Supporting information for: Direct Evidence of Chelated Geometry of Catechol on TiO2 by a Combined Solid State NMR and DFT Study

Daniel Finkelstein-Shapiro,*,† Stephen K. Davidowski,† Paul B. Lee,¶ Chengchen Guo,† Gregory P. Holland,§ Tijana Rajh,‖ Kimberly A. Gray,¶ Jeffery L. Yarger,† and Monica Calatayud‡

Department of Chemistry and Biochemistry, Arizona State University, Tempe AZ 85282, Sorbonne Universits, UPMC Univ Paris 06, CNRS, Laboratoire de Chimie Thorique, CC 137 - 4, place Jussieu F. 75252 PARIS CEDEX 05 - France, Department of Civil and Environmental Engineering, Northwestern University, Evanston IL 60202, Department of Chemistry and Biochemistry, San Diego State University, 5500 Campanile Drive, San Diego, CA 92182-1030, Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, and Institut Universitaire de France, France

E-mail: dfs@asu.edu

Phone: +0046 721-889855

Experimental Chemical Shift Anisotropies

CSA patterns were measured for neat catechol (see Fig. S1) and catechol on TiO_2 (see Fig. S2) at slow spinning speeds of 1.5 and 6 kHz, respectively. Fitting for the sidebands for neat catechol (see Table S1) shows good agreement between experiments and predictions. For the TiO_2-catechol sample a good fitting of the spectra is not possible because of spectral congestion. The skew parameter seems to be slightly positive which can be consistent with the chelated conformer in a defective surface (which is very close to $\kappa = 0$).

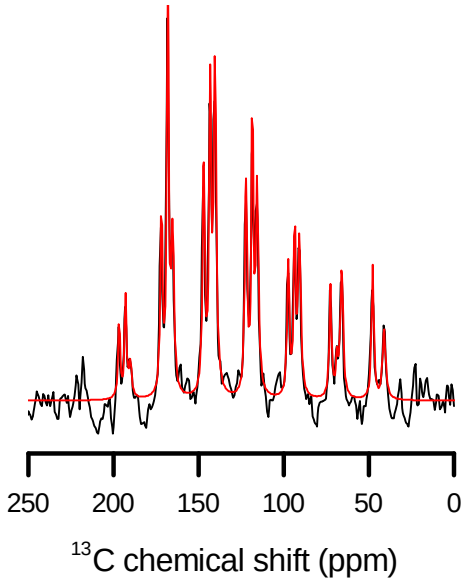

Figure S1: CP-MAS of neat catechol at a spinning speed of 2.5 kHz (black) and fit (red).

*To whom correspondence should be addressed
†Department of Chemistry and Biochemistry, Arizona State University, Tempe AZ 85282
‡Sorbonne Universits, UPMC Univ Paris 06, CNRS, Laboratoire de Chimie Thorique, CC 137 - 4, place Jussieu F. 75252 PARIS CEDEX 05 - France
¶Department of Civil and Environmental Engineering, Northwestern University, Evanston IL 60202
§Department of Chemistry and Biochemistry, San Diego State University, 5500 Campanile Drive, San Diego, CA 92182-1030
‖Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439
⊥Institut Universitaire de France, France

Table S1: CSA parameters for neat catechol

	δ_{iso}		Ω		κ	
	theory	exp.	theory	exp.	theory	exp.
α-C	143	143	147	133	0.24	0.31
β-C	116	116	156	167	0.33	0.28
γ-C	122	121	228	201	0.20	0.19

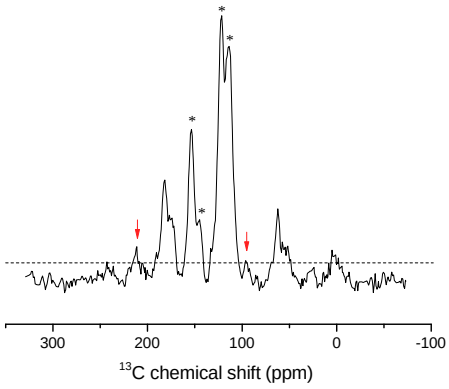

Figure S2: CP-MAS of catechol on TiO_2 at 6 kHz. The isotropic shifts are marked by an asterisk. The ± 1 sidebands of the most downfield shift of the α carbon signal are marked by a red arrow, and a horizontal line has been drawn to aid the eye in comparing intensities.

Full table of chemical shifts

The full chemical shifts for the α, β, γ and α', β', γ' carbons is shown in Table S2.

facet	binding mode	α-Carbon			α′-Carbon			β-Carbon			β′-Carbon			γ-Carbon			γ′-Carbon		
		δ_{iso}	Ω	κ	δ_{iso}	Ω	κ	δ_{iso}	Ω	κ	δ_{iso}	Ω	κ	δ_{iso}	Ω	κ	δ_{iso}	Ω	κ
101	bidentate	161.1	126.7	0.63	160.9	128.0	0.62	120.8	154.5	0.28	121.5	156.0	0.24	123.1	197.9	0.13	123.5	199.0	0.14
100	bidentate	162.2	128.1	0.65	162.7	128.0	0.64	120.6	155.1	0.30	120.9	155.1	0.28	121.7	195.7	0.13	121.8	196.3	0.14
001	bidentate	161.4	125.0	0.63	161.1	125.8	0.63	120.0	156.3	0.27	120.1	156.7	0.26	121.6	196.4	0.12	121.4	196.4	0.13
101	chelated	160.1	-131.1	0.33	163.8	-138.1	0.09	110.1	138.6	0.42	108.9	137.7	0.35	122.7	204.0	0.02	123.3	203.3	0.06
100	chelated	166.3	142.1	0.16	163.1	-125.4	0.04	110.6	141.0	0.34	109.9	139.2	0.37	123.2	201.5	0.06	122.3	199.7	0.06
001	chelated	161.8	-138.7	0.40	161.5	-146.0	0.27	109.5	138.3	0.41	110.3	140.9	0.39	122.6	202.8	0.04	124.3	205.2	0.05
001-defect	chelated	163.8	124.5	-0.08	160.8	134.9	0.05	107.2	137.9	0.25	112.7	147.5	0.35	124.6	202.1	0.12	122.9	201.6	0.09
101	monodentate	160.0	126.4	0.57	150.6	131.6	0.09	119.2	152.4	0.34	123.9	173.0	0.20	125.1	202.0	0.13	123.5	197.8	0.16
100	monodentate	162.5	127.5	0.64	162.7	126.9	0.64	120.9	155.2	0.30	120.9	155.0	0.29	122.8	197.0	0.16	122.9	197.2	0.16
001	monodentate	146.6	134.8	0.24	152.9	115.0	0.62	117.3	154.7	0.01	121.5	154.9	0.20	119.5	193.1	0.13	122.0	198.9	0.12
101	molecular	143.6	129.7	0.27	145.6	131.7	0.33	115.0	155.2	0.12	116.6	163.2	0.24	120.5	194.7	0.13	122.3	198.3	0.14
100	molecular	143.9	133.8	0.29	147.3	136.8	0.42	114.0	155.3	0.13	116.2	163.4	0.24	118.2	192.9	0.10	121.0	198.6	0.10
001	molecular	144.6	135.5	0.27	147.8	138.8	0.38	115.1	160.0	0.18	117.7	167.0	0.23	120.1	195.5	0.12	122.3	201.4	0.11

Table S2: Full chemical shift tensor parameters obtained from DFT calculations for all models generated in this work.