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Push-Pull Porphyrins *via* β-Pyrrole Functionalization: Evidence of Excited State Events Leading to High-Potential Charge-Separated States

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Abstract. A new set of free-base and zinc(II) metallated, β-pyrrole functionalized unsymmetrical push-pull porphyrins were designed and synthesized via β-mono- and dibrominated tetraphenylporphyrins by the Sonogashira cross-coupling reaction. The ability of donor and acceptor on the push-pull porphyrins to produce high-potential charge separated states was investigated. The porphyrins were functionalized at the opposite β,β'- pyrrole positions of porphyrin ring carrying triphenylamine push groups and naphthalimide pull group. Systematic studies involving optical absorption, steady-state and time-resolved emission revealed existence of intramolecular type interactions both in the ground and excited states. The push-pull nature of the molecular systems was supported by frontier orbitals generated on optimized structures, wherein delocalization of HOMO over the push group and LUMO over the pull group connecting the porphyrin π-system was witnessed. Electrochemical studies were performed to visualize the effect of push and pull groups on the overall redox potentials of the porphyrins. Spectroelectrochemical studies combined with frontier orbitals helped in characterizing the one-electron oxidized and reduced porphyrins. Finally, by performing transient absorption studies in polar benzonitrile, the ability of push-pull porphyrins to produce charge-separated states upon photoexcitation was confirmed and the measured rates were in the range of ~10^9 s^{-1}. The lifetime of the final charge separated state was ~ 5 ns. The present study ascertains the importance of push-pull porphyrins in solar energy conversion and diverse optoelectronic applications, where high-potential charge-separated states are warranted.

Introduction

Solar energy harvesting technology, basically derived from natural photosynthetic reaction center, has provided major driving force for building and studying a new generation of molecular materials for light energy conversion.[1-14] The energy-transfer and electron-transfer processes in the light-harvesting capability of porphyrin chromophores have been well studied for organic photovoltaics and photodynamic therapy.[15] Structurally close to naturally occurring chlorophylls,[16] porphyrins, have served as perfect building blocks for electron donor-acceptor conjugates.[17] Porphyrins can be peripherally modified with diverse electron donor or acceptor entities using established synthetic protocols, which would also allow one to fine-tune their photophysical and redox properties to a desired level. In recent years, push-pull porphyrins have attracted intense attention in the field of dye-sensitized solar cells (DSSCs).[18] The introduction of electron donating push-groups and electron withdrawing pull-groups on the porphyrin periphery have made outstanding impact on light energy conversion efficiencies due to the possibility of promoting vectorial electron transfer, when immobilized on semiconducting nanoparticles.[19-21] In fact, the best performing DSSCs to-date have been derived from this novel concept. Generally, the push and pull groups are relatively weaker electron donor and acceptor groups, which is in contrast to stronger electron donor and acceptor groups used in building multi-modular donor-acceptor systems to observe excited state electron transfer leading to charge separated states.[7-9] The stronger electron donor and acceptor groups are characterized by their redox potentials, that is, they are easier to oxidize and reduce compared to photosensitizing primary electron donor, porphyrin.

For the molecular design, both *meso*- and β-pyrrole functionalized porphyrins have been successfully adopted, although β-pyrrole functionalized porphyrins are better in terms of promoting intramolecular interactions due to direct attachment of the addend groups to the porphyrin π-system. However, it may be mentioned here that studies on β-pyrrole functionalized push-pull porphyrins are limited in number due to associated synthetic difficulties.[21-22] The synthesis of di- and tri-substitution on the β-pyrrole ring was first reported by Callot in 1974.[23] Although when connected with push and pull groups at the opposite side of the porphyrin ring, intramolecular charge transfer type interactions both in the ground and the excited state are expected to occur; evidence for generation of charge separated states upon photoexcitation in such closely positioned molecular systems has been limited,[24] due primarily the weak electron donating and accepting nature of the push and pull groups.

The synthesis and regiochemistry of *β*-disubstituted porphyrins and metalloporphyrins are largely unexamined due to the formation of mixture of products. Bhyrappa *et. al*. have reported the synthesis of partial *β*-pyrrole brominated TPP with isomers and the crystal structures of the complexes.[25] Recently Pizzotti *et al*. synthesized *β*-disubstituted push–pull tetraaryl Zn^{II} porphyrinates and explored its DSSC applications.[26] Sankar *et. al*. have reported the synthesis of mixed antipodal *β*-substituted porphyrins and studied their electronic and the redox properties.[27] Tagliatesta *et al*. have synthesized 2,12 positions of *β*-substituted porphyrin and its electron-transfer processes were investigated.[28]

In the present study, we have designed and synthesized push−pull porphyrins **1**–**6** *via β*-pyrrole functionalization wherein the push group, triphenylamine (TPA) and the pull group, naphthalimide (NI) units have been incorporated in the porphyrin π-system (Figure 1). Upon complete characterization, the ability to promote intramolecular interactions leading to charge separated states especially in electron transfer favoring polar solvents are investigated.

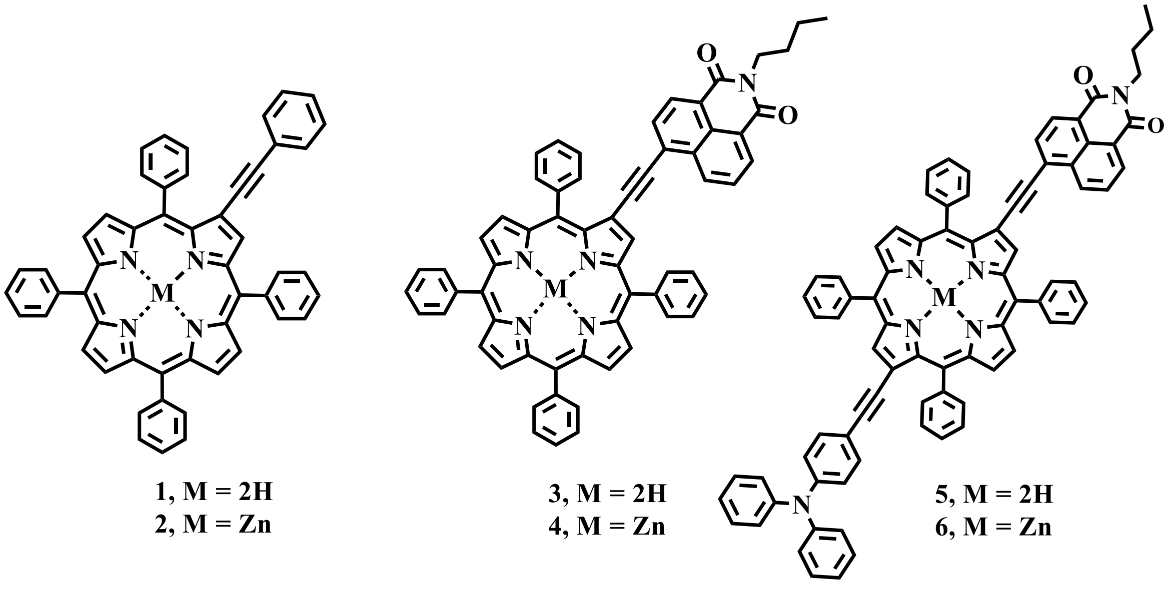
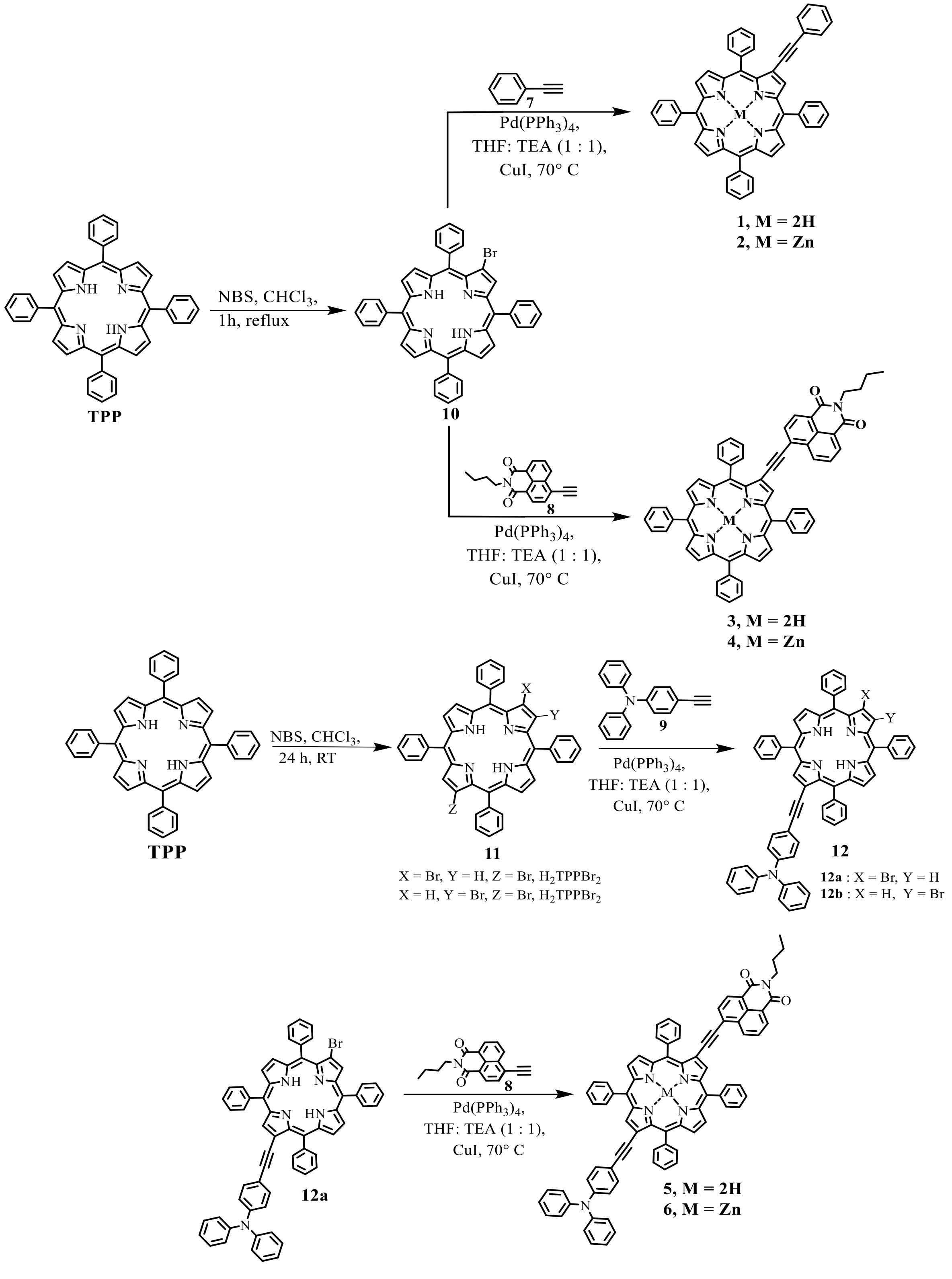


Figure 1. Structure of the push-pull porphyrins, **5-6**, and the control compounds, **1-4**, used in the present study.

Results and Discussion

Synthesis

The synthesis of push-pull porphyrin and its zinc derivatives **1**–**6** are shown in Scheme 1. The tetraphenylporphyrin (TPP) and monobrominated TPPBr, **10** were synthesized as per the reported procedures.[29] The synthesis of β-dibrominated TPP, **11** was carried out using controlled amount of N-bromosuccinimide (NBS) (1.8 equiv) in $CHCl_3$ at room temperature for 24 hours, which resulted in H_2TPPBr_2, **11** as mixture of products (Scheme 1). [25b] The control compounds **13** and **14** were synthesized according to the reported procedures (Figure S5).[30] The Pd-catalyzed Sonogashira cross-coupling reaction using phenylacetylene **7** with TPPBr in the presence of $Pd(PPh_3)_4$ at 70 °C in THF solvent resulted in porphyrin **1** with 53% yield (Scheme 1). The Sonogashira cross-coupling reaction of β-monobrominated TPPBr with 1 equiv of 2-butyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione **8** resulted in porphyrin **3** with 78% yield. The H_2TPPBr_2 **11** mixture was subjected to Sonogashira cross-coupling reaction with 4-ethynyl-N, N-diphenyl aniline **9** resulted in porphyrin **12** (**12a** and **12b**) isomers in 79% yield. The porphyrin **12a** and **12b** were separated by silica gel column chromatography. The separation of the porphyrin **12a** was evidenced from ^1H NMR characterization. However, it may be mentioned here that we were unable to discriminate the positions of bromination, whether it was at the 2,12- or 2,13 positions. Although we have clear ^1H NMR evidence that only one dibrominated product was isolated.[26] The Sonogashira cross-coupling reaction was further carried out on porphyrin **12a** with 1 equiv of 2-butyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione **8** resulted in porphyrin **5** with 47% yield. The zinc insertion on porphyrins **1**, **3** and **5** were carried out with $Zn(OAc)_2$ in $MeOH/CHCl_3$ (3:1) mixture, which resulted in zinc porphyrin **2**, **4** and **6** with 87%, 86% and 81% yields, respectively. The porphyrin and its zinc derivatives **1**–**6** were purified and well characterized by ^1H and ^{13}C NMR, HR-MS and MALDI-TOF mass spectra. (see supporting information for spectral details).



Scheme 1. Synthesis of porphyrins **1**−**6**.

Absorption and Emission Studies

Figure 2a and b show the normalized absorption and fluorescence spectra of the free-base and zinc(II) derived push-pull porphyrins along with their respective control compounds. Free-base porphyrins were characterized by an intense broad Soret and four visible bands, whereas the zinc derivatives were characterized by a broad Soret and two visible bands. Mono- and bis-pyrrole functionalization had marked changes in the absorption spectral behavior. Compared to pristine *meso*-tetraphenylporphyrin, H_2TPP and its zinc analog, ZnTPP, compounds **1** and **2** having a phenylacetylene entity at the β-pyrrole position revealed broadening of the Soret and visible bands with a small red-shift. Replacing the phenyl entity, with an electron deficient, naphthalimide entity in **3** and **4** caused additional red-shift and spectral broadening. Upon appending the push group, triphenylamine and the pull group naphthalimide at the opposite β, β'- pyrrole positions of porphyrin ring (**5** and **6**) had much more pronounced effects, that is, substantial broadening with red-shift approaching the near-IR region of the spectrum was witnessed (see Table 1). There was a gradual increase in the calculated full width at half maxima (FWHM) values for the Soret band (Table 1) for a given series, affirming the existence of ground state interactions between the porphyrin π-system and the appended entities in both sets of porphyrin derivatives. Additionally, the Q-bands gained in intensity for both push-pull porphyrins, **5** and **6**, a result that is consistent with our earlier observation on this type of systems.[24]

Noticeable changes in the emission behavior was also observed for the investigated push-pull porphyrins. As shown in Figure 2c and d, progressive red-shift in the fluorescence emission maxima for both free-base and zinc porphyrin series (**1** > **3**> **5** and **2** > **4** > **6**) was observed (Table 1). Interestingly, fluorescence quenching in free-base porphyrin derivative **3** was minimal (< 5%) which was in contrast to zinc porphyrin derivative **4** where about 65% of the original fluorescence intensity was quenched, although both were appended with the electron acceptor, NI. In the case of free-base porphyrin **5** having both NI and TPA entities, substantial quenching (80%) was observed. For the zinc derivative **6** this quenching was about 33%. These results reveal the significance of push-pull effects caused by the presence of both electron donor and acceptor entities on their excited state properties such as electron and energy transfer.[31]

The ascertain excited state interactions in the push-pull porphyrins, fluorescence lifetimes were also measured using time correlated single photon counting (TCSPC) method (Figure 3).

The decay could be satisfactorily fitted to one to three exponentials. The average lifetime of free-base porphyrin derivatives, **1**, **3** and **5** were found to be 8.73, 7.27 and 1.72 ns while that for the zinc porphyrin derivatives, **2**, **4** and **6**, they were 1.72, 1.08 and 0.66 ns. The lifetimes of compounds **1** and **2** were close to those of H_2TPP (9.6 ns) and ZnTPP (1.82 ns), and they tracked well with the earlier discussed steady-state measurements. Response: Figure 3 has been revised according to referee suggestion. The appearance of multiexponential decays could be due to aggregation, existence of different solution conformers, or return of the charge separated state to locally excited S_1 state due to high energy of charge-separated state (*vide infra*).

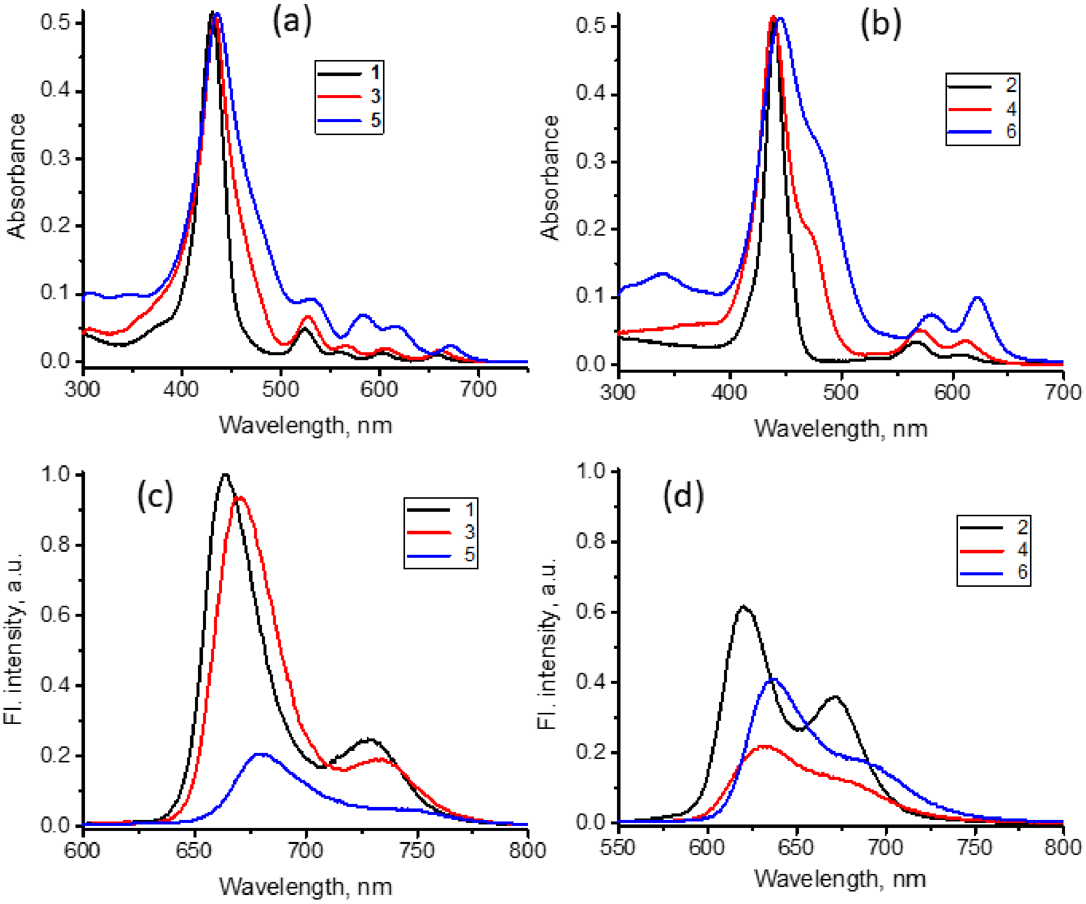


Figure 2. Normalized to the Soret band absorption (a and b) and fluorescence (c and d) of free-base porphyrin (a and c) and zinc porphyrin (b and d) derived push-pull porphyrins and their control compounds in benzonitrile. The samples were excited at the Soret band maxima.

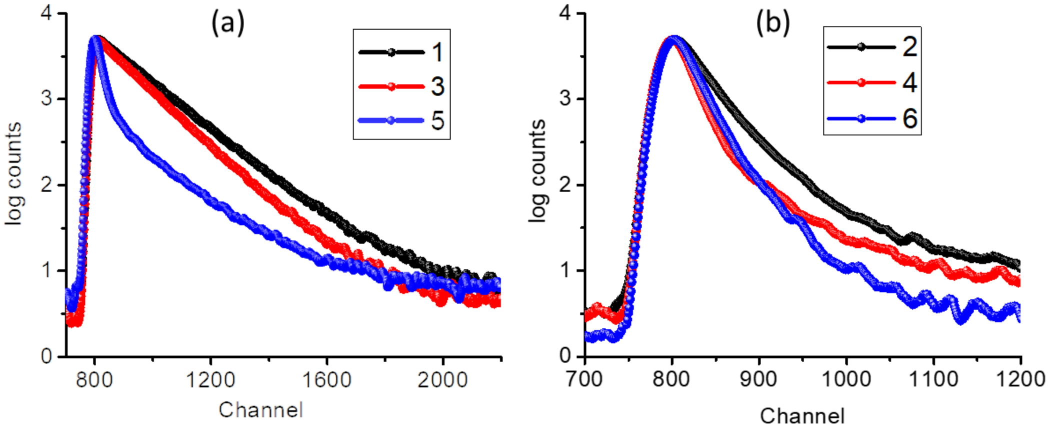


Figure 3. Fluorescence decay curves of (a) free-base porphyrin and (b) zinc porphyrin derivatives in benzonitrile. The samples were excited using nanoLED excitation sources and the emission was collected at the emission peak maxima.

Electrochemistry, Frontier Orbitals, and Spectroelectrochemistry

In order to understand the electronic effects caused by the push-pull entities on the porphyrin π-system, electrochemical studies were performed using cyclic voltammetry (CV) technique. Figure S1 show the CVs of free-base and zinc porphyrins in benzonitrile containing 0.1 M $(TBA)ClO_4$ while the data are summarized in Table 1. Relatively difficult oxidation and easier reduction for free-base porphyrin derivatives compared to related zinc(II) porphyrin derivatives was witnessed. The presence of push-pull groups shrunk the electrochemical HOMO-LUMO gap (i.e., difference between the first oxidation and reduction potentials) by lowering the reduction potentials while such changes in oxidation potentials were minimal. In order to realize the redox potentials of push and pull groups, electrochemical studies on two control compounds, viz., phenylacetylene functionalized TPA **13** and phenylacetylene functionalized NI **14** were performed (Figure S2). The first reduction of the former compound was located at -1.48 V vs. Fc/Fc^+ while the first oxidation of the latter compound was located at 0.56 V vs. Fc/Fc^+. These results suggest that the TPA oxidation occurs only after the first oxidation of free-base and zinc porphyrin entities in the push-pull porphyrins. However, the presence of directly linked electron rich TPA entity could make the oxidation process of porphyrin entity easier and could involve both TPA and porphyrin entities. Due to easier reduction of NI compared to ZnP, the first reduction in compounds **4** and **6** could be ascribed to the reduction of NI entity, however, for free-base porphyrins the first reduction of NI and H_2P were close and was difficult to assign the site of electron transfer. However, it may be noted that the presence of NI would make porphyrin reduction relatively easier involving the directly connected NI and porphyrin entities, a trend that is obvious from the electrochemical data shown in Table 1.

Table 1. Absorption maxima, fluorescence maxima and singlet excited lifetime, and electrochemical redox potentials of the investigated push-pull porphyrins in benzonitrile.

Compound	λ_{max}, nm	fwhm, cm^{-1}	λ_{flu}, nm	τ, ns	Potential V vs. Fc/Fc^+	
					E_{red}	E_{ox}
1	430, 520, 561, 600, 658	$1.57x10^3$	664, 727	8.73	-1.86, -1.59	0.48, 0.72
3	433, 526, 567, 605, 660	$2.13x10^3$	669, 736	7.27	-1.69, -1.50	0.48
5	435, 533, 583, 617, 671	$2.96x10^3$	679, 749	1.72	-1.65, -1.41	0.43, 0.59
2	440, 566, 607	$1.047x10^3$	620, 670	1.78	-1.79	0.30, 0.62
4	438, 474, 569, 612	$1.76x10^3$	633, 677	1.08	-1.77, -1.65	0.33
6	340, 444, 475, 580, 621	$3.36x10^3$	636, 689	0.66	-1.69, -1.42	0.32, 0.49
13						0.53
14					-1.48	

To gain further support for the above rationale additional studies involving computational and spectroelectrochemical studies were performed. The frontier orbitals were generated on B3LYP/6-31G* optimized structures [32] as shown in Figure 4. While majority of the HOMO and LUMO of **1** and **2** were located on the porphyrin π-system with little contributions on the phenylacetylene group, results for other porphyrin systems were significantly different. In the case of **3** and **5**, the HOMO was located mainly on the porphyrin π-system while the LUMO were on both porphyrin and NI entities. In the case of **5** and **6** push-pull systems, majority of HOMO on TPA with some contributions on the porphyrin entity while the LUMO was on the porphyrin-NI entity. These results suggest the push and pull groups directly interacting with the porphyrin π-system, rather than behaving as individual entities. It may be mentioned here that position of NI entity either at the **12a** or **12b** positions of porphyrin ring in the triads is expected not to change the geometry and electronic structures significantly, as demonstrated earlier by Parsa et. al. in push-pull porphyrins.[33]

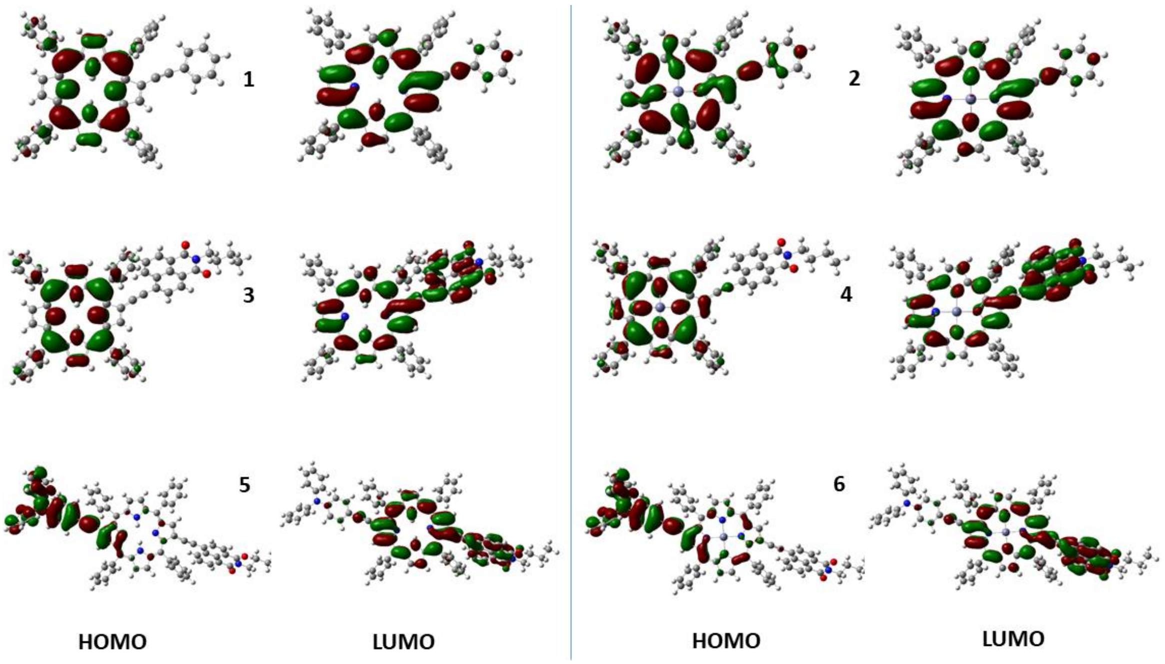


Figure 4. Frontier HOMO and LUMO on B3LYP/6-31G* optimized structures of the investigated compounds.

Spectroelectrochemical results shown in Figure S3 were supportive of oxidation involving the porphyrin π-system. Peaks corresponding to porphyrin π-radical cation covering the 600–800 nm range in the case of **3** and **5**, and 650–950 nm range in the case of **6** were clear. One or more isosbestic points were also observed. Due to β-pyrrole functionalization of the push-pull groups, the radical cation spectra were much more red-shifted compared to those of pristine samples. During reduction, the changes were not so clear. An overall increase in optical density was observed during first reduction of **5** and **6** suggesting that the NI entity is mainly involved in reduction (lacking absorption peaks in the visible range) and the porphyrin to a lesser extent.

Free-Energy Calculations

From the optical and electrochemical data, the driving forces for charge recombination ($-\Delta G_{\mathrm{CR}}$) and charge separation ($-\Delta G_{\mathrm{CS}}$) were calculated according to eqns. (1) and (2):[34]

$$-\Delta G_{\mathrm{CR}} = E_{\mathrm{ox}} - E_{\mathrm{red}} + \Delta G\mathrm{s} \qquad (1)$$

$$-\Delta G_{\mathrm{CS}} = \Delta E_{0,0} - (-\Delta G_{\mathrm{CR}}) \qquad (2)$$

where E_{ox} is the first oxidation potential of the porphyrin, E_{red} is the first reduction potential of the porphyrin, $\Delta E_{0,0}$ is the energy of the 0-0 transition between the lowest excited state of the porphyrin, evaluated as the mid-point of 0,0 transitions of absorption and fluorescence peaks. These values were respectively, 1.87, 1.99, 1.85 and 1.97 eV for **3**, **4**, **5**, and **6**. The ΔG_S refers to the static energy, calculated by using the 'Dielectric Continuum Model' according to eqn. (3).

$$\Delta G_S = -e^2/(4\pi\varepsilon_0\varepsilon_S R_{Ct\text{-}Ct}) \qquad (3)$$

The symbols ε_0 and ε_s represent vacuum permittivity and dielectric constant of benzonitrile (8.85 x 10^{-12} C^2/Nm and 26), respectively. The calculated ΔG_S value for **3** and **4** was 0.06 eV, and for **5** and **6** it was 0.03 eV. These values and the redox potentials were used to evaluate -ΔG_{CR} and were found to be 1.92, 1.92, 1.82 and 1.71 eV, respectively, for **3**, **4**, **5**, and **6**. These values directly represent the energy stored in the charge-separated states. The magnitude of which suggests possibility of generation of high-potential charge separated states. Finally, the -ΔG_{CR} values were combined with $\Delta E_{0,0}$ values which led to ΔG_{CS} values of 0.05, -0.07, -0.03 and -0.26 eV, respectively, for **3**, **4**, **5**, and **6**. These free-energy values suggest moderate thermodynamic feasibility of excited state charge separation in compounds **4**, and **5**, and exergonic reaction in **6**, however, such calculations suggested thermodynamic unfeasibility of excited state charge transfer in the case of **3**.

Femtosecond Transient Absorption (fs-TA) Spectral Studies

The fs-TA spectra at indicated delay times for compounds **1** and **2** are shown in Figures S4a and b, respectively. For **1**, immediately after excitation, the instantaneously formed ^{1}**1***revealed positive peaks at 484, 544, 623, 860, 1102 and 1280 nm. In addition, negative peaks at 522, 560, 600, 662 and 736 nm were observed. By comparison with the earlier discussed absorption and fluorescence spectra, the first three negative peaks were attributed to ground state bleaching while the latter two peaks were attributed to stimulated emission. The near-IR peak at 1280 nm was attributed to singlet-singlet transition as such a trend was observed earlier for pristine porphyrins.[35] With time, decay of the positive signals were noticed, however, within the 3 ns time window of our instrument most of the signal persisted which is in agreement with longer lifetime of **1** (8.73 ns). In the case of **2**, the instantaneously form ^{1}**2*** had positive peaks at 480, 586, 630, 732, 836 and 1320 nm. Negative peaks at 565, 609 and 673 nm were also observed. The first peak was due to ground state bleaching while the latter two peaks were due to stimulated emission. Decay of the positive peaks was accompanied by a strong near-IR peak at 858 nm corresponding to ^{3}**2***.

The fs-TA spectral characterization of porphyrins, **3** and **4**, bearing an electron withdrawing group, NI was subsequently performed. The earlier discussed free-energy calculations were suggestive of lack of charge separation in **3** while possibility for such a process in **4** upon photoexcitation in polar benzonitrile. Figure 5a and b show the fs-TA spectra at the indicated delay times for **3** and **4** in benzonitrile. For **3**, the spectral features were close to that observed for **1**, that is, the instantaneously formed ^{1}**3*** revealed decay/recovery of positive and negative peaks without providing strong evidence of charge separated state. If there was charge

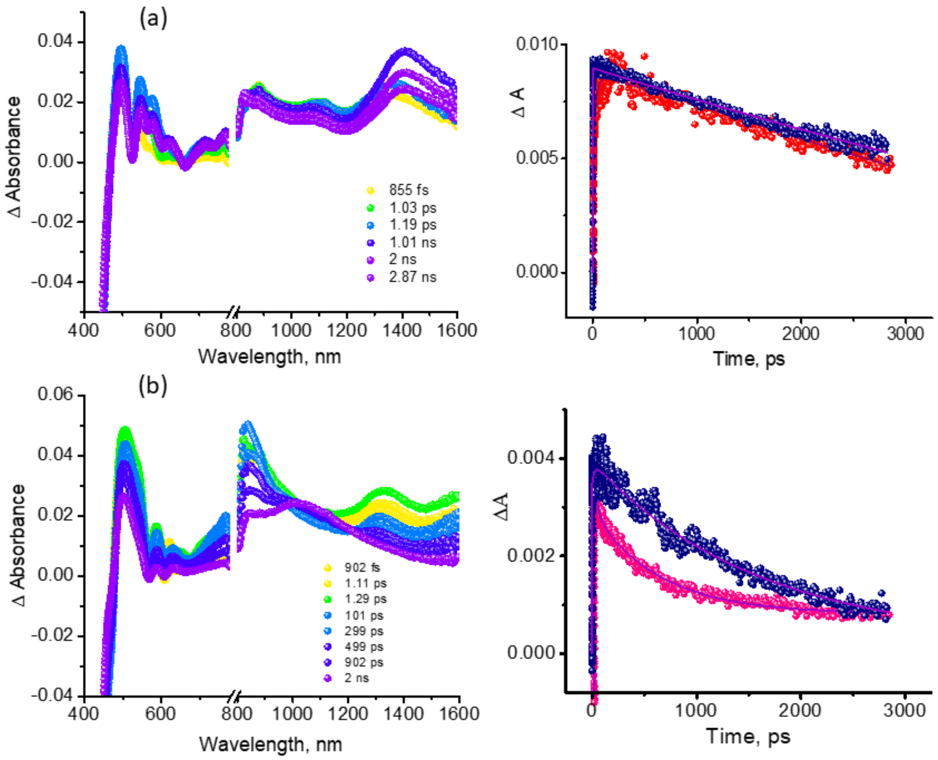


Figure 5. Fs-TA spectra at the indicated delay times for (a) **3** and (b) **4** in benzonitrile. The first sample was excited at 433 nm while the second one was excited at 438 nm. The right panel shows the decay curves for the near-IR bands of **1** (1325 nm) and **3** (1420 nm) (blue and red, upper panel), and **2** (1320 nm) and **4** (1308 nm) (blue and red, lower panel).

separation then one would expected to see a new transient peak covering the 600-800 nm range corresponding to free-base porphyrin cation radical. The decay curve of the near-IR band shown on the right-hand panel of Figure 5a for **1** and **3**, revealed only a moderate level of accelerated relaxation supporting lack of charge separation in **3**.

On the contrary, spectral features observed for **4** were indicative of charge separation in this molecular system (Figure 5b). In this case, the relatively rapid decay of the ^{1}**4*** transient peaks as shown in Figure 5b lower panel for the decay of near-IR peaks of **2** and **4**. This was accompanied by new transient peaks having spectral signature of zinc porphyrin radical cation as shown in Figure S3, suggesting $ZnP^{\cdot +}$-$NI^{\cdot -}$ to be the charge separated state.

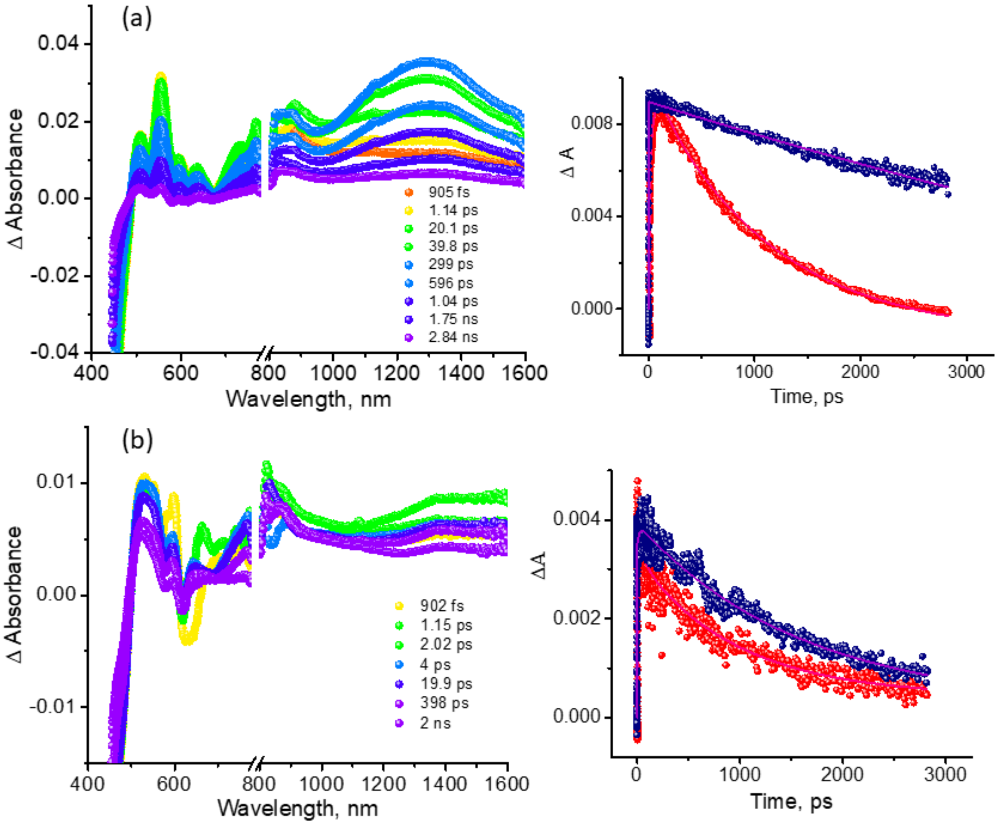


Figure 6. Fs-TA spectra at the indicated delay times for (a) **5** and (b) **6** in benzonitrile. The first sample was excited at 435 nm while the second one was excited at 444 nm. The right panel shows the decay curves for the near-IR bands of **1** (1325 nm) and **5** (1287 nm) (blue and red, upper panel) and **2** (1320 nm) and **6** (1378 nm) (blue and red, lower panel).

Finally, fs-TA spectral characterization of push-pull porphyrins, **5** and **6** were performed. As discussed earlier, free-energy calculations suggested that the excited state charge separation is indeed possible in these systems in polar solvent generating high-energy charge separated states. Figure 6a and b show the transient spectra at the indicated delay times for **5** and **6**, respectively. In both cases, rapid decay/recovery of the corresponding singlet excited state generated new transient spectra characteristic of charge separated states. As shown in the right-hand panel of each figure, the decay curves corresponding to the singlet excited state revealed rapid decay compared to the control **1** and **3**.

In order to estimate the rate of charge separation, k_{CS}, the earlier discussed fluorescence lifetimes were used according to equation 4.[36]

$$k_{CS} = 1/\tau_{DA} - 1/\tau_{probe} \qquad (4)$$

where τ_{DA} is the fluorescence lifetime of the donor-acceptor systems, **3**–**6** and τ_{probe} is the lifetime of probe molecules, **1** and **2** having no push or pull groups. The k_{CS} thus calculated were found to be 4.67×10^8 s^{-1} for **4**, 3.6×10^8 s^{-1} for **5** and 9.4×10^8 s^{-1} for **6** in benzonitrile indicating moderate rates of charge separation. In all of the cases, the charge-separated states lasted for few nanosecond (3–5 ns) although they were all high-energy states. The relatively faster recombination could be attributed to closely spaced push-pull groups on the porphyrin macrocycle and low-lying triplet excited states of porphyrins (E_T = 1.4 – 1.55 eV). Nonetheless, generating high-potential, charge separation in these push-pull porphyrins has been successful.

Summary

The push-pull porphyrins, newly synthesized in the present study, revealed several interesting results and insights. First, appending the electron push and pull groups to the *β*-pyrrole positions, instead of commonly utilized *meso*-positions, is shown to promote significant intramolecular interactions both in the ground and excited states due to their proximity to porphyrin π-system. Delocalization of HOMO over the push group and the central porphyrin π-system, and LUMO over the pull group and porphyrin π-system were key in visualizing the push-pull effects in the case of both free-base and zinc porphyrin derived systems. Spectral broadening accompanied by reduction in fluorescence intensity and lifetime provided first evidence of intramolecular push-pull effects. The important question of whether push-pull effects could promote excited state reactions to generate high-potential charge-separated states was answered by studies performed using fs-TA studies. Compounds **4**, **5** and **6**, were able to generate charge-separated states that lasted for few ns prior returning to ground state by populating their individual, low-laying triplet excited states. These findings suggest usefulness of push-pull porphyrins in relevant optoelectronic applications.

Experimental Section

General: All chemicals were used as received unless otherwise noted. All moisture sensitive reactions were performed under argon/nitrogen atmosphere. The NMR spectra were recorded at room temperature (298 K). Chemical shifts are given in ppm with respect to tetramethylsilane as internal standard ($CDCl_3$, 7.26 ppm, 77.0 ppm). ^1H NMR and ^{13}C NMR spectra were recorded using a 400 MHz and 100 MHz spectrometer. Tetra-n-butylammonium perchlorate, $n\text{-}Bu_4NClO_4$, used in electrochemical studies was from Fluka Chemicals. The density functional theory (DFT) calculation were carried out at the B3LYP/6-31G** level for C, N, H in the Gaussian 09 program. HRMS was recorded on TOF-Q mass spectrometer.

Instrumentation

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. A right angle detection method was used. Fluorescence lifetimes were determined using time correlated single photon counting using nanoLED excitation sources.

Cyclic voltammograms were recorded on an EG&G 263A potentiostat/galvanostat 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.

Spectroelectrochemical study was performed by using a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised of a Pt counter electrode, a 6 mm Pt

Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt Gauze working electrode.

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 1.45 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 Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of 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.

Synthesis

Synthesis of 5,10,15,20-tetraphenyl-7-(phenylethynyl) porphyrin (1).

7-bromo-5,10,15,20-tetraphenylporphyrin **10** (0.150 g, 0.21 mmol), ethynylbenzene **7** (0.033 g, 0.32 mmol) in THF: TEA (1: 1, v/v), palladium(0)-tetrakis(triphenylphosphine) (0.070 g, 0.06 mmol), and CuI (0.010 g, 0.05 mmol) were added under argon atm at room temperature. The reaction mixture was stirred for 12 h at 70 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane (20: 80) mixture to produce (0.080 g, 53%) of compound **1** as purple solid. ^1H NMR (400 MHz, $CDCl_3$): δ ppm= -2.66 (s, 2 H) 7.37 (m, 4 H) 7.64 - 7.82 (m, 13 H) 8.23 (s, 8 H) 8.76 - 8.89 (m, 6 H) 9.09 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm= 85.58, 98.48, 119.58, 119.69, 119.74, 120.04, 123.47, 126.28, 126.37, 127.43, 128.25, 131.64, 134.12, 134.16, 140.80, 141.43,

141.67, 141.72, 141.77. HRMS (ESI-TOF): m/z calculated for $C_{52}H_{34}N_4$ [M+nH] $^+$ 715.2856, found 715.2834.

Synthesis of 5,10,15,20-tetraphenyl-7-(phenylethynyl)porphyrin, zinc (2).

5,10,15,20-tetraphenyl-7-(phenylethynyl) porphyrin **1** (0.100 g, 0.14 mmol), Zn $(OAc)_2$, (0.289 g, 1.32 mmol) in MeOH: $CHCl_3$ (3 : 1, v/v), were added and the reaction mixture was stirred for 1 h at room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM/water and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane (40: 60) mixture to produce (0.095 g, 87%) of compound **2** as red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm= 7.35-7.40 (m, 4 H), 7.60 - 7.78 (m, 13 H) 8.23 (s, 8 H) 8.89-8.95 (m, 6 H) 9.26 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm= 86.41, 99.28, 121.38, 121.74, 124.22, 126.22, 126.76, 126.85, 128.07, 128.72, 132.30, 134.41, 134.62, 139.17, 142.21, 142.83, 148.49, 150.36, 150.90, 151.01, 151.32. HRMS (ESI-TOF): m/z calculated for $C_{52}H_{32}N_4Zn$ [M+nH] $^+$ 777.1991, found 777.1996.

Synthesis of 2-butyl-6-((5,10,15,20-tetraphenylporphyrin-7-yl) ethynyl)-1H-benzo[de] isoquinoline-1,3(2H)-dione (3).

7-bromo-5,10,15,20-tetraphenylporphyrin **10** (0.200 g, 0.28 mmol), 2-butyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione **8** (0.104 g, 0.37 mmol) in THF: TEA (1: 1, v/v), palladium(0)-tetrakis(triphenylphosphine) (0.070 g, 0.06 mmol), and CuI (0.010 g, 0.05 mmol) were added under argon atm at room temperature. The reaction mixture was stirred for 12 h at 70 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane (30: 70) mixture to produce (0.195 g, 78%) of compound **3** as black solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm= -2.66 (s, 2 H), 1.02 (t, J=7.28 Hz, 3 H), 1.46 - 1.54 (m, 2 H), 1.79 (quin, J=7.53 Hz, 2 H), 4.22 (m, 2 H), 7.28 - 7.35 (m, 3 H), 7.52 (t, J=7.65 Hz, 2 H), 7.69 (d, J=7.78 Hz, 1 H), 7.72 - 7.85 (m, 10 H), 8.20 - 8.27 (m, 7 H), 8.53 (d, J=7.53 Hz, 1 H), 8.61 (dd, J=10.79, 7.78 Hz, 2 H), 8.75 - 8.79 (m, 2 H), 8.83 - 8.88 (m, 1 H), 8.92 (s, 2 H), 9.21 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm= 13.90, 20.45, 29.71, 40.33, 95.09, 96.02, 120.06, 120.38, 120.42, 120.58, 121.53, 122.78, 126.77, 126.84, 126.87, 126.95, 127.88, 128.05, 128.55, 128.72, 129.09, 130.07, 130.90, 131.25, 131.41, 133.25, 134.44, 134.55, 134.59, 134.63, 141.23, 141.73, 141.92, 141.97, 163.90, 164.15. HRMS (ESI-TOF): m/z calculated for $C_{62}H_{43}N_5O_2$ $[M+nH]^+$ 890.3490, found 890.3493.

Synthesis of 2-butyl-6-((5,10,15,20-tetraphenylporphyrin-7-yl)ethynyl)-1H-benzo[de] isoquinoline-1,3(2H)-dione, Zinc (4).

2-butyl-6-((5,10,15,20-tetraphenylporphyrin-7-yl) ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione **3** (0.100 g, 0.11 mmol), Zn (OAc)$_2$, (0.270 g, 1.23 mmol) in MeOH: $CHCl_3$ (3 : 1, v/v), were added and the reaction mixture was stirred for 1 h at room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM/water and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane (50: 50) mixture to produce (0.090 g, 86%) of compound **4** as black solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm= 0.81 (t, J=7.28 Hz, 3 H) 1.11 - 1.19 (m, 2 H) 1.26 - 1.32 (m, 2 H) 3.30 (t, J=7.40 Hz, 2 H) 7.20 - 7.25 (m, 1 H) 7.46 (t, J=7.65 Hz, 3 H) 7.52 - 7.56 (m, 1 H) 7.64 (dt, J=15.62, 7.62 Hz, 2 H) 7.73 - 7.82 (m, 9 H) 8.09 - 8.14 (m, 3 H) 8.19 - 8.25 (m, 6 H) 8.52 (d, J=8.28 Hz, 1 H) 8.72 (d, J=5.02 Hz, 1 H) 8.86 (d, J=4.77 Hz, 1 H) 8.90 - 8.95 (m, 3 H) 9.28 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm= 13.62, 20.01, 29.70, 39.32, 95.17, 96.48, 120.30, 120.77, 121.22, 121.32, 121.50, 121.92, 124.21, 126.52, 126.65, 126.74, 127.58, 127.74, 128.36, 128.55, 129.80, 130.82, 131.17, 131.98, 132.38, 132.56, 132.89, 133.15, 134.23, 134.47, 138.90, 142.04, 142.57, 142.59, 163.95, 164.10. HRMS (ESI-TOF): m/z calculated for $C_{62}H_{41}N_5O_2Zn$ $[M+nH]^+$ 952.2624, found 952.2644.

Synthesis of 4-((17-bromo-5,10,15,20-tetraphenylporphyrin-7-yl)ethynyl)-N,N-diphenyl aniline (12a).

4-ethynyl-N, N-diphenyl aniline **9** (0.078 g, 0.28 mmol), $TPPBr_2$ mixture **11** (0.45 g, 0.58 mmol) in THF: TEA (1: 1, v/v), palladium(0)-tetrakis(triphenylphosphine) (0.100 g, 0.08 mmol), and CuI (0.010 g, 0.05 mmol) were added under argon atm at room temperature. The reaction mixture was stirred for 12 h at 70 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane

(20: 80) mixture to produce (0.211 g, 79%) compound **12** mixture with slight separation of substituted $TPPBr_2$ mixture on TLC Figure S13. However, compound **12** isomer were separated by silica gel column chromatography. The separation of the porphyrin **12a** isomer was evidenced from the ^{1}H NMR characterization Figure S14. However, it has to be mentioned that we have clear ^{1}H NMR evidence that only one dibrominated product was isolated as black solid. ^{1}H NMR of 12 isomers (400 MHz, $CDCl_3$): δ ppm= -2.79, -2.67 (s,s, 4 H) 6.95 - 7.02 (m, 4 H) 7.05 - 7.12 (m, 4 H) 7.13 - 7.22 (m, 12 H) 7.29 - 7.35 (m, 8 H) 7.69 - 7.80 (m, 23 H) 8.04 - 8.11 (m, 3 H) 8.15 - 8.25 (m, 13 H) 8.67 - 8.78 (m, 4 H) 8.78 - 8.92 (m, 7 H) 8.95 - 8.99 (d, 1 H) 9.03 (s, 1 H). ^{1}H NMR of 12a (400 MHz, $CDCl_3$): δ ppm= -2.65 (s, 2 H) 7.01 (d, J=8.55 Hz, 2 H) 7.10 (t, J=7.32 Hz, 2 H) 7.15-7.25 (m, J=8.54 Hz, 6 H) 7.30 - 7.37 (m, 4 H) 7.55 (d, J=8.55 Hz, 1 H) 7.70 - 7.80 (m, 11 H) 8.19 - 8.24 (m, 7 H) 8.72 (d, J=4.88 Hz, 1 H) 8.78 (s, 2 H) 8.82 (d, J=4.88 Hz, 1 H) 8.87 (s, 2 H) 9.04 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm= 85.5, 99.6, 119.9, 120.1, 120.5, 121.9, 123.5, 125.0, 126.7, 126.8, 127.8, 127.9, 128.6, 129.4, 133.1, 134.6, 141.9, 142.1, 147.3, 147.6. HRMS (ESI-TOF): m/z calculated for $C_{64}H_{42}N_5Br$ $[M+2]^+$ 962.2681, found 962.2686.

Synthesis of 2-butyl-6-((17-((4-(diphenylamino)phenyl)ethynyl)-5,10,15,20-tetraphenyl porphyrin-7-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (5).

4-((17-bromo-5,10,15,20-tetraphenylporphyrin-7-yl)ethynyl)-N,N-diphenylaniline **12a** (0.100 g, 0.10 mmol), 2-butyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione **8** (0.034 g, 0.12 mmol) in THF: TEA (1: 1, v/v), palladium(0)-tetrakis(triphenylphosphine) (0.070 g, 0.06 mmol), and CuI (0.010 g, 0.05 mmol) were added under argon atm at room temperature. The reaction mixture was stirred for 12 h at 70 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane (25: 75) mixture to produce (0.054 g, 47%) compound **5** as black solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm= -2.66 (s, 2 H) 1.01 (t, *J*=7.63 Hz, 3 H) 1.48 (dd, *J*=14.95, 7.63 Hz, 2 H) 1.69 - 1.79 (m, 2 H) 4.19 (t, *J*=7.63 Hz, 2 H) 6.99 (d, *J*=7.93 Hz, 2 H) 7.08 (t, 2 H) 7.15 - 7.21 (m, 5 H) 7.26 - 7.35 (m, 5 H) 7.50 (td, *J*=7.63, 3.66 Hz, 2 H) 7.60 - 7.66 (m, 1 H) 7.69 - 7.80 (m, 11 H) 8.19 - 8.26 (m, 8 H) 8.47 (t, *J*=7.32 Hz, 1 H) 8.52 - 8.61 (m, 2 H) 8.69 (s, 1 H) 8.74 (s., 1 H) 8.84 (d, *J*=7.93 Hz, 1 H) 8.91 (s, 1 H) 8.98 (d, *J*=4.27 Hz, 1 H) 9.16 (d, *J*=3.05 Hz, 1 H). ^{13}C NMR (100

MHz, $CDCl_3$): δ ppm= 13.9, 20.4, 22.7, 29.70, 40.3, 85.5, 95.2, 96.0, 100.0, 121.8, 123.5, 125.0, 126.8, 126.9, 128.7, 129.4, 130.9, 131.4, 133.1, 134.4, 134.6, 140.9, 141.1, 141.7, 141.9, 147.3, 147.6, 163.9, 164.1. HRMS (ESI-TOF): m/z calculated for $C_{82}H_{56}N_6O_2$ $[M+nH]^+$ 1157.4538, found 1157.4544.

Synthesis of 2-butyl-6-((17-((4-(diphenylamino)phenyl)ethynyl)-5,10,15,20-tetraphenyl porphyrin -7-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione, Zinc (6).

2-butyl-6-((17-((4-(diphenylamino)phenyl)ethynyl)-5,10,15,20-tetraphenylporphyrin-7-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione **5** (0.050 g, 0.04 mmol), Zn $(OAc)_2$, (0.104g, 0.47 mmol) in MeOH: $CHCl_3$ (3 : 1, v/v), were added and the reaction mixture was stirred for 1 h at room temperature. The solvent was then evaporated under reduced pressure and the resultant mixture was diluted with DCM/water and the organic layer was collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using a DCM: hexane (40: 60) mixture to produce (0.039 g, 81%) of compound **6** as green solid. ^1H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 9.15 (s, 1H), 8.91 (s, 1H), 8.84 (dd, J = 4.7, 1.6 Hz, 1H), 8.74 (dd, J = 4.7, 3.2 Hz, 1H), 8.67 (s, 1H), 8.60 (d, J = 8.9 Hz, 1H), 8.48 (d, J = 7.2 Hz, 1H), 8.14 – 8.24 (m, 8H), 7.68 – 7.78 (m, 11H), 7.47 – 7.51 (m, 3H), 7.32 (t, J = 12.9, 4.8 Hz, 5H), 7.21 – 7.24 (dd, 2H), 7.16 (d, J = 8.4 Hz, 4H), 7.09 (t, J = 7.3 Hz, 2H), 7.00 (m, 2H), 3.91 (t, 2H), 2.33 (t, J = 7.5 Hz, 2H), 1.35 – 1.41 (m, 2H), 0.95 (t, 3H). MS (MALDI-TOF) m/z: calculated for $C_{82}H_{54}N_6O_2Zn$ $[M]^+$ 1220.75, found 1220.60.

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Conflict of interest

The authors declare no conflict of interest.

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Table of contents

Push-Pull Porphyrins *via* β-Pyrrole Functionalization: Evidence of Excited State Events Leading to High-Potential Charge-Separated States

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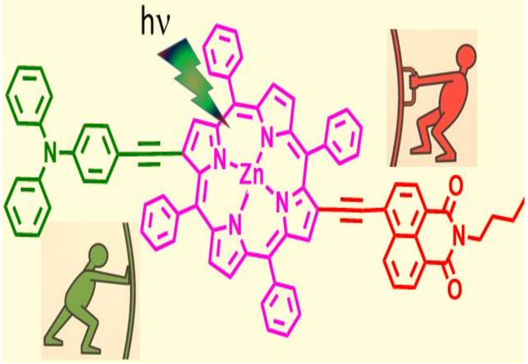

Push-Pull for Charge Separation: Creation of high-potential charge separated states in a series of push-pull porphyrins fearing triphenylamine push groups and naphthalene imide pull groups is reported.