Supporting Information

How Do Transition-Metal-Substituted POMs Modify Photoanode of Dye-Sensitized Solar Cells? A DFT Study

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1.1 Details about the heat maps of transition density matrix (TDM)

The TDM can be contracted to atom based form according to correspondence between basis functions and atoms, it will be symbolized as p. In Multiwfn, below construction ways are available:

Way 1: $p_{AB} = \sum\limits_{\mu \in A} \sum\limits_{v \in B} (P_{\mu v}^{tran})^2$

Way 2: $p_{AB} = \sqrt{\sum\limits_{\mu \in A} \sum\limits_{v \in B} (P_{\mu v}^{tran})^2}$

Way 3: $p_{AB} = \sum\limits_{\mu \in A} \sum\limits_{v \in B} \left| P_{\mu v}^{tran} \right|$

Way 4: $p_{AA} = \sum\limits_{\mu \in A} \left| P_{\mu\mu}^{tran} \right|$, $p_{A \neq B}^{tran} = \sqrt{\sum\limits_{\mu \in A} \sum\limits_{v \in B} (P_{\mu v}^{tran})^2}$

where μ and v denote the basis functions centered at atom A and on B, respectively. Both original form and symmetrized form of TMD could be employed here.

If way 1 is employed, the p will correspond to the matrix of so-called correlated electron-hole probability diagram (CEHPD), its (A,B) element was interpreted as the probability of simultaneously finding a hole in atom A and an electron in atom B (this interpretation is not strictly true in general cases).

*If the p are constructed in way 2, 3 or 4, the resulting matrix may be referred to as atom transition density matrix. For example, the way 4 has been employed in Chem. Rev., **102**, 3171 (2002). However, using way 2 or 3 is more preferred because that the diagonal terms obtained in way 4 is often too large compared to the off-diagonal terms.*

Assume that the TDM used to construct p was not symmetrized, the general structure of the resulting p could be expressed in below form

$$p \equiv electron \begin{bmatrix} 1,N & 2,N & L & N,N \\ M & M & N & M \\ 1,2 & 2,2 & L & N,2 \\ 1,1 & 2,1 & L & N,1 \end{bmatrix}$$
$$hole$$

In complete analogy with the discussion about TDM, the physical meaning of the matrix elements of p can be roughly understood as follows, irrespective of the choice of the specific way of constructing the p:

● Diagonal terms: If (A,A) is large, it implies that atom A has large contribution to both hole and electron, therefore the electron excitation should result in evident charge reorganization within atom A.

● Off-diagonal terms: If (A,B) is large, then atom A should have large contribution to hole and meantime atom B should have large contribution to electron, implying that electron excitation leads to CT from A to B.

If symmetrized form of TDM was used to build p, then CT directional information will not be reflected by p. In this case, if off-diagonal term (A,B)=(B,A) is large, then we can simply say that coherence between atoms A and B is strong during the electron excitation, in other words, change transfer occurs between atoms A and B. The heat map of p is particularly useful for analyzing large-size and highly conjugated molecules.
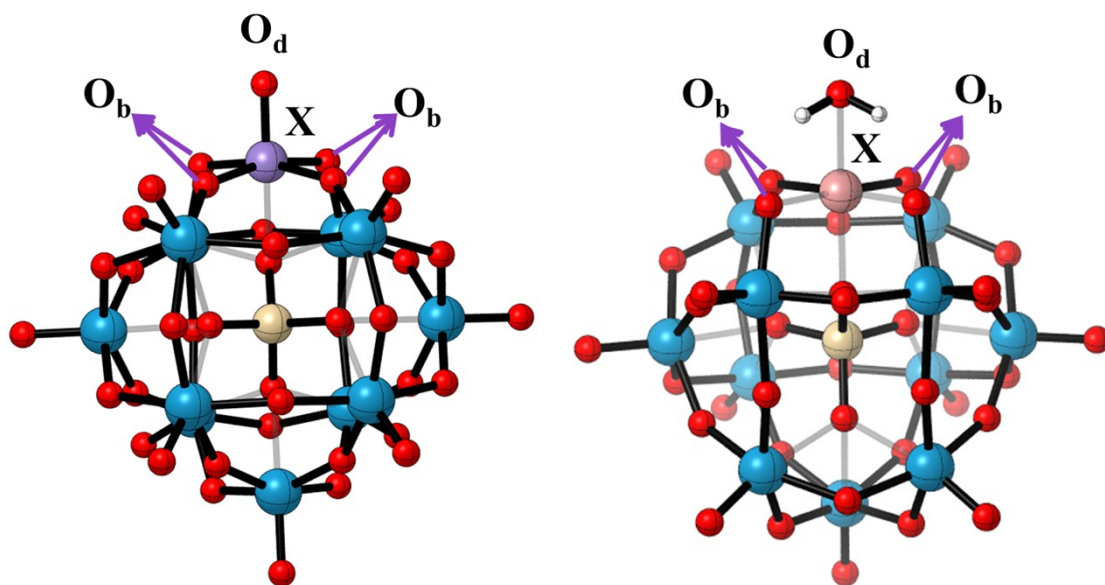
Figure S1. Geometrical structures of $SiW_{11}X^{n-}$. $X = Mn^{4+}$, Mn^{6+}, Ru^{6+}, Re^{6+} and Os^{6+}
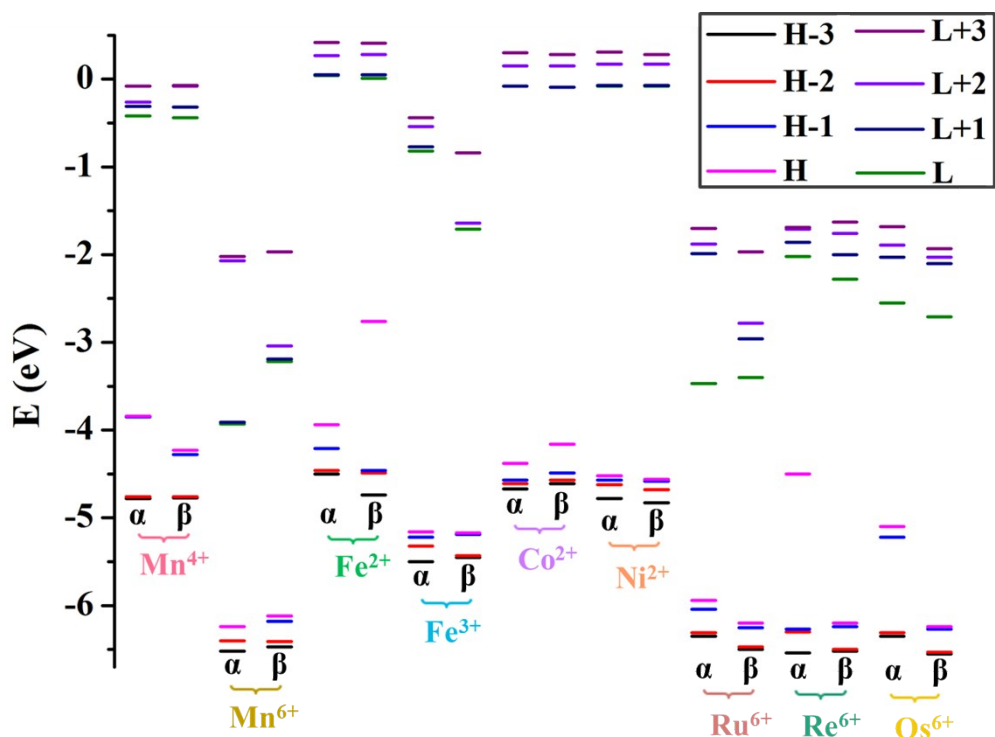
(left), $X = Fe^{2+}$, Fe^{3+}, Co^{2+} and Ni^{2+} (right).

Figure S2. The energy level diagram of $SiW_{11}X^{n-}$ ($X = Mn^{4+}$, Mn^{6+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ru^{6+}, Re^{6+} and Os^{6+}).
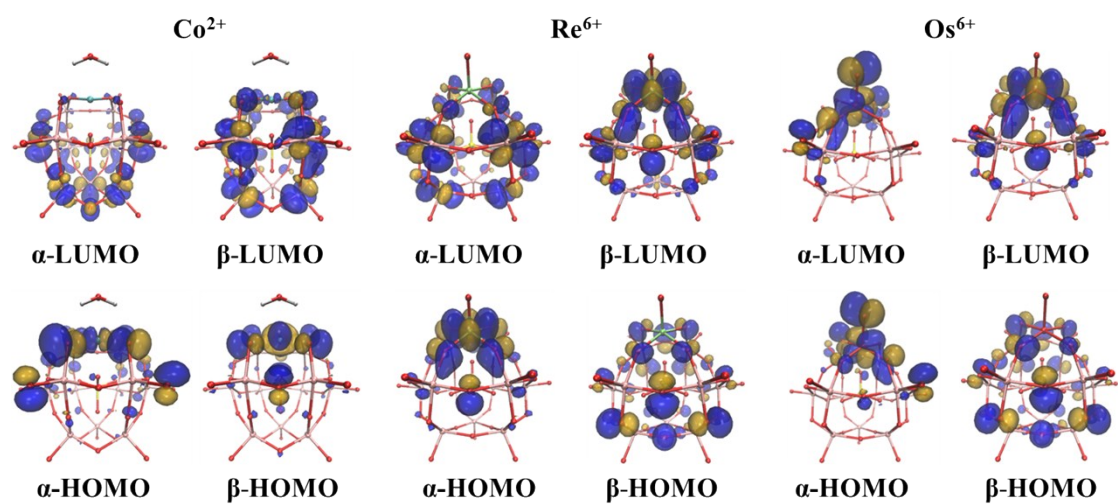
Figure S3. The frontier molecular orbital diagrams of $SiW_{11}X^{n-}$ ($X = Co^{2+}$, Re^{6+} and Os^{6+}).

Table S1. The bond lengths of substituted transition metals (X) and oxygens (O_b and O_d) in $SiW_{11}X^{n-}$ (X = Mn^{4+}, Mn^{6+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ru^{6+}, Re^{6+} and Os^{6+}) and the ionic radius (IR) for corresponding X.

X	X–O_b	X–O_d	IR
Mn^{4+}	1.917~1.965	1.653	0.53
Mn^{6+}	1.741~1.902	1.556	0.39
Fe^{2+}	2.076~2.108	2.219	0.77
Fe^{3+}	1.952~2.009	2.168	0.63
Co^{2+}	2.020~2.151	2.281	0.72
Ni^{2+}	2.021~2.094	2.248	0.63
Ru^{6+}	1.848~2.026	1.727	0.70
Re^{6+}	1.908~1.946	1.692	0.69
Os^{6+}	1.862~1.999	1.741	0.69

Table S2. Excitation energy E_v (eV), maximum absorption wavelengths λ_{max} (nm), and oscillator strengths f of $SiW_{11}Co^{6-}$ by different functionals.

$SiW_{11}Co^{6-}$	E_v	λ_{max}	f
Exp.	4.88	254	—
PBE0	4.35	285	0.035
	4.77	260	0.028
M06-2X	5.28	235	0.103
	5.04	246	0.046

Table S3. The relationship of the redox potentials E_{red} (eV) and the H–L gaps (eV) and the maximum absorption wavelengths λ_{max} (nm) for $SiW_{11}X^{4-}$ (X = Mn^{6+}, Ru^{6+} and Os^{6+}).

system	E_{red}	H–L gaps	λ_{max}
$SiW_{11}Mn^{4-}$	2.20	2.31	332
$SiW_{11}Ru^{4-}$	1.62	2.47	248
$SiW_{11}Os^{4-}$	0.84	2.55	232