# Investigation of the push-pull effects on β-functionalized zinc porphyrin coordinated to C$_{60}$ donor-acceptor conjugates

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Investigation of the push-pull effects on β-functionalized zinc porphyrin coordinated to C$_{60}$ donor-acceptor conjugates

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Abstract

Two novel β-functionalized push-pull zinc porphyrins with amine or phenyl push groups and cyclic imide or carboxylic esters pull-groups have been newly synthesized for light energy harvesting applications. The ethynylphenyl spacers extended the conjugation of the porphyrin π-systems, as reflected by their red-shifted absorbance and fluorescence spectra. Computational studies performed at the B3LYP/6-31G* level indicated no steric hindrance between the porphyrin π-system and the substituents. The calculated HOMO and LUMO orbitals displayed significant delocalization in 1, where the electron density in the HOMO was localized over the push groups while the LUMO was extended over the porphyrin π- and pull groups. On the other hand, 2 did not display significant orbital segregation which is attributed to its weaker push-pull character. Electrochemical studies revealed smaller HOMO-LUMO gaps for the push-pull zinc porphyrins. As a consequence of the push-pull effects, reduction in fluorescence intensity and lifetime was observed. Femtosecond transient absorption spectral studies revealed successful formation of singlet excited state in both of the push-pull porphyrins. Donor-acceptor conjugates were subsequently built and characterized by coordinating an electron acceptor, C₆₀Im, via metal-ligand axial coordination. Efficient photoinduced charge separation in both donor-acceptor conjugates was witnessed wherein the charge separated states persisted tens of nanoseconds prior returning to the ground state.

Keywords: push-pull zinc porphyrin • fullerene • metal-ligand axial coordination• photoinduced electron transfer
**Introduction**

Push-pull porphyrins have been of intense research interest in recent years owing to their exceptional performance in dye-sensitized solar cells. The important roles of the push (electron-donating) and the pull (electron-withdrawing) groups on electro- and photophysical properties of porphyrins have been demonstrated in their ability to significantly improve the solar energy conversion efficiency of dye-sensitized solar cells. Push-pull porphyrins have also shown potentials in non-linear optical applications, photosynthetic modelling, and in other organic electronics.

As compared with their meso-functionalized counterparts, β-functionalized push-pull porphyrins have been rarely investigated owing to their synthetic difficulties. Nevertheless, functionalization at β-positions could bring novel set of electronic and optical properties to porphyrins, which are different from those of meso-functionalized porphyrins. In recent years, we have engaged in the development of synthetic methodologies to access β-functionalized π-extended porphyrins. In a previous work, we reported the synthesis and preliminary characterizations of a series of β-functionalized push-pull dibenzoporphyrins carrying amine (electron-donating) groups and cyclic imide/ester (electron-withdrawing) groups. Our studies show that the inclusion of an amine group and an ethynylphenyl bridge in the donor (push) component make remarkable impact on their electronic and optical properties.

In order to further investigate these interesting compounds, in this work, we present the zinc analogues of these push-pull porphyrins, 1 and 2 (see Figure 1 for structures). Their spectral and chemical properties were elucidated through various spectral, electrochemical, computational and transient spectral techniques. Further, these porphyrins were allowed to interact with C\textsubscript{60} functionalized with a phenylimidazole entity, C\textsubscript{60}Im, via metal-ligand axial coordination to form the donor-acceptor conjugate. The structural integrity of the conjugates was arrived by performing systematic physico-chemical studies. In addition, excited state events occurring in the push-pull porphyrin-C\textsubscript{60} conjugates, as probed by time-resolved emission and transient absorption studies operating at different time scales, are also presented.
Figure 1. Structures of the push-pull zinc porphyrins, 1 and 2, and phenylimidazole functionalized fulleropyrroldine, C$_{60}$Im.

Experimental

Chemicals

Buckminsterfullerene, C$_{60}$ (+99.95%), was obtained from SES Research, (Houston, TX). All the reagents were from Aldrich Chemicals (Milwaukee, WI) while the bulk solvents utilized in the syntheses were from Fischer Chemicals. Tetra-$n$-butylammonium hexafluorophosphate, ($n$-Bu$_4$N)PF$_6$, used in electrochemical studies was from Fluka Chemicals.

Spectral Measurements

The UV-visible spectral measurements were carried out with a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. The fluorescence lifetimes were evaluated by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right angle detection method was used. The $^1$H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Cyclic voltammograms were recorded on an EG&G model 263A electrochemical analyzer using a three electrode system. A platinum button electrode was used as
the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas.

**General Procedure for the Synthesis of Zinc Dibenzoporphyrins 1 and 2**

Dibenzoporphyrin (1 equiv) and Zn(OAc)$_2$ (10 equiv) were dissolved in a solvent mixture of MeOH/CHCl$_3$ (v/v, 1/3). The mixture was reflux for 12h. The progress of the metallation reaction was monitored with absorption spectroscopy. After the reaction was completed, the solvent was removed, and the residue was re-dissolved in CHCl$_3$, washed with water and brine. Final product was recrystallized in CH$_2$Cl$_2$/ MeOH to give the pure compounds.

**Compound 1**, Green solid (mp > 300 °C), 11 mg, 0.007 mmol, 93%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.98 (d, J = 4.7 Hz, 2H), 8.93 (d, J = 4.6 Hz, 2H), 8.06 – 7.99 (m, 10H), 7.94 (t, J = 1.7 Hz, 2H), 7.60 (dd, J = 7.8, 1.5 Hz, 4H), 7.46 – 7.37 (m, 6H), 7.32 (s, 2H), 6.99 (s, 2H), 3.89 (s, 6H), 1.51 (s, 36H), 1.48 (s, 36H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.64, 150.39, 150.31, 150.04, 144.89, 143.73, 142.27, 142.08, 140.76, 139.13, 131.49, 131.43, 131.20, 129.21, 128.34, 128.17, 128.06, 127.75, 127.68, 126.03, 123.91, 122.01, 121.75, 121.64, 120.70, 120.29, 92.46, 89.87, 52.12, 35.16, 35.10, 31.72, 31.65. HRMS (MALDI) m/z: [M]$^+$ Calcd for C$_{104}$H$_{108}$N$_4$O$_4$Zn 1540.7662; Found 1540.7687.

**Compound 2**, Green solid (mp > 300 °C), 12 mg, 0.007 mmol, 95%. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.07 (s, 4H), 8.21 – 7.98 (m, 12H), 7.59 – 7.50 (m, 8H), 7.48 (s, 2H), 7.40 (br.s, 1H), 6.95 (s, 2H), 6.78 (d, J = 7.9 Hz, 4H), 3.08 (s, 12H), 1.56 (s, 36H), 1.53 (s, 36H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.34, 151.15, 150.58, 150.51, 150.03, 149.90, 146.28, 143.72, 143.07, 141.94, 141.64, 138.52, 132.79, 132.38, 132.11, 131.39, 129.05, 128.67, 127.82, 127.65, 127.45, 126.61, 123.36, 122.35, 121.94, 121.65, 121.16, 120.47, 111.94, 111.05, 94.20, 88.11, 40.32, 35.23, 35.23, 31.80, 31.72. HRMS (MALDI) m/z: [M]$^+$ Calcd for C$_{112}$H$_{117}$N$_7$O$_2$Zn 1655.8560; Found 1655.8579.

**Femtosecond Pump-Probe Transient Spectroscopy**

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode
locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.10 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of the Libra (Compressed output 1.15 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a harmonic generator which produced second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of a white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

**Nanosecond Laser Flash Photolysis**

The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with second and third harmonics OPO (tuning range 410-2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with the powers of 1.0 to 3 mJ per pulse. The transient absorption measurements were performed using a Proteus UV-Vis-NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic which delivered white probe light and either a fast rise Si photodiode detector covering the 200-1000 nm range or a InGaAs photodiode detector covering 900-1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope.

**Results and Discussion**

**Synthesis of Compounds 1 and 2**

The synthesis of compounds 1 and 2 started with 1a-1c and 2a shown in Scheme 1, according to our previous publication (see experimental section for details). Metallation of porphyrin 1c and 2a with zinc acetate gave compounds 1 and 2. The structural integrity of these compounds was established from $^1$H and $^{13}$C NMR, and HR-mass techniques.
Scheme 1. Synthesis of push-pull zinc porphyrins 1 and 2. Reagents, conditions and yields: (a) NBS, CHCl₃, reflux, 8h, 92%; (b) but-3-en-1-yn-1-ylbenzene, Pd[P(tBu)₃]₂, K₂CO₃, THF, 25%; (c) Zn(OAc)₂, CHCl₃, MeOH, reflux, 12h, 95%; (d) aniline, pyridine, reflux, 72h, 85%; (e) NBS, CHCl₃, reflux, 8h, 96%; (f) 4-(but-3-en-1-yn-1-yl)-N,N-dimethylaniline, Pd[P(tBu)₃]₂, K₂CO₃, THF, 21%; (g) Zn(OAc)₂, CHCl₃, MeOH, reflux, 12h, 90%.

Absorbance and Fluorescence Properties of Push-Pull Zinc Porphyrins, 1 and 2

Zinc porphyrin 1 bears an electron-withdrawing cyclic imide group on one fused benzene ring and two electron-donating 4-amino-phenylethynyl groups on the opposite fused benzene ring. Compound 2 bears two electron-withdrawing ester groups on one fused benzene ring and two weakly electron-donating phenylethynyl groups on the other fused benzene ring. The UV-visible and fluorescence spectra of 1 in toluene is shown in Figure 2a and b (blue line). Peaks at 416, 478, 590, and 618 nm were observed. Excitation of 1 at the Soret band located at 478 nm revealed two emission peaks at 635 and 701 nm, respectively (Figure 2b, blue line). This was also the case when compound 1 was excited using one of their visible band peak maxima. UV-visible and fluorescence spectra of 2 in toluene are also shown in Figures 2a and 2b (red lines). Peaks at 460, 585, and 624 nm were observed. Excitation of 2 at the Soret band located at 460 nm revealed two emission peaks at 630 and 697 nm (see Figure 2b, red line). This spectral
behavior of 1 and 2 is different from what has been reported for pristine zinc
tetraphenylporphyrin, ZnTPP, where blue-shifted absorption and fluorescence spectra compared
to that of 1 and 2 were reported. The red-shifted spectral features in 1 and 2 could be attributed
to extended π-conjugation caused by the two benzo groups at the β-pyrrole positions, thus
narrowing the overall HOMO-LUMO gap and extending the absorption into the 650 nm range.
This effect is little more pronounced in the case of 1 having higher degree of extended
conjugation due to the presence of cyclic amide group. In addition to the red-shift considerable
broadening of the spectral bands was also observed. The full width at half maximum (fwhm)
calculated for the Soret band was found to be 1438 and 1168 cm\(^{-1}\), respectively for 1 and 2. The
observed red shift is not as a result of intermolecular association involving N or O atoms of
peripheral substituents coordinating to Zn center was clarified by concentration dependance
studies. No noticeable spectral shifts of both absorption and fluorescence peaks were observed
in the concentration range of 0.1 µM-1 mM, suggesting lack of intermolecular association.

![Figure 2.](image-url) (a) Absorption and (b) fluorescence spectra of 1 (blue lines) and 2 (red lines) in
toluene. The compounds were excited at the Soret peak maxima.

The fluorescence lifetime of 1 and 2 were also measured in toluene using time correlated
single photon counting (TCSPC) technique and nanoLED excitation sources (see Figure S1 in
SI). The monoexponential decay with a lifetimes of 1.49 ns (\(\chi^2 = 0.73\)) for 1 and 1.19 ns (\(\chi^2 =
0.64\)) for 2 were obtained. These lifetimes are about 20-40% smaller compared to ZnTPP being
1.85 ns in toluene.\(^{21}\) These observations suggest excited state events occurring within the zinc
porphyrin that likely involve the peripheral push-pull substituents.\(^{22}\)
Formation of 1:ImC\textsubscript{60} and 2:ImC\textsubscript{60} Supramolecular Donor-Acceptor Conjugates

Metal-ligand axial coordination approach has been one of the widely used methods to build self-assembled donor-acceptor conjugates.\textsuperscript{19,20} Here, metalloporphyrin or metallophthalocyanine with coordinatively unsaturated metal in the porphyrin cavity is allowed to interact with an electron donor or acceptor functionalized with one or more Lewis bases. Excited state electron and energy transfer in such donor-acceptor conjugates have been successfully demonstrated mimicking the primary events of photosynthesis. In the present study, we have extended this approach of building donor-acceptor conjugates derived from push-pull zinc porphyrins, 1 and 2 using fullerene, C\textsubscript{60} functionalized with a phenylimidazole functionality (C\textsubscript{60}Im in Figure 1). The formation of the donor-acceptor conjugates was monitored by optical absorption and fluorescence spectroscopy. Figure 3 shows the spectral changes observed during increased addition of ImC\textsubscript{60} to a solution of 1 and 2 in toluene. In both cases, the Soret band experienced a red-shift with an isosbestic point, characteristic of axial coordination to the central zinc ion.\textsuperscript{23} The presence of isosbestic point indicated the presence of only one equilibrium process, that is, formation of a 1:1 supramolecular complex. The binding constant, \(K\), was estimated by constructing a Benesi-Hilderbrand plot\textsuperscript{24} as shown in Figure 3 insets. From the slope and intercept, binding constants of \(4.6 \times 10^{4}\) and \(3.7 \times 10^{4}\) M\textsuperscript{-1} for the formation of 1:ImC\textsubscript{60} and

![Figure 3](https://mc06.manuscriptcentral.com/cjc-pubs)

**Figure 3.** Spectral changes observed during increasing addition of C\textsubscript{60}Im to a solution of (a) 1 and (b) 2 in toluene.
\textbf{2:ImC}_{60}, respectively, were recorded. The magnitude of these values indicate moderately stable complex formation. The fluorescence spectra recorded during the titration revealed quenching of zinc porphyrin upon binding to \textit{C} \textit{60}Im and such effect was more for \textbf{1} compared to \textbf{2} at a given concentration of added \textit{C} \textit{60}Im. These results indicate occurrence of excited state events, such as electron or energy transfer in the supramolecular donor-acceptor conjugates.

\textbf{Electrochemical and Spectroelectrochemical Properties of 1 and 2 and their Donor-Acceptor Conjugates}

First, electrochemical and spectroelectrochemical properties of the push-pull zinc porphyrins were investigated in dichlorobenzene containing 0.1 M (TBA)PF$_6$ by cyclic and differential pulse voltammetry (DPVs) techniques. The first two oxidations of \textbf{1} were found to be closely located and appeared at 0.32 and 0.40 V vs Fc/Fc$.^+$ The first two oxidations of \textbf{2} were located at 0.32 and 0.56 V vs Fc/Fc$.^+$. The first oxidation potential of both compounds was about 30 mV anodically shifted compared to ZnTPP due to the push-pull substituents. In the case of \textbf{1}, additional oxidations were also observed perhaps due to the presence of terminal amino substituents. During the cathodic scan reduction processes were also observed. The first reduction of \textbf{1} and \textbf{2} was located at -1.68 and -1.67 V vs Fc/Fc$,^+$ respectively. The electrochemical HOMO-LUMO gap (potential difference between the first oxidation and first reduction) was found to be 2.00 and 1.99 V, smaller by about 40 mV compared to pristine ZnTPP. Further, spectroelectrochemical studies were performed to ascertain that the redox reactions involve the porphyrin $\pi$-system and not the peripheral substituents. Figure 4a and b bottom panels show the spectral changes observed during the first oxidation. During the oxidation, there was a decrease in the Soret band of each compound along with a development and concurrent increase at 745 and 715 nm for \textbf{1} and \textbf{2}, respectively. The drastic change of the zinc porphyrin (ZnP) Soret band clearly shows that the oxidation occurs on the ZnP center suggesting the peripheral substituents are not directly involved.
Figure 4. Differential pulse voltammogram (top panel) and spectral changes during first oxidation (bottom panel) of (a) 1 and (b) 2 in dichlorobenzene containing 0.1 M (TBA)PF$_6$ as supporting electrolyte.

The electrochemical studies performed on the supramolecular 1:ImC$_{60}$ and 2:ImC$_{60}$ donor-acceptor systems revealed peaks corresponding to both porphyrin and C$_{60}$Im entities, however, without any significant noticeable differences (see Figure S2 in SI). The first two reductions corresponding to C$_{60}$ were located at -1.01 and -1.43 V vs Fc/Fc$^+$ for both 1:ImC$_{60}$ and 2:ImC$_{60}$ conjugates while the first two oxidations corresponding to the ZnP were located at 0.32 and 0.40 V vs Fc/Fc$^+$ for 1:ImC$_{60}$ and at 0.32 and 0.56 V vs Fc/Fc$^+$ for 2:ImC$_{60}$. Under the cyclic voltammetry time scale all four redox processes were fully reversible. The HOMO-LUMO gap for the donor-acceptor systems, that is, potential difference between the first oxidation of zinc porphyrin and first reduction of fullerene was found to be 1.32 V.

Geometry Optimization and Electronic Structure of 1 and 2

DFT calculations at the B3LYP/6-31G* level$^{25}$ were performed for 1 and 2 to provide insight into the electronic properties of these compounds. The HOMO of 1 is distributed along the amino groups and ethynylphenyl spacers while the LUMO is delocalized around the porphyrin core and the cyclic amide group. The HOMO of 2 is primarily on the porphyrin core.
but has delocalization to both the ethynylphenyl push groups and the ester pull groups while the LUMO is found completely on the porphyrin core. (see Figure 5a and b) The difference in these compounds can be attributed to the stronger push-pull substituents on 1. These frontier orbitals suggest that the electron-donating amino groups play a much more important role than the electron-withdrawing groups in the HOMO/LUMO orbital segregation.

The geometry and electronic structure of both conjugates was deduced from a computational study performed at the B3LYP/6-31G* level (see Figure 5c and d). Upon coordination of ImC$_{60}$ to form 1:ImC$_{60}$, the HOMO was found to be still delocalized over the two electron-donating amino groups and porphyrin core while the LUMO was fully localized on the fullerene entity. In 2:ImC$_{60}$, the HOMO was delocalized over the porphyrin core and phenylimidazole entity while the LUMO was fully localized on the fullerene entity.

![Frontier HOMO and LUMO of B3LYP/6-31G* optimized structures of (a) 1, (b) 2, (c) 1:ImC$_{60}$ and (d) 2:ImC$_{60}$.](image)

**Figure 5.** Frontier HOMO and LUMO of B3LYP/6-31G* optimized structures of (a) 1, (b) 2, (c) 1:ImC$_{60}$ and (d) 2:ImC$_{60}$.

The free energy change for charge recombination ($\Delta G_{CR}$) and charge separation ($\Delta G_{CS}$) for each conjugate was evaluated from the singlet excited state energies of 1 or 2 using spectroscopic, computational, and electrochemistry data following Rehm-Weller’s approach, according to equations i-ii.$^{26}$

\[-\Delta G_{CR} = E_{ox} - E_{red} + \Delta G_{S} \]  

(i)
\[ -\Delta G_{CS} = \Delta E_{00} - (-\Delta G_{CR}) \]  

(ii)

where \( \Delta E_{00} \) and \( \Delta G_S \) correspond to the energy of singlet excited state of either 1 or 2 \( (\Delta E_{00} = (1240/\lambda_{\text{Abs}} + 1240/\lambda_{\text{Fl}})/2) \), and electrostatic energy calculated according to dielectric continuum model (see equation iii), respectively. The \( E_{\text{ox}} \) and \( E_{\text{red}} \) represent the oxidation potential of the electron donor (1 or 2) and the reduction potential of the electron acceptor (ImC\(_{60}\)), respectively.

\[
\Delta G_s = e^2 / 4\pi\varepsilon_0 \left[ \left( \frac{1}{2} R_+ + \frac{1}{2} R_- \right) \Delta \left( \frac{1}{\varepsilon_R} \right) - \frac{1}{R_{\text{CC}} \varepsilon_R} \right]
\]

(iii)

The symbols \( \varepsilon_0 \), and \( \varepsilon_R \) represent vacuum permittivity and dielectric constant of the solvent used for photochemical and electrochemical studies, respectively. \( R_+ \) and \( R_- \) represent radii of the cation and anion, respectively. \( R_{\text{CC}} \) is the center-to-center distance between donor and acceptor entities of each conjugate being 12.3 Å. Values of \( \Delta G_{CR} \) calculated by this approach was found to be -1.32 for both \( 1:\text{ImC}_{60} \) and \( 2:\text{ImC}_{60} \), while values for charge separation \( \Delta G_{CS} \) was found to be -0.62 and -0.64 eV, respectively, for \( 1:\text{ImC}_{60} \) and \( 2:\text{ImC}_{60} \). These data show thermodynamic feasibility of both charge separation from the singlet excited state of both \( 1^* \) and \( 2^* \) and subsequent dark charge recombination processes. It is also important to note that the \( 3\text{C}_{60}^* \) \( (E_T = 1.55 \text{ eV}) \) and \( 3\text{ZnP}^* \) \( (E_T = 1.50 \text{ eV}) \) energy levels are above the energy level of the charge separated state (see Figure S3). Under these conditions, the charge separated state could directly relax to the ground state.

**Femtosecond Transient Absorption Studies**

Femtosecond transient spectral studies of 1 and 2 were carried out in toluene at the excitation wavelength of 400 nm where the majority of absorption was from the zinc porphyrin entity. Figure 6a shows the transient spectra at the indicated delay times for compound 1. The transient spectra of 1 showed instantaneous formation of \( 1^* \) within 2 ps with peak maxima located at 523, 664, and 1248 nm. Negative peaks at 487, 590, 622, and 703 nm were also observed. The positive peaks at 523, 664, and 1248 nm are attributed to singlet-singlet excited peaks originating from \( 1^* \) while the positive peak in the 520-580 nm and 925 nm range appeared at latter delay times is attributed to a triplet excited state, \( 3^1* \) formed via the intersystem crossing process. Negative peaks at 487, 590, and 622 nm due to ground state...
bleaching and a peak at 702 nm peak due to stimulated emission was also observed. The decay
of the near-IR peak at 1248 nm corresponding singlet-singlet transition of $^1$1* was
monoeXponential with a time constant of 1.23 ns that was in close agreement with the earlier
discussed fluorescence lifetime of 1 (for decay profile, see Figure 6a right, blue curve). In the
second system, 2, instantaneous formation of $^1$2* was observed within 2 ps with peak maxima
located at 515, 665, 722 and a broad peak in the 1000 nm range (Figure 7a). Negative peaks at
467, 590, 630 and 700 nm were also observed. The positive peaks are attributed to singlet-singlet
excited peaks originating from $^1$2* while the first negative peaks are attributed to ground state
bleaching and the latter two negative peaks to stimulated emission. A positive peak emerged
with time at 525 nm has been ascribed to $^3$2* populated via intersystem crossing of $^1$2*. The
decay of the near-IR peak at 1078 nm corresponding singlet-singlet transition of $^1$2* was
monoeXponential with a time constant of 1.05 ns (for decay profile, see Figure 6a right, blue
curve) that was in close agreement with the earlier discussed fluorescence lifetime of 2.

![Figure 6](https://mc06.manuscriptcentral.com/cjc-pubs)

**Figure 6.** Femtosecond differential transient spectra of (a) 1 and (b) $^1$1*:ImC$_{60}$ at the indicated
delay times in deaerated toluene (400 nm, 100 fs pulse width). The right hand panel in Figure 6a
show the time profile of the near-IR band at 1248 nm for $^1$1* (blue) and $^1$1*:ImC$_{60}$ (red). The
right hand panel in Figure 6b shows the time profile of the fullerene radical anion peak at 1010 nm.

The transient spectra of push-pull zinc porphyrins discussed here have revealed successful formation of their singlet excited states that eventually undergoing intersystem crossing to populate their respective triplet excited state. In general, the push-pull effect has promoted the excited state deactivation. This observation of diminished excited state lifetimes is similar to that reported us by on push-pull porphyrins derived from free-base porphyrin derivatives.\textsuperscript{18,27}

Figure 6b shows the femtosecond transient spectra at the indicated delay times of the 1:ImC\textsubscript{60} conjugate in Ar-saturated toluene. To form the conjugate, 1.2 equivalents of ImC\textsubscript{60} was used to coordinate the zinc porphyrin. Under such conditions an equilibrium mixture of bound and unbound zinc porphyrin could be envisioned.\textsuperscript{23} The decay of the singlet-singlet peaks and recovery of the ground state bleach and stimulated emission peaks in 1:ImC\textsubscript{60} were much more faster (for time profile, see Figure 6a right red line), and also, peak of the triplet zinc porphyrin was at minimal indicating occurrence of additional photochemical events. In this case, instantaneously formed 1*:ImC\textsubscript{60} revealed expected transient peaks of the 1*: ImC\textsubscript{60} charge separated state. That is, a transient peak at 745 nm corresponding to ZnP*: and another peak at 1010 nm corresponding to ImC\textsubscript{60}: were observed. The decay of the 1248 nm peak corresponding to 1* in the conjugate was found to be biexponential with lifetimes of 66 and 843 ps. This biexponential decay could be attributed to two geometric isomers wherein in one case the fullerene entity being close to the push-group (electron rich amine) and the other in an almost vertical to plane of porphyrin. Using these lifetimes and that of pristine 1 at this peak, the rate of charge separation, k\textsubscript{CS} was estimated. The k\textsubscript{CS} thus calculated were found to be 1.4 x 10\textsuperscript{10} s\textsuperscript{-1} and 1.1 x 10\textsuperscript{9} s\textsuperscript{-1}. For the determination of rate of charge recombination, the decay of ImC\textsubscript{60} peak at 1010 nm was monitored, as shown in Figure 6b (right panel). This decay was also biexponential with a faster component at 69 ps and a slower component with appreciable signal intensity lasting beyond 3 ns, suggesting charge stabilization in the 1*:ImC\textsubscript{60} conjugate.

Photoinduced charge separation was also witnessed in the 2*: ImC\textsubscript{60} conjugate as shown in Figure 7b. In this case, the decay/recovery of the positive/negative peaks of the instanteneouly formed 1* revealed new peaks corresponding to 2*: ImC\textsubscript{60} charge separated state. That is, a
transient peak at 715 nm corresponding to ZnP•⁺ and another peak at 1010 nm corresponding to ImC₆₀•⁻ were observed. The decay of the 1100 nm peak corresponding to 12* in the conjugate was found to be biexponential with lifetimes of 40 and 780 ps, suggesting two geometric isomers, ‘close and far’, similar to that observed in the case of 1:ImC₆₀ conjugate. Using these lifetimes and that of pristine 2 at this peak, the rate of charge separation, $k_{CS}$ calculated were found to be $2.4 \times 10^{10}$ s⁻¹ and $1.2 \times 10^9$ s⁻¹, respectively. For the determination of $k_{CR}$, the decay of ImC₆₀•⁻ peak at 1010 nm was monitored, as shown in Figure 7b (right panel). This decay was biexponential with a lifetime of 270 ps and another one lasting beyond the 3 ns monitoring time window of our instrument suggesting charge stabilization in the 12*:ImC₆₀ conjugate.

**Figure 7.** Femtosecond differential transient spectra of (a) 2 and (b) 12*:ImC₆₀ at the indicated delay times in deaerated toluene (400 nm, 100 fs pulse width). The right hand panel in Figure 7a show the time profile of the near-IR band at 1248 nm for 12* (blue) and 12*:ImC₆₀ (red). The right hand panel in Figure 7b shows the time profile of the fullerene radical anion peak at 1010 nm.
Since the transient peaks corresponding to $1^{+}:\text{ImC}_{60}^{+}$ and $2^{+}:\text{ImC}_{60}^{+}$ charge separated states persisted beyond 3 ns, nanosecond transient studies were performed. As shown in Figure S4, nanosecond spectral features were devoid of any spectral features within the monitored wavelength region of 800-1200 nm. The broad signal observed here was due to the $3^{1*}$ and $3^{2*}$ species. These results suggest that the lifetime of $1^{+}:\text{ImC}_{60}^{+}$ and $2^{+}:\text{ImC}_{60}^{+}$ charge separated states is less than 25 ns, the lower detection limit of our nanosecond transient spectrometer (8 ns excitation pulses were used.

A comparison between the photochemical results obtained for the present push-pull zinc porphyrin-C$_{60}$ systems to other simple zinc porphyrin-C$_{60}$ suggest the following. First, the push-pull substituents and the electronic effect caused by them did not hinder C$_{60}$Im binding to zinc center or drastically change the redox properties (except for the small effect due to peripheral substituents). Second, the kinetics of charge separation and charge recombination, however, revealed two distinct rates. In the axially bound equilibrium process, it is likely that the electron deficient fullerene bends close to the electron donor substituents on the porphyrin ring promoting faster charge separation and recombination. A second configuration where such interactions are minimal, results in slower charge separation and recombination.

**Conclusion**

The push-pull zinc porphyrins studied here have made few noteworthy observations. In the studied porphyrins where both push and pull groups are directly connected to the porphyrin $\pi$-system, the push-pull effects were clearer from the location of the frontier orbitals, more so in the case of 1. The push-pull groups caused red-shifted absorption peaks with considerable spectral broadening. Importantly, the push-pull groups did not affect the binding of C$_{60}$Im to the metal center due to any geometric constraints. In fact, the magnitude of the determined binding constants were almost the same as that of C$_{60}$Im binding to pristine zinc porphyrin. Both 1 and 2 revealed faster excited state relaxation of the singlet excited state. Furthermore, efficient photoinduced charge separation and relatively slower charge recombination was witnessed in both $1:\text{ImC}_{60}$ and $2:\text{ImC}_{60}$ conjugates, although the rise and decay profiles were bi-exponentials due to different solution geometry. The present study brings out the importance of push-pull effects in governing ground and excited state properties of zinc porphyrin derived donor-acceptor conjugates.
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References


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