Polyphenylsilole multilayers - Insight by X-ray electron spectroscopy and density functional theory

Supporting Information

Katharina Diller,*[a,b] Yong Ma,[c,d] Yi Luo,[c] Francesco Allegretti,[a] Jianzhao Liu,[e] Ben Zhong Tang,[e] Nian Lin,*[f] Johannes V. Barth,[a] and Florian Klappenberger*[a]

[a] *Physik Department, E20, Technische Universität München, 85748 Garching, Germany;*
E-mail: katharina.diller@tum.de, florian.klappenberger@tum.de
[b] *current: Institute for Condensed Matter Physics, École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[c] *Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden.*
[d] *current: College of Physics and Electronics, Shandong Normal University, Jinan, Shandong 250014, People's Republic of China*
[e] *Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China.*
[f] *Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China;*
E-mail: phnlin@ust.hk

I. SIMULATION OF SI L-EDGES

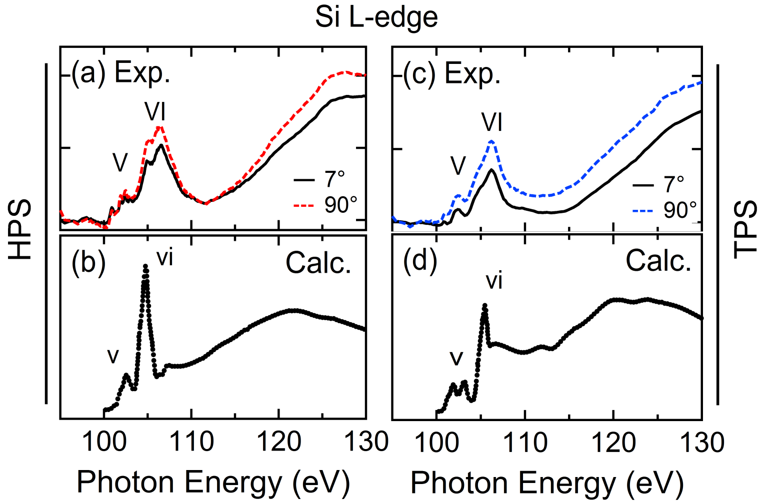


FIG. S 1. Experimental (top) and simulated (bottom) NEXAFS Si L-edge spectra of HPS (left) and TPS (right) multilayers.

The Si L-edge NEXAFS spectra were calculated at the DFT level by using the StoBe program.[1] Similarly to the C K-edge the full core hole approximation was used to simulate the spectrum. In contrast to the carbon edge, however, simulations for metal L-edges are more difficult, as the spin-orbit interaction from electrons in the p-orbitals has to be taken into account. In general, the interactions between electrons (and hence molecular orbitals) are non-trivial to predict. Unexpected effects can for example include transitions from p-orbitals to p-levels which normally should be forbidden by dipole selection rules, but become possible in some silicon compounds due to the mixing of p and d orbitals.[2] One possibility to treat the complicated structure is the utilization of multiple scattering approaches, as demonstrated, for example, by Chaboy, Benfatto, and Davoli for the Si L-edge of SiO_2[3] and by Xiong and co-workers for hexamethyldisilane.[4] On a DFT level, typical simulations of metal L-edges employ time-dependent codes which take into account spin-orbit splitting (as for example done for Fe L-edges in ref.[5]).

In the present work the focus of the NEXAFS simulations lies in assigning the peaks in the experimental NEXAFS spectrum to the different carbon species. The DFT code StoBe together with the double basis set technique[6] has been shown to yield excellent results for carbon edges[7,8] and is generally well suited for the simulation of NEXAFS spectra. However, the accurate treatment of spin-orbit interactions is not implemented in the present version of the code. For the Si L-edges shown in Fig. S1 we therefore use an approximation based on experimental values; the spin-orbit split

$2p_{1/2}$ and $2p_{3/2}$ components were approximately simulated by the calculated spectra of $2p_{x,y,z}$ with energy splitting of 0.6 eV and intensity ratio 1:2 (experimental values: 0.63 eV for methylsilane,[9] 0.6 eV for silicon oxide[10]).

II. CALCULATED PARTIAL CHARGES

TABLE S I. Calculated partial charges for HPS

Atom No.	Type	Mulliken / e	NBO / e	Atom No.	Type	Mulliken / e	NBO / e
1	Si	1.064458	1.67131	42	H	0.134604	0.21048
2	C	-0.402763	-0.34128	43	H	0.135180	0.21020
3	C	0.066390	-0.04666	44	H	0.125251	0.20666
4	C	0.066412	-0.04758	45	H	0.125558	0.20670
5	C	-0.402822	-0.34126	46	H	0.123850	0.20549
6	C	-0.012638	-0.06796	47	H	0.134604	0.21048
7	C	-0.109305	-0.18358	48	H	0.135177	0.21020
8	C	-0.108427	-0.18709	49	H	0.125251	0.20666
9	C	-0.136717	-0.19815	50	H	0.125557	0.20670
10	C	-0.136441	-0.19710	51	H	0.123850	0.20549
11	C	-0.116400	-0.20333	52	H	0.138005	0.20927
12	C	-0.012634	-0.06825	53	H	0.138322	0.20610
13	C	-0.109306	-0.18357	54	H	0.126893	0.20677
14	C	-0.108431	-0.18708	55	H	0.126657	0.20629
15	C	-0.136717	-0.19816	56	H	0.127854	0.20601
16	C	-0.136441	-0.19710	57	H	0.138002	0.20927
17	C	-0.116401	-0.20333	58	H	0.138318	0.20610
18	C	-0.212758	-0.48262	59	H	0.126891	0.20677
19	C	-0.162178	-0.18047	60	H	0.126655	0.20629
20	C	-0.164286	-0.18291	61	H	0.127851	0.20601
21	C	-0.112957	-0.20182	62	H	0.139731	0.20944
22	C	-0.114939	-0.20397	63	H	0.138965	0.21219
23	C	-0.130441	-0.19253	64	H	0.122468	0.20482
24	C	-0.212724	-0.48261	65	H	0.123361	0.20542
25	C	-0.162179	-0.18047	66	H	0.121335	0.20433
26	C	-0.164315	-0.18291	67	H	0.139723	0.20944
27	C	-0.112956	-0.20182	68	H	0.138967	0.21219
28	C	-0.114936	-0.20397	69	H	0.122468	0.20482
29	C	-0.130444	-0.19253	70	H	0.123360	0.20542
30	C	0.055698	-0.09177	71	H	0.121335	0.20433
31	C	-0.172416	-0.19756				
32	C	-0.116622	-0.18162				
33	C	-0.137036	-0.20021				
34	C	-0.137846	-0.19772				
35	C	-0.118140	-0.20665				
36	C	0.055669	-0.09178				
37	C	-0.172411	-0.19755				
38	C	-0.116624	-0.18162				
39	C	-0.137032	-0.20021				
40	C	-0.137848	-0.19772				
41	C	-0.118140	-0.20665				

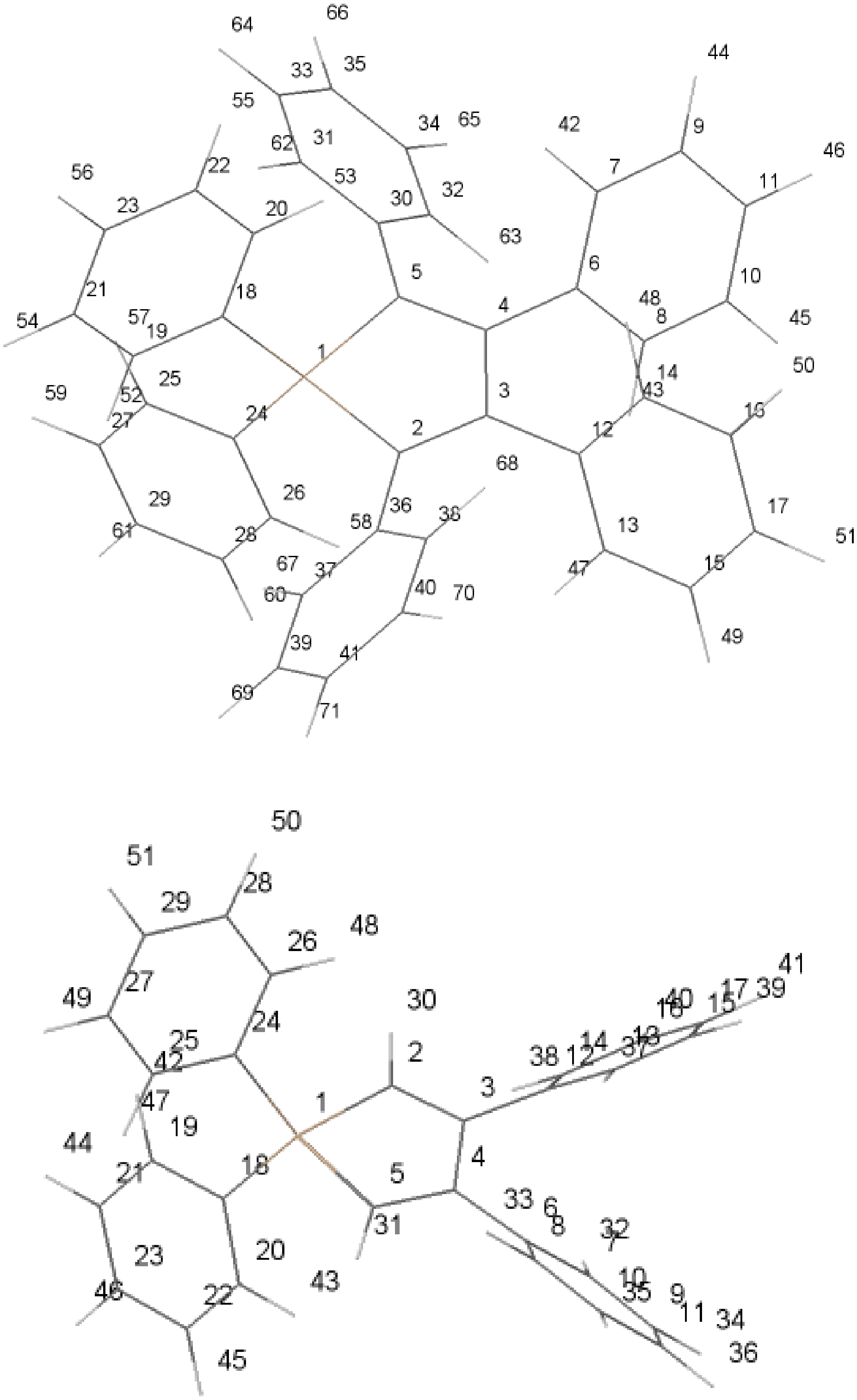
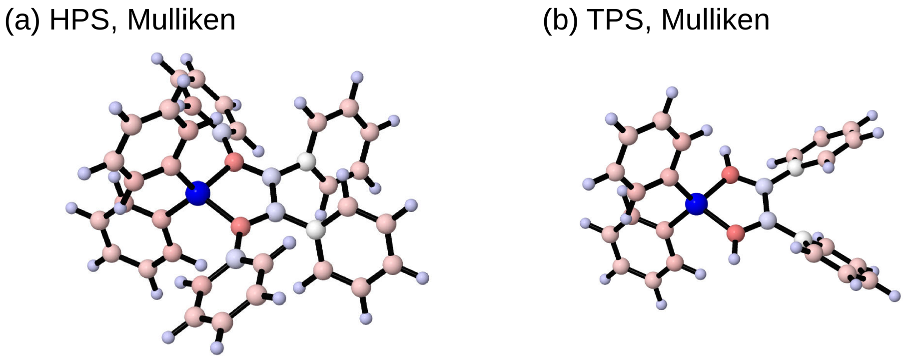


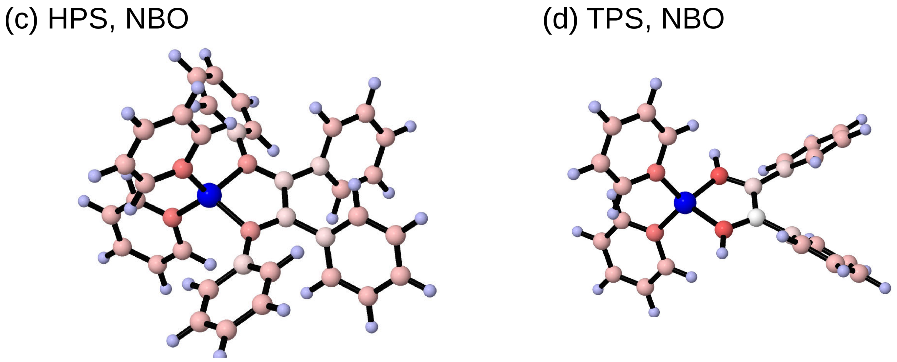
FIG. S 2. HPS (top) and TPS (bottom): atom numbers as used in Tables I and II.

TABLE S II. Calculated partial charges for TPS

Atom No.	Type	Mulliken / e	NBO / e	Atom No.	Type	Mulliken / e	NBO / e
1	Si	0.959972	1.57727	30	H	0.127911	0.21865
2	C	-0.482917	-0.57805	31	H	0.127913	0.21962
3	C	0.072684	-0.03392	32	H	0.140816	0.21361
4	C	0.072694	-0.03134	33	H	0.134177	0.21069
5	C	-0.482924	-0.58170	34	H	0.126629	0.20759
6	C	0.017271	-0.07075	35	H	0.125369	0.20705
7	C	-0.116814	-0.18175	36	H	0.124648	0.20626
8	C	-0.135418	-0.18830	37	H	0.140815	0.21362
9	C	-0.137051	-0.19839	38	H	0.134177	0.21067
10	C	-0.135999	-0.20150	39	H	0.126629	0.20759
11	C	-0.116680	-0.20405	40	H	0.125369	0.20705
12	C	0.017274	-0.07074	41	H	0.124647	0.20626
13	C	-0.116816	-0.18178	42	H	0.138134	0.20951
14	C	-0.135419	-0.18830	43	H	0.138793	0.21116
15	C	-0.137050	-0.19841	44	H	0.125745	0.20662
16	C	-0.135999	-0.20152	45	H	0.126053	0.20679
17	C	-0.116680	-0.20407	46	H	0.126980	0.20622
18	C	-0.197215	-0.45963	47	H	0.138136	0.20952
19	C	-0.162461	-0.18806	48	H	0.138795	0.21116
20	C	-0.163429	-0.18107	49	H	0.125745	0.20662
21	C	-0.113223	-0.20601	50	H	0.126053	0.20679
22	C	-0.112632	-0.20529	51	H	0.126981	0.20622
23	C	-0.131362	-0.19598				
24	C	-0.197226	-0.45957				
25	C	-0.162455	-0.18805				
26	C	-0.163421	-0.18098				
27	C	-0.113225	-0.20602				
28	C	-0.112634	-0.20531				
29	C	-0.131360	-0.19597				


(a) HPS, Mulliken

(b) TPS, Mulliken


(c) HPS, NBO

(d) TPS, NBO

FIG. S 3. Visualization of the partial charges listed in Tables I and II.

III. SIMULATED CORE LEVEL SHIFTS

TABLE S III. Simulated core level shifts for the carbon atoms in HPS, given with respect to the C-Si atom in the silole core. For the atom numbering see Fig. S2. Broadening of these values results in the spectrum diplayed in Fig. 2b.

Atom No.	relative core level shift
2	0.00 eV
3	0.91 eV
12	1.15 eV
13	0.87 eV
14	0.85 eV
15	1.05 eV
16	1.06 eV
17	0.96 eV
24	0.71 eV
25	1.03 eV
26	1.06 eV
27	1.18 eV
28	1.17 eV
29	1.16 eV
36	1.08 eV
37	0.56 eV
38	0.56 eV
39	0.88 eV
40	0.86 eV
41	0.68 eV

TABLE S IV. Simulated core level shifts for the carbon atoms in TPS, given with respect to the C-Si atom in the silole core. For the atom numbering see Fig. S2. Broadening of these values results in the spectrum diplayed in Fig. 4b.

Atom No.	relative core level shift
2	0.00 eV
3	1.45 eV
12	1.43 eV
13	1.07 eV
14	1.12 eV
15	1.26 eV
16	1.28 eV
17	1.17 eV
24	0.84 eV
25	1.18 eV
26	1.17 eV
27	1.32 eV
28	1.32 eV
29	1.30 eV

REFERENCES

[1] K. Hermann, L. Pettersson, M. Casida, C. Daul, A. Goursot, A. Koester, E. Proynov, A. St-Amant, D. S. C. V. Carravetta, H. Duarte, C. Friedrich, N. Godbout, J. Guan, C. Jamorski, M. Leboeuf, M. Leetmaa, M. Nyberg, S. Patchkovskii, L. Pedocchi, F. Sim, L. Triguero, and A. Vela, "Stobe-demon version 3.0, http://w3.rz-berlin.mpg.de/ hermann/stobe/index.html," (2007).

[2] P. L. HANSEN, R. BRYDSON, and D. W. MCCOMB, Microsc. Microanal. Microstruct. **3**, 213 (1992).

[3] J. CHABOY, M. BENFATTO, and I. DAVOLI, Phys. Rev. B **52**, 10014 (1995).

[4] J. Z. Xiong, D. T. Jiang, Z. F. Liu, K. M. Baines, T. K. Sham, S. G. Urquhart, A. T. Wen, T. Tyliszczak, and A. P. Hitchcock, Chem. Phys. **203**, 81 (1996).

[5] R. K. Hocking, E. C. Wasinger, F. M. F. de Groot, K. O. Hodgson, B. Hedman, and E. I. Solomon, Journal of the American Chemical Society **128**, 10442 (2006), http://dx.doi.org/10.1021/ja061802i.
[6] L. Triguero, L. G. M. Pettersson, and H. Ågren, Phys. Rev. B **58**, 8097 (1998).
[7] K. Diller, F. Klappenberger, M. Marschall, K. Hermann, A. Nefedov, C. Wöll, and J. V. Barth, J. Chem. Phys. **136**, 014705 (2012).
[8] K. Diller, F. Klappenberger, F. Allegretti, A. C. Papageorgiou, S. Fischer, A. Wiengarten, S. Joshi, K. Seufert, D. Ecija, W. Auwärter, and J. V. Barth, J. Chem. Phys. **138**, 154710 (2013).
[9] U. Ekström, H. Ottosson, and P. Norman, J. Phys. Chem. C **111**, 13846 (2007).
[10] D. Li, G. M. Bancroft, M. Kasrai, M. E. Fleet, R. A. Secco, X. H. Feng, K. H. Tan, and B. X. Yang, Am. Min. **79**, 622 (1994).