1.012  | 1.391       | 2.403  | 0.024 | 0.403 | 3.818 |
| MQ(S1)1.028 | 1.356  | 2.958       | 4.314  | 2.383 | 3.286 | 3.986 |
| BQ(H1)-13.382 | 1.279  | 5.853       | 7.131  | 6.251 | 14.661 | 19.235 |
| BQ(H2)-13.382 | 1.279  | 5.853       | 7.131  | 6.251 | 14.661 | 19.235 |
| BQ(N1)1.813  | 1.607  | 2.232       | 3.839  | 0.206 | 0.419 | 5.651 |
| BQ(N2)2.373  | 2.081  | 2.833       | 4.915  | 0.292 | 0.460 | 7.288 |
| BQ(N3)1.813  | 1.607  | 2.232       | 3.839  | 0.206 | 0.419 | 5.651 |
| BQ(N4)2.373  | 2.081  | 2.833       | 4.914  | 0.292 | 0.460 | 7.288 |
| BQ(S1)-0.657 | 1.058  | 1.322       | 2.380  | 0.402 | 0.665 | 3.037 |
| BQ(S2)-0.657 | 1.058  | 1.322       | 2.380  | 0.402 | 0.665 | 3.037 |
Figure S18. Left: transient UV-Vis absorption spectra of 1 obtained during the picosecond time regime (on the inset the time decay evolution is shown). Right: TRIR picosecond time evolution of the $\nu$(C=N) band of 1.

Table S13. Adiabatic and vertical excitation energies (in eV) for optimized excited state of neutral 1 computed at the CAM-B3LYP/6-31+G(d) level. Oscillator strength in parenthesis.

|     | $\Delta E_{ad}$ | $\Delta E_v$ |
|-----|----------------|-------------|
| $S_1$ | 1.57           | 1.33 (0.163) |
**Figure S19.** Lateral manipulation of 1 on Au(111). The manipulation was performed by allowing the STM tip to vertically approach the molecular assembly and laterally moving it along the path marked by the white arrow in (a). Manipulation parameters: $V_b = -0.015$ V, $I_t = 45$ nA. a,b) STM images before and after the manipulation event. The blue dashed circles highlight the individual molecule that was laterally manipulated. Scanning parameters: (a,b) $V_b = -0.7$ V, $I_t = 100$ pA . Scale bars = 5 nm.

**DFT-simulation of the on-surface self-assembled molecular phase**

On the basis of the experimentally obtained representative distances for the self-assembled molecular phase shown in Fig. 6a, we have carried out a set of DFT simulations to get some insight on the molecular stabilization in the ordered molecular ad-layer. For that purpose, we have simulated several starting-point configurations (varying on-surface adsorption sites) consistent with the experimental evidence to evaluate the strength of the intermolecular interaction, as well as other quantities obtained for the on-surface diluted molecular phase for comparison.

Figure S20a shows the top and side views of the DFT-optimized geometry of the most-stable optimized configuration obtained in an attempt to reproduce the self-assembled molecular ad-layer of Fig. 6a. The unit cell used in the calculations has a size of $(11.64 \times 25.02)$ Å$^2$, directly related with the unavoidable molecular commensuration with the Au(111) substrate from the theoretical point of view. In the most stable configuration shown in Fig. S20a all the molecules, with alternating $180^\circ$ orientation, prefer to lie on the surface with the molecular central C-ring located “on top” a surface Au atom at an average perpendicular distance from the surface of $3.1$ Å ($3.0$ Å for the isolated molecule on the surface). The other three configurations tested (with the central C-ring lying on an
Au—Au bridge, and on hcp and fcc hollows) result to be less stable than the preferred configuration within an energy window of 0.2 eV.

**Figure S20.** a) Top (upper panel) and side (lower panel) views of the DFT-optimized geometry of the most-stable optimized configuration reproducing the self-assembled molecular ad-layer of Fig. 6a. Unit cell (and lattice parameters) used in the simulations is depicted as a red dashed-line box. b) Simulated Keldish-Green STM image of the self-assembled molecular ad-layer for the most-stable optimized configuration shown in panel a). Molecular configuration is shown superimposed to the computed STM image for a better comparison.

The intermolecular interactions caused by this dense molecular distribution induce a slightly more pronounced bending of the molecules in comparison with the isolated molecule on the surface, which tend to maximize the intermolecular interactions. The computed interaction energy results in 0.32 eV per molecule, and is responsible for the stabilization of the molecules in such a dense arrangement. Interestingly, this slight increasing of the molecular distortion induces an out-of-plane pointing-down molecular dipole of 0.53 D per molecule (to be compared with the value of 0.45 D for the case of the molecular dilute phase). Stabilization of the molecules by the emerging intermolecular interactions seems to exhibit a slight “decoupling effect” of the molecular ad-layer from the surface with a computed binding energy and charge transfer per molecule of around 1.62 eV and 0.37 e−, respectively, (to be compared with the values of 1.9 eV and 0.41 e− for the case of the molecular dilute phase). Additionally, figure S20b shows the simulated Keldish-Green STM image of the computed most stable self-assembled molecular ad-layer shown in Fig. S20a. The comparison with the
experimental evidence is moderately good and, as expected, all the molecules seems to be equivalent according to the STM registry.
### Optimized coordinates in DCM

#### Neutral

| Atom | X               | Y               | Z               |
|------|-----------------|-----------------|-----------------|
| C    | 0.673932        | -1.433239       | -0.039107       |
| C    | -0.681946       | 1.054224        | -0.088609       |
| C    | -0.673186       | -1.433488       | 0.040035        |
| C    | 1.423951        | -0.187561       | -0.043904       |
| C    | 0.681664        | 1.054555        | 0.087949        |
| C    | -1.423721       | -0.188117       | 0.044034        |
| C    | -2.746948       | -0.376176       | 0.292696        |
| C    | -3.116888       | -1.762983       | 0.410369        |
| S    | -1.736610       | -2.818254       | 0.200436        |
| C    | 2.747256        | -0.375227       | -0.292450       |
| C    | 3.117772        | -1.761955       | -0.409232       |
| S    | 1.737931        | -2.817665       | -0.198626       |
| C    | -1.203790       | 2.388963        | -0.378778       |
| C    | 1.202978        | 2.389691        | 0.377252        |
| C    | -2.348856       | 2.764473        | -1.019878       |
| C    | 4.383708        | -2.229099       | -0.655189       |
| C    | -4.382629       | -2.230494       | 0.656632        |
| H    | -3.485014       | 0.402415        | 0.421840        |
| H    | 3.484994        | 0.403592        | -0.422101       |
| C    | 2.599985        | 4.156375        | 1.254829        |
| N    | 2.791322        | 5.282737        | 1.436586        |
| C    | 3.300362        | 1.882506        | 1.613135        |
| N    | 4.082942        | 1.225605        | 2.155416        |
| C    | 5.479985        | 4.156375        | 1.254829        |
| N    | 6.362758        | -0.02425        | -0.995681       |
| C    | 4.654699        | -3.625704       | -0.743595       |
| N    | 4.849511        | -4.765376       | -0.811433       |
| C    | -4.653039       | -3.627155       | 0.745939        |
| N    | -4.847376       | -4.766864       | 0.814515        |
| C    | -5.476582       | -1.333866       | 0.840734        |
| N    | -6.362351       | -0.604433       | 0.961412        |
| C    | -3.301032       | 1.880181        | -1.614253       |
| N    | -4.083389       | 1.222640        | -2.156082       |
| C    | -2.601488       | 4.154543        | -1.257479       |
| N    | -2.793260       | 5.280711        | -1.439977       |

#### Anion

| Atom | X               | Y               | Z               |
|------|-----------------|-----------------|-----------------|
| C    | 0.676843        | -1.383994       | -0.042593       |
| C    | -0.703100       | 1.069549        | -0.091996       |
| C    | -0.676155       | -1.384248       | 0.043444        |
| C    | 1.438796        | -0.151535       | -0.033818       |
| C    | 0.702765        | 1.069894        | 0.091366        |
| C    | -1.438621       | -0.152112       | 0.033946        |
| C    | -2.787713       | -0.377484       | 0.244300        |
| C    | -3.130331       | -1.745830       | 0.366481        |
| S    | -1.719258       | -2.783725       | 0.193833        |
| C    | 2.787991        | -0.376468       | -0.243974       |
| C    | 3.131183        | -1.744744       | -0.365328       |
| S    | 1.720531        | -2.783122       | -0.192141       |
| C    | -1.217958       | 2.385430        | -0.357656       |
| C    | 1.217095        | 2.386150        | 0.356176        |
| S    | -0.000705       | 3.609399        | -0.001045       |
| C    | 2.398516        | 2.793258        | 0.943527        |
| C    | -2.399494       | 2.791721        | -0.945350       |
| C    | 4.390924        | -2.268158       | -0.611487       |
| C    | -4.389840       | -2.269625       | 0.613016        |
H    -3.545438  0.386483  0.337684
H     3.545403  0.387760  0.337763
C     2.683309  4.187023  1.073573
N     2.901658  5.321261  1.169117
C     3.307618  1.925768  1.613555
N     4.042432  1.263579  2.217230
C     5.508280  1.407532  0.798519
N     6.410930  0.701475  0.968973
C     4.604851  3.669579  0.716128
N     4.754749  4.819015  0.796623
C     5.507546  1.409357  0.799607
N     6.410479  0.701475  0.968973
C     4.603179  3.671075  0.716128
N     4.752602  4.819015  0.796623
C     5.507546  1.409357  0.799607
N     6.410479  0.701475  0.968973
C     4.604851  3.669579  0.716128
N     4.754749  4.819015  0.796623

Dianion
C     0.680510  -1.356764  -0.048031
C    -0.718595   1.078716  -0.082762
C    -0.679903  -1.357019   0.048868
C     1.443658  -0.133323  -0.037350
C     0.718171   1.079062   0.082084
C    -1.443570  -0.133904   0.037470
C    -2.813615  -0.379894  -0.227529
C    -3.136787  -1.727701   0.340483
S     1.715861  -2.757216  -0.196327
C    -1.234868   2.379787  -0.307721
C     1.233941   2.380474   0.306179
S    -0.000743   3.596206  -0.001010
C     2.463852   2.810114   0.817720
C    -2.464838   2.808674  -0.819765
C     4.410195  -2.299272  -0.556575
C    -4.409124  -2.300803   0.558378
H    -3.568729   0.385232   0.329963
H     3.568635   0.386544  -0.329879
C     2.794724   4.191846   0.816553
N     3.058241   5.323123   0.807448
C     3.343175   1.981178  1.555190
N     4.061525   1.340640  2.205615
C     5.551081  -1.475264  -0.670511
N     6.484028  -0.786107  -0.765982
C     4.589842  -3.693780  -0.674996
N     4.722419  -4.846758  -0.769422
C    -4.588163  -3.695318   0.677637
N    -4.720243  -4.848296   0.772748
C    -5.550342  -1.477213   0.672013
N    -6.483563  -0.788391   0.767234
C    -3.343555   1.979103  -1.557245
N    -4.061397   1.338033  -2.207706
C    -2.796222   4.190283  -0.819383
N    -3.060169   5.321464  -0.810921