

Supporting Information

Electronic structure and stability of fluorophore-nitroxide radicals from ultra high vacuum to air exposure

R. Kakavandi,[†] P. Ravat,[‡] S.-A. Savu,[†] Y. B. Borozdina,^{‡,†} M. Baumgarten,[‡] M. B. Casu^{†*}

[†]Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

[‡]Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

*E-mail: benedetta.casu@uni-tuebingen.de

This Supporting Information provides:

- 1) C 1s and N 1s core level spectra of powder PPN embedded in indium foil together with the best fit procedure and the tables of the fitting parameters.
- 2) Fit results for energy position and relative intensities of the photoemission lines in the C 1s and N 1s spectra for a 3.3 nm nominally thick film, as shown in Figure 1.
- 3) The peak-fit analysis for the freshly evaporated 1.3 nm nominally thin film shown in Figures 5b and 5c.
- 4) The C 1s and N 1s peak-fit analysis of the spectra for the 25h air-exposed 1.3 nm nominally thin film shown in Figures 5b and 5c.

1)

As a reference, we have also measured the core level spectra of PPN powder embedded in indium foil without evaporation. The comparison of the XPS signals of the two systems does not reveal any relevant energy shift or changes in lineshape (the slight broadening of the XPS lines and the small binding energy differences in the spectra of the powder are due to the typical charging phenomena occurring in photoemission in organic crystals). The additional signals detected in the C 1s region were assigned to indium carbide present as former contaminant of the supporting indium foil due to the ambient storing conditions prior to preparation.

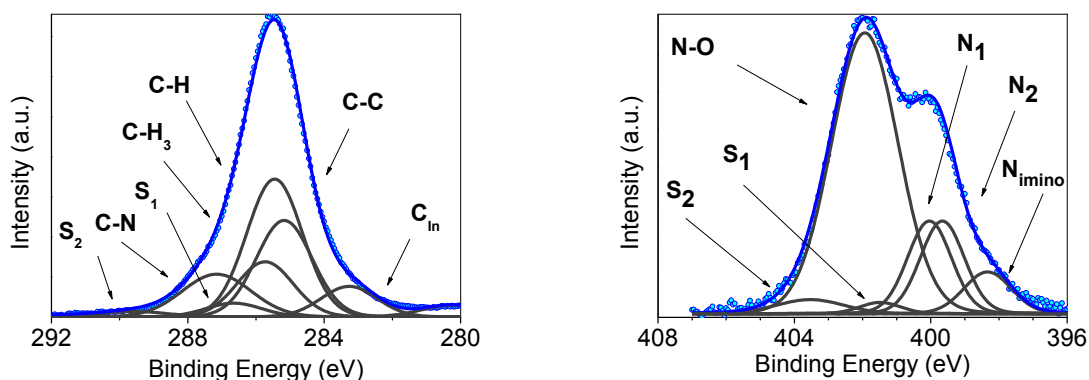


Figure 1S. C1s and N1s core level spectra PPN powder. The peak-fit analysis is also shown.

Table S1 and Table S2: Fit results for energy position and relative intensities of the photoemission lines in the C 1s and N 1s spectra for powder.

Table S1

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
C-C	285.36	0.08	1.90	26.54
C-H	285.74	0.08	1.90	37.86
C-H₃	286.02	0.08	1.90	15.15
C-N	287.45	0.08	2.35	14.41
S₁	286.94	0.08	1.90	3.79
S₂	289.75	0.08	2.35	1.88

Table S2

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
N-O	402.17	0.1	2.25	61.80
N₂	400.28	0.1	1.46	13.50
N₁	399.78	0.1	1.46	13.50
N_{imino}	398.58	0.1	1.58	6.53
S₁	401.72	0.1	1.46	1.52
S₂	402.67	0.1	2.25	3.10

The expected stoichiometric values are:

C = 81.25 %

N = 12.50 %

O = 6.25 %

C-C = 27 %

For the C 1s elemental analysis:

C-H = 42 %

$\text{CH}_3 = 15 \%$

$\text{C-N} = 15 \%$

For the N 1s elemental analysis:

$\text{N-O} = 50 \%$

$\text{N}_1 = 25 \%$

$\text{N}_2 = 25 \%$

2)

Table S3 and Table S4: Fit results for energy position and relative intensities of the photoemission lines in the C 1s and N 1s spectra for a 3.3 nm nominally thick film, as shown in Figure 1.

Table S3

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
C-C	284.98	0.08	1.42	24.84
C-H	285.26	0.08	1.42	39.98
C-H₃	285.54	0.08	1.34	14.18
C-N	286.97	0.08	1.75	12.91
S₁	286.46	0.08	1.42	5.46
S₂	289.41	0.08	1.75	3.12

Table S4

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
N-O	402.04	0.1	1.79	47.31
N₁	400.15	0.1	1.44	18.88
N₂	399.65	0.1	1.44	18.31
N_{imino}	398.64	0.1	1.44	8.21
S₁	401.59	0.1	1.44	3.86
S₂	403.64	0.1	1.79	3.44

3)

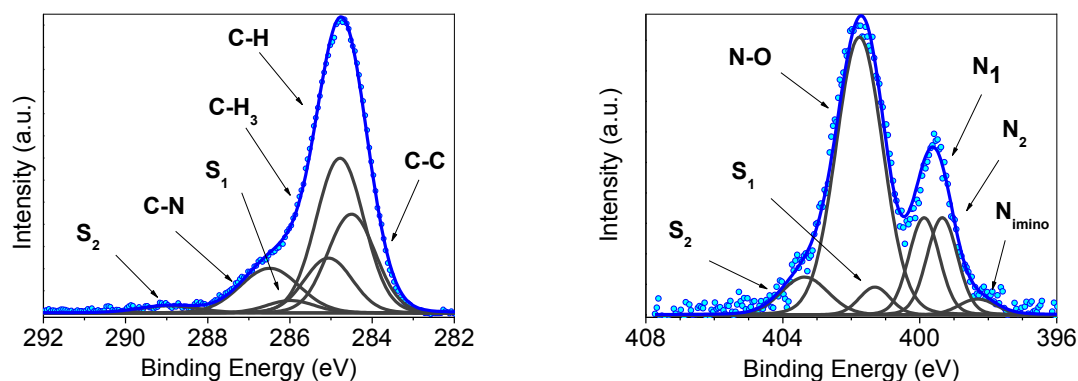


Figure 2S. The peak-fit analysis for the freshly evaporated 1.3 nm nominally thin film shown in Figures 5b and 5c.

Table S5 and Table S6: Fit results for energy position and relative intensities of the photoemission lines in the C 1s and N 1s spectra for a 1.3 nm nominally thick film, as shown in Figures 5b and 5c, and Figure 2S.

Table S5

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
C-C	284.50	0.08	1.33	25.72
C-H	284.78	0.08	1.33	40.29
C-H ₃	285.06	0.08	1.33	14.27
C-N	286.49	0.08	1.65	14.24
S ₁	285.98	0.08	1.33	3.22
S ₂	288.93	0.08	1.65	2.26

Table S6

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
N-O	401.77	0.1	1.56	58.44
N ₁	399.87	0.1	1.00	13.52
N ₂	399.38	0.1	1.00	13.52
N _{deg}	398.18	0.1	1.21	2.67
S1	401.32	0.1	1.00	3.92
S2	403.37	0.1	1.55	7.94

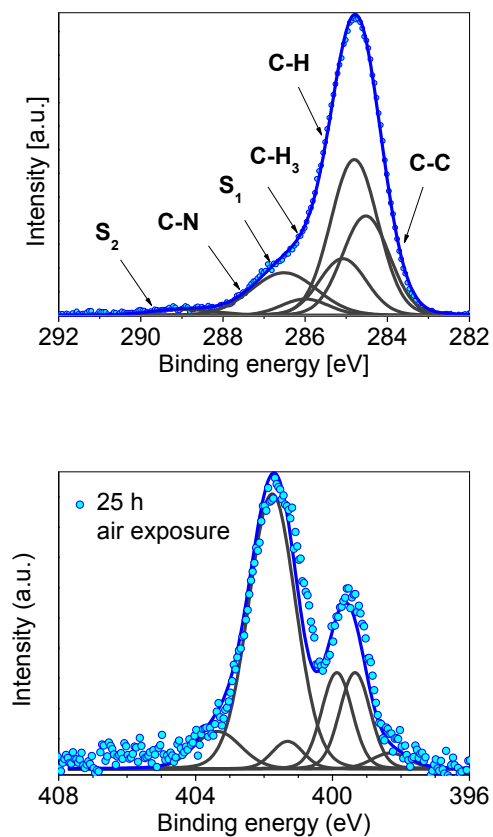


Figure 3S. The C 1s and N 1s peak-fit analysis of the spectra for the 25h air-exposed 1.3 nm nominally thin film shown in Figures 5b and 5c. The fitting parameters are exactly the same as in Table S5 and Table S6, for the freshly evaporated film.