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Challenges in controlled thermal deposition of organic diradicals

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ABSTRACT

We demonstrate that it is possible to evaporate diradicals in a controlled environment obtaining thin films in which the diradical character is preserved. However, evaporation represents a challenge. The presence of two radical sites makes the molecules more reactive also in the case of very stable single radicals. We have explored the parameters that play a role in this phenomenon. We found that the higher the formation energies of the crystal, the more difficult is the evaporation of intact radicals. Large delocalization of the unpaired electrons helps the diradical to stand evaporation. We have also investigated the lifetime of the films when exposed to X-rays or to air. The onset of thermal degradation plays a role in the film lifetime. In fact, the lower the evaporation temperature with respect to the onset temperature, the longer is the film lifetime. The evaporation of different diradicals can be successfully addressed considering our findings.

INTRODUCTION

Technology based on quantum phenomena, such as entanglement and superposition, is taking the lead in various fields. Its fast development involves a strong multidisciplinary approach including a new technological vision in terms of applications and devices, new algorithms, and materials. The latter implies not only the strategic use of materials, but also their discovery and design.¹ Among the materials candidate to play a role in emerging quantum technologies, organic materials and, particularly, radicals have recently attracted much attention.²⁻⁶ Inert organic radicals and their derivatives are metal-free carbon-based molecules with one unpaired electron that are demonstrated to be stable enough to match technical requirements, such as evaporation and film processing.⁷⁻¹³ The restriction to a single spin per molecule constitutes a limitation for many spintronic applications,^{2, 4-5} so the synthesis and the controlled growth of films of multi-spin radicals constitute a paramount step forward in the field. Diradicals have two unpaired electrons, each localized in a specific chemical group in the molecule. The singlet and the triplet state in these molecules are in competition as a ground state. High spin diradicals with large energy gap between the triplet and the singlet states are interesting because of their potential use in applications, such as sensors, memories, and quantum gates.¹⁴⁻¹⁸ These technologies require a very high degree of control in attaching to a surface single or few spin systems in quantum gates or a larger number of spins for sensors.

However, the implementation of diradicals in real devices has been hampered by the fact that their controlled evaporation and deposition onto a substrate was considered practically impossible to achieve because of their high reactivity. Huang et al.¹⁹ stated that the general rule of thumb is that the more unpaired electrons in a molecule are, the worse its thermal stability is. Thus, they excluded that diradicals could be evaporated because they would decompose during sublimation.¹⁹

Inspired by the promising technological opportunities offered by diradicals, we have tackled the problem of their evaporation. The nitronyl nitroxide (NN)²⁰ and the Blatter single radicals²¹ are stable against evaporation and they have good film forming properties, when fused to suitable substituents such as

pyrene.^{7-8, 22} Controlled preparation techniques using Knudsen cell evaporation and electrospray deposition are a good choice for growing films of sensitive molecules, or single molecule magnets.^{13, 23-}
²⁴ Thus, we chose organic molecular beam evaporation (OMBD), which allows tuning the preparation parameters to suit the film forming properties of the molecule.²⁵ The thin films were prepared in situ under ultrahigh vacuum (UHV) conditions by using opportunely calibrated Knudsen cells. Here we report the successful controlled evaporation of a diradical obtained fusing the NN radical to a derivative of the Blatter radical ($C_{26}H_{25}N_5O_2$, NN-Blatter, Figure 1, $S=1$)¹² and a derivative of the benzodithiophene decorated with two NN radicals ($C_{26}H_{32}N_4O_6S_2$, BTD-NN, Figure 1, $S=1/2$)²⁶ to identify the specific parameters that play a role for evaporation and film stability (Table 1). To fully investigate the problem of diradical evaporation, we have also evaporated a third diradical, a di-nitroxide diradical with $S=1$ ($C_{18}H_{26}N_2O_4$, Figure 1)²⁷.

We have investigated the thin films (in the nano-thickness regime) by using X-ray based techniques and ab-initio calculations, focusing on diradical film processes and the consequent challenges that must be addressed to successfully evaporate and grow diradical thin films. Furthermore, we investigated the film lifetime under X-ray and air exposure.

RESULTS AND DISCUSSION

We used X-ray photoelectron spectroscopy (XPS) to investigate the thin films because it is proved an efficient tool for the investigation of organic radical thin films.¹³ The method is element-sensitive, and allows insight into the stoichiometry of the film, and it is sensitive towards the different chemical environments of atoms of the same element.²⁸

We focus on the C 1s and N 1s core level spectra (for NN-Blatter in Figure 2). The O 1s core level spectrum is the sum of the substrate ($SiO_2/Si(111)$ wafers) and molecule signals, making the analysis less reliable. Important is that the spin densities are mainly localized in the nitrogen centres.^{8, 26, 29-30} Therefore, the information on the radical is substantially delivered by the N 1s core level spectra. The NN-Blatter N

1s spectrum is composed of two main features. Two contributions originated by the photoelectrons emitted by the nitrogen atoms in the 2- and 4-position of the 1,2,4-benzotriazinyl moiety are visible and centered around 400 eV. At higher binding energies, the emitted photoelectrons from the two chemically equivalent nitrogen atoms of the nitronyl nitroxide moiety combine with those of the nitrogen atom in the 1-position of the 1,2,4-benzotriazinyl moiety to form a broad peak with its highest intensity above 402 eV. The C 1s core level spectrum shows a main line at around 285 eV and a pronounced shoulder at higher binding energies. The main line contains the contributions from the emission of photoelectrons in the aromatic rings, as well as the contributions from carbon atoms bound to other carbon atoms and hydrogen atom (C-C, C-H, C-H₃). The shoulder is due to the signal of the photoelectrons emitted from carbon atoms bound to nitrogen atoms, which lie at higher binding energies due to the shift of charge towards the more electronegative nitrogen and the resulting decrease in electron density on the carbon atoms.

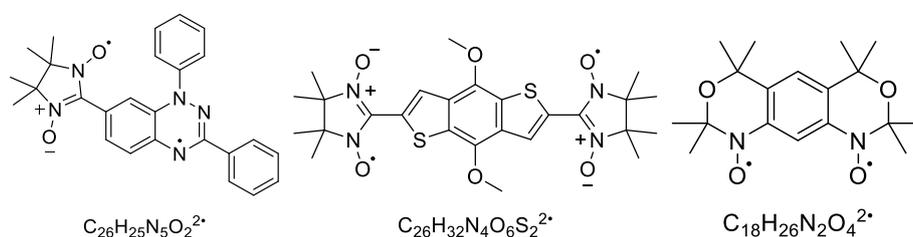
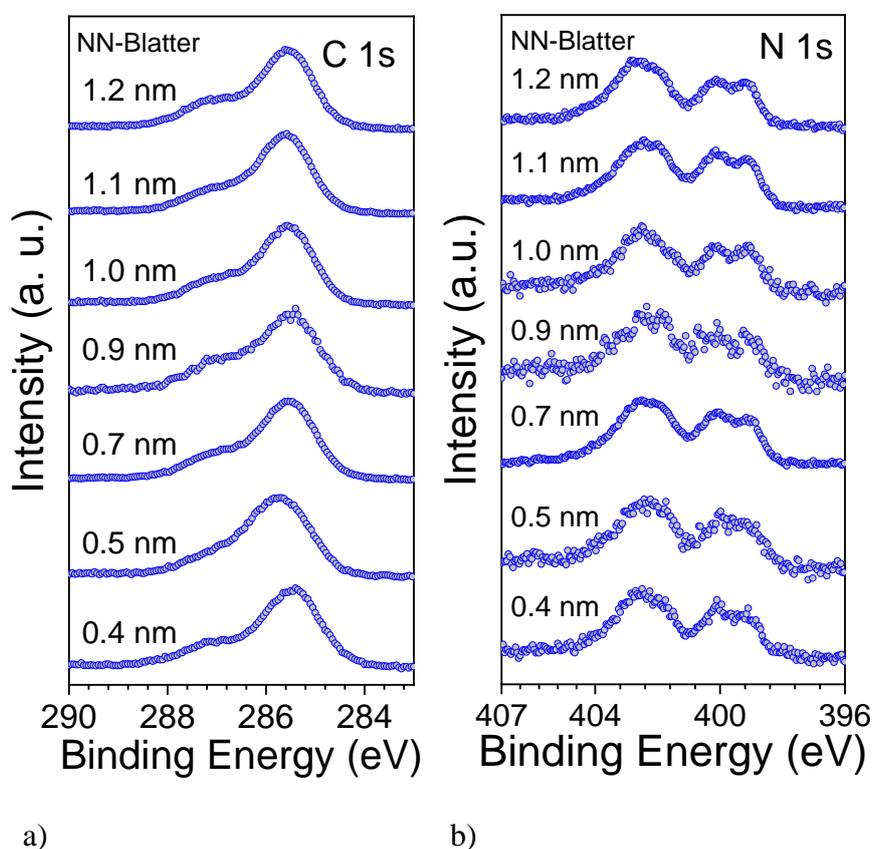
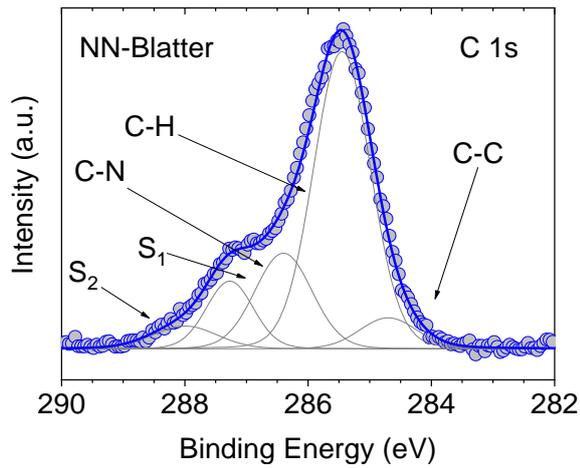


Figure 1. NN-Blatter (left), BTD-NN (middle) and diNitroxide (right) structures are shown.

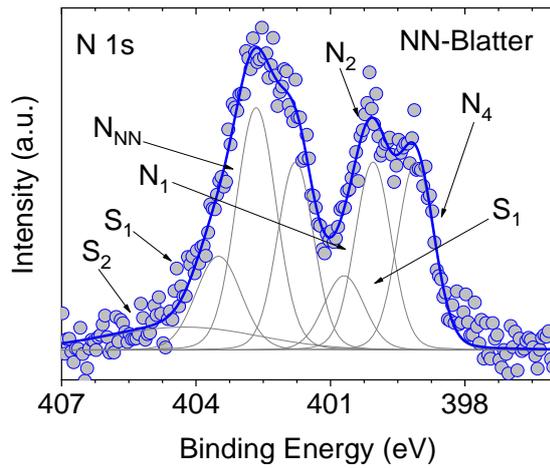
Figure 2 shows the thickness-dependent C 1s and N 1s core level spectra and it includes the best fit curves for the two core level spectra. The fit is forced by tight physical and chemical constraints (for details see the supporting information and Refs. ^{7, 12, 31-32}). The result indicates that the stoichiometry of the diradical film after evaporation and deposition corresponds to the theoretical values and, thus, that the diradical character of the molecule is maintained throughout the complete process.¹²

We also observe that there is a difference in the binding energy of the emitted photoelectrons when adopting a stepwise evaporation instead of a direct evaporation. The stepwise evaporation leads to a shift of the N 1s and C 1s spectra towards lower binding energies (Figure 3). This shift may be understood in terms of a change in the film morphology.³³ In fact, the increase of the thickness in organic thin films (e.g., monolayer vs. islands) leads to a less efficient screening of the core-hole, created upon photoemission, by the corresponding substrate mirror charge.³³

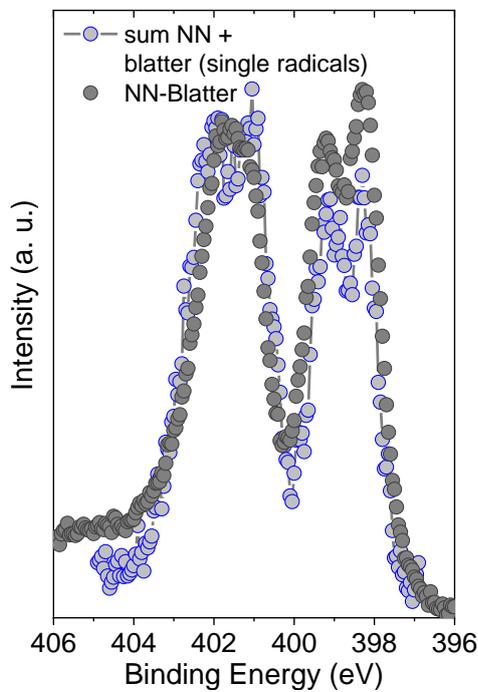




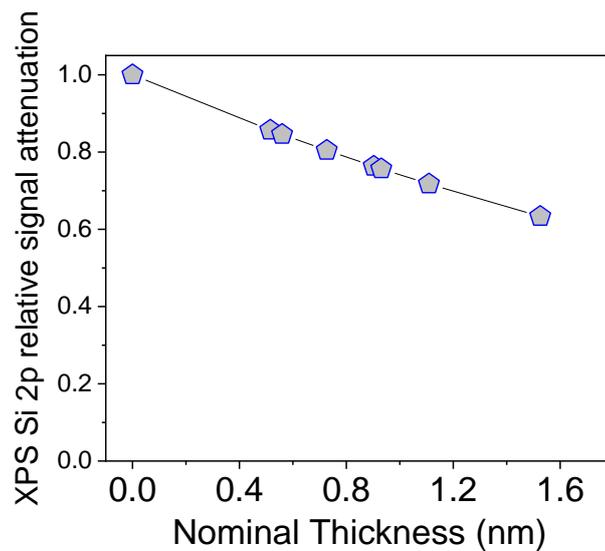
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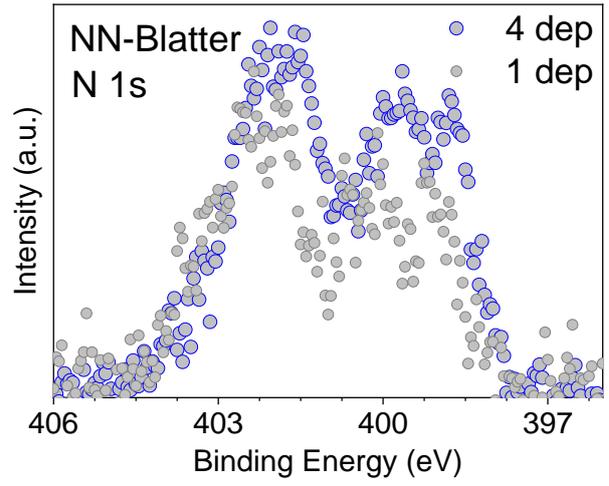
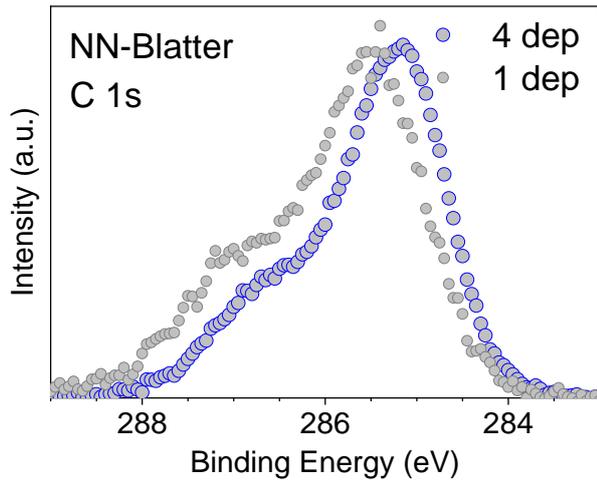
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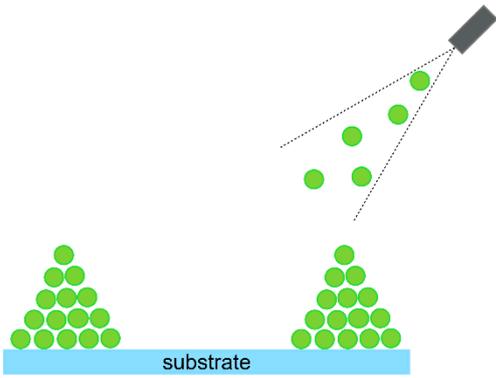
f)

Figure 2. NN-Blatter a) C 1s and b) N 1s thickness-dependent core-level spectra of the NN-Blatter thin films, thickness as indicated. NN-Blatter c) C 1s and d) N 1s spectra with their best fit for the nominally 0.4 nm thick film. e) N 1s core level spectrum obtained as a sum of the core level spectra of the single radicals (NN + Blatter radical⁷⁻⁸) compared to the NN-Blatter N1s core level spectrum as in b). f) Attenuation of the Si 2p XPS signal, normalized to the corresponding clean substrate signal, as a function of the film nominal thickness (the line is a guide to the eye).

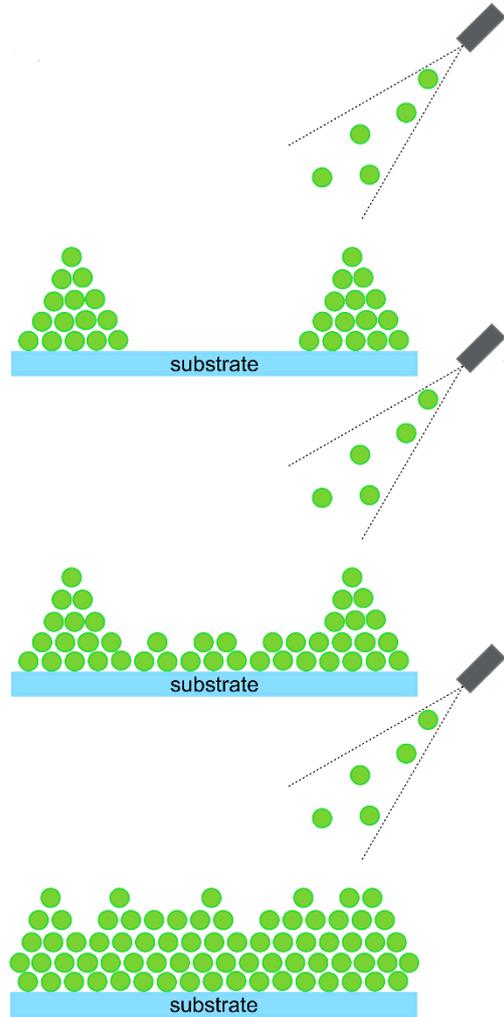
We explain our result considering that the NN-Blatter films grow following the Volmer–Weber (VW) growth mode,¹² i.e., purely island growth in case of direct evaporation, as it is also confirmed by the atomic force microscopy images of the films that clearly show island formation (Figure 3). Once the islands are formed during deposition, a successive evaporation adds molecules on the substrate left free from the first deposition. This leads to contributions in the XPS spectra due to photoelectrons coming from thinner regions of the assembly, that is, closer to the substrate and characterized by a more efficient screening of the core-hole (Figure 3). Note that the screening of the core-hole by an image charge is observable at the organic/metal-oxides interface, however, its effect is weaker than in metal substrates.³⁴ We also observe that the shift is non-rigid (0.4 eV for the N 1s and 0.2 eV for the C 1s main line, respectively). Non-rigid shifts may have different reasons: the image charge of the core-hole originates in elements at different height from the substrate because the molecules are not completely planar or from a fractional charge transfer from the substrate to the adsorbate in physisorption.³⁵⁻³⁶ To investigate this aspect, we performed an annealing experiment and we measured near-edge X-ray fine structure (NEXAFS) spectroscopy. In general, the island growth mode in thin films is driven by the intermolecular interaction being stronger than the interaction between the adsorbate and the substrate that cannot hence act as a template.³⁷ To evaluate the role played by the interaction with the substrate, an annealing experiment is very useful. The films were subsequentially annealed at 323, 388 and 483 K, respectively, for 30 minutes at each temperature step (Figure 4). The complete desorption at 483 K indicates that the interaction with the substrate is very weak: the molecules are physisorbed on the SiO₂ surface. We also note that the films are remarkably stable up to 388 K (Figure 4). To investigate the orientation of the molecules on the substrate, we performed NEXAFS spectroscopy which provides information on the unoccupied states and the film structure (see the Supporting Information and Figure S1). We observe a NEXAFS dichroism that indicates that the molecules are not aligned with respect to the substrate,³⁸ generating a different image charge for carbon and nitrogen atoms, because of the different distance from the substrate. This is reflected by and it is the reason for the XPS non-rigid shift.



a)



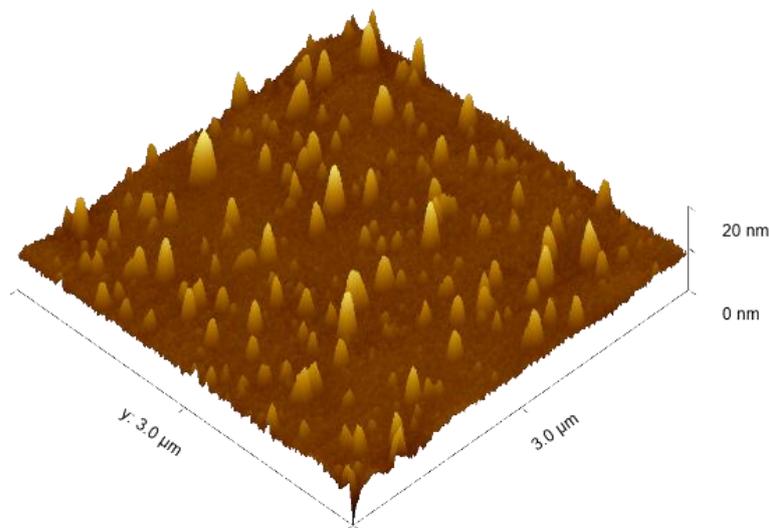
b)



direct evaporation

step-wise evaporation

c)



d)

Figure 3. NN-Blatter a) C 1s and b) N 1s core level spectra: direct versus stepwise deposition (substrate kept at room temperature in both cases). c) Sketch of the growth mode in the two cases. d) A typical 3 μm x 3 μm atomic force microscopy image of a NN-Blatter thin film (direct evaporation).

The poor air stability of the NN-Blatter thin films¹² hinders *ex-situ* investigations traditionally used to directly probe the radical persistence, such as electron paramagnetic resonance spectroscopy. To dispel any doubts on the radical character in the films, besides using the fit procedure, we adopted several strategies: 1) the comparison of the thin film core-level spectra with the same spectra obtained for the powder that show the same features, confirming the stoichiometry argument (see Ref. ¹² and the supporting information). 2) The comparison of the N 1s core level spectra with N 1s core level spectra obtained as a stoichiometric sum of the single radical thin films, i.e., the NN and the Blatter radical,⁷ as shown in Figure 2, that prove the agreement between the NN-Blatter experimental N 1s core level spectrum and the N 1s core level sum spectrum. 3) The use of *ab-initio* calculations to further verify that

the experimental occupied and unoccupied states correspond to intact diradicals (see below). This approach clearly shows that we evaporated the NN-Blatter without degradation.

To figure out which physical quantities play a role in growing diradical thin films by evaporation, we evaporated a second diradical (BTD-NN, Figure 1) adopting the same procedure as for the NN-Blatter thin films. We have chosen BTD-NN because it is a diradical that forms weakly antiferromagnetically coupled spin dimers of $S = \frac{1}{2}$ moieties.²⁶ The distance between the two NN groups in the molecule is 0.7 nm (0.987 nm is the distance between the carbon atoms that are the radical centers). Its density is similar to and its molecular weight is slightly higher than NN-Blatter.²⁶ The idea behind this choice is to explore the influence of the magnetic coupling as well as the radical interaction on the film evaporation, growth and stability (see also Table 1). The core level spectra are shown in Figure 5, together with the powder spectra.

Analogously to what we observed for NN-Blatter, we found that the BTD-NN film C 1s spectrum is characterized by a main line at 285.8 eV due to photoelectrons emitted from the atoms in the aromatic ring and the carbon atoms bound to hydrogen atoms. The shoulder at higher binding energy is due to contributions from the electrons emitted from hetero-bound carbon atoms. The two nitrogen atoms belonging to the nitronyl nitroxide radical have an equivalent chemical environment, thus, we expect a single line in the N 1s spectrum. Indeed, this is the case with the main line at 403 eV. We also observe signal intensity at lower binding energy, indicating that a very small amount of nitronyl nitroxide radicals switched to the imino nitroxide radicals.^{20, 22, 39} This switch is already present in the powder, as shown by the N1s line shape (Figure 5e). Note that in this case we do not observe any binding energy shift with thickness, although we have deposited also very (nominally) thin films (Figure 5 a and b). This indicated that the diradicals are very weakly physisorbed on the SiO₂ wafer, without creating any image charge at the interface, similarly to the single radical NN derivative on inert substrates.⁷ To shed light on the growth mode of the BTD-NN films, we followed the XPS core level signal of the substrate (Si 2p) by looking at its attenuation upon film deposition (Figure 5g). The curve is characterized by a very slow decay. This

intensity trend is typical of the Volmer-Weber growth mode, i.e., island growth.⁴⁰ The atomic force microscopy ex-situ images are consistent with this observation, clearly showing a film morphology dominated by islands (Figure 5h).

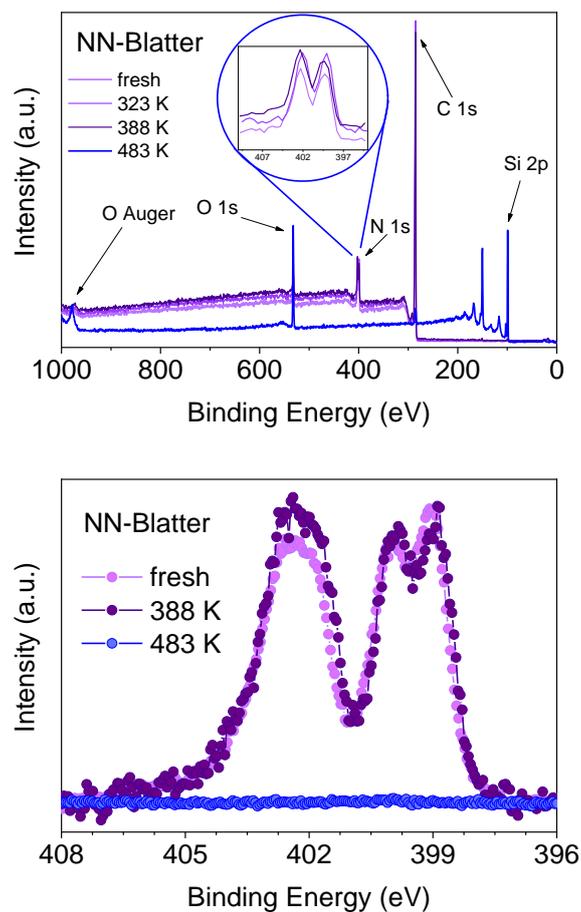
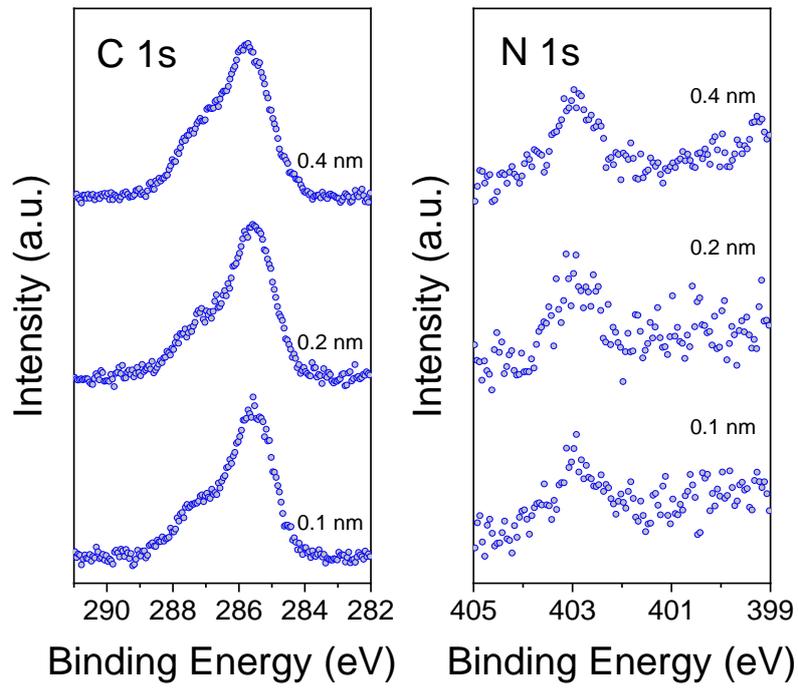


Figure 4. (upper panel) NN-Blatter XPS survey spectra (lower panel) together with the detailed N 1s core level spectra at different annealing temperatures, as indicated.

Following the same argument as for NN-Blatter, we can conclude that the evaporation of the BTD-NN films is successful, because of 1) the agreement of the film stoichiometry with the theoretical values, 2) the agreement between film and powder spectra (see Tables S3 and S4 and Figure 5) the ab-initio

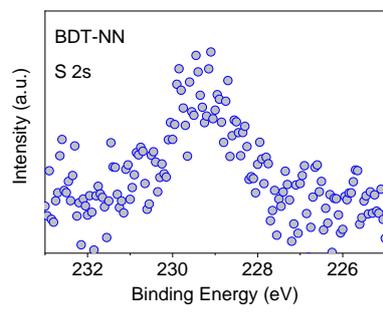
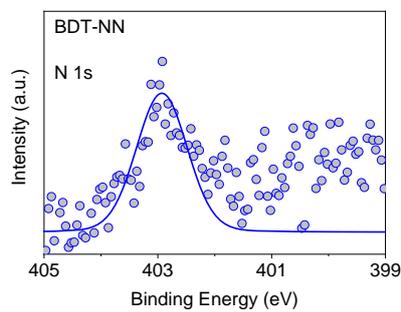
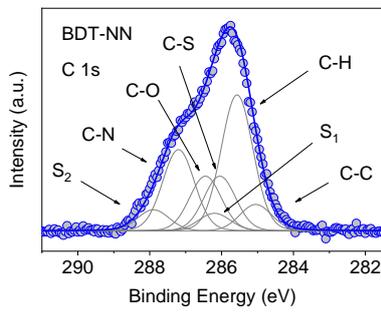
calculations (see the Supporting Information). Also in this case the evaporation temperature (373-383 K) is lower than in the case of the single NN.⁷ In the case of the BTD-NN films, we also observed an enhanced beam sensitivity with respect to the single NN radical derivatives that hinders the extensive use of X-rays techniques such as NEXAFS (Figure S3). The diradical samples were measured like the single radical derivative at room temperature using a monochromatized Al K α lab source. The radiation damage occurs on a shorter time scale in comparison with the single radical derivative and it does not depend on the sample thickness. (see also Table S5 in the Supporting Information).

In order to gain further insight, we carried out a first principles study, based on density functional theory (DFT), of the structural, electronic and magnetic properties of both diradicals in the isolated (i.e., single molecule) and aggregated (i.e., bulk-like) phases. DFT calculations cannot always assess the right exchange interaction and, thus, the magnetic character of the radical systems, also in the case of the Blatter radical.^{30, 41} On the contrary, our method shows a nice agreement with the experimental determined magnetic character (see the Supporting Information for details).



a)

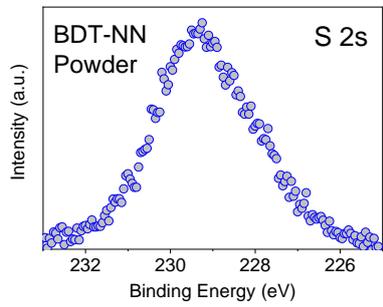
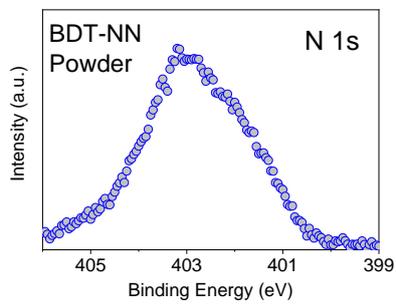
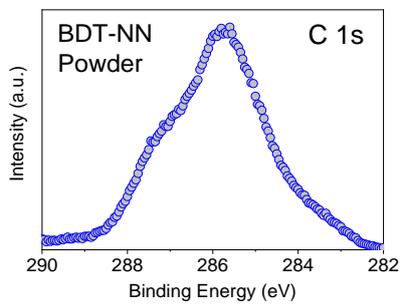
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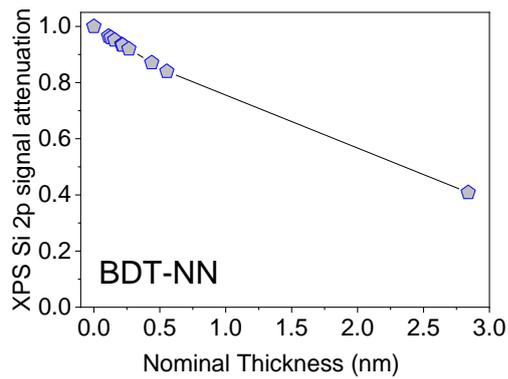
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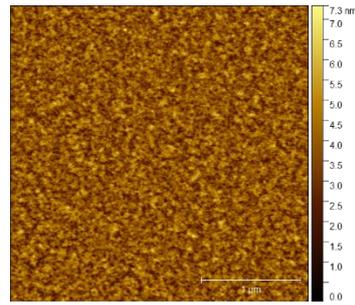
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g)

h)



i)



j)

Figure 5. BTD-NN a) C 1s and b) N 1s thickness-dependent core-level spectra of the BTD-NN thin films, thickness as indicated. c) C 1s, d) N 1s and e) S 2s core-level spectra of the BTD-NN thin films (0.1 nm nominal thickness), compared to the correspondent spectra of the powder, f)-h), as indicated. i) Attenuation of the Si 2p XPS signal, normalized to the corresponding saturation signal, as a function of film nominal thickness (the line is a guide to the eye). j) A typical 5 μm x 5 μm atomic force microscopy image (2.9 nm nominal thickness).

Our results, for the relative energetic stability are summarized in Figure 6. In the ground state, the NN-Blatter solid phase exhibits a different short-range (intra-molecular) and long-range (inter-molecular) spin alignment distribution, which corresponds to a $M_T=0\mu_B/\text{cell}$ and $M_A=8.2\mu_B/\text{cell}$. The spins remain parallelly oriented ($\uparrow\uparrow$) within each single molecule, while they arrange in chains with AF order between next-neighbor molecules, ($\uparrow\uparrow - \downarrow\downarrow$), in agreement with the experimental evidence.^{12, 26} The fully parallelly oriented spin configuration, i.e., the FM state ($\uparrow\uparrow-\uparrow\uparrow$), is energetically less favored by 41 meV/mol than the AF phase.

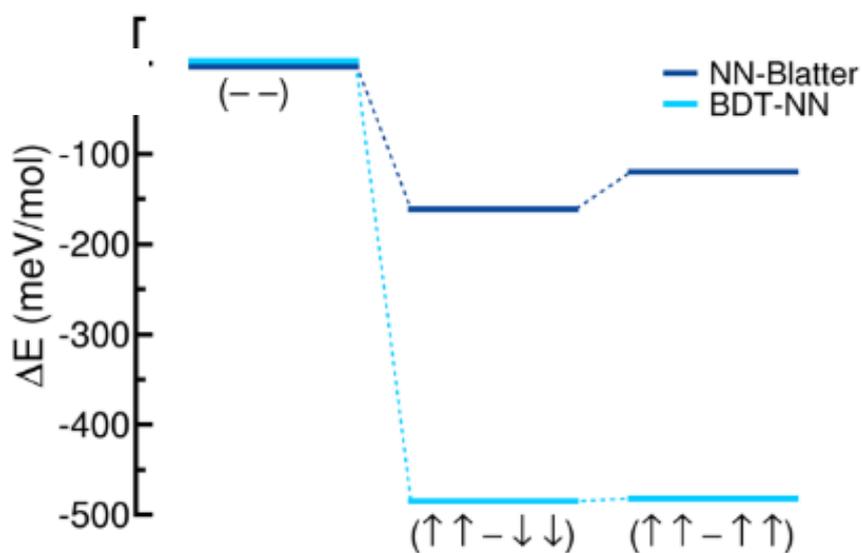


Figure 6. Total energy difference ΔE of the bulk crystals, as a function of the total magnetization, with respect to the non-magnetic (- -) phase. Labels ($\uparrow\uparrow-\downarrow\downarrow$) and ($\uparrow\uparrow-\uparrow\uparrow$) correspond to AF and FM long-range (inter-molecular) spin alignment, and correspond to $M_T=0$, and $8\mu_B/\text{cell}$, respectively.

BDT-NN crystal may be stabilized in both FM and AF phase at the same total energy, being the AF state only 2 meV/mol more stable than the FM one. In both cases, the absolute magnetization is $M_A \sim 8.5 \mu_B/\text{cell}$, while $M_T = 8.0 \mu_B/\text{cell}$ and $M_T = 0 \mu_B/\text{cell}$, for the FM and AF state, respectively. The weak AF behavior detected in the experiments can be thus interpreted as a sequence of weak interacting $S=1/2$ NN radicals. The different long-range spin arrangement also affects the DOS of the two bulk crystals as shown in Figure S6.

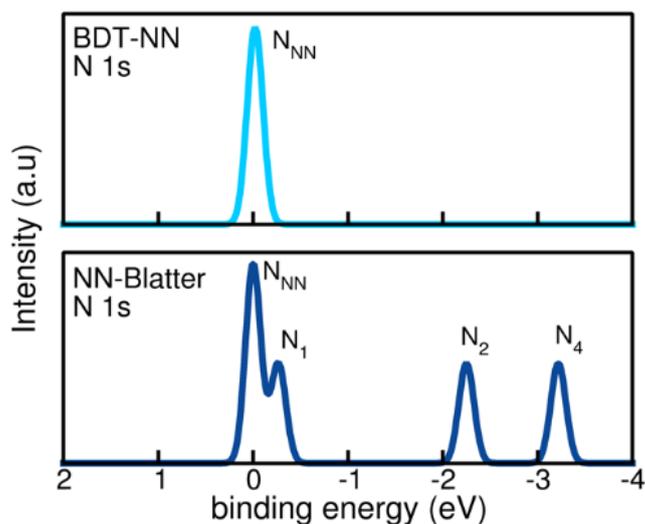


Figure 7. Simulated X-Ray N 1s core level spectra of BDT-NN (upper panel) and NN-Blatter (bottom panel) in the isolated molecule configuration. NN peak is assumed as zero energy reference for all spectra.

To confirm this analysis, we simulated the N 1s X-ray spectra for the two diradicals (Figure 7), in the single molecule configuration. The XPS spectra of BDT-NN (top panel) is dominated by one single peak relative to the N_{NN} atoms that result to be almost indistinguishable. Solid state packing does not change this picture, in agreement with the experimental results. We conclude that each NN unit, both in the molecular and in the solid-state phase, remain intrinsically independent and weakly coupled to the rest of the molecule or to the environment (i.e., $S=1/2$ single radicals). On the contrary, the intramolecular interactions affect the N 1s spectra of the NN-Blatter (bottom panel). Four peaks are clearly visible, the one at higher binding energy corresponds to the NN site, the other three (N_1 , N_2 , N_4) to the Blatter component, in very good agreement with the analysis of experimental data in Figure 2d.

The agreement between experiments and calculations that can describe both the magnetic character and the electronic structure of the diradicals allows using the calculations to shed light on the complexity of the diradical evaporation.

A large variety of novel, chemically stable radicals under ambient conditions were synthesized in recent years.^{20-21, 42-48} It was found that, among them, the radicals that can stand evaporation are characterized either by protection of the unpaired spin centers with steric hindrance or by very large delocalization of the unpaired electron.^{13, 49} The controlled evaporation in UHV of a radical is more complicated than in the case of closed shell molecules: the temperature window left for a successful evaporation is very narrow, and it is difficult to keep the evaporation rate stable. In general, the Knudsen cell temperature for radical evaporation in UHV varies in the range between 390 and 420 K (Figure 8). Using higher evaporation temperatures damages the radical. This is a clear difference in comparison with closed shell systems that stand much higher temperatures.⁵⁰⁻⁵¹ In the case of NN-Blatter, the optimized evaporation temperature is significantly lower than in the case of the NN and Blatter radicals taken separately (373 K, versus 393 and 418 K, respectively⁷⁻⁸). The space of evaporation parameters, such as pressure, substrate temperature, evaporation temperature, is very limited: on the one hand the evaporation temperature must be low enough to avoid damaging the radical (the upper limit is given by the onset of degradation in the thermal gravimetric analysis (TGA)), on the other hand, it must be high enough to overcome the intermolecular interaction, leading to sublimation. Similar arguments also apply for the substrate temperature and for post-growth temperature treatments.

Thus, we investigated the thermodynamic stability of the two compounds, by evaluating the formation energies of the crystal bulk (E_{for}), with respect to the single molecule components: $E_{\text{for}}=(E_{\text{cry}}-4E_{\text{mol}})/4.0$, where E_{cry} is the total energy of the crystalline bulk including 4 diradicals per cell and E_{mol} is the total energy of the isolated molecules. Both bulk structures are energetically very stable with $E_{\text{for}}=-1.6$ eV/mol and -0.9 eV/mol, for BDT-NN and NN-Blatter, respectively. We further checked the effect of the dichloromethane units that stabilize the NN-Blatter crystal structure.¹² We prepared and re-optimized the

atomic structure of a second crystal that does not include the CH_2Cl_2 molecules. Note that their presence has no effect on the magnetic order of the system but affects its stability. In fact, the formation energy of NN-Blatter reduces to -0.4 eV/mol when dichloromethane is not included in the system.

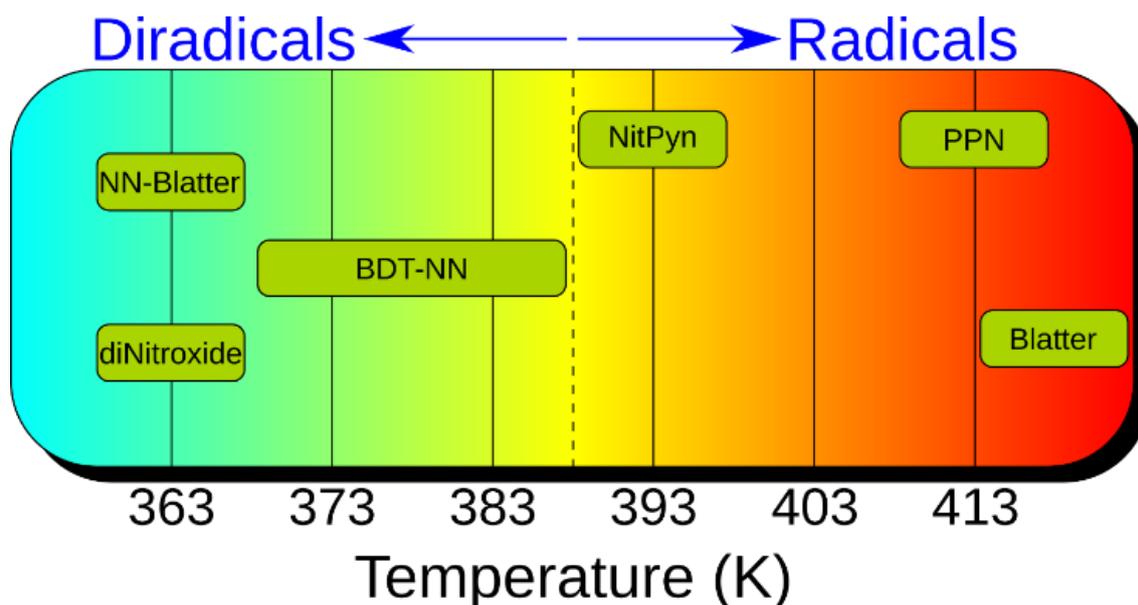


Figure 8. Schematic diagram of the evaporation temperature range for several diradicals and radicals.

We have gained at this point a full picture of the systems that allows us to answer the initial question on why the diradicals are difficult to evaporate. Our results show that the strength of the antiferromagnetic interaction does not play a role, since we observe a very similar behavior for both radicals that have different strength and sign of interactions. While NN-Blatter possesses a strong ferromagnetic interaction between the two radical sites with a weak antiferromagnetic intrachain formation, the BDT-NN has medium sized antiferromagnetic interaction between the spin centers. Other parameters that intuitively could play a role do not contribute either: in fact, the distance between the radical sites does not influence (in this case 1.0 nm versus 0.7 nm) nor does the spin (1 versus two $\frac{1}{2}$). Thermodynamics is the key. The

two diradicals assemble in stable aggregates (high E_{for}), which includes both the initial powder (before evaporation) and the final films (after deposition). On the one hand, to evaporate the molecules it is necessary to provide enough thermal energy (i.e., increasing the temperature) to release each molecule to its gas phase from the initial crystalline powder. On the other hand, temperature cannot be arbitrarily increased to avoid compromising the integrity of the molecules. Once the molecules reach the substrate, they easily tend to re-aggregate growing in compact island rather than in ordered planar films (Figures 3 and 5). Kinetics most probably affects the morphology and the size rather than the formation of the molecular islands.

Finally, we find that the diradical film stability in ambient air is extremely limited in comparison with the one observed for the NN and the Blatter radical thin films⁷⁻⁸ (Figure S2). Therefore, at this point, we intend to address the enhanced instability of the diradical films, when exposed to X-ray and to air. X-ray exposure is important not only to correctly perform the present experiments, but it gives a direct comparison with standard closed shell organic molecules that are known to be stable under the soft X-rays.

The air stability is of special significance for investigations with ex-situ techniques and for applications. In both case the term stability indicates the film lifetime, i.e., how long the films can stand beam or air exposure at room temperature, without showing changes in the electronic structure that indicate radical degradation.

We observe that comparing diradical to radical films, the number of radical sites (radical versus diradical) makes a difference, also when comparing the same radical in single or diradical configuration, e.g., films of single NN derivatives are more stable than the BTD-NN films (see Table S5). However, the NN-Blatter thin films are more robust than the BTD-NN thin films. If we look at the molecular structure, BTD-NN carries two NN, with the two unpaired electrons delocalized over the two NO groups, one in each radical. NN-Blatter on the contrary carries only one NN radical and one Blatter radical. The delocalization of the unpaired electron in the present Blatter radical derivative is quite extended, as proved by the calculations

(see the Supporting Information). In general, the films of the Blatter radical derivatives are more stable than those of the NN derivatives.^{8, 22} This difference is strongly enhanced when two NN radicals are present in the same molecules, as it is the case for BDT-NN that, for example, is very sensitive to X-ray exposure (see Figure S3). The onset of degradation in the TGA also plays a role on the film lifetime. We find a correlation between the film lifetime and the TGA onset: the larger is the difference between the evaporation temperature and the TGA onset temperature, the longer is the lifetime. (Table S5). This correlation is not trivial because there is no thermal treatment involved since the samples are kept at room temperature in darkness. A new feature N* appears upon air exposure and it grows with the duration of air exposure (Figure S2). A similar feature also appeared in the Blatter single radical films after long air exposure (several months) due to possible hydrogenation of the radical.⁸ The longer film lifetime depending on the TGA onset suggests that the film degradation triggered by air exposure might have patterns similar to the degradation caused by annealing, as seen in the case of other organic thin films and nanoparticles.⁵² These observations are fully backed up by the preliminary results obtained on a dinitroxide diradical (Figure S7). In this case the very low TGA onset (~ 103 °C) and the limited delocalization of the unpaired electrons over the N-O groups make the evaporation of the intact diradical very difficult and the film stability poor, forming films extremely sensitive also to short X-Ray exposure.

CONCLUSIONS

We have demonstrated that it is possible to evaporate diradicals in a controlled environment obtaining thin films in which the diradical character is preserved. We have explored the parameters that might play a role in this phenomenon. We found that the strength of the antiferromagnetic interaction and the distance between the radical sites do not play a role nor does the spin. Bulk formation thermodynamics play the major role. The higher the formation energies of the crystal, the more difficult is the evaporation of intact radicals. The film lifetime under ambient air is correlated with the delocalization of the unpaired electrons and the onset of decomposition in TGA. The larger the delocalization and the higher the onset, the more

stable are the films exposed to X-rays and air, making them attractive for applications. The evaporation of different diradicals can be successfully addressed considering our findings.

Table 1. Main properties of the investigated diradicals.

	BDT-NN	NN-Blatter	di-nitroxide
Formula	$C_{26}H_{32}N_4O_6S_2$	$C_{26}H_{25}N_5O_2$	$C_{18}H_{26}N_2O_4$
Formula weight (g/mol)	560.67	481.97	334.41
Density (g/cm ³)	1.332	1.363	1.297
Spin	1/2	1	1
Magnetic interaction	weak AFM	strong AFM	weak AFM
Intramolecular ordering	dimer	1D chains	1D chains
Evaporation Temperature (K)	373 – 383	363	363

METHODS

Experimental Section

Thin films were prepared in situ under UHV conditions by OMBD using a Knudsen cell. Our measurements showed that the residual powder in the cell that underwent four evaporation cycles led to some minor degradation in the films, therefore, we grew the films using the same residual powder in the Knudsen cell for not more than three successive evaporation cycles.

Native SiO₂ grown on single-side polished n-Si(111) wafer was used as the substrate for all thin films. The wafers were cleaned in an ultrasonic bath by immersion in ethanol and acetone for one hour each and annealed at around 500 K for several hours. Cleanness was verified by XPS. Nominal films thicknesses were calculated from the attenuation of the substrate signal. The NN-Blatter deposition rate was 0.03

nm/min. The substrate was kept at room temperature during deposition. The thin films were grown by direct deposition, unless specified differently in the text. The UHV system was composed of a dedicated OMDB chamber connected to an analysis chamber (2×10^{-10} mbar base pressure) in which the XPS measurements were conducted. It is equipped with a monochromatic Al K α source (SPECS Focus 500) and a SPECS Phoibos 150 hemispherical electron analyzer. Survey spectra were measured at 50 eV pass energy and individual core level spectra at 20 eV pass energy. Both were subsequently calibrated to the Si 2p signal at 99.8 eV. To minimize potential radiation damage, only freshly prepared films were measured, and radiation exposure was limited. For measurements probing stability, beam exposure was further limited after air exposure to attribute the damage exclusively to the degradation by air exposure. This results in a worse signal to noise ratio in those spectra.

NEXAFS measurements were performed at the third-generation synchrotron radiation source BESSY II at the Low-Dose PES end station installed at the PM4 beamline ($E/\Delta E = 6000$ at 400 eV). This end station was equipped with a similar setup as the one described above. The same calibrated Knudsen cells used to grow the films for the XPS measurements were mounted to a preparation chamber attached to the NEXAFS measuring chamber to reproduce the same preparation conditions, as for XPS. The measurements were carried out in multibunch hybrid mode (ring current in top up mode = 300 mA). The spectra were measured in total electron yield and normalized with the clean substrate signal as well as the ring current. Subsequently they were scaled to give an equal absorption edge jump.

Atomic force microscopy was measured ex situ and under ambient conditions with a Digital Instruments Nanoscope III Multimode microscope using tapping mode. Note that while the XPS information on the decay of the substrate signal is obtained in situ without breaking the vacuum, the images are obtained after air exposure. The information obtained with the two techniques is correlated, but since the samples underwent a gradient of pressure from UHV to ambient conditions before microscopy, in this work we use the images only to further support the XPS results on the Volmer–Weber (VW) growth mode without a quantitative evaluation.

Computational Section

Single molecules and crystalline systems have been simulated by using first principles approaches based on DFT, as implemented in the Quantum-Espresso suite of codes.⁵³ Spin-unrestricted geometry optimizations were performed at the PBE-GGA level,⁵⁴ and van der Waals corrections were included within the semiempirical method proposed by Grimme (DFT-D2).⁵⁵ The electronic structure is described by using B3LYP hybrid-functional in order to correct the DFT deficiencies in reproducing the bandgap, without further atomic relaxation on the optimized PBE structures. Spin degrees of freedom are treated within the local spin density approximation. Atomic potentials are described by ultrasoft pseudopotential as available in the SSSP library.⁵⁶ Single particle wavefunctions (charge) are expanded in planewaves up to a kinetic energy cutoff of 30 Ry (300 Ry), respectively. The first Brillouin zone of bulk systems is sampled with a (2x2x2) k-point grid; center-zone Γ -point is used in the case of single molecules. All structures were fully relaxed until forces on all atoms become lower than 0.03 eV/Å.

The N 1s core level spectra were calculated in the pseudopotential framework using the final state theory.⁵⁷ This approach provides only the relative shift between the core level binding energies of inequivalent atoms, while their absolute value is not defined. The choice of the reference does not change the analysis.

ASSOCIATED CONTENT

Supporting Information. Stoichiometry: NN-Blatter. NEXAFS Spectra. Film stability upon air exposure: NN-Blatter. Stoichiometry: BDT-NN. Stability under X-rays. Bulk crystals: Calculated Density of states. Temperature onset of degradation in thermal gravimetry analysis (TGA) for several radicals and diradicals and their film stability. Preliminary results obtained for diNitroxide.

Supporting Information References. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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