Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary Information

Colour tunable cool pigments based on $TiZn_2O_4$ inverse spinels

Deepak Joshy[a], C. P. Jijil[a], Sheethu Jose[b], Yahya A. Ismail[a], Pradeepan Periyat[c]*

[a]Department of Chemistry, University of Calicut, Kerala, India-673635.

[b]Department of Chemistry, Central University of Kerala, India-671316

[c]Department of Environmental Studies, Kannur University, Kerala, India

E-mail:pperiyat@uoc.ac.in/pperiyat@kannuruniv.ac.in

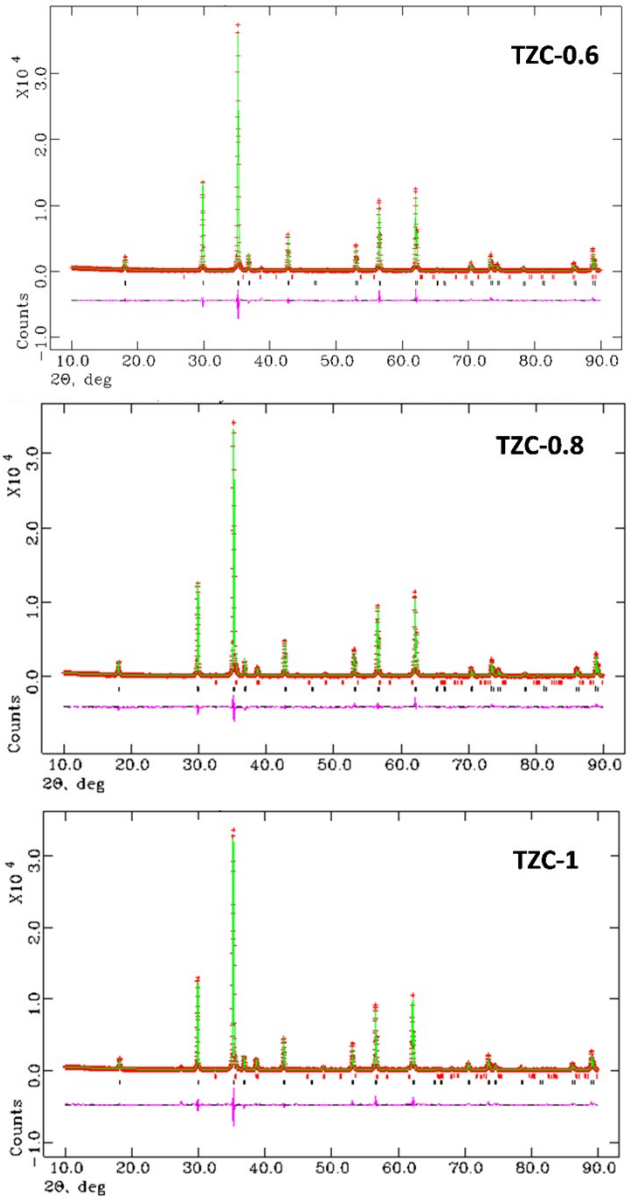

Figure S1- The experimental and refined patterns obtained on Rietveld analysis of TZC-0.6, TZC-0.8 and TZC-1 samples

Table S1 - The fractional coordinates, sites occupied and extent of occupancy obtained upon Rietveld refinement for TZF-0.6, TZF-0.8 and TZF-1 composition

TZC-0.6						
Atom	**Site**	**x**	**y**	**z**	**Uiso**	**Occupancy**
Zn(1)	8a	0.125	0.125	0.125	0.02135	1
Ti	16d	0.5	0.5	0.5	0.01398	0.5
Zn(2)	16d	0.5	0.5	0.5	0.01331	0.2
Cu	16d	0.5	0.5	0.5	0.01701	0.3
O	32e	0.257709	0.257709	0.257709	0.02291	1
TZC-0.8						
Atom	**Site**	**x**	**y**	**z**	**Uiso**	**Occupancy**
Zn(1)	8a	0.125	0.125	0.125	0.01915	1
Ti	16d	0.5	0.5	0.5	0.01069	0.5
Zn(2)	16d	0.5	0.5	0.5	0.00132	0.1
Cu	16d	0.5	0.5	0.5	0.02192	0.4
O	32e	0.260400	0.260400	0.260400	0.02022	1
TZC-1						
Atom	**Site**	**x**	**y**	**z**	**Uiso**	**Occupancy**
Zn	8a	0.125	0.125	0.125	0.01876	1
Ti	16d	0.5	0.5	0.5	0.01396	0.5
Cu	16d	0.5	0.5	0.5	0.02094	0.5
O	32e	0.257047	0.257047	0.257047	0.02313	1

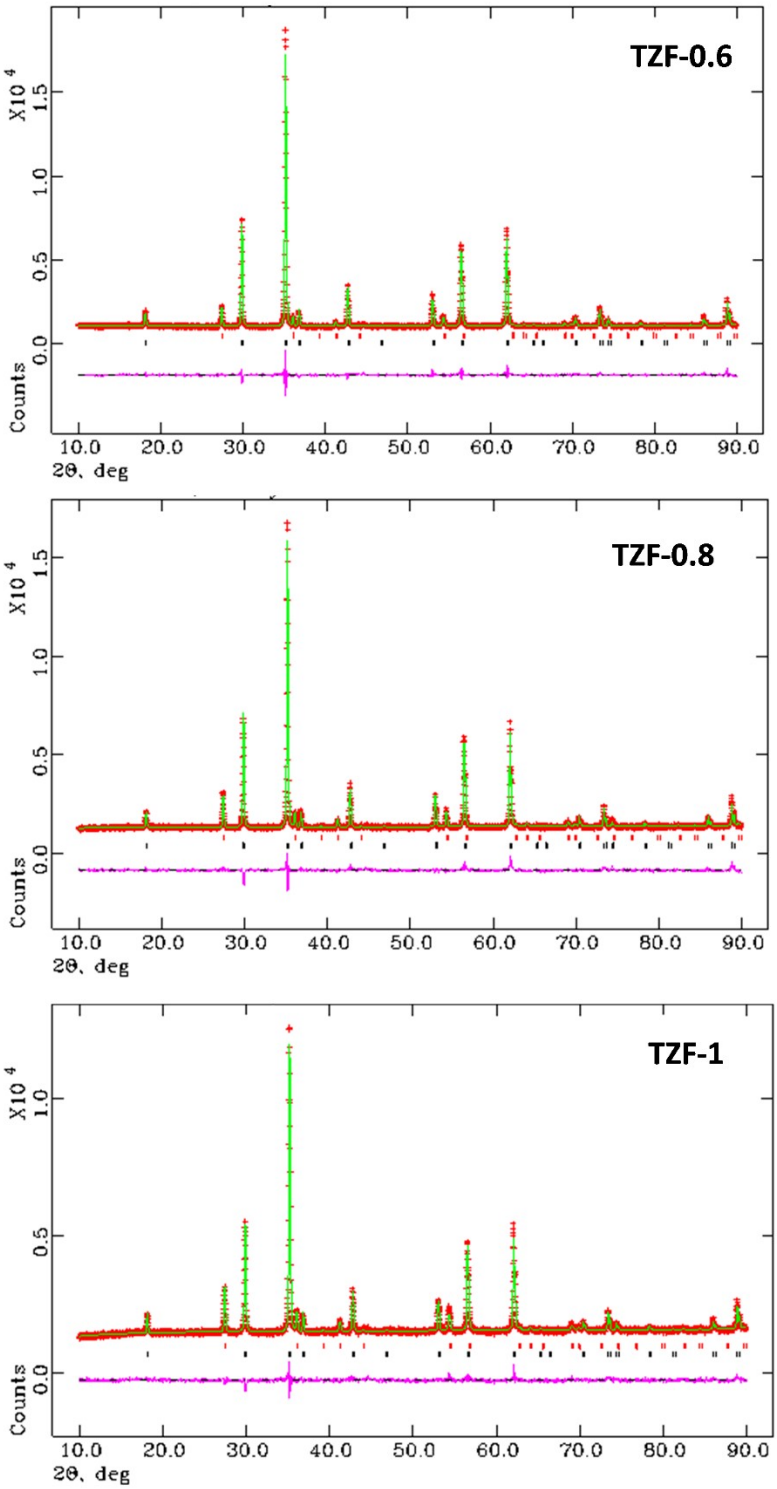

Figure S2- The experimental and refined patterns obtained on Rietveld analysis of TZF-0.6, TZF-0.8 and TZF-1 samples

Table S2 - The fractional coordinates, sites occupied and extent of occupancy obtained upon Rietveld refinement for TZF-0.6,TZF-0.8 and TZF-1 composition

TZF-0.6						
Atom	**Site**	**x**	**Y**	**z**	**Uiso**	**Occupancy**
Zn(1)	8a	0.125	0.125	0.125	0.01784	1
Ti	16d	0.5	0.5	0.5	0.00340	0.5
Zn(2)	16d	0.5	0.5	0.5	0.00674	0.2
Fe	16d	0.5	0.5	0.5	0.0250	0.3
O	32e	0.259159	0.259159	0.259159	0.01668	1
TZF-0.8						
Atom	**Site**	**x**	**y**	**z**	**Uiso**	**Occupancy**
Zn(1)	8a	0.125	0.125	0.125	0.01995	1
Ti	16d	0.5	0.5	0.5	0.02500	0.5
Zn(2)	16d	0.5	0.5	0.5	0.02500	0.1
Fe	16d	0.5	0.5	0.5	0.0250	0.4
O	32e	0.259902	0.259902	0.259902	0.01520	1
TZF-1						
Atom	**Site**	**x**	**y**	**z**	**Uiso**	**Occupancy**
Zn	8a	0.125	0.125	0.125	0.02145	1
Ti	16d	0.5	0.5	0.5	0.02500	0.5
Fe	16d	0.5	0.5	0.5	0.00213	0.5
O	32e	0.260221	0.260221	0.260221	0.01354	1

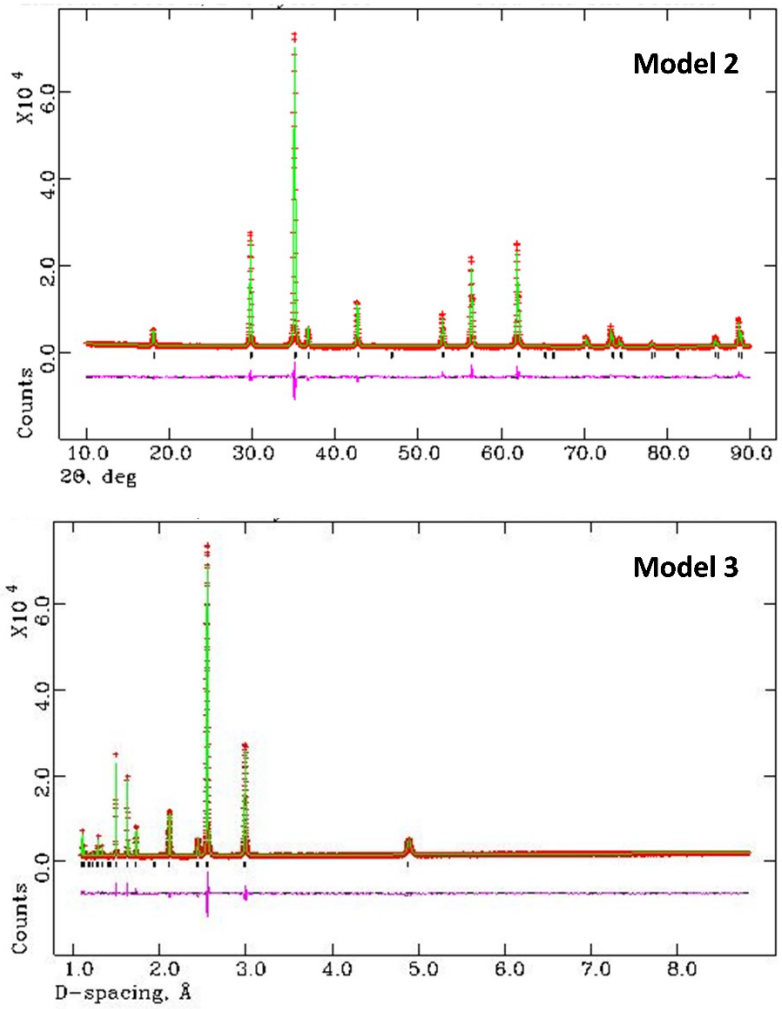

Figure S3- The experimental and refined patterns obtained on Rietveld analysis of TZF-0.2 as per model 2 and 3.

Table S3 - The fractional coordinates, sites occupied and extent of occupancy obtained upon Rietveld refinement for TZF-0.2 as per model 2 and 3.

Model 2

Atom	Site	x	y	z	Uiso	Occupancy
Zn(1)	8a	0.125	0.125	0.125	0.01240	0.8
Ti	16d	0.5	0.5	0.5	0.01245	0.5
Zn(2)	16d	0.5	0.5	0.5	0.02060	0.5
Fe	8a	0.125	0.125	0.125	0.02500	0.2
O	32e	0.257162	0.257162	0.257162	0.01976	1

Model 3

Atom	Site	x	y	z	Uiso	Occupancy
Zn(1)	8a	0.125	0.125	0.125	0.01456	0.9
Ti	16d	0.5	0.5	0.5	0.01055	0.5
Zn(2)	16d	0.5	0.5	0.5	0.01936	0.45
Fe(1)	8a	0.125	0.125	0.125	0.01986	0.1
Fe(2)	16d	0.5	0.5	0.5	0.0250	0.05
O	32e	0.25848	0.25848	0.25848	0.0250	1

Table S4 - The percentages of main and secondary phases calculated through Rietveld refinement for the developed pigment compositions.

Composition	Percentage of phases present
TZ	90.01 (Main phase) 7.57 (ZnO) 2.366 ($ZnTiO_3$)
TZC-0.2	91.29 (Main phase) 8.70 (ZnO)
TZC-0.4	93.7 (Main phase) 6.3 (ZnO)
TZC-0.6	99.5 (Main phase) 0.49 (TiO_2)
TZC-0.8	94.36 (Main phase) 5.63(CuO)
TZC-1	92.73 (Main phase) 7.263 (CuO)
TZF-0.2	100 (Main phase)
TZF-0.4	100 (Main phase)
TZF-0.6	90.72 (Main phase) 9.2 (TiO_2)
TZF-0.8	86.65 (Main phase) 13.34 (TiO_2)
TZF-1	77.11 (Main phase) 22.88 (TiO_2)

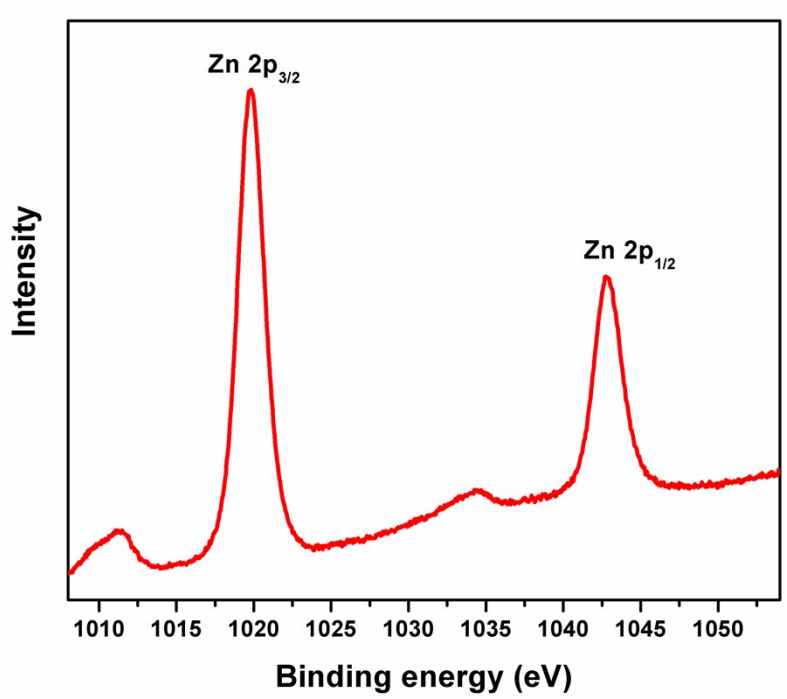

Figure S4- High resolution XPS of Zn $2p_{3/2}$ and Zn $2p_{1/2}$

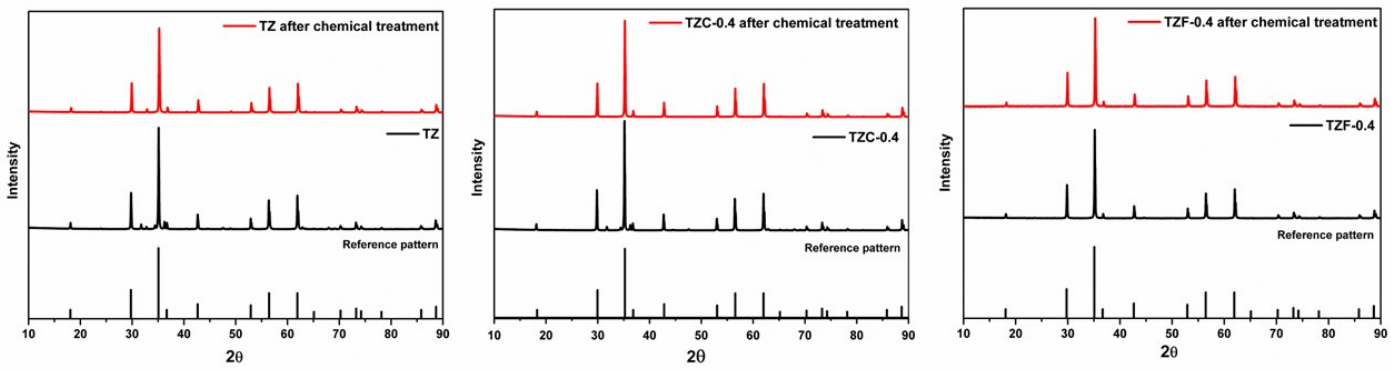

Figure S5- XRD patterns of TZ, TZC-0.4 and TZF-0.4 after chemical treatment, given in comparison with XRD patterns of reference and untreated samples.