Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Exploring the Influence of Electron Donating/ Withdrawing Groups on Hexamolybdate-Based Derivatives for Efficient *p*-Type Dye-Sensitized Solar Cells (DSSCs)

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Cartesian coordinate of final optimized geometries of systems **1-5**

System **1**: **E**=-2483.54730080 a.u.

Mo	-0.38521700	0.70716300	0.00000000
Mo	0.00235700	-1.54657900	2.34617200
Mo	2.35355900	-1.16214600	0.00000000
Mo	-2.34222200	-1.95716000	0.00000000
Mo	0.00235700	-1.54657900	-2.34617200
Mo	0.41037700	-3.91044300	0.00000000
O	0.00127100	-1.49838900	0.00000000
O	0.01195200	-1.58810500	4.05779400
O	4.06203700	-1.05780900	0.00000000
O	-4.04662700	-2.11426600	0.00000000
O	0.01195200	-1.58810500	-4.05779400
O	0.54612300	-5.61469300	0.00000000
O	-2.13808500	0.11335900	0.00000000
O	-0.14547500	0.31938200	1.91963100
O	1.73990300	0.56042400	0.00000000
O	-0.14547500	0.31938200	-1.91963100
O	0.16257000	-3.43427800	1.85154300
O	-1.87609700	-1.72374100	1.87273600
O	1.88947500	-1.41032500	1.86471200
O	2.12086100	-3.26296000	0.00000000
O	1.88947500	-1.41032500	-1.86471200

O	-1.67964900	-3.66608800	0.00000000
O	-1.87609700	-1.72374100	-1.87273600
O	0.16257000	-3.43427800	-1.85154300
N	-0.57161100	2.46109000	0.00000000
C	-0.71926100	3.81720600	0.00000000
C	-2.00618600	4.37237100	0.00000000
C	-2.11814000	5.77487500	0.00000000
H	-3.11546100	6.19952000	0.00000000
C	-1.02763700	6.63402000	0.00000000
C	1.48915100	6.87736500	0.00000000
H	1.39194900	7.95445200	0.00000000
C	2.74764700	6.30248900	0.00000000
C	2.87237100	4.89496700	0.00000000
H	3.86719400	4.46027700	0.00000000
C	1.75191200	4.09260600	0.00000000
H	1.85771400	3.01285100	0.00000000
C	0.45364100	4.66080000	0.00000000
C	0.30771300	6.08825700	0.00000000
C	-3.25542700	3.52712200	0.00000000
H	-3.03261700	2.45900500	0.00000000
H	-3.86921900	3.74917000	-0.88195200
H	-3.86921900	3.74917000	0.88195200
C	-1.29320800	8.09703500	0.00000000
O	-0.46601800	8.99634700	0.00000000
O	-2.61977500	8.39284400	0.00000000
H	-2.67328600	9.36690400	0.00000000
N	3.96205300	7.08986400	0.00000000
H	3.96222200	7.71078100	-0.80954300
H	3.96222200	7.71078100	0.80954300

System **2**: **E**= -2542.72608523 a.u

Mo	-0.54439800	-0.54499200	-0.00004500
Mo	1.67080300	0.02423800	2.34639000
Mo	1.09793900	2.33807500	0.00015600
Mo	2.26832700	-2.27937000	-0.00013600
Mo	1.67083800	0.02454400	-2.34637100
Mo	3.99494200	0.62211500	0.00006700
O	1.61777900	0.01832900	0.00000900
O	1.71267100	0.03764300	4.05768500
O	0.85631200	4.03296000	0.00026600
O	2.56349900	-3.96562300	-0.00024700
O	1.71273300	0.03817200	-4.05766300
O	5.68283500	0.89478300	0.00009200
O	0.18403900	-2.24578200	-0.00015200
O	-0.17543500	-0.27668800	1.92072000
O	-0.56851600	1.58657300	0.00008700
O	-0.17541000	-0.27643800	-1.92076900
O	3.53945500	0.33701000	1.85116600
O	2.00083700	-1.83362300	1.87263500
O	1.38250000	1.89386500	1.86529600
O	3.20784500	2.27382800	0.00017000
O	1.38253500	1.89410900	-1.86503700
O	3.91812500	-1.47909200	-0.00006600
O	2.00087000	-1.83337900	-1.87285300
O	3.53948000	0.33724700	-1.85107600
N	-2.28475500	-0.83653200	-0.00006400
C	-3.63791200	-1.01672200	-0.00005400
C	-4.15952400	-2.32031600	-0.00003700
C	-5.55608100	-2.46487000	-0.00002100
H	-5.95919500	-3.47113400	-0.00000700
C	-6.44352000	-1.39371100	-0.00002800
C	-6.76094900	1.10977700	-0.00005000
H	-7.83001000	0.96909500	-0.00003500

C	-6.20468200	2.37612100	-0.00007200
C	-4.79709800	2.54584900	-0.00008300
H	-4.39268000	3.55343900	-0.00009800
C	-3.97432200	1.44796000	-0.00007100
H	-2.89830000	1.58373600	-0.00007100
C	-4.50925700	0.13095300	-0.00005600
C	-5.93246500	-0.04573100	-0.00004600
C	-3.27985700	-3.54621200	-0.00003000
H	-2.21862500	-3.29167000	-0.00004000
H	-3.48242300	-4.16633600	-0.88218000
H	-3.48240900	-4.16631900	0.88213500
C	-7.89752000	-1.69418700	-0.00001100
O	-8.81760100	-0.88876500	0.00007900
O	-8.16410600	-3.02756400	0.00014300
H	-9.13682400	-3.10134500	0.00022800
O	-6.92109600	3.53403100	-0.00008900
C	-8.34220000	3.44600500	-0.00019100
H	-8.70939700	2.92756100	-0.89420700
H	-8.70954500	2.92763700	0.89380700
H	-8.70480100	4.47517100	-0.00026500

System **3**: **E**= -2585.45706744 a.u.

Mo	-0.24825100	0.62177500	-0.20248400
Mo	2.04508300	-0.28947700	-2.37169200
Mo	1.17511400	-2.33456800	0.17688300
Mo	2.61404800	2.20043100	-0.16242300
Mo	1.73418300	0.15406200	2.38749800
Mo	4.12377600	-0.77183500	0.21584800
O	1.84645900	-0.05218000	0.00311900
O	2.17203100	-0.26582700	-4.08019300
O	0.73878500	-3.99003400	0.12859400
O	3.10990900	3.83880200	-0.10648300

O	1.67206700	0.11193000	4.09938400
O	5.76424600	-1.24862000	0.28510000
O	0.66445400	2.31088400	-0.02873600
O	0.22467800	0.46103400	-2.03721300
O	-0.42832400	-1.38806700	-0.12096600
O	-0.01951400	0.43759300	1.83420800
O	3.80394600	-0.56944300	-1.76345700
O	2.51871000	1.75001800	-1.92701200
O	1.44814000	-1.94969200	-1.91393700
O	3.14987800	-2.39855100	0.04246300
O	1.29373800	-1.88423700	1.94241200
O	4.21116200	1.20100800	0.13755200
O	2.35913900	1.80501200	1.93044000
O	3.57568000	-0.60070500	1.99786300
N	-1.95044600	1.09087000	-0.24544800
C	-3.27144600	1.41247400	-0.16784100
C	-3.64426200	2.76370600	-0.12674700
C	-5.01423500	3.06406700	-0.04330500
H	-5.30062800	4.10852800	-0.00918200
C	-6.01296700	2.09644800	-0.00188000
C	-6.59112500	-0.36626200	-0.00641400
H	-7.63638100	-0.10284200	0.05957500
C	-6.21291000	-1.70087000	-0.04833300
C	-4.82910400	-1.99752300	-0.13142000
H	-4.49109200	-3.02682100	-0.16523400
C	-3.88216900	-0.99624900	-0.16934100
H	-2.82890700	-1.25144900	-0.22647000
C	-4.26202000	0.36578300	-0.12922100
C	-5.65415000	0.69997900	-0.04571300
C	-2.60889200	3.85666300	-0.16831600
H	-2.00212100	3.79630200	-1.07960200
H	-1.91161500	3.77836900	0.67391400

H	-3.08256000	4.84195400	-0.13373800
C	-7.42348400	2.55693700	0.08756400
O	-8.42791100	1.86062800	0.09939100
O	-7.53447200	3.90999100	0.16065300
H	-8.49124700	4.09367400	0.21060900
C	-7.29080600	-2.80161700	0.00513700
C	-8.28084900	-2.61550500	-1.16947500
C	-6.69006400	-4.21740300	-0.09473900
C	-8.06053200	-2.69681200	1.34384800
H	-8.78054400	-1.64216000	-1.13074300
H	-7.76450600	-2.69087700	-2.13355200
H	-9.05539800	-3.39171700	-1.13731200
H	-6.01012500	-4.43432300	0.73686500
H	-7.49581300	-4.95967800	-0.06392400
H	-6.14115300	-4.36318900	-1.03210800
H	-8.83653900	-3.47062500	1.39759400
H	-7.38447300	-2.83410600	2.19578700
H	-8.54807900	-1.72266100	1.45495900

System **4**: **E**= -2616.77466126 a.u.

Mo	-0.59051100	0.44821300	0.00000000
Mo	0.03613000	-1.75356900	2.34592800
Mo	2.33379200	-1.11791400	0.00000000
Mo	-2.25352200	-2.40767200	0.00000000
Mo	0.03613000	-1.75356900	-2.34592800
Mo	0.69135000	-4.06114000	0.00000000
O	0.02810800	-1.69794500	0.00000000
O	0.04849000	-1.79109000	4.05699700
O	4.02274100	-0.84022500	0.00000000
O	-3.93286100	-2.73890700	0.00000000
O	0.04849000	-1.79109000	-4.05699700
O	1.00180800	-5.74217100	0.00000000

O	-2.27129300	-0.32152900	0.00000000
O	-0.31071000	0.08686000	1.91612800
O	1.54489600	0.52995000	0.00000000
O	-0.31071000	0.08686000	-1.91612800
O	0.39379700	-3.61172200	1.85183100
O	-1.81319800	-2.12629800	1.87185500
O	1.89634200	-1.41625800	1.86460700
O	2.32199200	-3.23557300	0.00000000
O	1.89634200	-1.41625800	-1.86460700
O	-1.41426600	-4.03693600	0.00000000
O	-1.81319800	-2.12629800	-1.87185500
O	0.39379700	-3.61172200	-1.85183100
N	-0.93925500	2.17955800	0.00000000
C	-1.18893500	3.51982300	0.00000000
C	-2.51285200	3.97871400	0.00000000
C	-2.73317100	5.36993100	0.00000000
H	-3.75993400	5.71718900	0.00000000
C	-1.71246400	6.30849800	0.00000000
C	0.77334300	6.74153600	0.00000000
H	0.59556100	7.80593000	0.00000000
C	2.06903100	6.25297200	0.00000000
C	2.31073600	4.85821600	0.00000000
H	3.33477400	4.50095500	0.00000000
C	1.25418600	3.97890300	0.00000000
H	1.43640200	2.90972100	0.00000000
C	-0.08423000	4.45160600	0.00000000
C	-0.34130100	5.86239800	0.00000000
C	-3.69354900	3.04128100	0.00000000
H	-3.38987100	1.99325900	0.00000000
H	-4.32179600	3.21744900	-0.88200700
H	-4.32179600	3.21744900	0.88200700
C	-2.08448200	7.75009000	0.00000000

O	-1.32266100	8.70428200	0.00000000
O	-3.42768300	7.94553000	0.00000000
H	-3.55665800	8.91267400	0.00000000
C	3.24389100	7.16349400	0.00000000
O	4.40522400	6.79358500	0.00000000
O	2.91021900	8.47551000	0.00000000
H	3.75000800	8.97257100	0.00000000

System **5**: **E**= -2632.70348366 a.u.

Mo	-0.59051100	0.44821300	0.00000000
Mo	0.03613000	-1.75356900	2.34592800
Mo	2.33379200	-1.11791400	0.00000000
Mo	-2.25352200	-2.40767200	0.00000000
Mo	0.03613000	-1.75356900	-2.34592800
Mo	0.69135000	-4.06114000	0.00000000
O	0.02810800	-1.69794500	0.00000000
O	0.04849000	-1.79109000	4.05699700
O	4.02274100	-0.84022500	0.00000000
O	-3.93286100	-2.73890700	0.00000000
O	0.04849000	-1.79109000	-4.05699700
O	1.00180800	-5.74217100	0.00000000
O	-2.27129300	-0.32152900	0.00000000
O	-0.31071000	0.08686000	1.91612800
O	1.54489600	0.52995000	0.00000000
O	-0.31071000	0.08686000	-1.91612800
O	0.39379700	-3.61172200	1.85183100
O	-1.81319800	-2.12629800	1.87185500
O	1.89634200	-1.41625800	1.86460700
O	2.32199200	-3.23557300	0.00000000
O	1.89634200	-1.41625800	-1.86460700
O	-1.41426600	-4.03693600	0.00000000
O	-1.81319800	-2.12629800	-1.87185500

O	0.39379700	-3.61172200	-1.85183100
N	-0.93925500	2.17955800	0.00000000
C	-1.18893500	3.51982300	0.00000000
C	-2.51285200	3.97871400	0.00000000
C	-2.73317100	5.36993100	0.00000000
H	-3.75993400	5.71718900	0.00000000
C	-1.71246400	6.30849800	0.00000000
C	0.77334300	6.74153600	0.00000000
H	0.59556100	7.80593000	0.00000000
C	2.06903100	6.25297200	0.00000000
C	2.31073600	4.85821600	0.00000000
H	3.33477400	4.50095500	0.00000000
C	1.25418600	3.97890300	0.00000000
H	1.43640200	2.90972100	0.00000000
C	-0.08423000	4.45160600	0.00000000
C	-0.34130100	5.86239800	0.00000000
C	-3.69354900	3.04128100	0.00000000
H	-3.38987100	1.99325900	0.00000000
H	-4.32179600	3.21744900	-0.88200700
H	-4.32179600	3.21744900	0.88200700
C	-2.08448200	7.75009000	0.00000000
O	-1.32266100	8.70428200	0.00000000
O	-3.42768300	7.94553000	0.00000000
H	-3.55665800	8.91267400	0.00000000
C	3.24389100	7.16349400	0.00000000
O	4.40522400	6.79358500	0.00000000
O	2.91021900	8.47551000	0.00000000
H	3.75000800	8.97257100	0.00000000

As system **4** has two carboxy groups at 1- and 7-positions, the system **4**-$(NiO)_4$ and **4′**-$(NiO)_4$ ($(NiO)_4$ connected with carboxy groups at 1- and 7-position, respectively.) were optimized at the level of B3LYP/6-31G* for nonmetal atoms (LANL2DZ for Mo and Ni). After BSSE correction, the E_{bind} decreases in the order: **4**-$(NiO)_4$ (-88.14eV) > **4′**-$(NiO)_4$ (-84.14eV). Therefore, the system **4**-$(NiO)_4$ is more stable than system **4′**-$(NiO)_4$.

Moreover, the FMOs of systems **4**-$(NiO)_4$ and **4′**-$(NiO)_4$ were studied and the results were shown in Fig. S1. For these two systems, the distributions of α-LUMO, β-HOMO and β-LUMO are similar to those of isolated dyes. In addition, the α-HOMO in system **4**-$(NiO)_4$ localizes over the organic groups and $(NiO)_4$ cluster. The α-HOMO in system **4′**-$(NiO)_4$ localizes over –COOH at 7-position and $(NiO)_4$ cluster. The distribution of occupied molecular orbitals and unoccupied molecular orbitals for system **4**-$(NiO)_4$ are in a straight line. And it may contribute to the intramolecular charge transfer. So, we selected system **4**-$(NiO)_4$ as a theoretical model system to study.

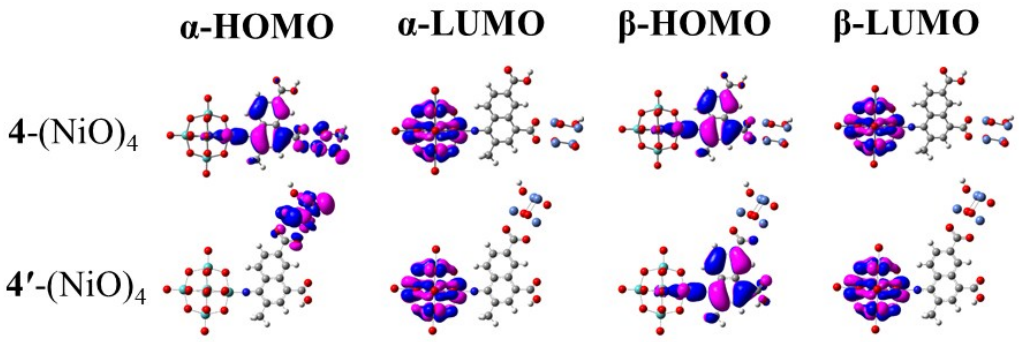

Fig. S1 Isosurfaces of selected frontier orbitals of systems **4**-$(NiO)_4$ and **4′**-$(NiO)_4$.