1,1'-bis-(diphenylphosphino)ferrocene appended d8- and d10-configuration based thiosquarates: The molecular and electronic configurational insights into their sensitization and co-sensitization properties for dye sensitized solar cells

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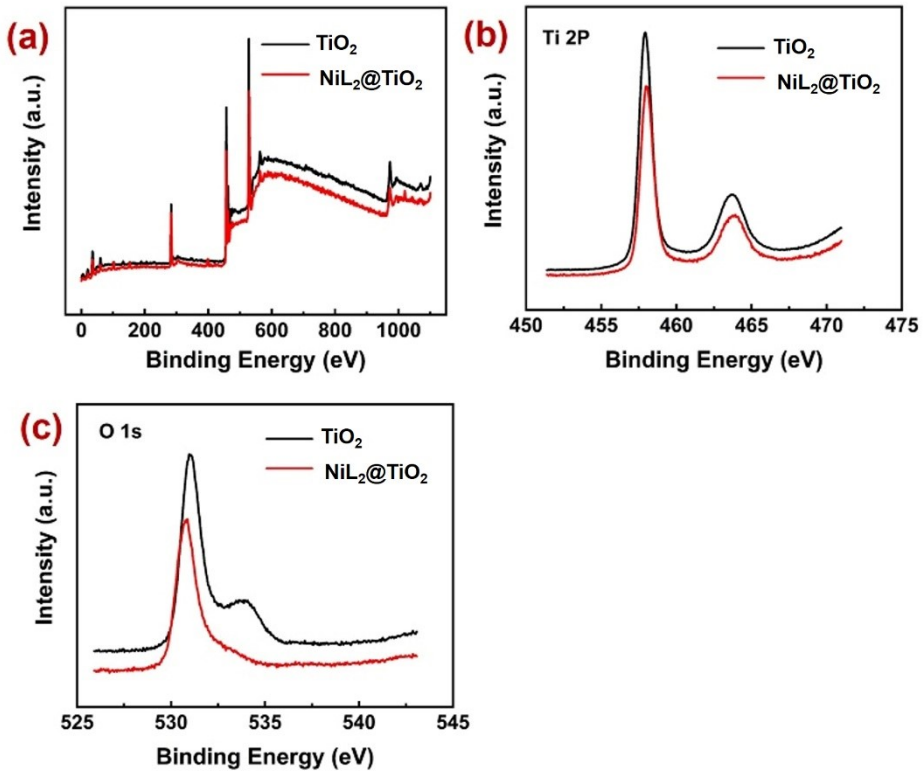

Fig. S1 XPS results for TiO_2 and $NiL_2@TiO_2$ (a) Full; (b) deconvoluted Ti 2p; (c) deconvoluted O1s.

Table S1 DSSC performances of some previously reported co-sensitizers.

Dyes	**J_{sc} (mA.cm^{-2})**	**V_{oc} (V)**	**FF**	***η*(%)**	**IPCE (%)**	**Ref**
Zn/N719	12.90±0.03	0.750±0.002	0.73±0.01	7.10±0.02	47±1	
Hg/N719	11.98±0.04	0.730±0.002	0.73±0.01	6.38±0.04	39±1	1
Cd/N719	12.35±0.03	0.740±0.003	0.73±0.01	6.68±0.03	42±1	
ZnL/N719/TiO_2	14.46	0.74	0.62	6.65	42	2a
CdL/N719/TiO_2	14.35	0.73	0.60	6.30	41	
HgL/N719/TiO_2	13.92	0.70	0.61	5.96	40	
1/N719/TiO_2	17.99	0.70	0.61	7.68	82	2b
4/N719/TiO_2	16.69	0.71	0.58	6.85	79	
1/N719/TiO_2	17.48	0.75	0.63	8.27	-	2c
2/N719/TiO_2	17.39	0.74	0.60	7.73	-	
2-Py-Zn/N719	10.43	-0.727	0.63	4.80	39	2d
3-Py-Zn/N719	10.93	-0.736	0.63	5.06	41	
4-Py-Zn/N719	14.08	-0.727	0.64	6.52	44	
N719/Zn-Fc	11.25 ± 0.06	0.776 ± 0.02	0.65 ± 0.02	5.71 ± 0.04	63 ± 2	3
N719/Cd-Fc	10.15 ± 0.04	0.758 ± 0.03	0.65 ± 0.01	5.00 ± 0.05	59 ± 1	
N719/Hg-Fc	9.38 ± 0.06	0.742 ± 0.02	0.66 ± 0.01	4.57 ± 0.03	57 ± 1	

Computational Details

To ascertain the electronic nature of all the sensitizers**,** density functional theory (DFT) calculations were performed. The molecular geometries of all the five sensitizers were optimized using the B3LYP exchange-correlation functional.[4] The MDF10 basis set for Fe,

Ni and Zn, while CEP-121G basis set was used for Cd while 6-31G** basis set for other atomic centers were employed to execute geometry optimization. These optimized structures were used for the time-dependent density functional theory (TD-DFT) calculations for first 30 vertical excitation were executed using CAM-B3LYP functional and polarised continuum model (PCM) having solvent parameters of dichloromethane. Also, TiO_2 cluster, $(TiO_2)_{30}$@**sensitizers** were optimized and the starting coordinates were taken from the relaxed geometry of $(TiO_2)_{30}$ cluster and sensitizers. All calculations were performed using the Gaussian 09 program.[5] In order to obtain the density of states plots for sensitizers, $(TiO_2)_{30}$ cluster and $(TiO_2)_{30}$@**3-Py-Ni** GaussSum 3.1 was used.[6]

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