Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

New insights on pertinent Fe-complex for the synthesis of iron through the instant polyol process

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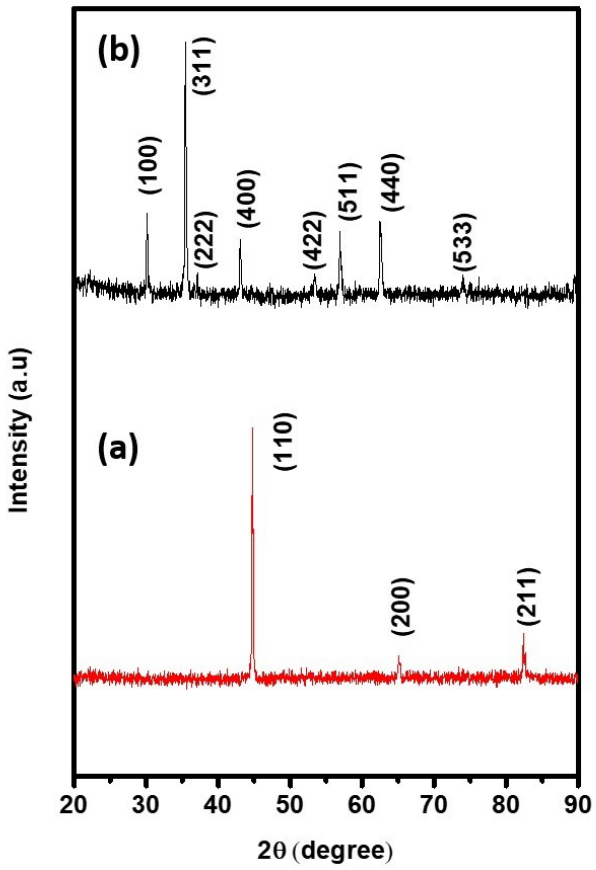

Fig. S1. XRD patterns of Fe and Fe oxide synthesized through a) PG and b) tPG, respectively.

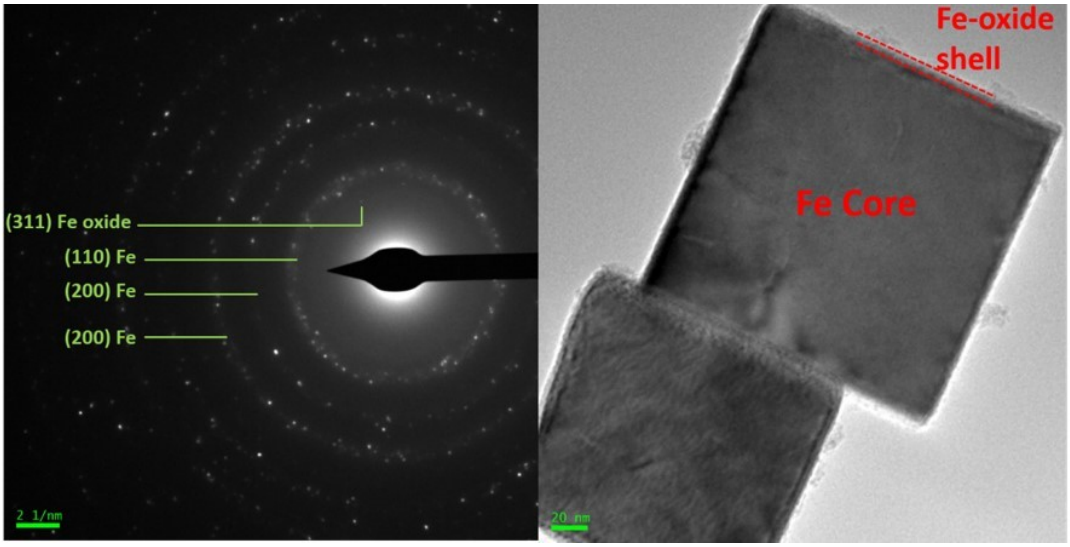

Fig. S2. SAED pattern (left) and TEM image (right) of single particle Fe synthesized through PG exhibiting a Fe core and Fe oxide shell.

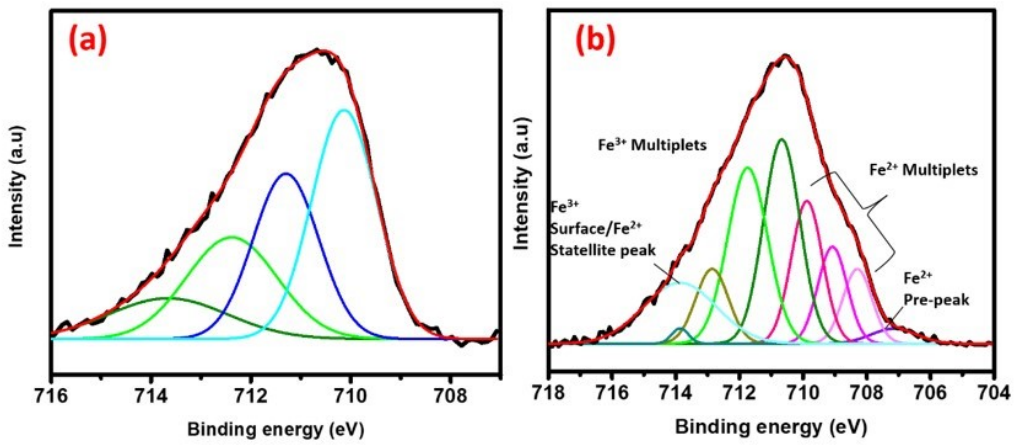

Fig. S3. XPS fitting of a) multiplets of Fe^{3+} peaks of γ-Fe_2O_3 and b) multiplets of Fe^{2+} and Fe^{3+} of Fe_3O_4.

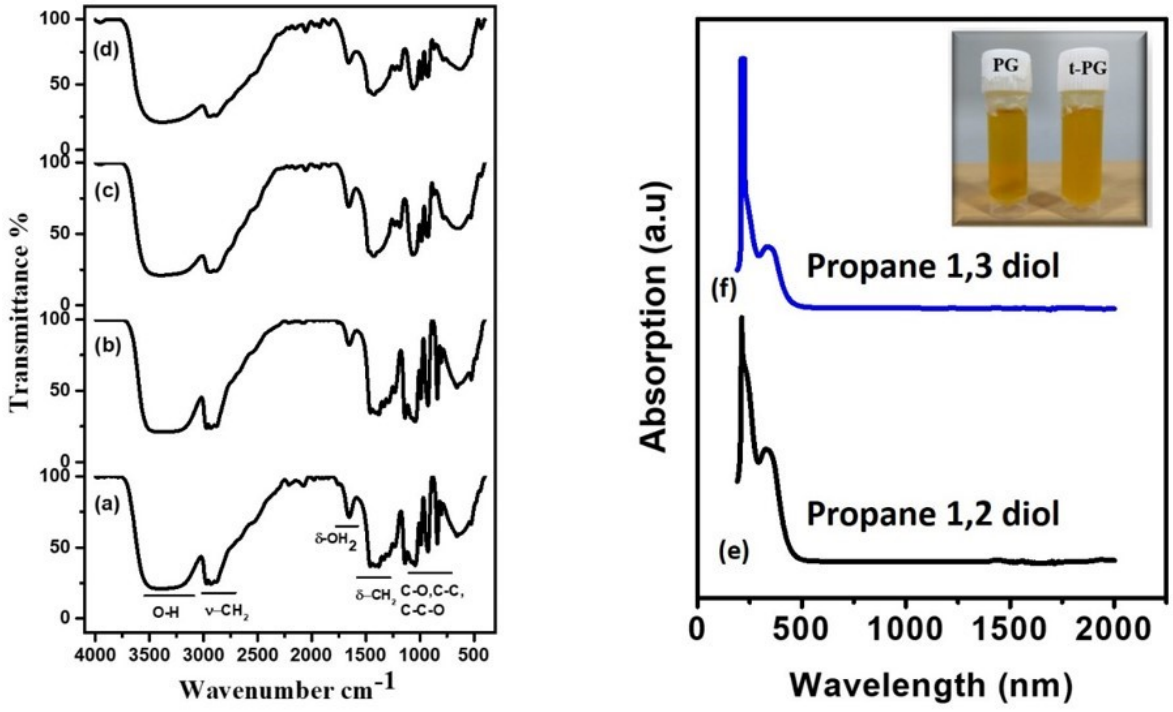

Fig. S4. FTIR spectra of (a) dehydrated PG (b) $FeCl_2.4H_2O$ dissolved in PG at 170 °C (c) dehydrated tPG and (d) $FeCl_2.4H_2O$ dissolved in tPG at 170 °C. UV-Visible spectra of the iron precursor introduced at 170 °C in e) PG and f) tPG (the inset picture shows similar color for both the samples).

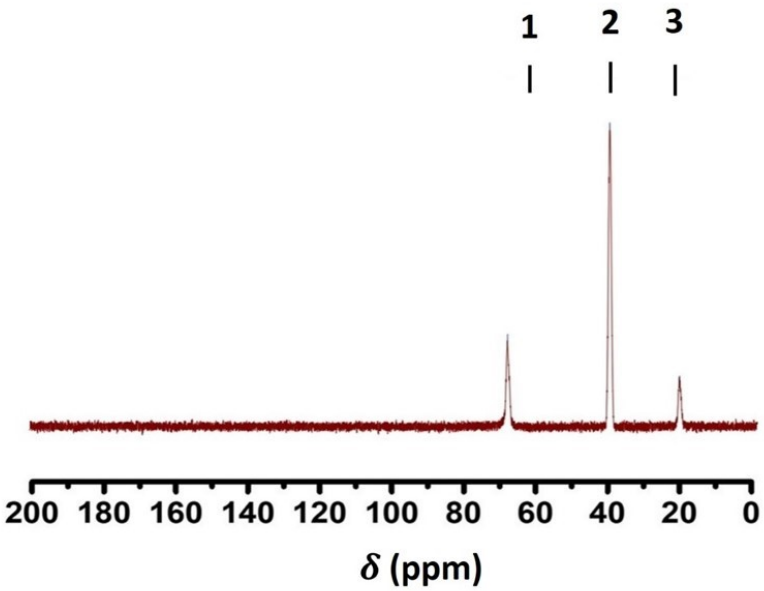

Fig. S5. ^{13}C NMR of polyol solution after introducing Fe precursor at 170 ^{o}C in PG. The chemical shifts of peaks marked 2, 3 and 1 represent the solvent peak DMSO, the carbon positions at methyl and -OH, respectively of 1,2 propanediol.

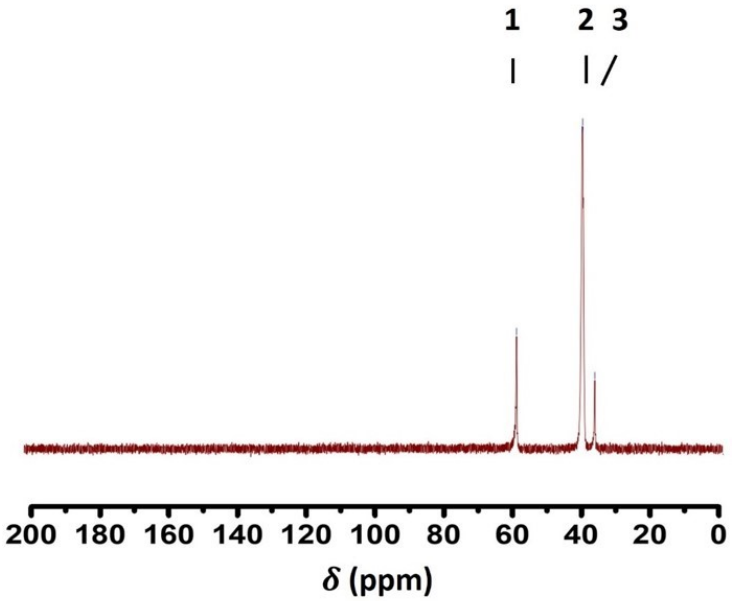

Fig. S6. ^{13}C NMR of polyol solution after introducing Fe precursor at 170 ^{o}C in tPG. The chemical shifts of peaks marked 2, 1 and 3 represent the solvent peak DMSO, the carbon positions at terminal and methylene carbon of 1,3 propanediol, respectively.

Computational details

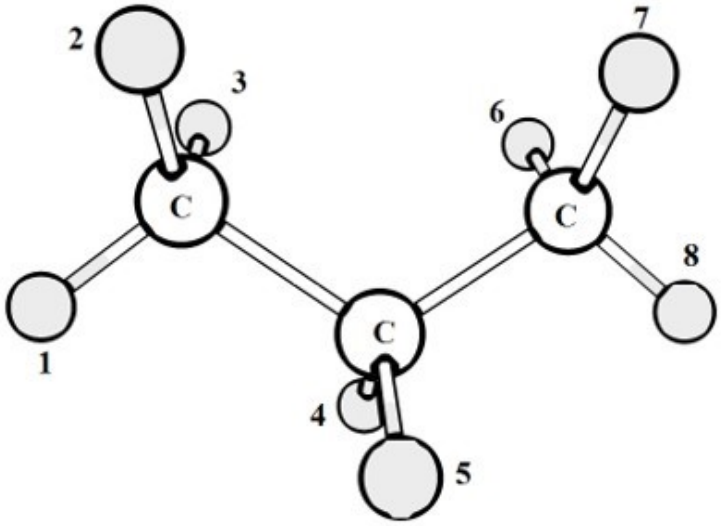

Fig. S7. The molecular structure of propane, where substitution of two (-OH) groups at either of 1 or 2 or 3 positions and either of 6 or 7 or 8 positions results in a terminal propanediol, while substitution at either of 4 or 5 and either of 1 or 2 or 3 or 6 or 7 or 8 results in a vicinal propanediol.

Depending on the site of substitution of two (-OH) groups, the polyols of propane (propanediol) could be classified into 21 isomers (9 combinations of terminal polyol and 12 combinations of vicinal polyol). Among the 21 isomers, only 9 structures (6 among terminal and 6 among vicinal) are structurally unique, while 12 other structures are repetitive (for instance, 2 and 8 substituted terminal polyol is the same as 1 and 7 substituted case). Hence the 9 identified unique structures were considered for further analysis. The cartesian coordinates of the optimized propanediol structures and the relative energy profile of 9 structures are presented in Tables S1 and S2, respectively.

Table S1. Cartesian coordinates of optimized propanediol structures.

Atom	**x**	**y**	**z**
Propanediol (1,8)			
C	-0.000017	-0.341973	0.000094
C	1.278104	0.496215	-0.006482
C	-1.278124	0.496208	0.006498
H	1.302056	1.157961	0.863313
H	1.305138	1.134262	-0.902145
H	-1.301892	1.157998	-0.863284
H	-1.305286	1.134171	0.902199

H	-0.021445	-0.994314	-0.881201
O	2.456707	-0.297186	0.090391
H	2.486769	-0.871794	-0.680948
H	0.021514	-0.994226	0.881465
O	-2.456682	-0.297178	-0.090499
H	-2.48683	-0.871839	0.680801
Propanediol (2,8)			
C	-0.043351	0.710845	-0.205968
C	-1.001843	-0.358398	0.315162
C	1.404329	0.519134	0.248089
H	-1.000366	-0.362759	1.40923
H	-0.675715	-1.353826	-0.020672
H	1.460818	0.526675	1.346383
H	-0.063876	0.712691	-1.302667
O	-2.353651	-0.120256	-0.061706
H	-2.395849	-0.13241	-1.023125
H	-0.401712	1.690541	0.129427
H	2.01444	1.349804	-0.112092
O	2.009202	-0.659903	-0.283726
H	1.663036	-1.418934	0.193266
Propanediol (3,8)			
C	0.044519	0.703877	-0.225049
C	0.9983	-0.366213	0.303364
C	-1.400511	0.527332	0.244632
H	0.678257	-1.354623	-0.036246
H	0.981437	-0.372043	1.404847
H	0.396808	1.691344	0.104233
O	2.32586	-0.219089	-0.186482
H	2.647074	0.644416	0.091566
H	0.074287	0.694548	-1.318586
H	-2.008874	1.355843	-0.123372
H	-1.449034	0.551511	1.343523
O	-2.015748	-0.654577	-0.264544
H	-1.654696	-1.411644	0.204562
Propanediol (2,7)			
C	0.029685	1.041292	-0.344056
C	-1.285071	0.476234	0.175725
C	1.266418	0.403793	0.297304
H	0.082728	0.900146	-1.428464
H	0.031826	2.120908	-0.15192
H	-2.132248	0.970665	-0.316835
H	1.175022	0.458581	1.395485
H	-1.364456	0.659157	1.256815
O	-1.310763	-0.935523	-0.091029
H	-2.089343	-1.31616	0.325145
H	2.15902	0.971163	0.020685

O	1.490273	-0.929039	-0.133306
H	0.635182	-1.375886	-0.080062
Propanediol (3,7)			
C	0.033487	1.133489	0.003962
C	-1.157856	0.309846	-0.471354
C	1.211031	0.25198	0.450358
H	-0.934257	-0.111526	-1.459047
H	0.3377	1.787993	-0.819634
H	-0.260822	1.774672	0.842102
H	2.126908	0.846095	0.486692
H	-2.045142	0.94823	-0.564537
O	-1.382972	-0.745725	0.474301
H	-2.1634	-1.234941	0.198771
H	1.018214	-0.125729	1.460256
O	1.463222	-0.828045	-0.44399
H	0.758826	-1.466528	-0.28489
Propanediol (3,6)			
C	-0.030064	1.041603	-0.343893
C	1.284663	0.476479	0.175992
C	-1.26678	0.403441	0.296894
H	1.363746	0.658806	1.257167
H	-0.032585	2.121096	-0.151272
H	-0.082688	0.900934	-1.42841
H	-2.159585	0.970124	0.019479
H	-1.176058	0.459117	1.395144
O	-1.489105	-0.929709	-0.132969
H	-0.633189	-1.37514	-0.080541
H	2.131874	0.971262	-0.316122
O	1.310806	-0.935169	-0.091559
H	2.087964	-1.316303	0.326818
Propanediol (5,1)			
C	-0.445828	0.027593	-0.337194
C	-1.784238	-0.602888	0.029513
C	0.750258	-0.738452	0.215286
H	-1.89611	-0.655225	1.115513
H	-1.86898	-1.613394	-0.381564
H	0.774484	-1.748356	-0.200991
H	0.64108	-0.819462	1.307722
O	-0.317914	1.348549	0.219396
H	-0.904265	1.941639	-0.258783
H	-0.336598	0.082088	-1.429048
H	-2.614929	-0.012303	-0.36779
O	1.971395	-0.112294	-0.135277
H	1.856324	0.817452	0.096351
Propanediol (5,2)			
C	0.568248	0.113742	0.453702

C	-0.947685	0.072751	0.640908
C	1.125581	-1.164933	-0.1559
H	-1.278553	1.0377	1.059993
H	2.203619	-1.065915	-0.295143
H	-1.183769	-0.705692	1.382119
H	0.659308	-1.34512	-1.124794
H	0.934397	-2.02249	0.494888
O	0.97604	1.182067	-0.399637
H	0.532821	1.986072	-0.112104
H	0.999203	0.252358	1.459402
O	-1.578597	-0.182257	-0.605903
H	-2.523434	-0.264765	-0.452293
Propanediol (5,3)			
C	-0.477205	-0.040892	-0.339706
C	0.799408	-0.64336	0.262981
C	-0.717315	1.394841	0.09848
H	0.7048	-0.648659	1.357645
H	-1.644584	1.77131	-0.337033
H	0.895315	-1.683097	-0.065087
H	0.098978	2.044104	-0.228561
H	-0.805657	1.449877	1.187826
O	-1.612573	-0.797051	0.09025
H	-1.536982	-1.685609	-0.271672
H	-0.384764	-0.071382	-1.434845
O	1.986731	0.010745	-0.169406
H	2.050303	0.850366	0.29445

Table S2. The total energy of propanediol conformers and relative energy of each conformer with respect to the minimum energy conformer calculated in kcal/mol.

Isomer	Relative Energy
Terminal	
Propanediol (1,8)	3.53
Propanediol (2,8)	3.51
Propanediol (3,8)	3.71
Propanediol (2,7)	0
Propanediol (3,7)	1.9

Propanediol (3,6)	0
Vicinal	
Propanediol (5,1)	0
Propanediol (5,2)	4.73
Propanediol (5,3)	2.87

*Note: The numbers proceeding Propanediol represent the position of -OH group as illustrated in Fig. S5.

From the Table S2 it is observed that propanediol (2,7) and propanediol (3,6) are stable conformers among terminal polyols, while propanediol (5,1) is the most stable conformer among the vicinal cases. It is also observed that the relative energies of all the other cases are above room temperature thermal energy of 0.58 kcal/mol.

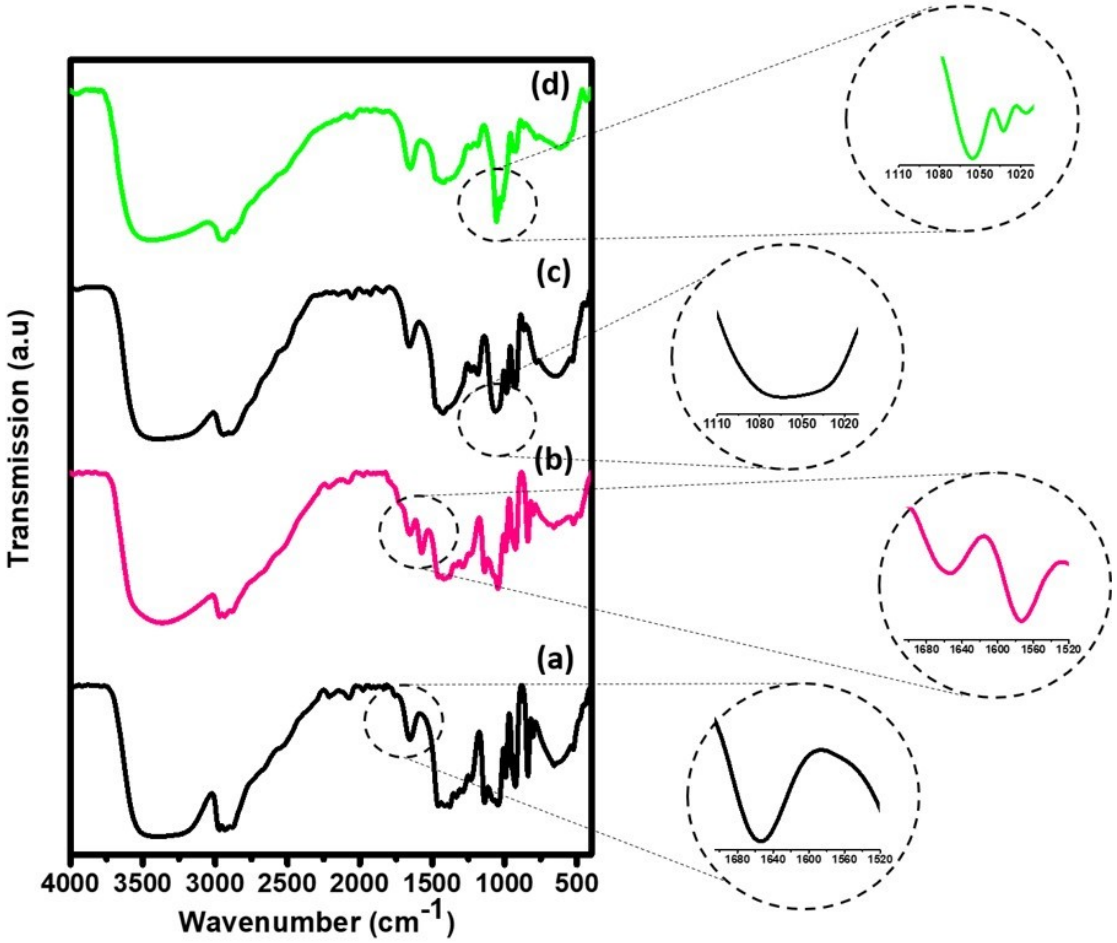

Fig. S8. FTIR patterns of a) Fe precursor in PG, b) Fe intermediate in PG, c) Fe precursor in t-PG and d) Fe intermediate in t-PG. The magnified regions show the difference in the patterns between the precursors and intermediates.

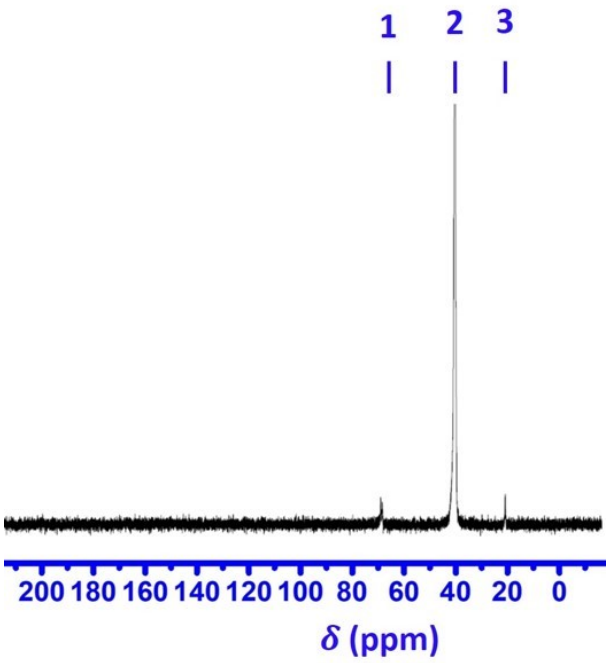

Fig. S9. ^{13}C NMR of polyol solution after capturing intermediate in PG. The chemical shifts of peaks marked 2, 3 and 1 represent the solvent peak DMSO, the carbon positions at methyl and -OH, respectively of 1,2 propanediol.

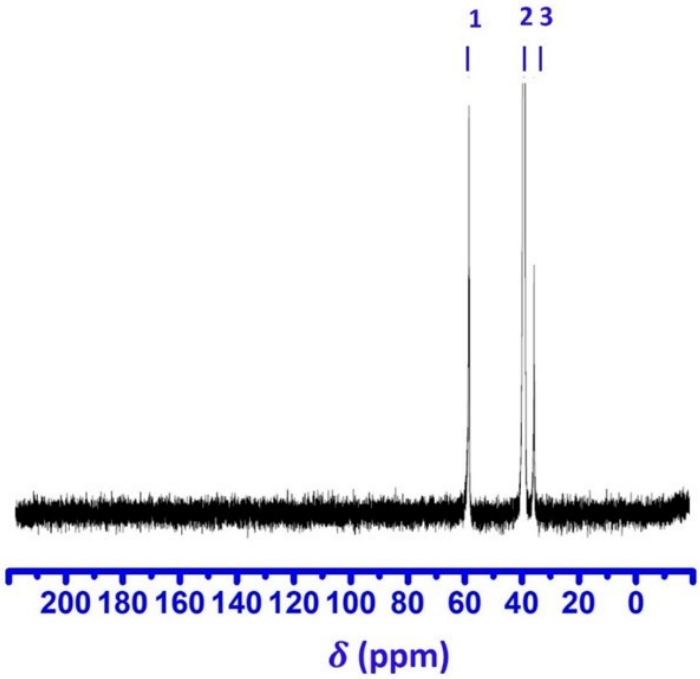

Fig. S10. ^{13}C NMR of polyol solution after capturing intermediate in tPG. The chemical shifts of peaks marked 2, 1 and 3 represent the solvent peak DMSO, the carbon positions at terminal and methylene carbon of 1,3 propanediol, respectively.

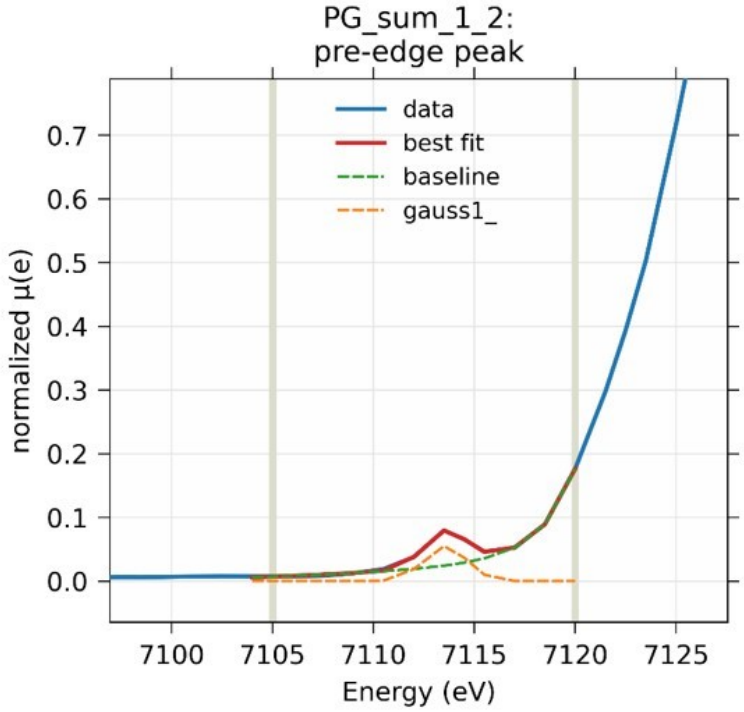

Fig. S11. The fitted pre-edge region of the XAS spectrum of the PG intermediate.

Table S3. The parameters obtained from fitting the pre-edge XAS spectrum of PG intermediate.

	Gauss1_center	Gauss1_amplitude	Gauss1_sigma	Gauss1_FWHM	χ^2	$Reduced\ \chi^2$
Nominal value	7113.55	0.146	1.06	2.5	1.507e-5	3.014e-6
error	0.04	0.009	0.04	0.1		

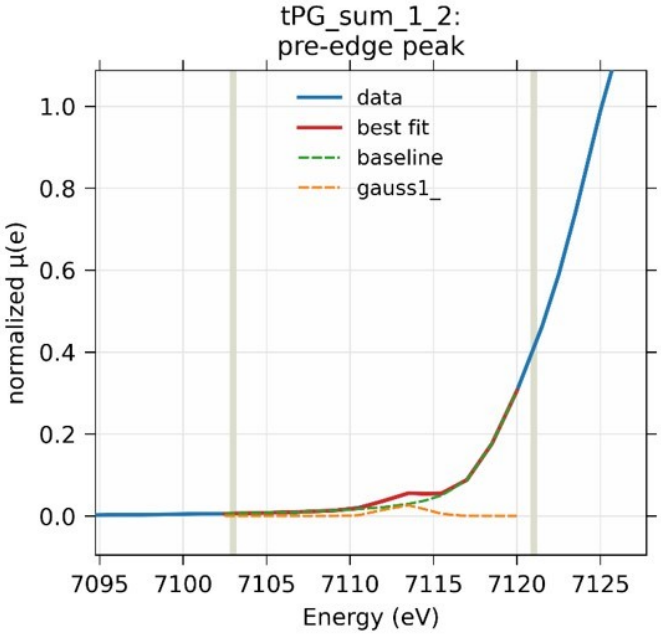

Fig. S12. The fitted pre-edge region of the XAS spectrum of the tPG intermediate.

Table S4. The parameters obtained from fitting the pre-edge XAS spectrum of tPG intermediate.

	Gauss1_center	Gauss1_amplitude	Gauss1_sigma	Gauss1_FWHM	χ^2	*Reduced* χ^2
Nominal value	7113.29	0.082	1.22	2.9	5.188 e-6	1.723e-6
error	0.05	0.005	0.06	0.1		

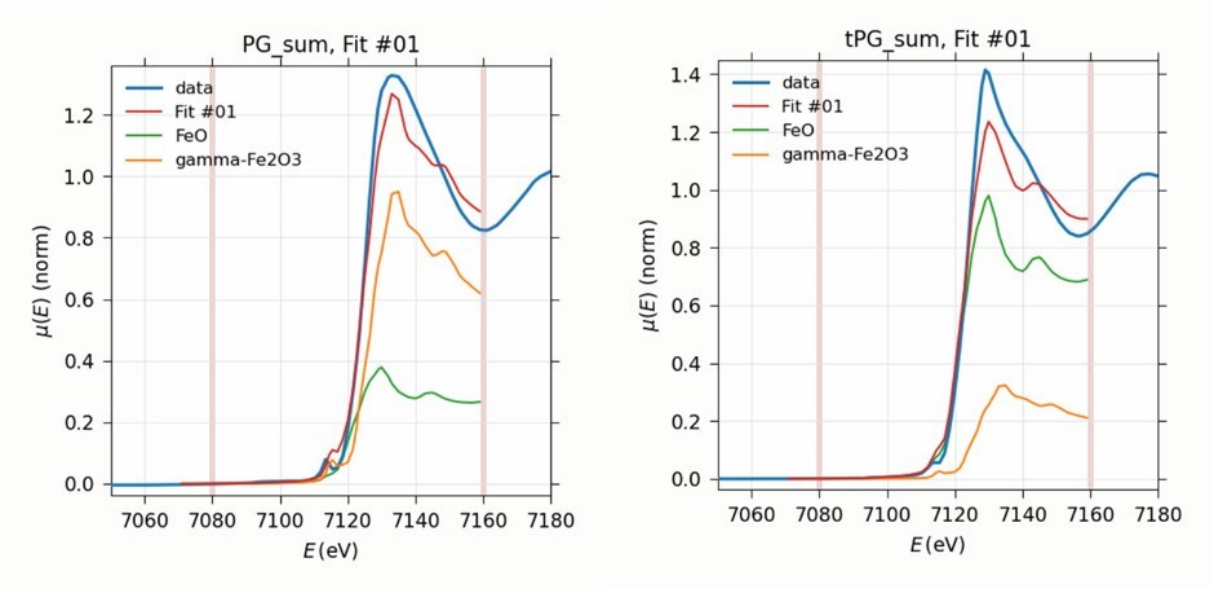

Fig. S13. Least square fitting of XANES regions of PG (left) and t-PG intermediate to known FeO and γFe_2O_3 system.

Table S5. The parameters from the least square fit of the XANES data corresponding to the intermediates obtained in PG and tPG.

Sample	FeO %	γ-Fe_2O_3 %	Function evals	Data points	variables	χ^2	$Reduced\ \chi^2$
PG	29 ± 4	75 ± 5	7	50	1	0.2093	0.0043
tPG	71 ± 4	24 ± 5	7	50	1	0.3281	0.0067

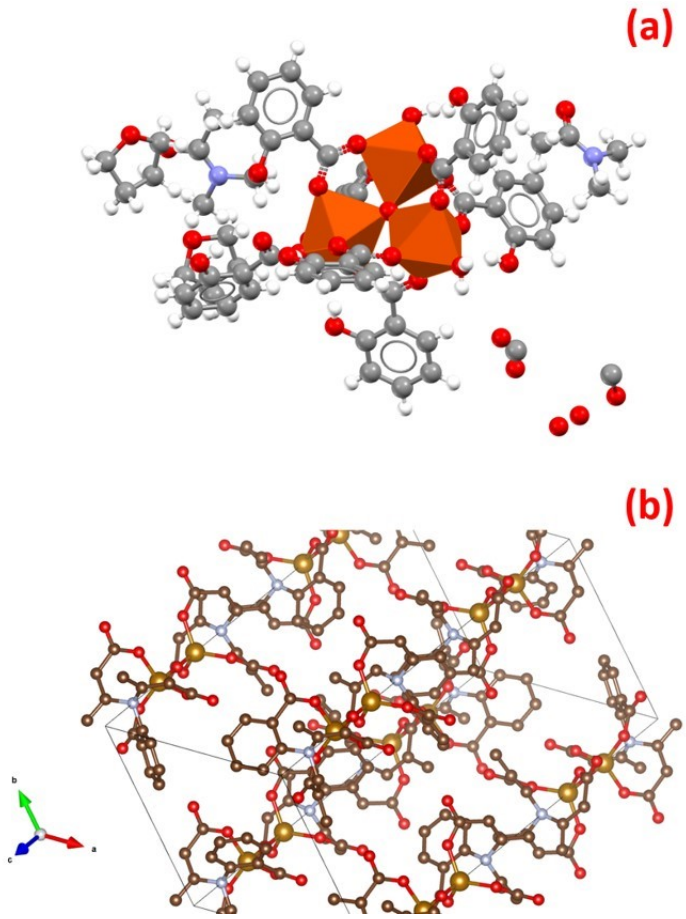

Fig. S14. Models used for fitting the EXAFS data a) BENQUJ for PG intermediate and b) HAHLEI for the tPG intermediate.

Table S6. Guessed parameters used for fitting the EXAFS data of PG complex.

amp	0.76 +/- 0.04
enot	2.3+/- 0.6
delr	0.004+/-0.002
ss	0.003+/-0.001
delr_C	-0.13 +/-0.02
ss_C	0.0006+/-0.0001
delr_Fe	-0.07+/-0.03
ss_Fe	0.011+/-0.007
ss_O2	0.004 +/-0.003
delr_O2	0.25+/-0.08

Table S7. Guessed parameters used for fitting the EXAFS data of tPG complex.

amp	1.3+/- 0.1
enot	0.7+/-0.2
delr	0.12+/-0.01
ss	0.008+/-0.002

delr_C1	0.34+/- 0.08
ss_C1	0.02+/- 0.009
delr_Fe	0.13+/-0.03
ss_Fe	0.005+/-0.004
ss_OFe	0.006+/-0.002
delr_OFe	-0.09 +/- 0.01