Electronic Supplementary Information

Experimental and computational investigation of the substituent effects on the reduction of Fe^{3+} by 1,2-dihydroxybenzenes.

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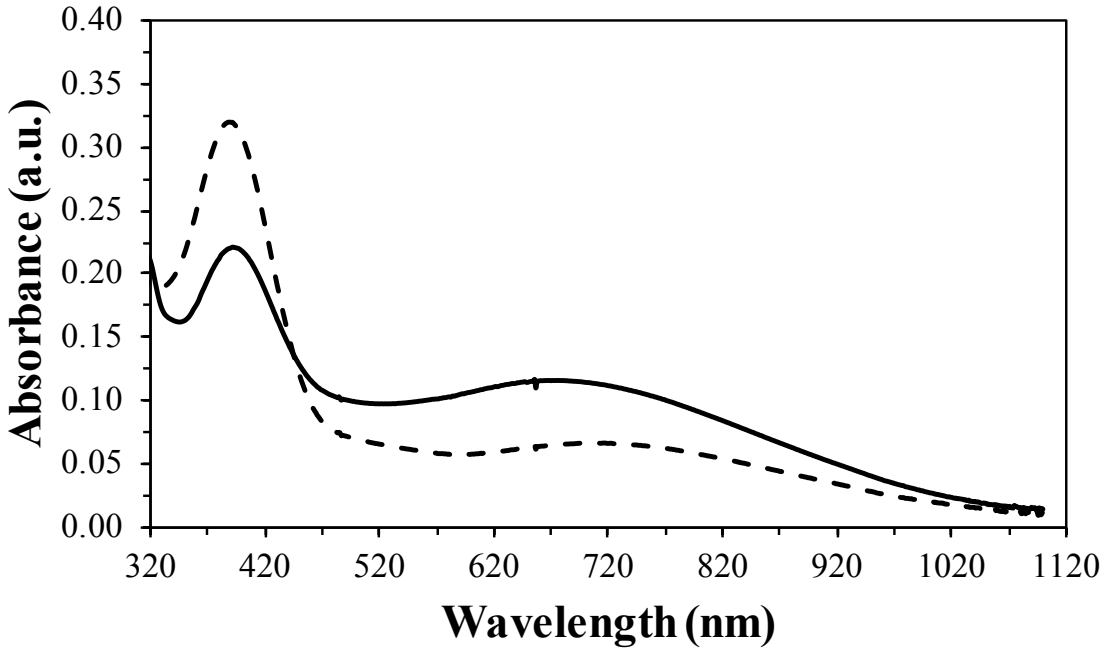

Figure S1: UV-visible absorption spectra of the mixtures of $1x10^{-4}$ mol/L of Fe^{3+} and $1x10^{-2}$ mol/L of catechol. Solid lines (-) indicates the UV-visible absorption spectra taken immediately after the mixture and dashed lines (--) show the spectra of the 1 minute after the mixture.

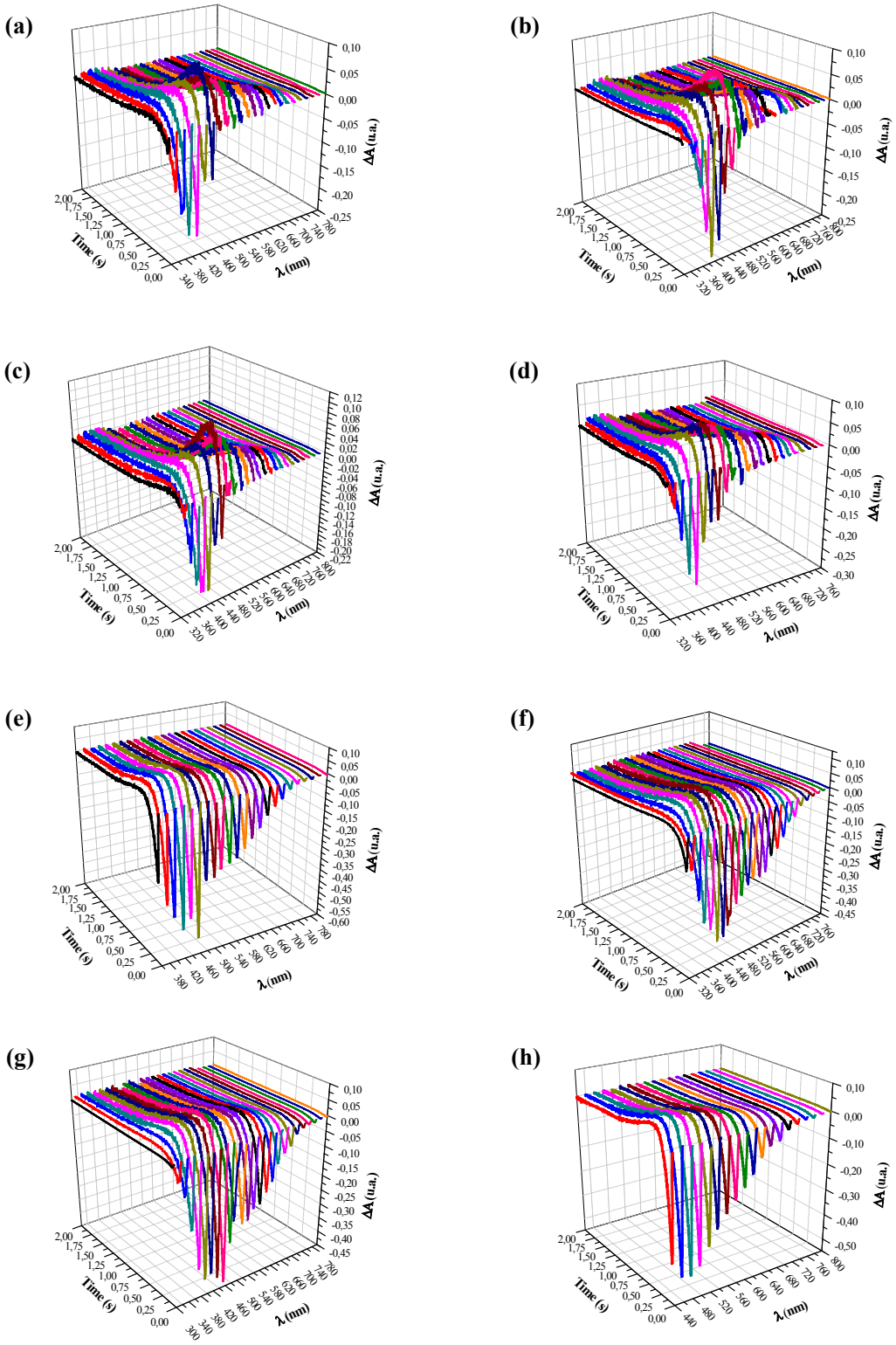

Figure S2. (a) 4-tert-butylcatechol, (b) 4-ethylcatechol, (c) 4-methylcatechol, (d) catechol, (e) 3,4-dihydroxybenzaldehyde, (f) 3,4-dihydroxybenzoic acid, (g) 3,4-dihydroxybenzonitrile and (h) 4-nitrocatechol.

Table S1. Rate constants obtained from the kinetics profiles for the reaction between Fe^{3+} $1.0x10^{-4}$ mol/L and the 1,2-DHBs $1.0x10^{-2}$ mol/L at pH= 3.0.

	Rate constant (s^{-1})		
1,2-dihydroxybenzenes	**b**	**d**	**f**
4-tert-butylcatecol	9.16 ± 0.16	2.28 ± 0.04	40.07 ± 0.54
4-ethylcatechol	8.98 ± 0.09	2.60 ± 0.07	40.64 ± 0.81
4-methylcatechol	9.27 ± 0.06	2.47 ± 0.05	39.87 ± 0.32
Catechol	9.38 ± 0.08	2.19 ± 0.06	41.14 ± 0.77
3,4-dihydroxybenzaldehyde	10.03 ± 0.11	1.55 ± 0.07	50.55 ± 0.93
3,4-dihydroxybenzoic acid	9.74 ± 0.07	1.63 ± 0.05	47.69 ± 0.95
3,4-dihydroxybenzonitrile	10.22 ± 0.12	1.45 ± 0.06	52.19 ± 0.31
4-nitrocatechol	10.72 ± 0.10	1.37 ± 0.08	57.66 ± 1.05

Table S2. Oscillator strengths for: species II or IV (green), species III (purple), species V (blue), species VI (light blue), species VII (red) and species VIII (grey).

λ (nm)	4-TC	4-EC	4-MC	CAT	4-CHO	4-COOH	4-CN	4-NO_2
300	0.0347							
302							0.382	
303	0.0512							
304	0.1771	0.1159						
305		0.0550						
306		0.0541				0.332		
307	0.0086							
308			0.0711	0.0551				
309						1.537		
310						0.786		
311						0.247		
313	0.0265							
314						0.417		
315					2.197		0.711	0.311
316	0.0126	0.0398						
319					0.267			
320				0.0468			0.105	
321		0.0137						
322		0.0207	0.0660					
324			0.0511		0.300			
325	0.0531						0.972	
329							0.193	
330					0.766	0.325	0.766	
332						0.297		
333			0.0170					
334							0.335	
335					0.097			
336				0.0243		0.371		1.250
337	0.0242	0.0248						
338					0.516			
339					0.331		0.155	
340					1.363			0.427
341							1.478	1.132
342						0.281		
344							0.914	0.345
345								0.570
346		0.0904	0.0132		0.312			
347	0.0120					0.853		
348		0.0182	0.0564	0.0270				
349				0.1299				
350	0.0712							
353	0.0222							
356	0.0134						1.366	
357	0.0120							
359					0.270			

360			0.1383		0.108	0.202		
361		0.0097	0.0187					0.138
362						0.183		0.289
363		0.1104			0.752		0.752	
365		0.0323	0.0182					
366							0.099	
368			0.0082					
369		0.0423						
370		0.0163						
371								0.520
372	0.0311	0.0118				0.392	0.226	
374				0.0305				
375					0.326			
376	0.0298							
379				0.0168				0.321
381			0.0130		0.478	0.826	0.478	
382		0.0250						
383							0.446	0.312
385				0.0542		0.258		
386			0.0138					
388				0.0352				
389		0.0137						
390	0.0682		0.0505					
391			0.0285					
392		0.0613						0.204
393						0.210		
394				0.0238				
395					0.584			
396						0.280		0.357
399			0.0153					
400			0.0204					
401							0.990	
402	0.0754	0.0177			0.071		0.071	
403		0.0234						
406					0.637			
407	0.0278					0.241		
410							0.240	
419								0.100
421	0.1420							
426					0.662			
427								0.741
436						1.190		
440								0.167
441					0.169			
445		0.0138						
446			0.0147					
453					0.063		0.063	
454				0.0431			0.364	0.150
457								0.131

458					0.347			
459								0.319
461								0.146
462				0.0312				
463			0.0473		0.039		0.039	
464		0.0589				0.327		
465	0.0328	0.0347			0.073			
470		0.0560						
472								0.131
474							0.371	
475			0.0518					
477			0.0343					
479								0.233
485						0.471		
487				0.0139				
492				0.0143				
494					0.952			
498					0.124			0.113
502			0.0230				0.625	
508		0.0237						
510	0.0246							
512						0.121		
519	0.0222							
522							0.289	
533							0.744	0.593
541				0.0334				
546						0.479		
547					0.533	0.397		
549								0.415
552		0.0245						
554	0.0398							
557			0.0353					
594							0.081	
605						0.364		
610					0.226			
616	0.0160							
618		0.0408						
623	0.0440							
624				0.0197				
625		0.0162						
626					0.182			
627								0.497
636							0.158	
647			0.0171					
649						0.135		
656								0.685
658								0.341
662				0.0129				
666					0.088			

676			0.0099					

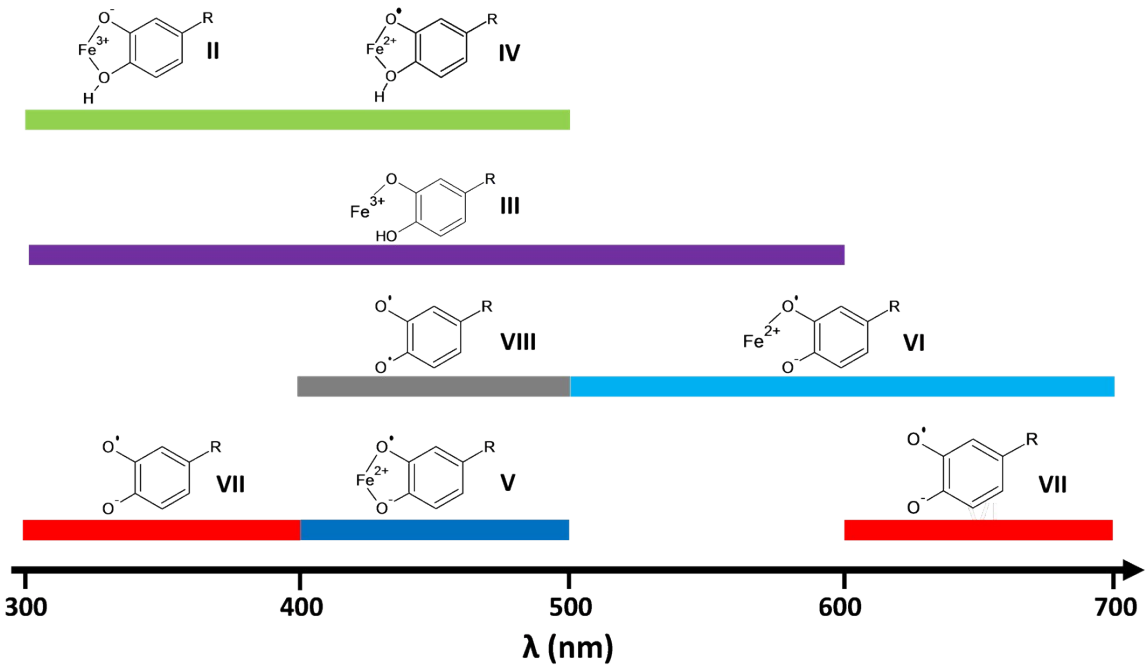

Figure S3. Wavelength regions where the calculated species mainly absorb.