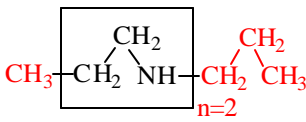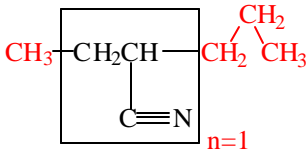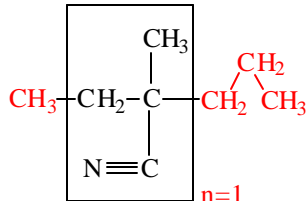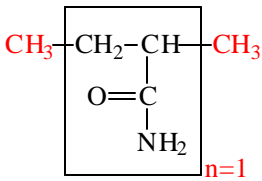# Sorption of Nitrogen Bases and XPS Study of Mesoporous Solid Acid SBA-15
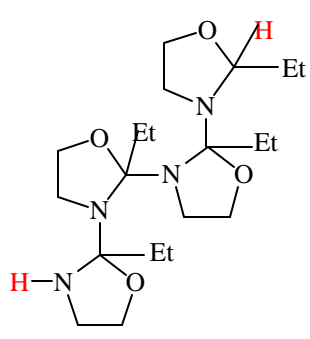
Jeremy L. Smith, Richard G. Herman, Courtney R. Terenna, Matthew R. Galler, and Kamil Klier[*]
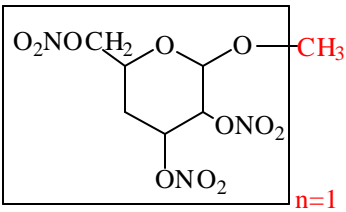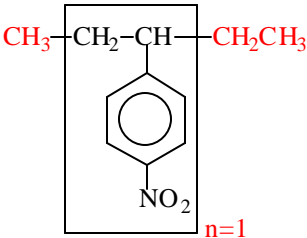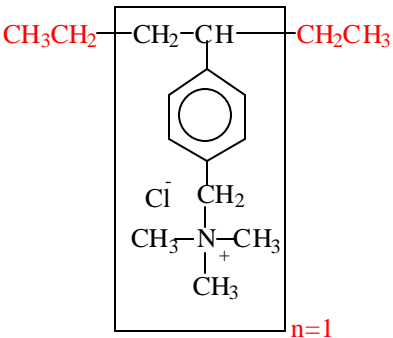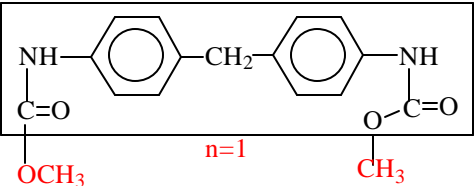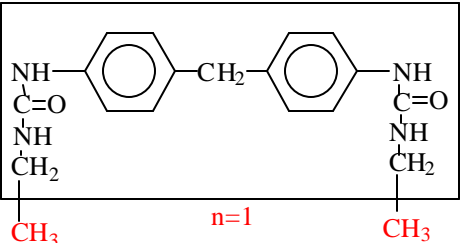
Supporting Information
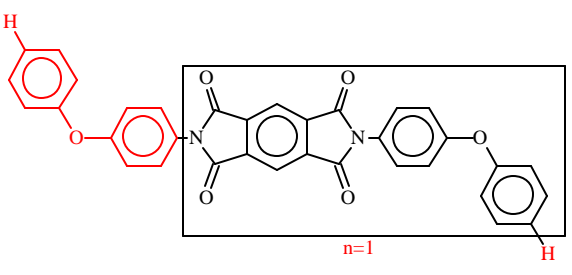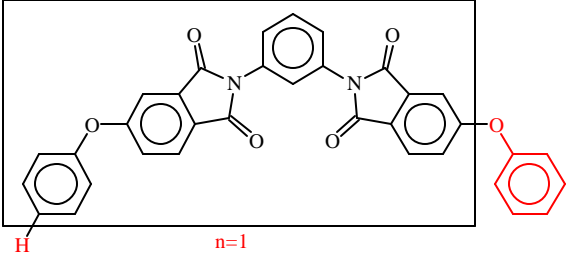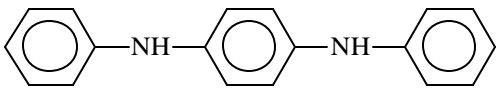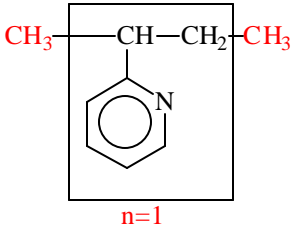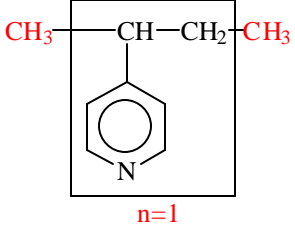
Table S1. Nitrogen-Containing Polymers and Molecular Models for Calculations of N1s Core Level Chemical Shifts
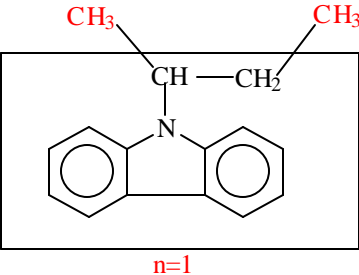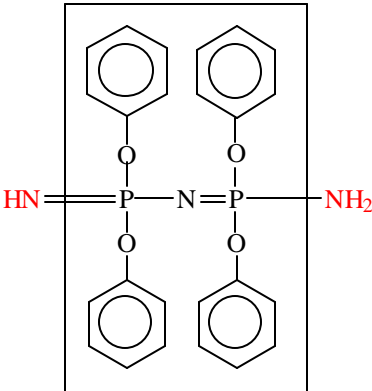
Acronym[a]	Name[a]	Polymer formula and Molecular Model[b]
PEI	Poly(ethyleneimine)	
PAN	Poly(acrylonitrile)	
PMAN	Poly(methacrylonitrile)	
PAM	Poly(acrylamide)	

[*] Corresponding author. Email: kk04@lehigh.edu.

PMAM	Poly(methacrylamide)	$CH_3-CH_2-\underset{\underset{NH_2}{\overset{\overset{CH_3}{|}}{O=C}}}{C}-CH_3$, n=1
PNVP	Poly(N-vinylpyrrolidone)	$CH_3-CH_2-CH-CH_3$ (N-vinylpyrrolidone ring), n=1
PEOx	Poly(2-ethyl-2-oxazoline)	(oxazoline structures with Et, O, N, H groups)
N6	Nylon 6	$CH_3-(CH_2)_5NH-\underset{O}{C}-(CH_2)_4-CH_3$
N12	Nylon 12	$CH_3-(CH_2)_5NH-\underset{O}{C}-(CH_2)_5-CH_3$
PAAMC	Poly(allylamide hydrochloride)	$CH_3-CH_2-\underset{\underset{Cl^--NH_3^+}{CH_2}}{CH}-CH_3$, n=1

CTN	Cellulose trinitrate	O_2NOCH_2 ... O ... O—CH_3, ONO_2, ONO_2, n=1
PNS	Poly(4-nitrostyrene)	CH_3—CH_2—CH—CH_2CH_3, NO_2, n=1
PVBTMAC	Poly(vinylbenzyl trimethylammonium chloride)	CH_3CH_2—CH_2—CH—CH_2CH_3, Cl^- CH_2, CH_3—$\overset{+}{N}$—CH_3, CH_3, n=1
PU	Poly(urethane)	NH——CH_2——NH, $C=O$ ... $C=O$, OCH_3, n=1, CH_3
PUa	Poly(urea)	NH——CH_2——NH, $C=O$ ... $C=O$, NH ... NH, CH_2 ... CH_2, CH_3, n=1, CH_3

KAP	Poly(ether imide) (Kapton HN)	n=1
ULT	Poly(ether imide) (Ultem 1000)	n=1
PA	N,N'-Diphenyl-1,4-phenylenediamine [poly(aniline) oligomer]	
P2VP	Poly(2-vinylpyridine)	n=1
P4VP	Poly(4-vinylpyridine)	n=1

P9VC	Poly(9-vinylcarbazole)	
PPP	Poly(phenoxy phosphazine)	

[a] Names of polymers are as in Beamson, G.; Briggs, D. *"High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database",* J. Wiley & Sons, **1992**, ISBN 0 471 93592 1.

[b] Segments of polymers are represented in black letters. The capping groups and multiplicities of the segments in the molecular models are marked red.

In Table S1, each of the nitrogen-containing polymers is represented by its acronym, full name and segment formula, while the corresponding molecular model is the segment formula with capping groups. The geometry of each molecular model was fully optimized at the DFT/BP/DN** level, and the optimized geometries are available as coordinate files from the authors.

The experimental BEs of nitrogen-containing polymers and the presently calculated theoretical KS core levels of the model capped segments are presented in Table S2. The KS orbital energies of the capping groups, marked red in Table S1, were excluded from calculations presented in Table S2. Thus only the inner segments marked black in Table S1, which are common to the polymers from the XPS database and the theoretical models, are being compared and rectified in Table S2.

Table S2. Experimental Binding Energies and Theoretical Core-Levels of Nitrogen Containing Polymers and Corresponding Molecular Models (eV).

1	2	3	4	5	6	7	8	9
No.	Polymer	N1s-expt	N1s-expt, rectified	C1s-expt, lowest	C1s-theor, lowest	Theor. shift from aliphatic C1s of Nylon 6	C1s-expt, rectified	N1s-theor
1	PEI	399.07	399.62	285.56	269.94	0.55	286.11	380.56
2	PAN	399.57	400.00	285.48	269.82	0.43	285.91	381.00
3	PMAN	399.57	399.79	285.00	269.61	0.22	285.22	380.96
4	PAM	399.83	400.15	285.00	269.71	0.32	285.32	381.66
5	PMAM	399.96	400.19	285.00	269.61	0.23	285.23	381.63
6	PNVP	399.88	400.11	285.00	269.61	0.23	285.23	381.70
7	PEOx	399.87	399.62	285.00	269.14	-0.25	284.75	380.96
8	N6	399.77	399.77	285.00	269.39	0.00	285.00	381.61
9	N12	399.84	399.77	285.00	269.32	-0.07	284.93	381.70
10	PAAMC	401.46	401.92	285.00	269.85	0.46	285.46	382.43
11	CTN	408.15	409.40	287.13	270.86	1.25	288.56	389.09
12	PNS	405.45	405.93	284.49	269.87	0.48	284.97	387.06
13	PVBTMAC	402.14	402.48	284.47	269.73	0.34	284.81	384.97
14	PU	400.32	400.60	284.64	269.67	0.28	284.92	382.32
15	PUa	399.89	400.38	284.58	269.88	0.49	285.07	381.97
16	KAP	400.60	401.26	284.70	270.05	0.66	285.36	383.07
17	ULT	400.40	400.80	284.72	269.79	0.40	285.12	382.67
18	PA	399.92	400.14	284.70	269.61	0.22	284.92	382.05
19	P2VP	399.30	399.45	285.00	269.54	0.15	285.15	380.83
20	P4VP	399.34	399.58	285.00	269.63	0.24	285.24	380.84
21	P9VC	400.22	400.30	284.67	269.47	0.08	284.75	382.22
22	PPP	397.93	398.27	284.70	269.73	0.34	285.04	380.19

Col. 1: Number of the polymer or model compound

Col. 2: Name of the polymer

Col. 3: N1s-expt = Experimental XPS BE from Beamson and Briggs, eV

Col. 4: N1s-expt, rectified = N1s-expt (Col. 3) + Theoretical shift from aliphatic C1s of Nylon 6 (Col. 7)

Col. 5: C1s-expt, lowest = Lowest experimental C1s BE in the respective nitrogen-containing polymer from Beamson and Briggs, eV

Col. 6: C1s-theor, lowest: Lowest theoretical C1s core-level energy in the respective nitrogen-containing model compound

Col. 7: Theoretical shift from aliphatic C1s of Nylon 6 = C1s-theor, lowest (Col. 6) for the given polymer - C1s-theor, lowest for Nylon 6 (row 8 in Col. 6)

<u>Col. 8:</u> C1s-expt, rectified = C1s-expt, lowest (Col. 5) − Theoretical shift from aliphatic C1s of Nylon 6 (Col. 7)

<u>Col. 9:</u> Theoretical N1s core-level energy in the model compound, eV.

In the Beamson-Briggs experimental database, the XPS core-level binding energies are referenced to a selected C1s energy, which is set at a certain value such as 285.0 eV for aliphatic carbon, as exemplified in Column 5, Rows 3-10 and 19-20 of Table S2. The carbon atoms are not equivalent, however, and calculations show a spread of some 0.2 eV around an average value for the aliphatic carbons in the different molecules, as in Column 6. Thus we refined the reference values in the following manner: we calculated the difference between the lowest C1s core-level energy in a given model molecule and the C1s core-level in the CH_2 groups of the model for Nylon 6 (Col. 7, Theoretical shift from aliphatic C1s of Nylon 6), and then added these shift values to each experimental C1s BE (Col. 8, C1s-expt, rectified) and N1s BE (Col. 4, N1s expt, rectified). The theoretically calculated N1s core-level energies (Col. 9) are then plotted against the rectified experimental N1s BEs of Column 4 in Figure S1.

Data: N1s: Y(DFT) *vs.* X(expt. BE, corr.)
Model: Y = -18.2 eV + A*X
Chi^2 = 0.15256
A = 0.99998 +/- 0.00029
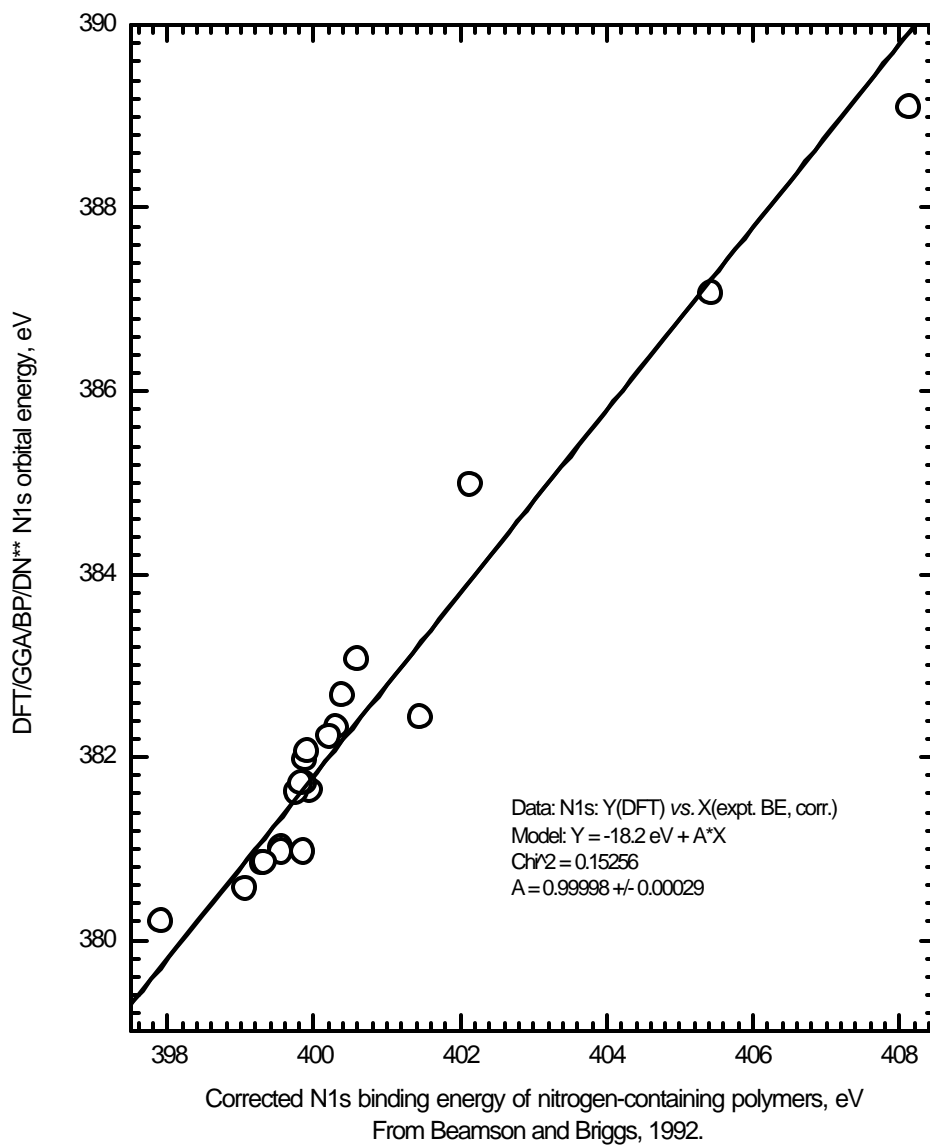
Figure S1. Correlation between the DFT N1s orbital energies (negative of the Kohn-Sham core-level energies) and the experimental N1s BEs of nitrogen-containing polymers. Identification of the models for polymer segments and data from Table S1.