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Structure and Absorption in C₆₀ – Zinc Tetra-Phenylporphyrin Composite Materials: A Computational Study

Izaak Mitchell^{1,2} and Alister J. Page^{*1,2}

¹ *Newcastle Institute for Energy and Resources*

² *School of Environmental and Life Sciences, Discipline of Chemistry, The University of Newcastle, NSW 2308, Australia*

*Corresponding author: Email: alister.page@newcastle.edu.au, Ph: +61-2-40333957

Abstract

We investigate structure and photo-excitation in C_{60} – zinc tetraphenylporphyrin (ZnTPP) and $C_{60}F_{48}$ -ZnTPP complexes, which are promising candidates for organic photovoltaic devices. The C_{60} -ZnTPP complex results from π - π stacking between the fullerene and porphyrin structures, and has a binding energy of 76.0 kJ/mol. Fluorination of the C_{60} cage leads to decrease in ZnTPP binding, due to reduced π - π stacking interaction. C_{60} -ZnTPP photo-excitation results largely from internal ZnTPP $\pi \rightarrow \pi^*$ transitions, although delocalised ZnTPP $\pi \rightarrow C_{60} \pi^*$ transitions are also observed below 300 nm. The more intense photo-excitations of $C_{60}F_{48}$ -ZnTPP arise solely from localised ZnTPP $\pi \rightarrow \pi^*$ transitions.

Graphical Abstract

1. Introduction

Since the structural characterisation of C₆₀ fullerene in 1985 [1], there has been extensive research into fullerene derivatives and fullerene composite materials. C₆₀ is amongst the most versatile molecules; it has unique chemistry [2-4], it can modify material properties [5-8] and can even act as an enzyme inhibitor [9]. One of the most intensely studied applications of C₆₀ is in the field of organic electronics. This is driven by the C₆₀ cage's ability to accept electrons, whilst maintaining good charge separation and low levels of charge recombination [10]. These properties have so far been exploited in devices including light emitting diodes [11, 12] and organic photovoltaics (OPVs) [13-15].

Fullerene OPVs generally use conjugated polymers and/or porphyrins as photo-active electron donors, although other donors such as TiO₂ have also been developed [16]. Porphyrins are naturally occurring electron donor molecules that exhibit excellent UV/Vis absorbance, and a number of fullerene/porphyrin OPVs have so far been reported [17-20]. The utility of these composite materials is limited by the limited interaction between the porphyrin and fullerene moieties, and a number of approaches towards increasing this interaction have recently been reported [20, 21]. Smets *et al.* [20] have demonstrated that a porphyrin/fluorinated C₆₀ fullerene (C₆₀F₄₈) composite exhibits a marked increase in both binding and charge transfer. However, the mechanisms responsible for this enhanced interaction and charge transfer remain unknown.

In this work we investigate the structure and absorption of C₆₀ and fluorinated C₆₀ (C₆₀F₄₈) zinc-tetraphenylporphyrin (ZnTPP) complexes, towards understanding how complexation influences the absorption of the ZnTPP moiety. We show that C₆₀-ZnTPP is weakly bound, yet highly symmetric, driven by π - π stacking interactions. Time dependent density functional theory (TD-DFT) calculations show that the C₆₀ cage has little effect on ZnTPP excitations in the C₆₀-ZnTPP complex between ~300 – 650 nm. The predominant excitations correspond to ZnTPP $\rightarrow$ ZnTPP transitions, consistent with the relatively weak binding in this complex. Fluorination of the C₆₀ cage decreases fullerene-ZnTPP interaction, since π - π stacking is overcome by electrostatic attractions between F (on C₆₀) and Zn (on the porphyrin). As a result, low-lying LUMOs in the C₆₀F₄₈-ZnTPP complex are lowered, which enhances absorption near 400 nm, with excitations being dominated by ZnTPP $\rightarrow$ C₆₀ molecular orbital (MO) transitions.

2. Computational Details

The structure of $(I_h)C_{60}$ -ZnTPP and $(S_6, D_3)C_{60}F_{48}$ -ZnTPP complexes has been studied here using a 2-layer ONIOM [22-25] approach. The S_6 and D_3 $C_{60}F_{48}$ structures characterised by Troyanov *et al.* [26] are employed here. Applying ONIOM to extended conjugated structures such as fullerenes presents special challenges. The importance of including a sufficiently large region of the C_{60} cage in the ONIOM high-level region has been demonstrated several times [27-32]. In this work, the high level includes the entire ZnTPP structure except for the four phenyl moieties, and the hemi-spherical C_{32} portion of the fullerene cage closest to the ZnTPP (Figure 1). The remaining atoms constitute the low level. For the fluorinated $C_{60}F_{48}$ cage, fluorine atoms bonded to high/low level carbon atoms were also included in the high/low levels, respectively. Solá *et al.* have previously demonstrated the importance of including dispersion corrections in DFT when modeling structure and reactivity in fullerenes and fullerene based materials [28]. On this basis, we use Truhlar's M06-2X functional [33] in conjunction with the 6-31G(d,p) basis set as the high level method, due to its ability in describing non-bonding and π - π interactions. A recent investigation [34] has highlighted that this functional describes structure in similar C_{60} composite systems well, although it slightly underestimates binding energies compared to the more accurate spin-component-scaled (SCS) MP2 method. For the low level, we employ the AM1 semi-empirical Hamiltonian. In comparison to the M06-2X/6-31G(d,p) $(S_6)C_{60}F_{48}$ structure, ONIOM(M06-2X/6-31G(d,p):AM1) yields root mean squared errors in bond lengths, angles and dihedral angles of only 0.179 Å, 0.868° and 1.81°.

Absorption spectra of C_{60} -ZnTPP and $(S_6, D_3)C_{60}F_{48}$ -ZnTPP at their respective ONIOM(M06-2X/6-31G(d,p):AM1)-optimised geometries were calculated using TD-DFT, at the ω B97-D/6-31G(d,p) level of theory. Lee *et al.* [35] have recently demonstrated that, for porphyrin-based molecules, Head-Gordon's ω B97-D exchange correlation functional [36] provided the most accurate excitation energies compared to a number of other functionals. Excitations up to 279.9 nm (4.43 eV) and 365.9 (3.39 eV) were calculated for C_{60} -ZnTPP and $(S_6)C_{60}F_{48}$ -ZnTPP, respectively. Numerical convergence issues prevented higher excitations from being calculated. However, absorption of $(D_3)C_{60}F_{48}$ -ZnTPP and $(S_6)C_{60}F_{48}$ -ZnTPP were consistent in this range. For $(D_3)C_{60}F_{48}$ -ZnTPP, only two additional higher energy excitations were observed at 356 nm ($f \sim 0.03$) and 323 nm ($f \sim 0.01$). However, we do not anticipate a notable difference between higher energy absorptions in $(S_6)C_{60}F_{48}$ -ZnTPP and $(D_3)C_{60}F_{48}$ -ZnTPP, based on their structural similarity, and the consistency in their absorption

spectra in this region. Our discussion here therefore focuses on the absorption of (*S*₆)C₆₀F₄₈-ZnTPP. All calculations reported here were performed using Gaussian09 [37].

3. Results and Discussion

3.1 Structure of the C₆₀-ZnTPP Complex

ONIOM(M06-2X/6-31G(d,p):AM1)-optimised geometries of the C₆₀-ZnTPP complex are shown in Figure 1(a). In order to identify the most stable local minimum, a number of starting configurations were considered for this complex, including those with the ZnTPP Zn atom directly over the C₆₀ pentagon, hexagon and individual carbon atoms in the C₆₀ cage. None of these configurations correspond to local minima. The only stable configuration of the C₆₀-ZnTPP complex found is one in which the Zn atom is located directly over the midpoint of the C=C double in the C₆₀ cage. The ZnTPP moiety binds to C₆₀ with an equilibrium Zn – C=C midpoint distance of 2.60 Å, and a binding energy (ΔE) of 76.0 kJ/mol. Binding energy is calculated here as,

$$\Delta E = E_{\text{C}_{60}\text{-ZnTPP}} - (E_{\text{C}_{60}} + E_{\text{ZnTPP}}) \quad (1)$$

where E is the electronic energy without zero-point and thermal corrections.

The proximity of the Zn atom to the C₆₀ C=C suggests that some formal bonding character may exist between the ZnTPP and the C₆₀ cage. However, this is not the case, and we conclude that the main factor binding the two fragments remains π - π stacking, as is the case for related (non-porphyrin) fullerene complexes [34]. Supplementary ONIOM calculations using the BP86 functional [38, 39] instead of M06-2X for the high-level reveal the importance of describing non-bonding interactions, such as the π - π stacking, in C₆₀ composite materials. For example, using ONIOM(BP86/6-31G(d,p):AM1), the Zn – C=C midpoint distance increases to 4.5 Å and the binding energy is reduced to ~4 kJ/mol.

In the configuration shown in Figure 1, the ZnTPP N atoms are also aligned directly and symmetrically over C-C bonds, at a distance of 3.45 Å. The phenyl groups in the ZnTPP moiety are twisted by 120° with respect to the plane of the porphyrin structure. As anticipated, these phenyl groups exhibit considerable conformational flexibility in the gas-phase, however this would be inhibited on a solid substrate such as Au(111) [20]. However, we do not anticipate substrate adsorption to influence structure in the remainder of the C₆₀-ZnTPP complex, since these phenyl groups are peripheral to the structure as a whole.

Figure 1. (a) ONIOM(M06-2X/6-31G(d,p):AM1) optimised structure of C₆₀-ZnTPP complex. Grey, blue, purple and white atoms are C, N, Zn and H, respectively. The two atom representations denote the ONIOM high and low level regions. (b) Dominant MOs in C₆₀-ZnTPP excitations between 279 and 580 nm (see Figure 3(a), Table 1). MO isosurfaces are shown at $0.02 e/a_0^3$.

3.1 Structure of (*D*₃, *S*₆)C₆₀F₄₈-ZnTPP Complexes

The structure of the (*S*₆)C₆₀F₄₈-ZnTPP and (*D*₃)C₆₀F₄₈-ZnTPP complexes are shown in Figure 2(a) and (b), respectively. The binding between the fluorinated fullerene cage and the ZnTPP moiety in these complexes decreases slightly compared to the C₆₀-ZnTPP complex. However, there is no strong correlation between ΔE and C₆₀F₄₈ symmetry (*D*₃ versus *S*₆).

For the (S_6)C₆₀F₄₈-ZnTPP complex, ONIOM(M06-2X/6-31G(d,p):AM1) predicts a ΔE value of 53.4 kJ/mol, while ΔE for the (D_3)C₆₀F₄₈-ZnTPP complex is 56.2 kJ/mol. The minimal distance between the C₆₀F₄₈ fluorine atoms and the plane of the ZnTPP moiety is 2.53 Å for (S_6)C₆₀F₄₈-ZnTPP, and 2.53 Å for (D_3)C₆₀F₄₈-ZnTPP; this is a slight contraction compared to the C₆₀ - ZnTPP distance in Figure 1.

Analysis shows that there is no bonding character between the two fragments in both of these C₆₀F₄₈-ZnTPP complexes. Consequently, both (S_6)C₆₀F₄₈ and (D_3)C₆₀F₄₈ structures retain their familiar ‘deflated’ cage structures [26]. Furthermore, there are limited π - π interactions between the two fragments. This is expected, since adding 48 fluorine atoms to C₆₀ (in both S_6 and D_3 isomers) results in only 6 isolated C=C double bonds in the fullerene cage. Moreover, the exohedral addition of fluorine atoms increases the effective diameter of the cage, preventing conjugated adsorbents from approaching close enough for any π - π interactions to become significant.

Figure 2. ONIOM(M06-2X/6-31G(d,p):AM1) optimised structure of (a) (S_6)C₆₀F₄₈-ZnTPP and (b) (D_3)C₆₀F₄₈-ZnTPP complexes. Grey, blue, purple, aqua and white atoms are C, N, Zn, F and H, respectively. The two atom representations denote the ONIOM high and low level regions.

Instead, π - π interactions in these complexes are not as strong as electrostatic attractions between the partial negative charges on C₆₀F₄₈ fluorine atoms and the partial positive charge

of the ZnTPP Zn atom. ONIOM(BP86/6-31G(d,p):AM1) calculations, which lack explicit dispersion corrections in the high-level region, corroborate this proposal; whereas C₆₀-ZnTPP is essentially dissociative at this level of theory (discussed above), both the (*S*₆)C₆₀F₄₈-ZnTPP and (*D*₃)C₆₀F₄₈-ZnTPP complexes are bound by ~ 16 kJ/mol, and exhibit Zn-F distances of 3.15 Å.

Figure 2 shows that, for both the *S*₆ and *D*₃ structural isomers, the C₆₀F₄₈ and ZnTPP fragments are arranged such that electrostatic Zn-F and N-F interactions are optimised. Ultimately this electrostatic attraction dominates binding between the two fragments. The greater binding for the *S*₆ isomer here presumably arises from a greater electrostatic attraction, due to the presence of more fluorine atoms in the immediate vicinity of the porphyrin core structure. The ZnTPP fragment is prevented from adsorbing more closely to the C₆₀F₄₈ structure by the steric repulsions between individual fluorine atoms and the ZnTPP phenyl groups. The latter remain out-of-plane in the fluorinated complex, as for the C₆₀-ZnTPP complex.

3.3 Absorption in C₆₀-ZnTPP

We have established binding in C₆₀-ZnTPP and C₆₀F₄₈-ZnTPP is dominated by π - π stacking and electrostatic interactions, respectively, between the two fragments. We now consider what impact this has on the electronic excitations in these complexes, which is of fundamental importance in understanding how these composite materials can be utilised in OPV devices.

The electronic transitions of C₆₀ (in the absence of the ZnTPP) consist of four distinct regions: a region of intense peaks between 190 – 350 nm; a region of weaker transitions between 350 – 430 nm; a weak continuum of transitions between 430 – 640 nm (with a maximum near 540 nm); and three weak bands between 640 – 690 nm [40-42]. In this work, we aim to characterise the influence of C₆₀ on the absorptivity of the ZnTPP complex, and understand the intermolecular transitions between C₆₀ and ZnTPP. These transitions are observed between 300 – 400 nm, and so we do not consider transitions below 300 nm (which will be dominated by the most intense C₆₀ – C₆₀ transitions in any case).

Figure 3. TD- ω B97-D/6-31G(d,p) absorption spectrum of (a) C₆₀-ZnTPP (>279.9 nm) and (b) (S₆)C₆₀F₄₈-ZnTPP (>365.9 nm), at the respective ONIOM(M06-2X/6-31G(d,p):AM1)-optimised geometries.

The simulated absorption spectrum of C₆₀-ZnTPP is shown in Figure 3(a). The corresponding excitation energies, oscillator strengths and principle MO transitions are listed in Table 1. Electronic excitations in the C₆₀-ZnTPP complex are dominated by ZnTPP $\pi \rightarrow \pi^*$ transitions. The main features of the C₆₀-ZnTPP absorption spectrum are the transitions at 377.2 and 378.4 nm. The 377.2 nm excitation is dominated by HOMO-1 $\rightarrow$ LUMO+3 and HOMO $\rightarrow$ LUMO+4 transitions, each of which is centered solely on the ZnTPP moiety. The four phenyl moieties in the ZnTPP structure lie out of the porphyrin plane, and so make little to no contribution to either of these low lying unoccupied MOs. The C₆₀-ZnTPP HOMO has limited contributions from these phenyl groups, and also the C₆₀ cage. The 378.4 nm

excitation is also dominated by HOMO-1 $\rightarrow$ LUMO+4 and HOMO $\rightarrow$ LUMO+3 transitions. However, there is a limited contribution from the HOMO-2 $\rightarrow$ LUMO+1 transition, which is $C_{60} \pi \rightarrow \pi^*$. ZnTPP $\pi \rightarrow \pi^*$ transitions are also largely responsible for the weaker bands near 570 nm. The continuum of weak C_{60} bands between 500 – 600 nm [42] is obscured by these stronger ZnTPP $\pi \rightarrow \pi^*$ transitions, and transitions from occupied MOs on the ZnTPP moiety to unoccupied MOs on the fullerene cage. The excitation at 572.3 nm arises due to ZnTPP $\pi \rightarrow \pi^*$ transitions alone. The dominant transition is the HOMO $\rightarrow$ LUMO+4, although there is considerable contribution also from HOMO-1 $\rightarrow$ LUMO+3. For the excitation at 576.2 nm, the HOMO $\rightarrow$ LUMO+3 and HOMO-1 $\rightarrow$ LUMO+4 ZnTPP $\pi \rightarrow \pi^*$ transitions are dominant, however, this excitation has a weak contribution from the HOMO $\rightarrow$ LUMO $\pi(\text{ZnTPP}) \rightarrow \pi^*(C_{60})$ transition.

Intermolecular transitions between C_{60} /ZnTPP moieties are observed near 280 nm, with only intermediate intensities. The absorption spectrum of C_{60} itself here includes a number of weak excitations [42], however these transitions are not observed here and presumably they are quenched by the presence of the ZnTPP moiety. The predominant excitation in this region (at 280.8 nm) is delocalised over several $\pi(C_{60}) \rightarrow \pi^*(\text{ZnTPP})$ and $\pi(\text{ZnTPP}) \rightarrow \pi^*(C_{60})$ transitions. The dominant transition here is the HOMO-14 $\rightarrow$ LUMO+2 transition; HOMO-14 is centred on the ZnTPP moiety, yet has C_{60} character as well. Similarly, $\pi(C_{60}) \rightarrow \pi^*(\text{ZnTPP})$ transitions between low-lying OMOs (HOMO-28, HOMO-24) and LUMO+2 contribute here. The weaker excitation at 293.3 nm is predominantly HOMO-1 $\rightarrow$ LUMO+5, and to a lesser extent HOMO-7 $\rightarrow$ LUMO, both of which are $\pi(\text{ZnTPP}) \rightarrow \pi^*(C_{60})$ transitions.

3.4 Absorption in $C_{60}F_{48}$ -ZnTPP

Fluorination of the C_{60} cage in C_{60} -ZnTPP leads to enhanced absorption between 300 – 400 nm, primarily since low-lying LUMOs are lowered in energy. Absorption in the $(S_6)C_{60}F_{48}$ -ZnTPP complex consists of a group of intense peaks near 365 nm, and a group of weaker peaks near 550 nm (Figure 3(b)). These excitations are characterised in Table 2; key MOs associated with these excitations are shown in Figure 4.

Table 1. Principle excitation energies (λ) and oscillator strengths (f) of C₆₀-ZnTPP (See Figure 3(a)).

λ (nm)	f	Main Transitions			
279.9	0.1092	HOMO-21	→	LUMO+3	0.13 ^a
		HOMO-6	→	LUMO+5	0.13
		HOMO-5	→	LUMO+3	0.19
		HOMO-5	→	LUMO+7	0.12
		HOMO-2	→	LUMO+3	0.49
		HOMO-2	→	LUMO+4	-0.17
		HOMO-2	→	LUMO+6	-0.14
280.8	0.1200	HOMO-28	→	LUMO+2	0.19
		HOMO-24	→	LUMO+2	-0.19
		HOMO-23	→	LUMO+2	-0.11
		HOMO-22	→	LUMO	0.15
		HOMO-14	→	LUMO+2	-0.33
		HOMO-12	→	LUMO	-0.16
		HOMO-12	→	LUMO+3	-0.13
		HOMO-9	→	LUMO+2	-0.12
		HOMO-8	→	LUMO+4	0.14
		HOMO-4	→	LUMO+5	0.15
		HOMO-3	→	LUMO+3	0.16
		HOMO-3	→	LUMO+7	0.15
		HOMO-1	→	LUMO+16	0.13
293.3	0.0377	HOMO-7	→	LUMO	0.10
		HOMO-1	→	LUMO+5	-0.66
377.2	0.8426	HOMO-4	→	LUMO	-0.12
		HOMO-1	→	LUMO+3	0.50
		HOMO-1	→	LUMO+4	0.16
		HOMO	→	LUMO+3	-0.12
		HOMO	→	LUMO+4	0.40
378.4	0.7651	HOMO-2	→	LUMO+1	-0.13
		HOMO-1	→	LUMO+3	-0.15
		HOMO-1	→	LUMO+4	0.50
		HOMO	→	LUMO+3	-0.39
		HOMO	→	LUMO+4	-0.12
572.3	0.0227	HOMO-1	→	LUMO+3	-0.39
		HOMO-1	→	LUMO+4	-0.19
		HOMO	→	LUMO+3	-0.24
		HOMO	→	LUMO+4	0.49
576.1	0.0205	HOMO-1	→	LUMO+4	0.36
		HOMO	→	LUMO	0.22
		HOMO	→	LUMO+3	0.48
		HOMO	→	LUMO+4	0.23

^a Configuration interaction coefficient.

Figure 4. Dominant MOs in $(S_6)C_{60}F_{48}$ -ZnTPP excitations between 365 - 600 nm (see Figure 3(b), Table 1). MO isosurfaces are shown at $0.02 e/a_0^3$. Low-lying LUMOs, including LUMO – LUMO+5 do not contribute to these excitations.

Table 2 shows also that these $C_{60}F_{48} \rightarrow \text{ZnTPP}$ transitions are significantly less delocalised compared to the transitions for C_{60} -ZnTPP (Table 1). For example, the most intense excitations at 365.9 and 366.1 nm each arise from HOMO/HOMO-1 $\rightarrow$ LUMO+6/+7 ZnTPP $\pi \rightarrow \pi^*$ transitions. These same transitions are responsible for the weaker, lower-energy excitations near 560 nm. Figure 4 shows that the ZnTPP phenyl groups make a limited contribution to these excitations; this was not the case for the unfluorinated C_{60} -ZnTPP complex. This contribution from the ZnTPP phenyl groups, in the presence of fluorine, suggests that absorption in $C_{60}F_{48}$ -porphyrin composite materials can potentially be enhanced by substituting larger conjugated structures onto the porphyrin moiety.

High-lying occupied MOs in both C_{60} -ZnTPP and $C_{60}F_{48}$ -ZnTPP correspond to π orbitals on the central porphyrin structure (Figure 1(b), Figure 4). Although several low-lying unoccupied MOs (LUMO+3, +4) for C_{60} -ZnTPP also reside on the porphyrin core, the lowest unoccupied MOs (LUMO - LUMO+5) in $C_{60}F_{48}$ -ZnTPP reside exclusively on the

fluorinated C₆₀ cage. Table 2 shows that these LUMOs do not contribute to the primary excitations near 365 nm. For the D₃ isomer, these MOs play a role for extremely weak excitations observed at 375.4 and 356.5 nm ($f = 0.02$ and 0.04 , respectively), and so there is evidence of $\pi(\text{ZnTPP}) \rightarrow \pi^*(\text{C}_{60}\text{F}_{48})$ character for these excitations. A number of similar delocalised transitions (not shown in Table 2) are also observed for (S₆)C₆₀F₄₈-ZnTPP between 300 – 315 nm, however are extremely weak ($f > 0.001$).

Table 2. Principle excitation energies (λ) and oscillator strengths (f) of (S₆)C₆₀F₄₈-ZnTPP (See Figure 3(b)).

λ (nm)	f	Main Transitions			
365.9	1.2078	HOMO-1	→	LUMO+6	0.31 ^a
		HOMO-1	→	LUMO+7	-0.43
		HOMO	→	LUMO+6	0.37
		HOMO	→	LUMO+7	0.27
366.1	1.1946	HOMO-1	→	LUMO+6	0.43
		HOMO-1	→	LUMO+7	0.31
		HOMO	→	LUMO+6	-0.27
		HOMO	→	LUMO+7	0.37
558.94	0.0129	HOMO-1	→	LUMO+6	-0.46
		HOMO	→	LUMO+7	0.52
559.5	0.0135	HOMO-1	→	LUMO+7	0.46
		HOMO	→	LUMO+6	0.52

^a Configuration interaction coefficient.

4. Conclusions

We have characterised the structure of the C₆₀-ZnTPP and C₆₀F₄₈-ZnTPP complexes, and determined the influence of the C₆₀/C₆₀F₄₈ on the excitation of the adsorbed porphyrin moiety. ONIOM calculations show that the C₆₀-ZnTPP structure is highly symmetric, with the porphyrin Zn atom arranging itself immediately over the C=C double bond of the fullerene cage. Complexation occurs through π - π interactions, and binding strength is concomitant with this mechanism ($\Delta E = 76.0$ kJ/mol). In contrast, binding in C₆₀F₄₈-ZnTPP is slightly weaker ($\sim \Delta E$ kJ/mol), because these interactions are largely removed. Fluorination of the C₆₀ cage leads to the low-lying LUMOs being lowered in energy, which yields a greater influence on ZnTPP absorption in C₆₀F₄₈-ZnTPP, compared to C₆₀-ZnTPP. The dominant excitations in C₆₀-ZnTPP correspond to $\pi(\text{ZnTPP}) \rightarrow \pi^*(\text{ZnTPP})$ transitions,

although there is evidence of $\pi(\text{ZnTPP}) \rightarrow \pi^*(\text{C}_{60})$ and $\pi(\text{C}_{60}) \rightarrow \pi^*(\text{ZnTPP})$ transitions as well, particularly in the less intense excitations. A common feature of many of these excitations is that they are delocalised over several MO $\rightarrow$ MO transitions. Conversely, the more intense photo-excitations observed for $\text{C}_{60}\text{F}_{48}\text{-ZnTPP}$ arise from only the HOMO/HOMO-1 $\rightarrow$ LUMO+6/+7 $\text{ZnTPP } \pi \rightarrow \pi^*$ transitions. However, both the D_3 and S_6 isomers of this complex show a number of very weak excitations that show $\pi(\text{ZnTPP}) \rightarrow \pi^*(\text{C}_{60}\text{F}_{48})$ and $\pi(\text{C}_{60}\text{F}_{48}) \rightarrow \pi^*(\text{ZnTPP})$ character.

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