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Supplementary Information

Using TOF-SIMS Spectrometry to Study the Kinetics of the Interfacial Retro Diels–Alder Reaction

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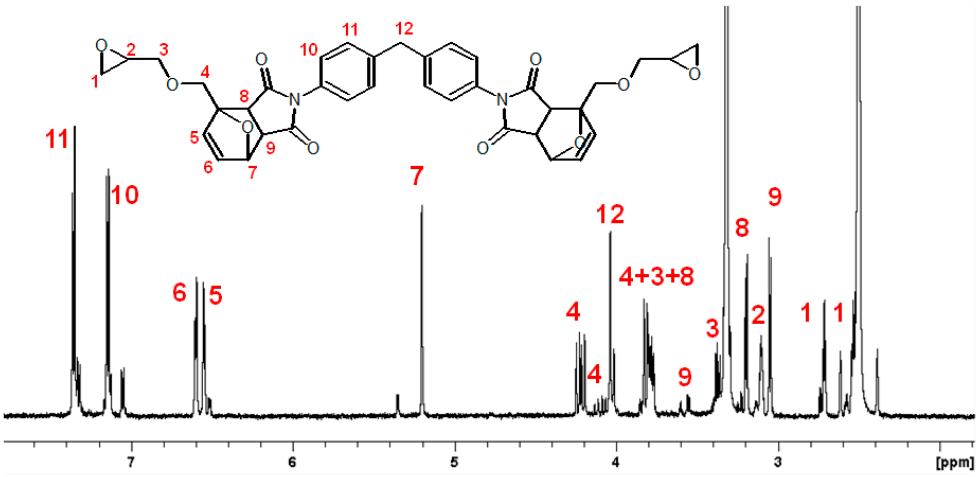

Figure S1. ^{1}H NMR spectrum of the DA molecule in DMSO at 298K.

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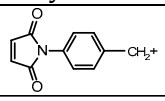
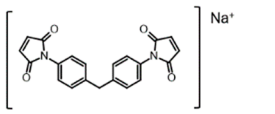
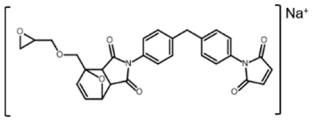
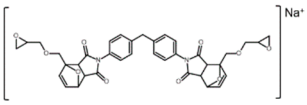
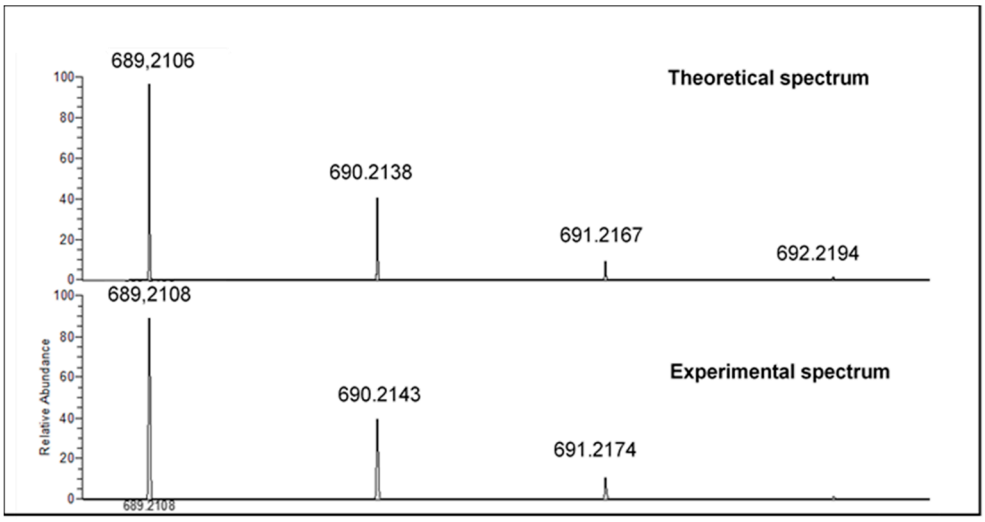
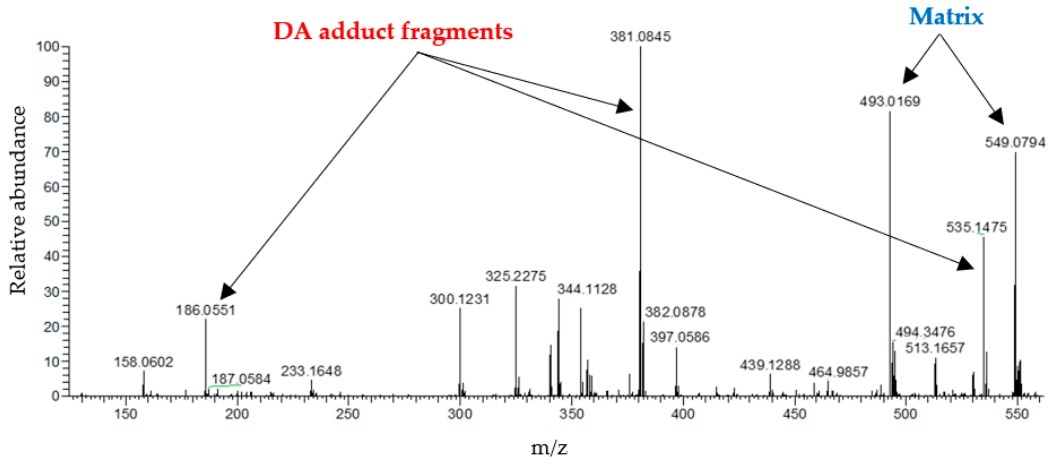
Table S1. Structural assignments for the main fragments of the adduct molecule detected by MALDI-HRMS.

N°	Exact Mass	Observed Mass	Chemical Formula	Secondary Ion Structure
1	186.0555	186.0551	$C_{11}H_8O_2N^+$	
2	381.0846	381.0845	$C_{21}H_{14}O_4N_2Na^+$	
3	535.1481	535.1475	$C_{29}H_{24}O_7N_2Na^+$	
4	689.2106	689.2108	$C_{37}H_{34}O_{10}N_2Na^+$	



(**a**)



(**b**)

Figure S2. (**a**) Comparison between experimental and theoretical MALDI-HRMS spectra of the DA adduct-containing molecule (**b**) Fragments of the DA molecule peaks detected by MALDI-HRMS.

Table S2. Values of the maleimide-fragment peak area as determined by TOF-SIMS, on SAMs.

Time (s)	**333 K**					**353 K**				
0	0.0655	0.0601	0.0554	0.0352	0.0531	0.0099	0.0104	0.0109	0.0104	0.0102
900	-	-	-	-	-	0.0099	0.0094	0.0070	0.0103	0.0105
1,800	0.0591	0.0538	0.0627	0.0557	0.0610	0.0091	0.0082	0.0093	0.0072	0.0076
3,600	0.0312	0.0313	0.0273	0.0305	0.0327	0.0086	0.0076	0.0072	0.0069	0.0061
10,800	0.0126	0.0116	0.0115	0.0125	0.0127	0.0038	0.0039	0.0037	0.0037	0.0040
Time (s)	**363 K**					**373 K**				
0	0.0253	0.0160	0.0142	0.0142	0.0164	0.0099	0.0104	0.0109	0.0104	0.0102
900	0.0170	0.0173	0.0166	0.0176	0.0173	0.0079	0.0078	0.0062	0.0078	0.0083
1,800	0.0144	0.0143	0.0154	0.0156	0.0154	0.0068	0.0081	0.0071	0.0069	0.0078
3,600	0.0131	0.0133	0.0134	0.0148	0.0135	0.0054	0.0057	0.0057	0.0060	0.0059
10,800	0.0069	0.0064	0.0062	0.0067	0.0066	0.0057	0.0060	0.0055	0.0059	0.0058
Time (s)	**383 K**					**393 K**				
0	0.0253	0.0160	0.0142	0.0142	0.0164	0.0655	0.0601	0.0554	0.0352	0.0531
900	0.0142	0.0142	0.0138	0.0133	0.0134	-	-	-	-	-
1,800	-	-	-	-	-	0.0104	0.0104	0.0102	0.0105	0.0110
2,700	0.0078	0.0066	0.0065	0.0077	0.0077	-	-	-	-	-
3,600	0.0058	0.0062	0.0059	0.0057	0.0057	0.0094	0.0079	0.0082	0.0067	0.0083

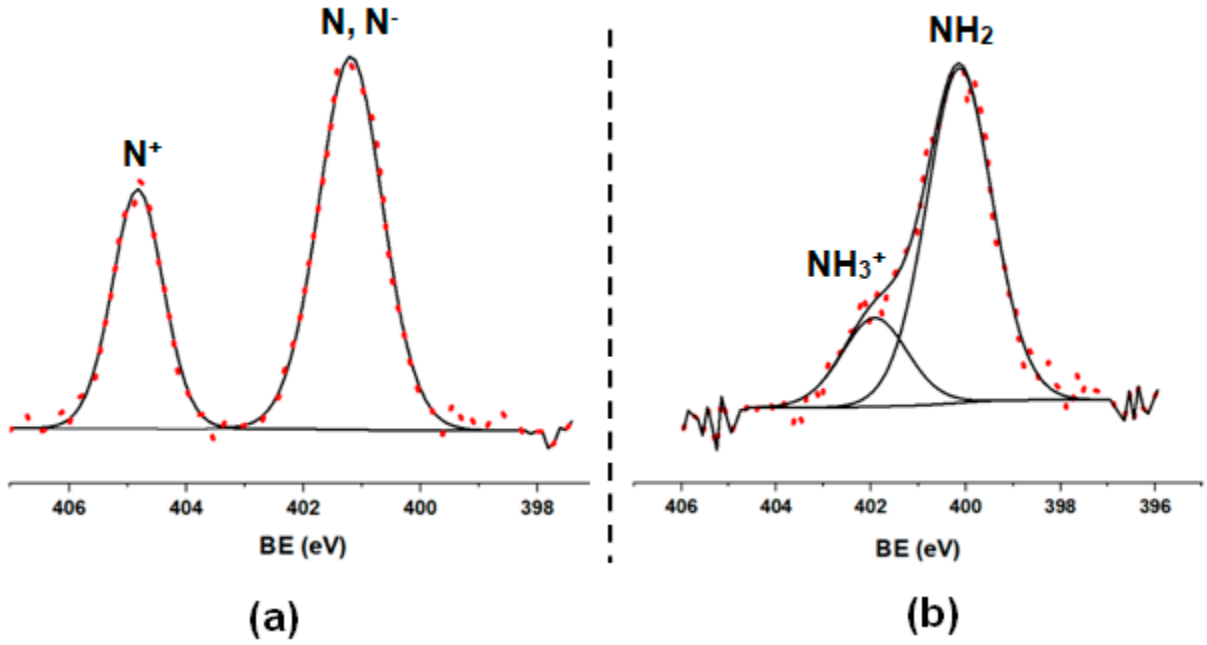


Figure S3. High resolution XPS N1s spectrum of (**a**) azide terminated SAMs that were finally transformed to (**b**) amine-terminated SAMs.

Methodology used for the determination of retro DA reaction conversion using ^{1}H NMR.

It is assumed that at the selected temperatures, the reverse reaction (DA reaction) can be neglected. The conversion rate of retro DA reaction (X_i) is then determined as the

fraction of formed furfuryl glycidyl ether (FGE), for different times and for different temperatures. It is calculated by the following formula: $Xi = \frac{A_{FGE}}{A_{FGE}+A_{Add}}$

A_{FGE}, A_{Add} are respectively the area of the peak characteristic of one proton in furan group (highlighted in Figure S1a) and the area of a peak representing one proton of the adduct (highlighted in Figure S1c).

The retro DA reaction conversion values of can be found in Table S2.

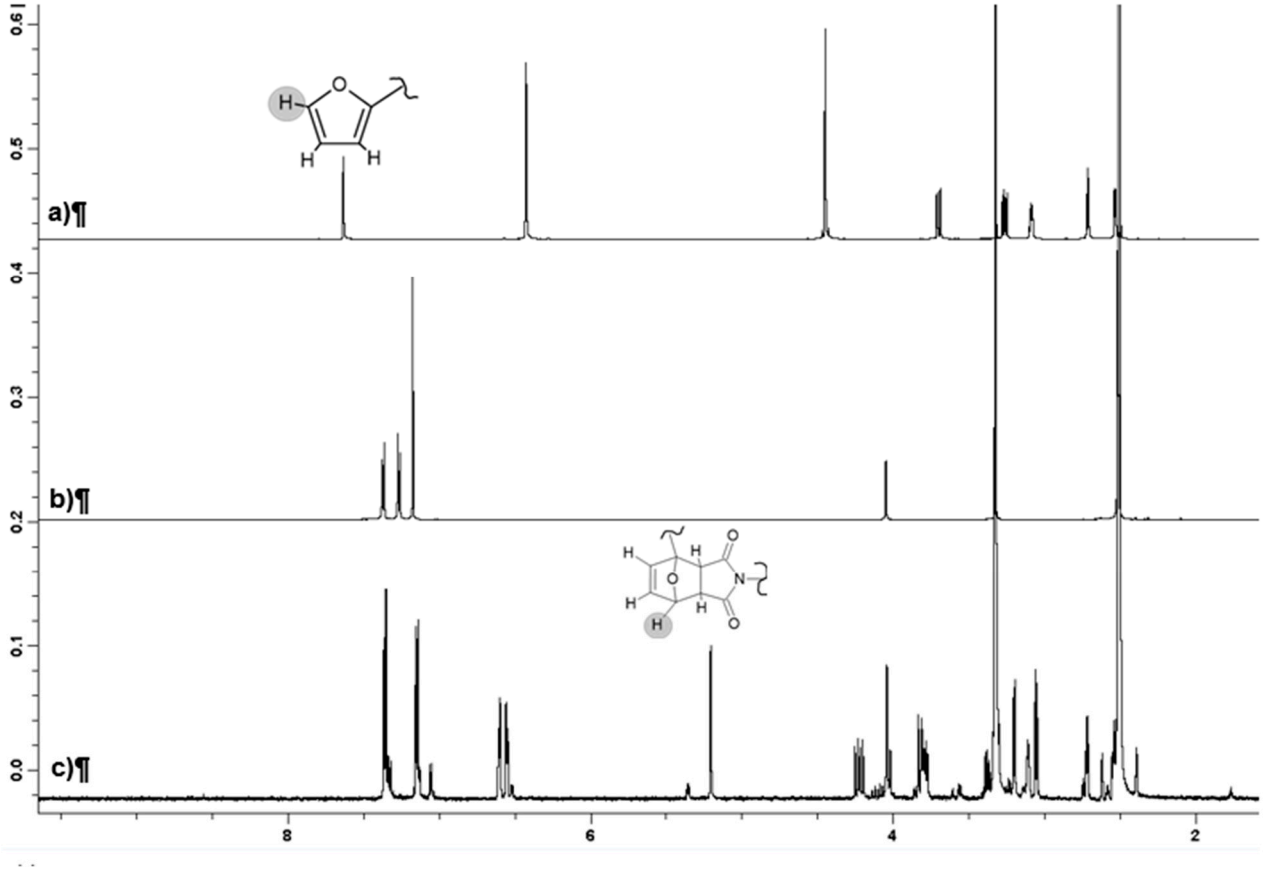


Figure S4. ^{1}H NMR spectra of (**a**) furfuryl glycidyl ether, (**b**) bismaleimide and (**c**) synthesised molecule containing the adduct.

Table S3. Retro DA conversion values determined by ^{1}H NMR spectrometry, for different temperatures.

Time (s)		343 K			353 K	
0	0.142	0.029	0.038	0.040	0.028	0.043
60	0.155	0.062	0.048	0.167	0.124	0.178
900	0.266	0.062	0.048	0.230	0.229	0.231
1,800	0.305	0.111	0.075	0.330	0.255	0.309
2,700	0.317	0.111	0.090	0.385	0.321	0.412
3,600	0.270	0.140	0.147	0.437	0.385	0.398
7,200	0.314	0.202	0.253	0.596	0.532	0.664
10,800	0.356	0.303	0.315	0.730	0.656	0.773
18,000	-	0.384	0.425	0.842	0.839	0.888
25,200	-	0.498	0.528	0.900	0.888	0.942

Time (s)		358 K			363 K	
0	0.040	0.043	-	0	0.034	0
60	0.196	0.199	-	0.285	0.291	0.285
900	0.348	0.324	-	0.436	0.463	0.436
1,800	0.476	0.473	-	0.559	0.606	0.559
2,700	0.579	0.543	-	0.684	0.674	0.684
3,600	0.678	0.649	-	0.75	0.773	0.75
7,200	0.854	0.837	-	1	0.886	1
10,800	0.933	0.919	-	1	0.957	1
18,000	0.983	0.983	-	1	0.942	1
25,200	1	0.988	-	1	0.955	1

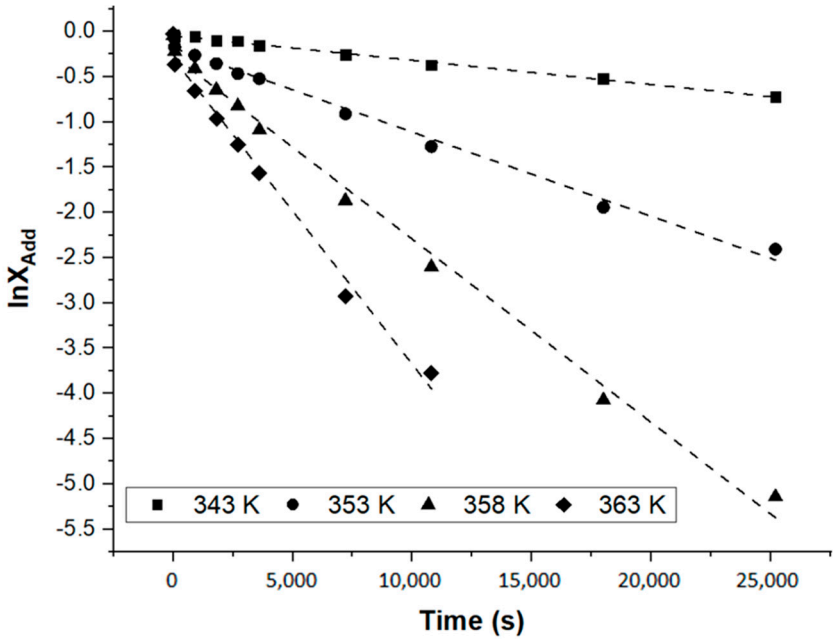


Figure S5. Linearization, according to a first order, of retro DA reaction rate law occurring in the DA molecule in solution performed at different temperatures.