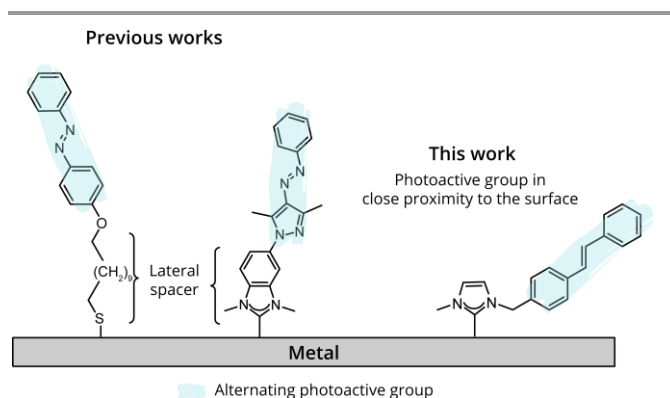


The Influence of Surface Proximity on Photoswitching Activity of Stilbene-Functionalized N-Heterocyclic Carbene Monolayers

Shahar Dery[†], Israel Alshanski[†], Evgeniy Mervinetsky[†], Daniel Feferman, Shlomo Yitzchaik*, Mattan Hurevich*, and Elad Gross *

Self-assembly of photo-responsive molecules is a robust technology for reversibly tuning the properties of functional materials. Herein, we probed the crucial role of surface-adsorbate interactions on the adsorption geometry of stilbene-functionalized N-heterocyclic carbenes (stilbene-NHCs) monolayers and its impact on surface potential. Stilbene-NHCs on Au film accumulated a vertical orientation that enabled high photoisomerization efficiency and reversible changes in surface potential. Strong metal-adsorbate interactions led to flat-lying adsorption geometry of stilbene-NHCs on Pt film, which quenched the photo-isomerization influence on surface potential. It is identified that photo-induced response can be optimized by positioning the photo-active group in proximity to weakly-interacting surfaces.

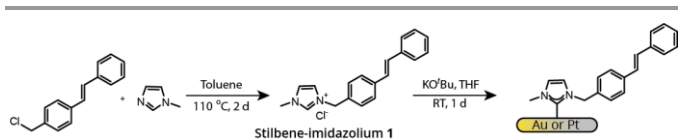
The use of light as a non-invasive stimulus and the wide chemical versatility of photoresponsive organic-based monolayers make these systems highly beneficial for photo-adjusting the surface properties of functional materials.^[1] These advantages led to utilization of photoresponsive organic-based monolayers in the fields of nanoscience^[2], electronics^[3], sensing^[4] and catalysis^[5]. Photoresponsive monolayers are constructed of two main segments: i. photoactive group, such as azobenzenes^[6], stilbenes^[7] and spiropyrans^[8]; ii. surface anchoring handle, which is frequently thiol-based for metallic surfaces and silane-based for oxide surfaces.^[2a] The metal or oxide surface on which the monolayer is anchored can potentially function as a third segment in the photoresponsive system and influence the photoswitchability. However, in most systems a lateral spacer separates the photoactive group from the surface-anchoring handle and partially decouple the surface properties from that of the photoactive group (Scheme 1).^[2a] It was recently demonstrated that N-heterocyclic carbene molecules (NHCs) can be utilized as a surface anchoring group for the formation of photoresponsive monolayers (Scheme 1).^[9] The metal-affinity of NHCs^[10] enabled to form robust monolayers in which a photoactive arylazopyrazole group was installed on the benzimidazole backbone.^[9] Since NHCs are anchored to the surface through the carbene of the imidazole ring,^[11] N-substitution of the imidazole provides a unique opportunity for positioning a responsive group in close proximity to the metal surface.^[12] The ability to position chemically-active groups of NHCs in proximity to metal supports was previously utilized for tuning the chemical reactivity of addressable groups^[12-13] and for adjusting the metal properties, i.e. surface potential.^[12d, 14]



Scheme 1. Photoresponsive thiol- and NHC-based monolayers in which the photoactive group is separated from the surface using an alkyl or benzimidazole spacer were previously shown (left). In this work, the photoactive group was positioned in close proximity to the metal surface, yielding a metal-dependent coupling of the photoelectronic effect (right).

In a similar way, N-substitution of the imidazole ring with photoactive groups will enable to optimally couple the light-induced responsiveness of the photoactive group and surface properties while benefiting from the high thermal stability of anchored NHCs. To the best of our knowledge, such system has not been reported yet. Herein, a photoactive stilbene group was positioned directly on the imidazole scaffold, thus yielding NHC-based monolayer in which the photoresponsive group is located in close proximity to the metal surface (Scheme 1).

Stilbene was chosen as the photoresponsive group since it enables evaluating the influence of surface proximity on both photo-induced *trans*-to-*cis* isomerization and thermal-induced *cis*-to-*trans* isomerization.^[7, 15] Photoactive NHC molecules were designed to include imidazole scaffold and photoresponsive stilbene functionality separated via a methylene group (Scheme 2, NMR data can be found in Fig. S1-S6). This design ensures close proximity of the stilbene to the metal surface while decoupling the imidazole and stilbene aromatic systems by sp^3 carbon in order to break their conjugation. The non-conjugated system provides an opportunity to exclusively measure the influence of photoinduced isomerization on surface properties. Activated carbene solution was prepared by deprotonation of stilbene-imidazolium (10 mM) using KO^tBu (2 eq.) in THF under inert conditions. Stilbene-NHC was self-assembled by immersion of Au and Pt films in the activated carbene solution (Scheme 2).



Scheme 2. Synthetic scheme for preparation of 1-p-methylstilbene-3-methyl-1H-imidazolium chloride (Stilbene-imidazolium, **1**) from 4-chloromethylstilbene and N-methylimidazole in toluene. Deprotonation of **1** led to the formation of stilbene-NHC that was self-assembled on Au and Pt films.

N1s XPS spectrum of stilbene-imidazolium **1** displayed a dominant peak centered at 402.0 eV (Figure 1a), while the N1s XPS spectra of stilbene-NHC that was self-assembled on Au and Pt films exhibited a peak positioned at 400.0 eV (Figure 1b and 1c, respectively).^[12a-e] The shift in the peak position was correlated to neutralization of the positive charge in stilbene-imidazolium and was identified in various NHC-based monolayers.^[12a] The XPS peak width (FWHM= 1.3 eV) is characteristic for NHCs on metal surfaces^[11b, 16].

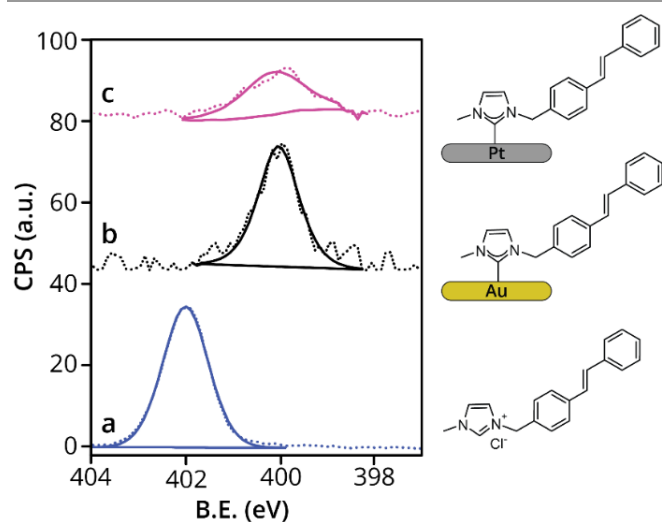


Figure 1. N1s XPS spectra of stilbene-imidazolium salt (a) and stilbene-NHCs that were anchored on Au (b) and Pt (c) films. The measured data is shown in dots and the lines represent the Gaussian fit.

Quantitative analysis of the N1s/Au4f and N1s/Pt4f XPS peaks area ratio indicated on similar surface coverage of stilbene-NHCs on the two metal films (Table S1). The higher carbon content on Pt is attributed to either the presence of base residues or to encapsulated solvent molecules^[11a, 12c]. Contact potential difference (CPD) measurements were performed to analyze the influence of stilbene-NHC monolayer on the work function (WF) values of Au and Pt. The WF values of Au and Pt films were changed by -0.36 eV and -0.25 eV, respectively, following surface-anchoring of stilbene-NHC. The decrease in WF values results from the interface dipole that is formed between the NHC and metal surfaces.^[14] The larger change in surface potential of Au, in comparison to Pt, can be associated with the higher order of stilbene-NHC on Au.^[12e]

The photoswitchability of surface-anchored stilbene-NHC and its impact on surface properties was examined by CPD measurements under irradiation. Each cycle consisted of one-hour irradiation (at 365 nm) followed by relaxation without illumination. Irradiation of stilbene-NHC that was self-

assembled on Au film led to a photo-induced increase of 90 ± 10 mV in CPD values (Figure 2a, green-colored bars). Stilbene isomerization lowered the molecular dipole pointing towards the surface, which increased the CPD value.^[1a, 17] Bare Au substrate demonstrated an average change of 23 ± 7 mV in CPD values following illumination (Figure 2a, orange-colored bars), attributed to the interaction of light with polycrystalline Au islands that were present on the corrugated Au film.^[18]

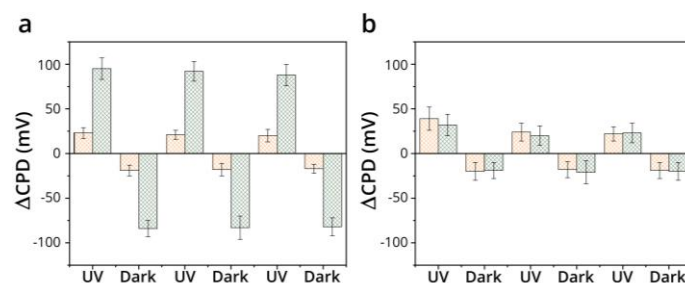


Figure 2. Δ CPD measurements under UV irradiation (365 nm) of bare and Stilbene-NHC coated metal films: (a) bare Au (orange-colored bars) and stilbene-NHC/Au (green-colored bars) and (b) bare Pt (orange-colored bars) and stilbene-NHC/Pt (green-colored bars). Error bars represent the SD values of three samples.

Thermal-induced relaxation (without illumination) yielded a decrease in CPD values due to *cis*-to-*trans* isomerization of the stilbene group.^[15b] Reversible changes in CPD values was demonstrated over several cycles with a relatively small decrease of 10 % in Δ CPD changes after the third cycle. The photo-degradation can be correlated to the susceptibility of $-C=C-$ bonds to undergo photo-induced transformations.^[19] Notably, the isomerization of stilbene-NHC on Au led to Δ CPD values that were in the same range as those measured for NHC that was functionalized with arylazopyrazole on its benzimidazole backbone and supported on Au film.^[9] This similarity in Δ CPD values indicates that surface proximity of the stilbene group did not quench its photo-induced isomerization impact on surface properties. The measured Δ CPD values of NHC-stilbene were 2-fold higher than that of thiol-based SAMs that were functionalized with azobenzene.^[20] It is hypothesized that the enhanced Δ CPD values of NHC-stilbene are correlated with higher degree of conformational freedom available to stilbene attached to NHC, resulting from its larger footprint^[21] in comparison to that of a thiolate ligand.

Photo-induced Δ CPD values of stilbene-NHC/Pt (Figure 2b, green-colored bars) were similar to the values measured for the bare Pt film (Figure 2b, orange-colored bars) and threefold lower than the Δ CPD values recorded for stilbene-NHC/Au. Since the surface density of stilbene-NHC on Au and Pt is comparable (Table S1), the differences in Δ CPD values imply that the effect of photoisomerization was quenched once stilbene-NHC was anchored on Pt. Photoactivity quenching on Pt can be correlated to the strong electronic interaction of the aromatic benzene rings of stilbene-NHC with the Pt film. It was previously demonstrated that strong interaction of benzene and benzene-functionalized molecules with Pt surface can lead to a flat-lying position of the benzene ring.^[12e, 22] Similarly, the interaction of stilbene-NHC with Pt can induce flat-lying

positioning of the stilbene and thus hinder its photo-tunability, leading to deteriorated photo-induced Δ CPD values.

For stilbene-NHC/Au, on the other hand, 15 minutes was measured as the half-life time for thermal-induced *cis*-to-*trans* isomerization, based on first-order decay analysis of Δ CPD values (Fig. S7). This result demonstrates that surface proximity does not lead to rapid thermal-induced *cis*-to-*trans* isomerization. As a control experiment, photo-inert dimethyl functionalized-NHCs were deposited on Au and Pt films and the effect of irradiation on WF values was measured. Photo-induced Δ CPD values of 20 ± 7 and 22 ± 8 mV were measured for dimethyl-NHC on Au and Pt films, respectively (Fig. S8). These values are similar to the values measured for the bare metal films (Figure 2), indicating that the photo-induced changes in Δ CPD of stilbene-NHC/Au stems from the stilbene group and were not induced by the imidazole scaffold. Control experiment was also performed with bulkier NO₂-functionalized NHCs (1,3-bis(2,4-dinitrophenyl)-1H-imidazol-3-ium) that was deposited on Au film. UV-irradiation led to Δ CPD values of 8 ± 3 mV, confirming that the conformational freedom of benzene rings has negligible influence on photoactivity of stilbene-NHC. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements of stilbene-NHC/Au and stilbene-NHC/Pt (Figure 3a and 3b, respectively) were performed under illumination and thermal relaxation (purple- and black-colored spectra, respectively) to probe the *trans* and *cis* isomers, respectively, of the stilbene group. The high sensitivity of PM-IRRAS measurements to dipoles that are perpendicular to the surface yields spectroscopic data with which the impact of illumination on the anchoring geometry of stilbene-NHC on Au and Pt can be deduced. Illumination led to the appearance of a peak at 740 cm⁻¹ on both Au and Pt films that were coated with stilbene-NHCs. This peak was attributed to the *cis*-stilbene isomer^[15b, 23] and was not detected under dark conditions. Additionally, surface illumination eliminated two vibrational signatures at 947 and 1648 cm⁻¹, assigned to C–H bending and C=C–H stretch of the *trans* double bond, respectively. The photo-induced variations in IR spectra validate that stilbene isomerization led to the observed changes in CPD values. The signals in the 1300-1600 cm⁻¹ range, assigned to the imidazole ring, were not significantly modified following illumination, indicating that the imidazole ring did not change its position during the light-dark cycles.

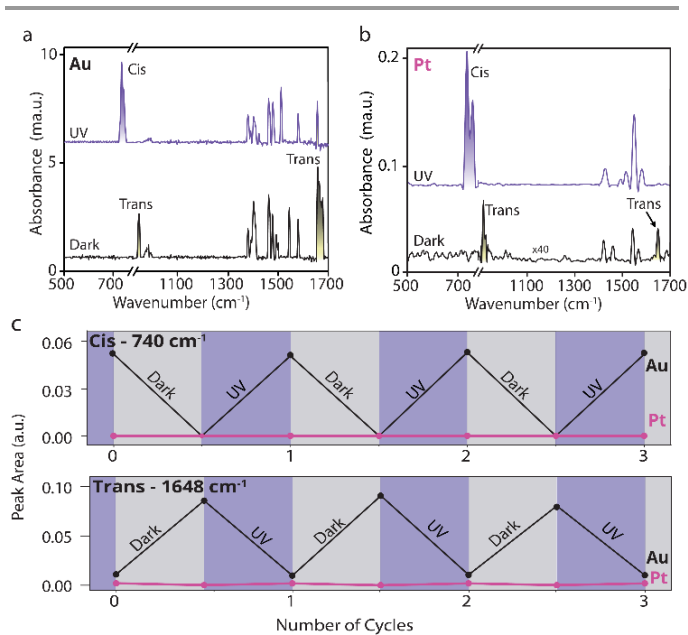


Figure 3. *In-situ* PM-IRRAS spectra of stilbene-NHC on Au (a) and Pt (b) films, measured under illumination and after thermal relaxation (purple- and black-colored spectra, respectively). (c) Peak area analysis of *cis*- and *trans*-related vibrations (740 and 1648 cm⁻¹, shown in upper and lower panels, respectively) of stilbene-NHC/Au (black) and stilbene-NHC/Pt (pink) during several cycles of irradiation (purple background) and thermal relaxation (gray background).

The amplitudes of the vibrational peaks were 20-fold higher for NHC-stilbene on Au than on Pt. Since the surface density of stilbene-NHC on Au and Pt is comparable (Table S1), the vast differences in the vibrational amplitude were correlated to dissimilarities in the adsorption geometry, induced by the strong interaction of stilbene-NHC with Pt. The deteriorated vibrational signals of stilbene-NHC on Pt indicate that the surface-anchored molecules were mostly oriented in a close to flat-lying position.^[12c-e] The absence of the vibrational fingerprint attributed to the imidazole ring at 1300-1600 cm⁻¹ on Pt further supports a flat-lying orientation of the aromatic imidazole ring. The flat-lying stilbene groups on Pt were photo-isomerized upon their illumination, as identified by the changes in the PM-IRRAS spectra (Figure 3b). However, due to the parallel position of the stilbene group in respect to the Pt surface, the photo-isomerization did not induce a noticeable influence on work function values (Figure 2b).

The reversible appearance and disappearance of a *cis*-related peak (740 cm⁻¹) and the disappearance and appearance of a *trans*-related peak (1648 cm⁻¹) under illumination and dark conditions, respectively, were monitored for stilbene-NHC on Au and Pt during three consecutive dark-light cycles (Figure 3c). High reversibility of photo-isomerization was detected for both stilbene-NHC/Au and stilbene-NHC/Pt. However, the vibrational signal amplitude variations for stilbene-NHC on Au were much higher than those measured on Pt, correlated to differences in metal-adsorbate interactions that influenced the adsorption geometry of anchored molecules.

In conclusion, *N*-substituted NHC with a stilbene group was synthesized and self-assembled on Au and Pt films, enabling to position a photoactive group in close proximity to the metal

surface. *In-situ* PM-IRRAS and Δ CPD measurements provided a holistic view of the influence of metal-adsorbate interactions on stilbene photoisomerization and its impact on surface properties. Stilbene-NHC that was anchored on the more inert and weakly interacting Au surface accumulated a vertical orientation, which led to structural flexibility and high isomerization efficiency that resulted reversible photoinduced changes of 90 ± 10 mV in CPD value. Once stilbene-NHC was supported on Pt film, the strong metal-adsorbate interactions led to flat-lying adsorption geometry of the stilbene group that quenched the influence of photoswitchability on CPD values. The presented results therefore identify the key impact of metal-adsorbate interactions on the adsorption geometry and the ability to photo-adjust the surface potential. It is demonstrated that in order to fully utilize the photo-induced response of monolayers for adjusting the metal properties the photo-active group should be positioned in high proximity to weakly-interacting metal surfaces.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the European Research Council under the Horizon 2020 research and innovation program (No. 802769, ERC Starting Grant “MapCat”). S.Y. thanks the Benjamin H. Birstein Chair in Chemistry. S.D. acknowledges the Israeli Ministry of Energy and the Azrieli Foundation for the award of an Azrieli Fellowship. I.A. is supported by The Hebrew University Center for Nanoscience and Nanotechnology PhD Scholarship.

References

- [1] a) E. Orgiu and P. Samori, *Advanced Materials* **2014**, *26*, 1827-1845; b) M. M. Russew and S. Hecht, *Advanced Materials* **2010**, *22*, 3348-3360; c) A. B. Grommet, L. M. Lee and R. Klajn, *Accounts of Chemical Research* **2020**, *53*, 2600-2610.
- [2] a) T. Bian, Z. Chu and R. Klajn, *Advanced Materials* **2020**, *32*, 1905866; b) A. J. Veinot, A. Al-Rashed, J. D. Padmos, I. Singh, D. S. Lee, M. R. Narouz, P. A. Lummis, C. J. Baddeley, C. M. Crudden and J. H. Horton, *Chemistry – A European Journal* **2020**, *26*, 11431-11434; c) Z. She, M. R. Narouz, C. A. Smith, A. MacLean, H.-P. Loock, H.-B. Kraatz and C. M. Crudden, *Chemical Communications* **2020**, *56*, 1275-1278; d) W. C. de Vries, M. Niehues, M. Wissing, T. Würthwein, F. Mäsing, C. Fallnich, A. Studer and B. J. Ravoo, *Nanoscale* **2019**, *11*, 9384-9391.
- [3] a) Y. Wang and H.-P. Cheng, *Physical Review B* **2012**, *86*, 035444; b) C. Zhang, M. H. Du, H. P. Cheng, X. G. Zhang, A. E. Roitberg and J. L. Krause, *Physical Review Letters* **2004**, *92*, 158301.
- [4] a) Y. He, R. Wang, C. G. Sun, S. F. Liu, J. X. Zhou, L. X. Zhang, T. F. Jiao and Q. M. Peng, *Acs Omega* **2020**, *5*, 3689-3698; b) K. T. Kim, N. Il Moon and H. K. Kim, *Sensors and Actuators a-Physical* **2010**, *160*, 19-21; c) R. M. Mayall, C. A. Smith, A. S. Hyla, D. S. Lee, C. M. Crudden and V. I. Birss, *ACS Sensors* **2020**, *5*, 2747-2752.
- [5] R. Dorel and B. Feringa, *Chemical Communications* **2019**, *55*, 6477-6486.
- [6] D. Bleger, A. Ciesielski, P. Samori and S. Hecht, *Chemistry-a European Journal* **2010**, *16*, 14256-14260.
- [7] J. Zhang, J. K. Whitesell and M. A. Fox, *Chemistry of Materials* **2001**, *13*, 2323-2331.
- [8] a) M. Ikbal, D. Balogh, E. Mervinetsky, R. Sfez and S. Yitzchaik, *Journal of Physical Chemistry C* **2017**, *121*, 27176-27181; b) P. K. Kundu, S. Das, J. Ahrens and R. Klajn, *Nanoscale* **2016**, *8*, 19280-19286.
- [9] D. T. Nguyen, M. Freitag, C. Gutheil, K. Sotthewes, B. J. Tyler, M. Bockmann, M. Das, F. Schluter, N. L. Doltsinis, H. F. Arlinghaus, B. J. Ravoo and F. Glorius, *Angewandte Chemie-International Edition* **2020**, *59*, 13651-13656.
- [10] a) C. M. Crudden, J. H. Horton, I. I. Ebraldize, O. V. Zenkina, A. B. McLean, B. Drevniok, Z. She, H. B. Kraatz, N. J. Mosey, T. Seki, E. C. Keske, J. D. Leake, A. Rousina-Webb and G. Wu, *Nature Chemistry* **2014**, *6*, 409-414; b) A. V. Zhukhovitskiy, M. G. Mavros, T. Van Voorhis and J. A. Johnson, *Journal of the American Chemical Society* **2013**, *135*, 7418-7421; c) A. V. Zhukhovitskiy, M. J. MacLeod and J. A. Johnson, *Chemical Reviews* **2015**, *115*, 11503-11532.
- [11] a) C. M. Crudden, J. H. Horton, M. R. Narouz, Z. Li, C. A. Smith, K. Munro, C. J. Baddeley, C. R. Larrea, B. Drevniok, B. Thanabalasingam, A. B. McLean, O. V. Zenkina, I. I. Ebraldize, Z. She, H.-B. Kraatz, N. J. Mosey, L. N. Saunders and A. Yagi, *Nature Communications* **2016**, *7*, 12654; b) A. Bakker, A. Timmer, E. Kolodzeiski, M. Freitag, H. Y. Gao, H. Mönig, S. Amirjalayer, F. Glorius and H. Fuchs, *Journal of the American Chemical Society* **2018**, *140*, 11889-11892.
- [12] a) S. Dery, S. Kim, D. Feferman, H. Mehlman, F. D. Toste and E. Gross, *Physical Chemistry Chemical Physics* **2020**, *22*, 18765-18769; b) S. Dery, S. Kim, D. Haddad, A. Cossaro, A. Verdini, L. Floreano, F. D. Toste and E. Gross, *Chemical Science* **2018**, *9*, 6523-6531; c) S. Dery, S. Kim, G. Tomaschun, I. Berg, D. Feferman, A. Cossaro, A. Verdini, L. Floreano, T. Klüner, F. D. Toste and E. Gross, *The Journal of Physical Chemistry Letters* **2019**, *10*, 5099-5104; d) S. Dery, S. Kim, G. Tomaschun, D. Haddad, A. Cossaro, A. Verdini, L. Floreano, T. Klüner, F. D. Toste and E. Gross, *Chemistry-a European Journal* **2019**, *25*, 15067-15072; e) S. Dery, I. Berg, S. Kim, A. Cossaro, A. Verdini, L. Floreano, F. D. Toste and E. Gross, *Langmuir* **2020**, *36*, 697-703; f) E. Amit, I. Berg and E. Gross, *Chemistry-a European Journal* **2020**, *26*, 13046-13052; g) I. Berg, L. Hale, M. Carmiel-Kostan, F. D. Toste and E. Gross, *Chemical Communications* **2021**, *57*, 5342-5345.
- [13] a) R. Ye, A. V. Zhukhovitskiy, R. V. Kazantsev, S. C. Fakra, B. B. Wickemeyer, F. D. Toste and G. A. Somorjai, *Journal of the American Chemical Society* **2018**, *140*, 4144-4149; b) M. J. MacLeod, A. J. Goodman, H.-Z. Ye, H. V. T. Nguyen, T. Van Voorhis and J. A. Johnson, *Nature Chemistry* **2019**, *11*, 57-63.
- [14] H. K. Kim, A. S. Hyla, P. Winget, H. Li, C. M. Wyss, A. J. Jordan, F. A. Larrain, J. P. Sadighi, C. Fuentes-Hernandez, B. Kippelen, J. L. Bredas, S. Barlow and S. R. Marder, *Chemistry of Materials* **2017**, *29*, 3403-3411.
- [15] a) S. T. Repinec, R. J. Sension, A. Z. Szarka and R. M. Hochstrasser, *Journal of Physical Chemistry* **1991**, *95*, 10380-10385; b) D. H. Waldeck, *Chemical Reviews* **1991**, *91*, 415-436.
- [16] G. Wang, A. Rühling, S. Amirjalayer, M. Knor, J. B. Ernst, C. Richter, H.-J. Gao, A. Timmer, H.-Y. Gao, N. L. Doltsinis, F. Glorius and H. Fuchs, *Nature Chemistry* **2017**, *9*, 152-156.
- [17] a) N. Delorme, J. F. Bardeau, A. Bulou and F. Poncin-Epaillard, *Langmuir* **2005**, *21*, 12278-12282; b) M. Kim, N. S. Safron, C. H. Huang, M. S. Arnold and P. Gopalan, *Nano Letters* **2012**, *12*, 182-187; c) J. Lu, A. Lipatov, N. S. Vorobeve, D. S. Muratov and A. Sinititskii, *Advanced Electronic Materials* **2018**, *4*, 1800021.
- [18] I. Zoric, M. Zach, B. Kasemo and C. Langhammer, *Acs Nano* **2011**, *5*, 2535-2546.
- [19] A. Galvan-Gonzalez, K. D. Belfield, G. I. Stegeman, M. Canva, S. R. Marder, K. Staub, G. Levina and R. J. Twieg, *Journal of Applied Physics* **2003**, *94*, 756-763.
- [20] S. Schuster, M. Fuser, A. Asyuda, P. Cyganik, A. Terfort and M. Zharnikov, *Physical Chemistry Chemical Physics* **2019**, *21*, 9098-9105.
- [21] E. Amit, L. Dery, S. Dery, S. Kim, A. Roy, Q. C. Hu, V. Gutkin, H. Eisenberg, T. Stein, D. Mandler, F. D. Toste and E. Gross, *Nature Communications* **2020**, *11*, 5714.
- [22] S. Lehwald, H. Ibach and J. E. Demuth, *Surface Science* **1978**, *78*, 577-590.
- [23] a) Z. Meic and H. Gusten, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* **1978**, *34*, 101-111; b) C. Pecile and B. Lunelli, *Canadian Journal of Chemistry* **1969**, *47*, 243-250.