

Supporting Information

Investigation on the edge doping process of nitrogen-doped carbon materials by in-situ pyrolysis mass spectrometry and laser-induced acoustic desorption mass spectrometry

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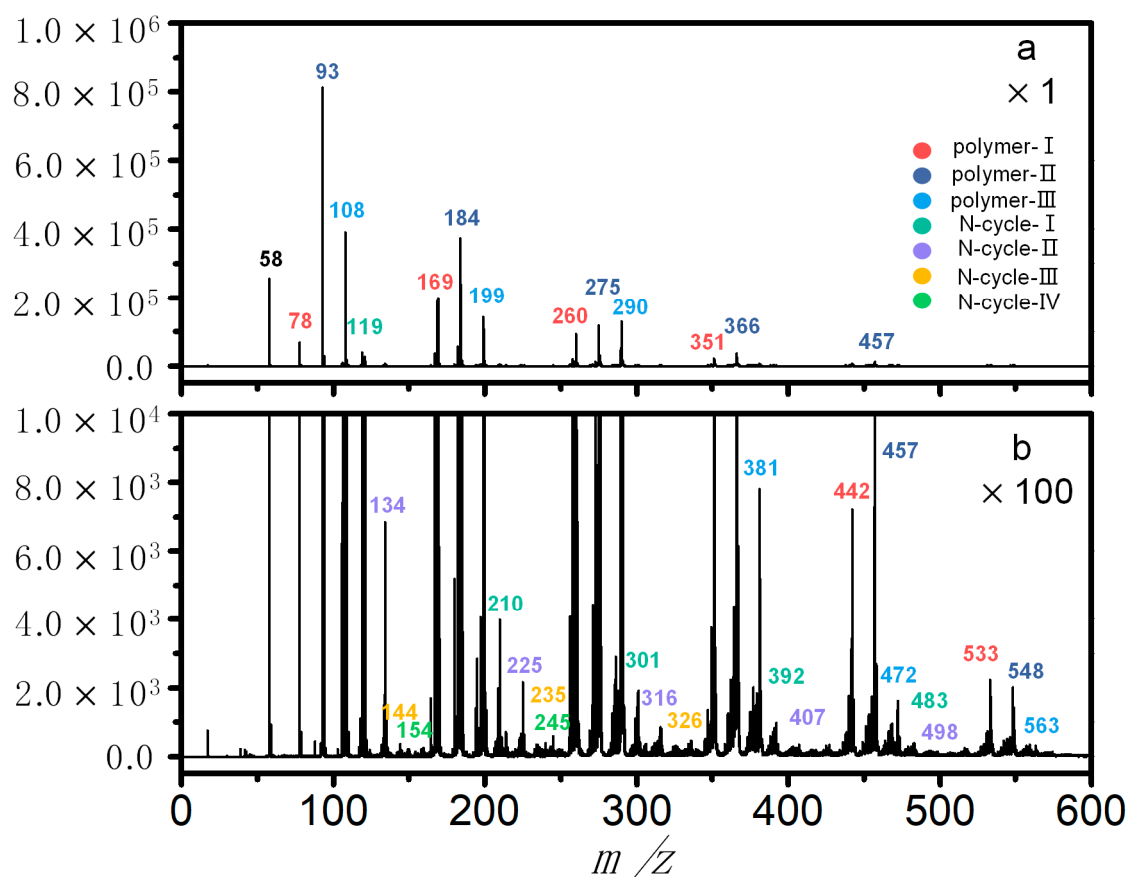


Figure S1. In-situ Py-PI-TOF MS spectra of in-situ pyrolysis of PANI (a) $\times 1$, (b) $\times 100$.

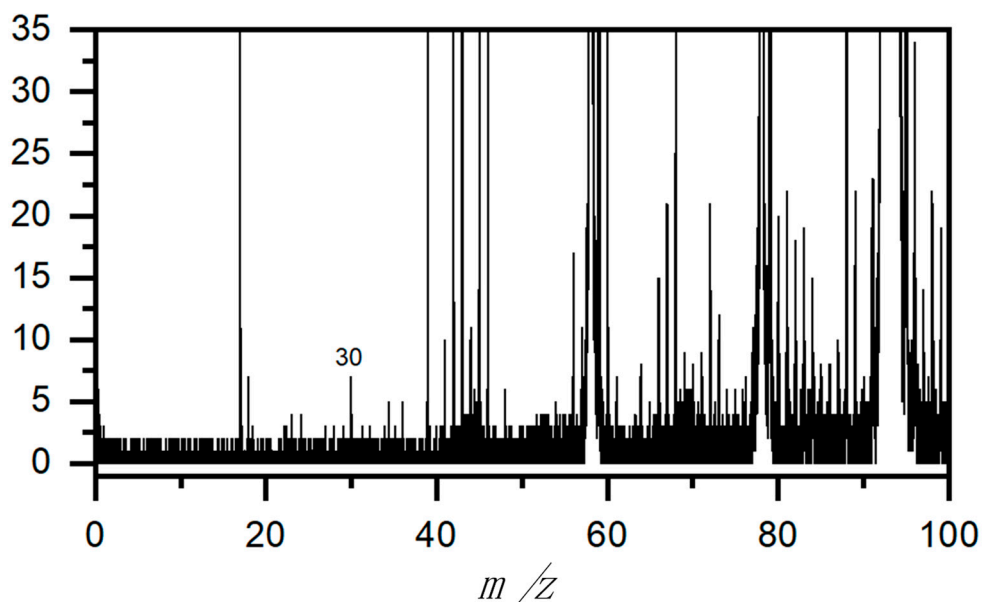


Figure S2. In-situ Py-PI-TOF MS spectra of in-situ pyrolysis of PANI (partial enlarged detail).

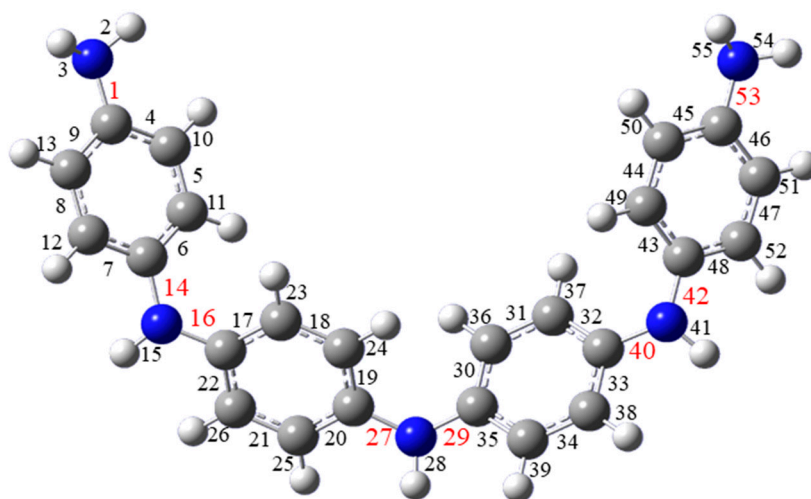


Figure S3. Bond order information of PANI (aniline tetramer), Blue represents N, gray represents C, and white represents H.

Number	Bond type	Bond order
1	C-N	0.982
2	N-H	0.822
3	N-H	0.820
4	C-C	1.520
5	C-C	1.541
6	C-C	1.513
7	C-C	1.525
8	C-C	1.549
9	C-C	1.519
10	C-H	0.894
11	C-H	0.905
12	C-H	0.899
13	C-H	0.895
14	C-N	0.853
15	N-H	0.808
16	C-N	0.917

17	C-C	1.502
18	C-C	1.540
19	C-C	1.503
20	C-C	1.519
21	C-C	1.545
22	C-C	1.510
23	C-H	0.904
24	C-H	0.901
25	C-H	0.898
26	C-H	0.890
27	C-N	0.870
28	N-H	0.806
29	C-N	0.904
30	C-C	1.510
31	C-C	1.536
32	C-C	1.501
33	C-C	1.515
34	C-C	1.545
35	C-C	1.512
36	C-H	0.901
37	C-H	0.904
38	C-H	0.893
39	C-H	0.895
40	C-N	0.881
41	N-H	0.808
42	C-N	0.890
43	C-C	1.508
44	C-C	1.553
45	C-C	1.510
46	C-C	1.526

47	C-C	1.534
48	C-C	1.524
49	C-H	0.899
50	C-H	0.894
51	C-H	0.890
52	C-H	0.896
53	C-N	0.979
54	N-H	0.820
55	N-H	0.817

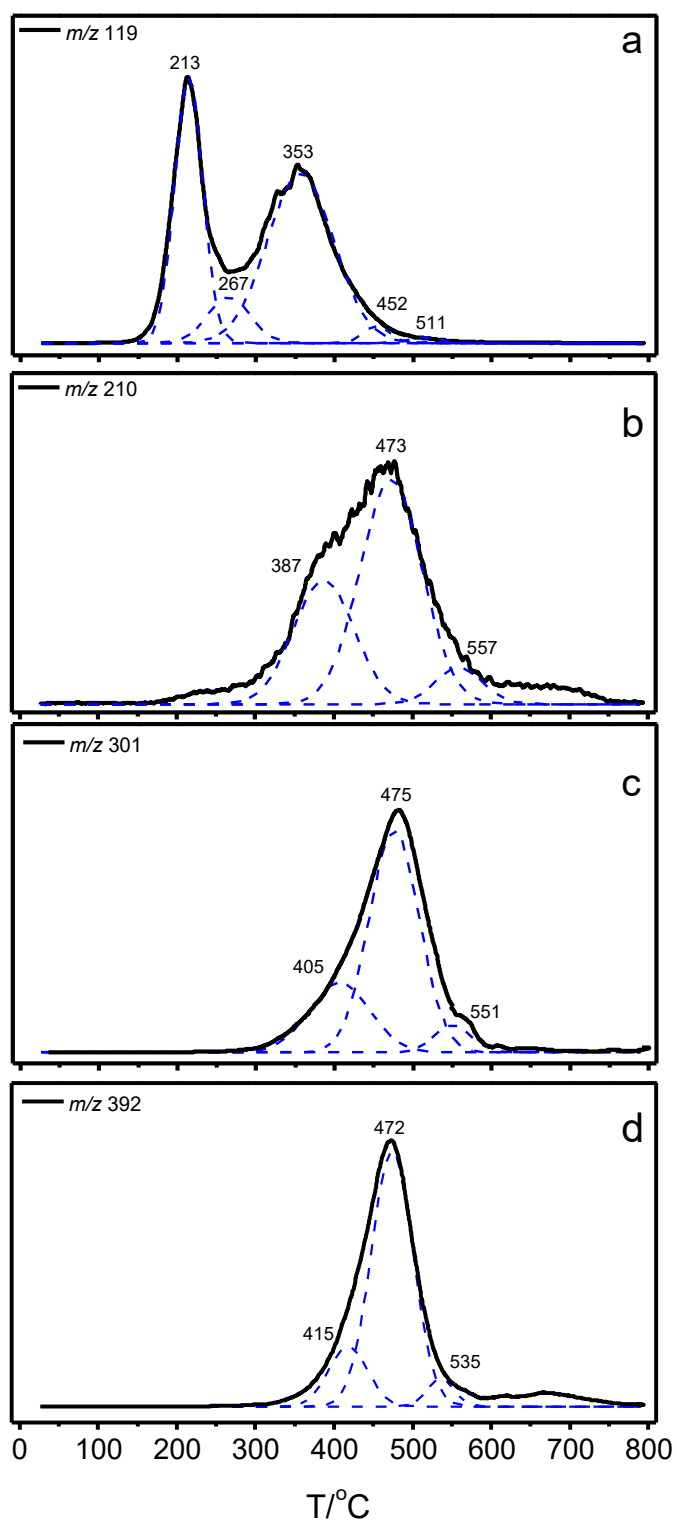


Figure S4. Ion current of N-cycle-I $n = 0$ (a), $n = 1$ (b), $n = 2$ (c), $n = 3$ (d).

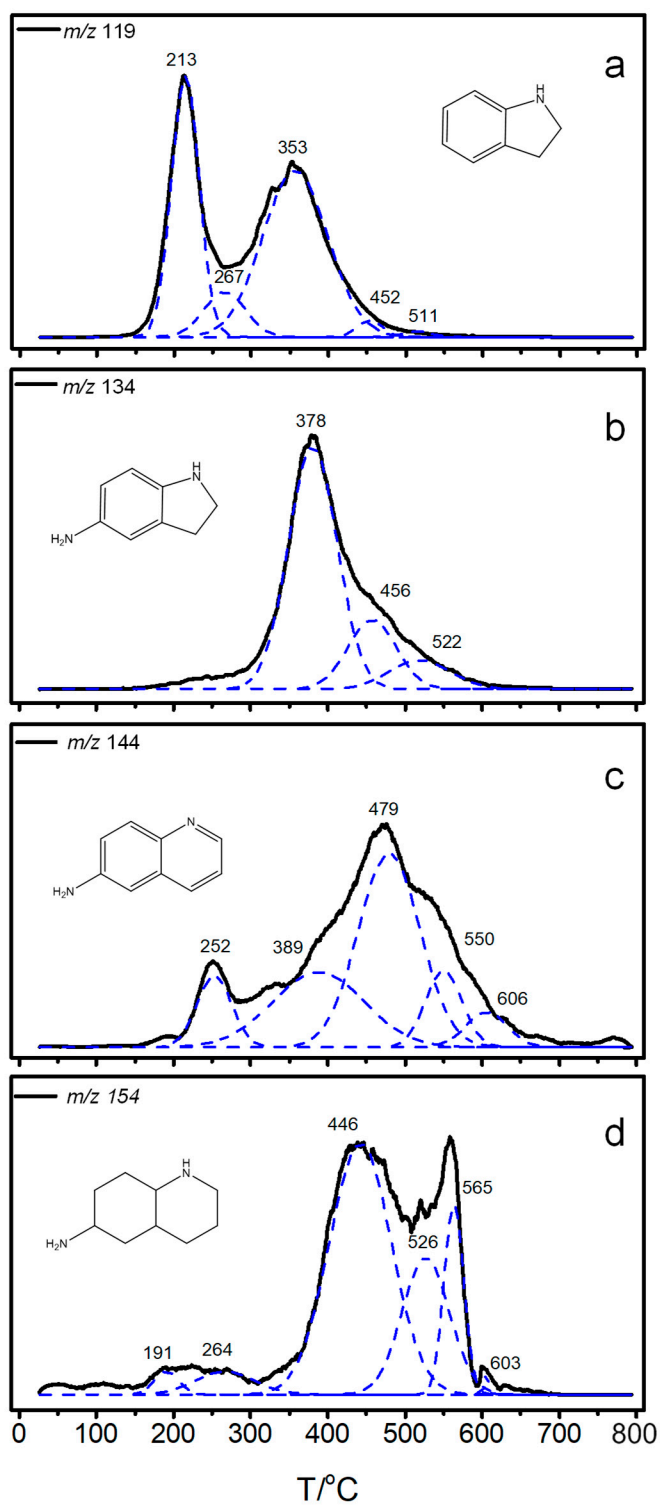


Figure S5. Ion current of N-cycle-I (a), N-cycle-II (b), N-cycle-III (c), N-cycle-IV (d) ($n = 0$).

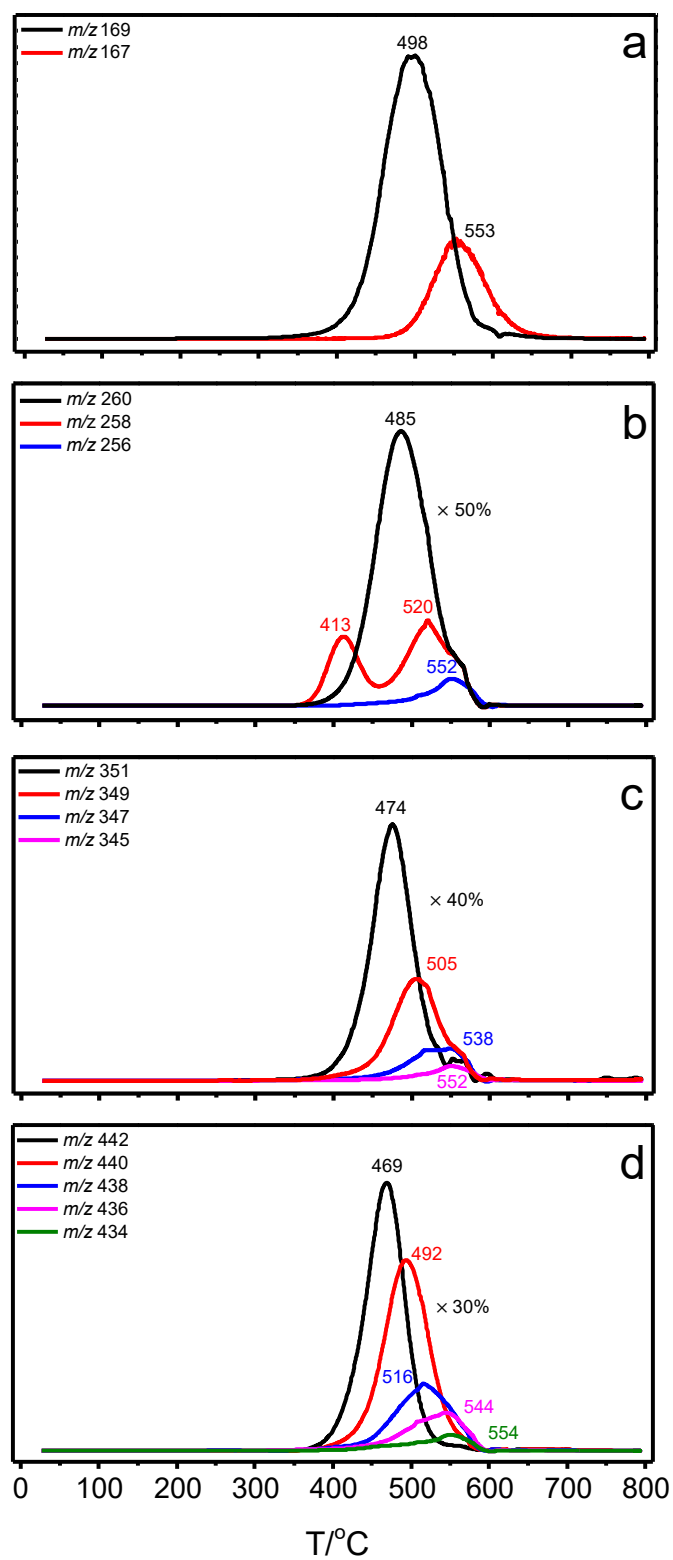


Figure S6. Ion current of polymer-I and its cyclization products (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$.

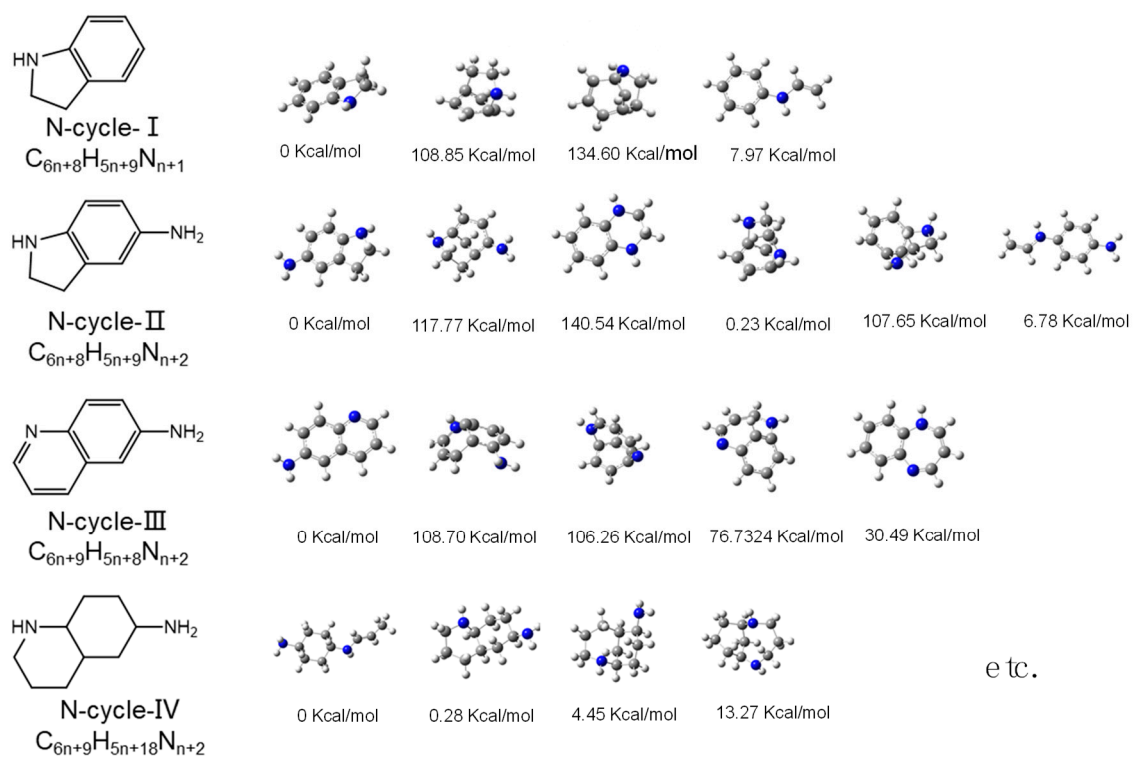


Figure S7. Possible isomers of nitrogen-containing heterocyclic compounds (N-cycle-I, N-cycle-II, N-cycle-III, N-cycle-IV).

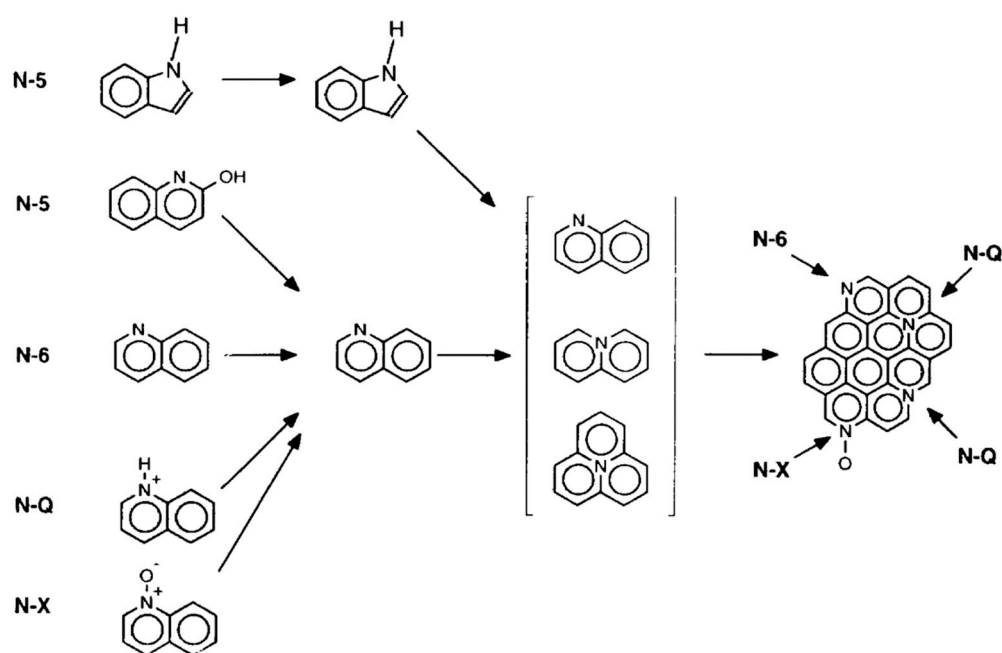


Figure S8. Visualisation of the evolution of nitrogen functionalities in carbonaceous materials during pyrolysis[1].

Table S1 The main initial pyrolysis products of PANI (by In-situ Py-PI-TOF MS)


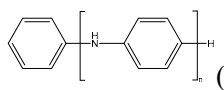
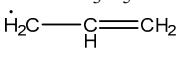
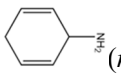
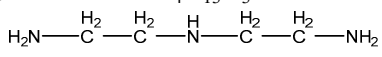
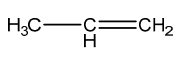
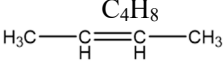
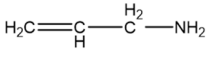



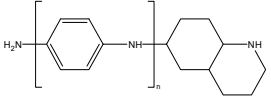

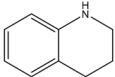
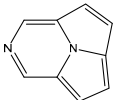
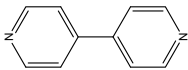
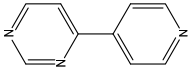
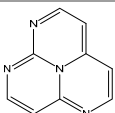
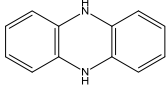
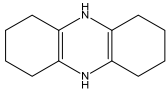
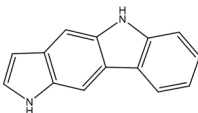
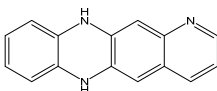
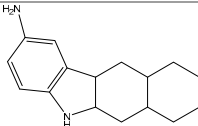
<i>m/z</i>	Formula	IE/eV	<i>m/z</i>	Formula	IE/eV
17	NH ₃	10.07	72	C ₃ H ₈ N ₂	9.16
18	NH ₄	4.73	91n+78	 C _{6n+6} H _{5n+6} N _n (I)	\
30	N ₂ H ₂ HN=NH	9.589	95	 C ₆ H ₉ N (<i>n</i> = 0-4)	\
41	C ₃ H ₅ · 	8.13	103	 C ₄ H ₁₃ N ₃ 	\
42	C ₃ H ₆ 	9.73	91n+93	C _{6n+6} H _{5n+7} N _{n+1} (II)	\
56	C ₄ H ₈ 	9.57	91n+108	C _{6n+6} H _{5n+8} N _{n+2} (III)	\
57	C ₃ H ₇ N 	8.80	91n+119	C _{6n+8} H _{5n+9} N _{n+1} (IV)	\
66	C ₄ H ₄ N· 	8.57	91n+134	C _{6n+8} H _{5n+9} N _{n+2} (V)	\
67	C ₄ H ₅ N 	8.27	91n+144	C _{6n+9} H _{5n+8} N _{n+2} (VI)	\
68	C ₃ H ₄ N ₂ 	8.81	91n+154	C _{6n+9} H _{5n+18} N _{n+2} (VII)	\
				 (<i>n</i> = 0-4)	

Table S2 Unique products of pyrolysis residue in m/z 0-300.

Molecular weight	Formula	Structure
m/z 85	$C_5H_{11}N$	
m/z 133	$C_9H_{11}N$	
m/z 142	$C_9H_6N_2$	
m/z 156	$C_{10}H_{10}N_2$	
m/z 157	$C_9H_7N_3$	
m/z 170	$C_9H_6N_4$	
m/z 182	$C_{12}H_{10}N_2$	
m/z 190	$C_{12}H_{18}N_2$	
m/z 206	$C_{14}H_{10}N_2$	
m/z 233	$C_{15}H_{11}N_3$	
m/z 242	$C_{16}H_{22}N_2$	

- [1] J.R. Pels, F. Kapteijn, J.A. Moulijn, Q. Zhu, K.M. Thomas, Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis, *Carbon*, 33 (1995) 1641-1653.