ESI for:

Spectroscopic Properties of Zn(Salphenazine) Complexes and their Application in Small Molecule Solar Cells

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Extension of parts of the DFT-calculated structure for complex 9:
Central part of the structure showing the octanuclear Zn₈ core. Zn atoms in purple and orange.
Figure S1: Comparison between absorption spectra of 1 in different solvents at a concentration of $1 \times 10^{-5}$ M.
Figure S2:

Figure S2: UV-Vis comparisons: (A) between di-substituted 5 and tetra-substituted 1; (B) comparison between tetra-substituted complexes 1-4. All UV-Vis spectra were recorded in THF at a concentration of 1 × 10⁻⁵ M.

1. R¹ = tBu ; R² = tBu
2. R¹ = R² = F
3. R¹ = R² = Cl
4. R¹ = R² = Br
5. R¹ = H ; R² = tBu
Figure S3: UV-Vis comparisons between di-substituted complexes 5-7:

5. $R^1 = t$Bu
6. $R^1 =$ allyl
7. $R^1 =$ Br

Figure S3: UV-Vis comparisons between di-substituted complexes 5-7.
EDDMs of transitions 7, 13 and 14 for complex 1·THF:

Transition 7:

Energy = 3.18 eV (389 nm)

$f = 0.92; \text{H-3→LUMO (69\%)}$
Transition 13:

Energy = 3.79 eV (327 nm)

\( f = 0.48; \text{H-2} \rightarrow \text{L+1} \ (75\%) \)

Transition 14:

Energy = 3.94 eV (315 nm)

\( f = 0.36; \text{H-3} \rightarrow \text{L+1} \ (75\%) \)
Calculated absorption spectra and relative EDDMs of transitions 1-4 for complex 10·THF:

The calculated spectra of complex 10 (vide infra), even though slightly overestimates the energy of the transitions, shows that the lowest absorption band is formed by 4 different transitions (EDDMs next page). In particular it has been observed that transition 2 (398 nm page S10) has a π-π* character with the electron density migrates from the two phenyl side groups towards the phenyl backbone. This type of transition, characterized by a charge transfer, is equivalent to the transition 2 in complex 1 (511 nm, see Fig 8C) but in the case of the latter the more extended π-system of the phenazine provoke a red-shift. Same considerations can be done for transition 3 of complex 10 (389 nm, see page S11) and transition 7 (395 nm, see page S7) of 1, but in this case the transitions are characterized by π-π* with no charge transfer character. Since this reason the more extended π-conjugated system of 1 causes a blue-shift of this transition.

TD-DFT Calculate spectra of 10
Transition 1:

Energy = 2.92 eV (424 nm)

\[ f = 0.26; \text{HOMO} \rightarrow \text{LUMO} \ (87\%) \]

Transition 2:

Energy = 3.16 eV (398 nm)

\[ f = 0.33; \text{H}-1 \rightarrow \text{LUMO} \ (92\%) \]
Transition 3:

Energy = 3.27 eV (395 nm)

$f = 0.32; \text{HOMO} \rightarrow \text{L+1} (93\%)$

Transition 4:

Energy = 3.37 eV (368 nm)

$f = 0.02; \text{H-1} \rightarrow \text{L+1} (87\%)$
Cyclic voltammetry for complex 1:

Conditions used: degassed CH$_3$CN, r.t., NBu$_4$PF$_6$ (0.1 M) as electrolyte. See further the experimental conditions in the main text described under “Differential Pulse Voltammetry” in the Experimental section.
NMR spectra (copies) for complexes 1, 2, 3, 5, 8 and 9:

Full NMR trace (DMSO-$d_6$)
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Full NMR trace (DMSO-$d_6$)
Aromatic region (DMSO-$d_6$)

Aliphatic region: the peaks at $\delta = 3.33$ and 2.55 ppm indicate MeOH and DMSO solvent impurities.
Full NMR trace (DMSO-d$_6$)
Aromatic region (DMSO-$d_6$)

Aliphatic region: the peak at $\delta = 2.55$ ppm indicates a DMSO solvent impurity.
Full NMR trace (DMSO-d$_6$)
Aromatic region (DMSO-$d_6$)

Aliphatic region: the peaks at $\delta = 3.51$ and 2.55 ppm indicate MeOH and DMSO solvent impurities.
Full NMR trace (DMSO-$d_6$)
Aromatic region (DMSO-$d_6$)

Aliphatic region: the peaks around 3.44 ppm indicate a MeOH solvent impurity.
Full NMR trace (DMSO-\textit{d}_6)
Aromatic region (DMSO-d$_6$)

Aliphatic region (DMSO-d$_6$): no sign of DMSO/MeOH impurities.
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Full NMR trace (DMSO-\textit{d}_6)
Aromatic region (DMSO-$d_6$)

Aliphatic region (DMSO-$d_6$): MeOH impurity located at $\delta = 3.17$ ppm.
Representative MALDI(+) MS spectra:

Chemical Formula: C$_{42}$H$_{48}$N$_{4}$O$_{2}$Zn
Exact Mass: 704.31
Molecular Weight: 706.24
Chemical Formula: C_{104}H_{58}N_{16}O_{16}Zn_{8}
Exact Mass: 2295.84
Molecular Weight: 2308.70

Full trace; zoom on the next page.
Zoom of the main peak around $m/z$ 2300: below the simulated pattern for complex 9.