

Photoinduced electron transfer in a directly linked *meso*-triphenylamine zinc porphyrin-quinone dyad

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Dedicated to Professor John A. Shelnutt on the occasion of his 65th birthday

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> **ABSTRACT:** A multimodular donor-acceptor system composed of three triphenylamine entities at the *meso*-positions of a zinc porphyrin macrocycle and a quinone at the fourth *meso*-position was newly synthesized and characterized. The triphenylamine entities acted as energy transferring antenna units in addition of improving the electron donor ability of the zinc porphyrin. Appreciable electronic interactions of the triphenylamine and quinone entities with the porphyrin π -system were observed. In agreement with the spectral and electrochemical results, the computational studies performed by the DFT B3LYP/3-21G(*) method revealed delocalization of the frontier HOMO over the triphenylamine and the porphyrin macrocycle while the LUMO to be fully localized over the quinone entity. Free-energy calculations suggested photoinduced electron transfer from the singlet excited zinc porphyrin to the directly linked quinone to be exothermic and this was experimentally confirmed by the time-resolved pump probe and up-conversion techniques. In the investigated system, the ET reaction path was found to depend upon the excitation wavelength. That is, when Zn porphyrin was predominantly excited, a rapid charge separation followed by equally fast charge recombination was observed. However, excitation of the peripheral TPA substituents resulted in an extremely long-lived CS state with triplet spin character *via* the TPA triplet and Zn porphyrin triplet states.

KEYWORDS: photoinduced electron transfer, triphenylamine, porphyrin, quinone.

INTRODUCTION

Electron transfer is ubiquitous in both biological and synthetic systems. Among different aspects, understanding the mechanism and control of electron transfer paths in natural and synthetic models are the widely investigated topics. The fundamental process of primary photosynthesis, for example, is characterized by a series of sequential electron transfer events in the reaction center producing long-lived charge separated states [1, 2]. The initial step involves transfer of an electron from the so-called 'special pair' chlorophyll dimer to the quinone located within the reaction center. The distant location of radical ion-pair species avoiding the energy wasting back electron transfer and a small overall reorganization energy ($\lambda_{reorg} \sim 0.2 \text{ eV}$) along with a well-balanced electronic coupling between different donor and acceptor entities results in high efficiency of charge separation [1, 2]. In order to further improve the understanding of the mechanistic details and the associated technological developments in the area of optoelectronics and solar energy harvesting, a

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Scheme 1. Structure of the porphyrin-quinone systems investigated in the present study

plethora of molecular structures comprised of donor and acceptor entities have been designed and photoinduced electron transfer relevant to early events of photosynthesis have been studied [3–11]. From these studies the role of free-energy of reaction, the magnitude of reorganization energy and the extent of electron coupling between the initial and final states have been established and theoretically modeled primarily by Marcus theory [12].

Among the different electron donor-acceptor systems reported to-date, the systems built on porphyrin (or other tetrapyrroles) as donor and the three-dimensional electron acceptor, fullerene have attracted wide attention [7-9, 11]. The relatively easy reduction [13] and low solvent and internal reorganization energies of fullerene in electron transfer reactions [14] along with the low susceptibility to solvent stabilization of the radical anion make it to be a superior electron acceptor. As a consequence, fullerenes in donor-acceptor dyads accelerate forward electron transfer (charge-separation; k_{CS}) and slow down the backward electron transfer (charge-recombination; $k_{\rm CR}$), thus generating the much desired long-lived chargeseparated (CS) states [7-9, 11], a result often next to impossible to achieve in the case of donor-acceptor systems having simple two-dimensional electron acceptors [3–5]. Further improvements in charge stabilization in porphyrin-fullerene systems have been accomplished by introducing one or more electron donor or acceptor entities to initiate sequential electron transfer for distant location of the radical ion-pairs [3–9].

Recently, we reported on a zinc porphyrin-fullerene system in which the donor, zinc porphyrin was functionalized at the *meso*-positions with triphenylamine (TPA) entities [15]. In this molecule, the TPA entities in the dyad played two important roles; first by promoting excitation transfer to the donor, and second, by stabilizing the charge separated states on the order of a few microseconds. DFT calculations suggested that the improved charge stabilization is due to the extensive delocalization of the highest occupied molecular orbital (HOMO) on the entire donor entity. Intrigued with these findings, in the present study, we have extended the study by replacing the fullerene entity by the well-known two-dimensional electron acceptor, quinone directly linked to the zinc porphyrin macrocycle, 1 (Scheme 1). Photoinduced electron transfer in 1 has been investigated using transient flash photolysis, pump-probe and up-conversion techniques, and compared with the results of a directly linked zinc porphyrin-quinone, 2 lacking the TPA *meso*substituents [16].

RESULTS AND DISCUSSION

Optical absorption and fluorescence studies

Figure 1a shows the optical absorption spectra of 1 along with a control compound, *meso*-tetrakis-(triphenylamine)porphyrinatozinc, (TPA)₄-ZnP, that is, a compound having four TPA entities at the four mesopositions and lacking the quinone entity, in benzonitrile. The Soret band of 1 was located at 444 nm while the Q-bands were located at 565 and 611 nm, respectively. The absorption due to TPA entities was located at 309 nm. These peak maxima of porphyrin macrocycle were found to be red shifted by up to 6 nm compared to the control compound lacking the quinone. These results indicate substantial interactions between the porphyrin π -system with the directly linked quinone entity. Additionally, the peak maxima for compound 2 were located at 418, 549 and 618 nm, respectively, for the Soret and Q-band transitions with much narrower bands compared to 1 (data not shown) [16, 17]. The large red shift of up to 26 nm for 1 along with broader bands as compared to 2 suggests strong electronic interactions between the TPA entities and the porphyrin π -system. These results suggest that both the triphenylamine and quinone substituents of 1 interact with the porphyrin π -system and modulate the electronic structure.

Figure 1b shows the fluorescence spectra of 1 along with the control compound. The emission band of 1 was



Fig. 1. (a) Absorption spectra normalized to the Soret band and (b) fluorescence spectra of (i) **1** and (ii) the control, *meso*-tetrakis(triphenylamine)porphyrinatozinc in PhCN. $\lambda_{ex} =$ 564 nm

found to be red shifted by about 9 nm compared with the control compound, (TPA)₄-ZnP, in addition to quenching of its intensity by more than 80%. Such quenching (more than 80%), accompanied with a small red shift, was also observed for 2 compared to its control compound, mesotetraphenylporphyrinatozinc(II), ZnTPP. In agreement with the absorption behavior, the emission maximum of 1 was found to be red shifted by ~ 25 nm compared with the emission maximum of 2 [17]. These results suggest occurrence of excited state events in 1 from the singlet excited zinc porphyrin entity. As reported earlier, when (TPA)₄-ZnP was excited at 318 nm corresponding to the absorption of TPA entities, a new emission at 480 nm was observed [15]. Control experiments performed using triphenylamine confirmed that this band is due to the emission of peripheral substituents. However, when compared with the emission intensity of triphenylamine, the emission of (TPA)₄-ZnP was found to be substantially quenched. Further scanning the emission wavelength into the red region revealed additional bands corresponding to porphyrin emission, which was not observed for ZnTPP lacking TPA entities. Excitation spectrum recorded by fixing the emission monochromator to the porphyrin emission maxima at 632 nm revealed absorption peaks of TPA entities [15]. These results indicate occurrence of excitation transfer from the TPA entities to the zincporphyrin of $(TPA)_4$ -ZnP [18]. Such a photophysical process is also possible in **1** due to structural similarities, although the emission bands were almost completely quenched due to the presence of the additional quinone entity. These observations suggest the occurrence of sequential energy transfer followed by electron transfer in **1** when the peripheral TPA entities are directly excited in polar benzonitrile solvent.

Electrochemistry and computational studies

Electrochemical studies using differential pulse voltammetric (DPV) technique were performed to evaluate the redox potentials of 1 in benzonitrile containing 0.1 M $(n-Bu_4N)ClO_4$, as shown in Fig. 2. The electrochemistry of 2 has earlier been reported by us [17, 19]. During anodic scan, compound 1 revealed oxidation processes corresponding to both the porphyrin macrocycle and the TPA entities while during cathodic scan reduction processes corresponding to both quinone and porphyrin were observed. The site of electron transfer was assigned based on comparative electrochemistry involving the control compounds and spectroelectrochemical studies [15, 20, 21]. The two one-electron anodic processes corresponding to the oxidation of the porphyrin macrocycle were located at 0.29 and 0.49 V vs. Fc/Fc⁺ while the third anodic process involving at least four-electrons was located at 0.72 V vs. Fc/Fc⁺ corresponding the oxidation of the peripheral TPA entities. The two one-electron cathodic processes corresponding to the quinone entity were located at -0.81 and -0.93 V vs. Fc/Fc⁺ while the porphyrin ring based one-electron reductions appeared at -1.80 and -2.01 V vs. Fc/Fc⁺, respectively. The reduction of the quinone entity of 1 was positively shifted compared to the first reduction of dyad 2 located at -0.85 V vs. Fc/Fc⁺ in benzonitrile. The electrochemically measured



Fig. 2. Differential pulse voltammograms of **1** (~0.5 mM) in benzonitrile containing 0.1 M (TBAP)ClO₄. DPV conditions: scan rate = 20 mV/s, pulse width = 50 ms, step time = 100 ms and pulse height = 0.025 V

HOMO–LUMO gap for 1, calculated from the first oxidation potential of porphyrin and the first reduction potential of quinone, was found to be 1.10 V PhCN, and is smaller by about 130 mV compared to 2 which could be attributed to the influence of the peripheral electron donating TPA entities.

In order to gain insights into the geometry and electronic structure, computational studies were performed using density functional methods (DFT) at the B3LYP/3-21G(*) level on 1 [22]. The B3LYP/3-21G(*) methods have recently been successfully used to predict the geometry and electronic structure of molecular and supramolecular donor-acceptor assemblies [23]. Compound 1 was optimized to a stationary point on the Born-Oppenheimer potential energy surface whose structure is shown in Fig. 3a. The porphyrin ring was found to be almost flat with no appreciable ring puckering due to the presence of the meso-substituents. The quinone entity attached at the meso-position of the porphyrin macrocycle was tilted at an angle of 78°. The molecular electrostatic potential map (MEP) for compound 1 in Fig. 3b clearly shows electron deficient site on the quinone entity. In the optimized structure, the HOMO was localized on the porphyrin macrocycle with considerable contribution also on the peripheral TPA entities, while the LUMO was fully localized on the quinone entity (Figs 3c,d). These results suggest that the triphenylamine-substituted porphyrin is an electron donor and quinone an electron acceptor in electron transfer reactions. The computed gas phase HOMO-LUMO gap was found to be 1.56 eV which was smaller than the HOMO-LUMO gap of 2 being 1.82 eV [19]. Although the electrochemical studies indicate involvement of ZnP entity in the first oxidation process, the appearance of part of the HOMO over the peripheral TPA substituents



(a)

(b)



Fig. 3. B3LYP/3-21G(*) optimized (a) geometry, (b) molecular electrostatic potential map, (c) highest occupied molecular orbital and (d) lowest unoccupied molecular orbital of porphyrin-quinone 1

is expected to stabilize the radical cation by delocalization, ultimately slowing down the charge recombination during the light induced electron transfer process.

The energy levels of the CS states (ΔG_{RIP}) were evaluated using the Weller-type approach [24] utilizing the redox potentials, and the dielectric constant of benzonitrile. By comparing these energy levels of the CS states with the energy levels of the excited states, the driving forces (ΔG_{CS}) were also evaluated, according to the following equations.

$$\Delta G_{\rm RIP} = E_{\rm ox} - E_{\rm red} - \Delta G_{\rm S} \tag{1}$$

where $\Delta G_{\rm S} = -e^2/(4\pi\epsilon_0\epsilon_{\rm R}R_{\rm Ct-Ct})$ and ϵ_0 and $\epsilon_{\rm R}$ refer to vacuum permittivity and dielectric constant of the solvent benzonitrile. This gives 1.26 eV and 1.39 eV as the energies of the CS states of **1** and **2**, respectively, in benzonitrile. The term $R_{\rm Ct-Ct}$ refers to the center-to-center distance (estimated as 3.5 Å) of the optimized structure shown in Fig. 3a. Furthermore, the driving force for charge separation can be calculated as

$$-\Delta G_{\rm CS} = \Delta E_{0-0} - \Delta G_{\rm RIP} \tag{2}$$

where $\Delta E_{0.0}$ is the energy of the lowest excited state (estimated from the first Q-band in the absorption spectrum as 2.03 eV and 2.01 eV for **1** and **2**, respectively).

Such calculations reveal that the generation of $((Ph_2N)_3$ -ZnP)*+-Q⁻⁻ in **1** and ZnP*+-Q⁻⁻ in **2** are exothermic *via* the singlet excited state of the porphyrin in PhCN [24].

Time-resolved spectroscopy studies

Femtosecond up-conversion measurements were carried out to determine the fluorescence lifetime of the first excited singlet state of Zn porphyrin in 1 and 2 in PhCN. A fast component with a lifetime close to the instrument time resolution was observed for both dyads (Fig. 4). In addition, another longer-living component was seen, although not very accurately resolved with the measured time range. For 2 this longer-living component is a minor one compared to the fast component (Fig. 4a), but for 1 the situation is reversed (Fig. 4b) [26]. There is no direct explanation for this longer-living fluorescence. However, the measurements were repeated after approximately two weeks and the longer-living component was found to be stronger in amplitude than in the first measurements. Thus it seems that the samples were not quite stable in time, even though the absorption spectrum measured before and directly after the up-conversion measurements showed no signs of sample degradation.

Transient absorption of the compounds was monitored with two systems in two different time scales. In the femtosecond pump-probe measurements mainly Zn porphyrin was excited at 410 nm. The global fitting of the pump-probe absorption decay curves of 1 in PhCN required four exponentials (Fig. 5). The component with a lifetime 1.1 ps shows characteristic cation absorption of TPA substituted Zn porphyrin above 700 nm [15] and can be attributed to the CS state. The 0.3 ps component is a mirror image of the 1.1 ps component and corresponds to the formation of the CS state from the singlet excited state of Zn porphyrin. The lifetime of the singlet excited state (0.3 ps) is in agreement with the shorter fluorescence decay component $(0.6 \pm 0.3 \text{ ps})$ detected in the up-conversion measurements. Similar behavior was observed for compound 2 (not shown): the CS state was formed in 0.37 ps and it decayed in 2 ps. The spectrum of the CS state in 2 corresponds well with that of ZnTPP radical cation, *i.e.* the broad radical cation band is at a lower wavelength range compared to that seen in **1**.

The time constants obtained for charge separation and charge recombination and the energies of the states can be used to estimate the reorganization energy, λ , of the electron transfer reaction. According to Marcus ET theory, the rate constants for charge separation, k_{cs} , and charge recombination, k_{cr} , are;

$$k_{cs} = k_0 \exp\left[-\frac{(\Delta G_{cs} - \lambda)^2}{4\lambda k_B T}\right] \text{ and}$$
$$k_{cr} = k_0 \exp\left[-\frac{(\Delta G_{cr} - \lambda)^2}{4\lambda k_B T}\right]$$
(3)



where k_0 is the rate for the passage through the transition state from the reactant state (the singlet excited

Fig. 4. Fluorescence decay curves of (a) **2** and (b) **1** in PhCN. The excitation wavelength was 410 nm and the signal was monitored at 620 nm. The lifetimes and the amplitudes (in brackets) obtained from the bi-exponential fitting are indicated in the figure



Fig. 5. Transient absorption decay component spectra of **1** in PhCN measured with the femtosecond pump-probe method (420 nm excitation). The spectra with time constants 0.3 and 1.1 ps correspond to the charge separation and recombination reactions, respectively, and the longer-lived components originates from the solvent response (see text for more details)

state or the charge-separated state for charge separation and charge recombination, respectively) to the product state (charge-separated state or ground state for charge separation and charge recombination, respectively), k_B is the Boltzmann constant and *T* is the temperature. If k_0 is assumed to be the same for both charge separation and charge recombination, dividing the equations 3 one by another and solving for λ gives:

$$\lambda = \frac{E_{ex}(2E_{cs} - E_{ex})}{4k_B T \ln \frac{k_{cs}}{k_{cr}} + 2(2E_{cs} - E_{ex})}$$
(4)

where E_{ex} and E_{cs} are the energies of the singlet excited state and the CS state, respectively. The calculated values for λ are 0.89 eV and 0.90 eV for **1** and **2**, respectively, and they are quite reasonable for porphyrin-quinone dyads [25].

The two longer-living components needed for the fitting of the pump-probe results are more difficult to interpret, because the solvent, benzonitrile, also participates in the signal. The measurements were carried out also for pure PhCN, and a long-living signal with a broad 600 nm centered absorption was observed. It was not possible to get rid of this solvent signal completely by reducing the excitation intensity, but it was taken into account while analyzing the data. Thus, the 6 ps component and the longest-living component, with a lifetime too long to be resolved with the instrument (time limit ~1 ns), originate most probably from the solvent, though some typical Q-band features of Zn porphyrin can be noticed in the spectra of the components around 560 nm and 600 nm.

The flash-photolysis measurements in the microsecond time-scale were carried out to investigate possible contribution of the triplet excited state to photoinduced electron transfer. The measurements were carried out under nitrogen flow to reduce triplet state quenching by molecular oxygen dissolved in the solvent. The excitation wavelength was 355 nm, which excites the TPA moieties predominantly. Energy transfer from the triphenylamines to Zn porphyrin was expected, because it was observed earlier for a similar dyad with fullerene as the acceptor instead of quinone [15], however the efficiency of the singlet-singlet energy transfer was estimated to be 80%, which indicates that a considerable part of excited TPA chromophores relax to the triplet excited state. One can also notice that through the multiple excitation of one and the same molecule by relatively long (15 ns) laser pulse at 355 nm the actual yield of the triplet state after the excitation may exceed 20%, thus generating relatively strong transient absorption response of the samples.

In the time domain of flash photolysis measurements (>20 ns) and selective excitation of TPA at 355 nm, one can expect to observe triplet excited states of TPA and ZnP chromophores, one formed as the result of intersystem crossing and another resulting from singlet state energy transfer from TPA to ZnP, respectively. The transient absorption spectrum of $(TPA)_4$ -ZnP measured right after excitation (Fig. 6a, spectrum denoted as "at t = 0") has a strong absorption band around 1000 nm, which is in agreement with previously published results [15]. In this wavelength range triplet state of regular ZnTPP has only weak and featureless absorption, whereas TPA is



Fig. 6. Transient absorption decay component spectra and calculated spectrum at 0 delay time of (a) (TPA)₄-ZnP and (b) **1** in PhCN measured with the microsecond flash-photolysis method (355 nm excitation)

expected to have spectrum similar to that presented in Fig. 6a at t = 0. The spectrum changes drastically with time constant of 50 µs, converting to less intense and virtually flat absorption over the measured near infra red region. This change can be attributed to the triplet-triplet energy transfer to the Zn porphyrin chromophore [15].

Comparison with the spectrum detected at 0 delay time for 1 (Fig. 6b) shows clearly that the first detectable state is the triplet state of the TPA chromophore also in 1. Global fitting of the transient absorption decays of 1 requires at least three exponential components which resulted in decay associated spectra presented in Fig. 6b. The triplet state of TPA chromophores relaxes by yielding two other intermediate states. At first a state with rather broad and featureless absorption appears (the spectrum at $t = 30 \ \mu s$ in Fig. 6b), and then a state with a broad but clear band around 1300 nm is formed (the longest-lived component, 840 us, in Fig. 6b). The latter can be attributed to the Zn porphyrin cation with triplet character, *i.e.* to the CS triplet state [15, 28]. Based on this observation three step relaxation of TPA triplet state can be proposed. The first step is intramolecular triplettriplet energy transfer from TPA chromophore to ZnP moiety with time constant 15 µs. Second is charge separation between the porphyrin and quinone moieties with 81 µs time constant, and finally the charge recombination with time constant 840 µs. Further studies involving time resolved EPR may be needed to confirm this long-lived charge separated state.

To confirm triplet nature of the CS, the measurements were repeated for air saturated sample and comparison of the transient absorption decays in air and under nitrogen is presented in Fig. 7 at the monitoring wavelength corresponding to the absorption of the CS state, 1480 nm. Atmospheric oxygen is known to quench efficiently the triplet state, which reduces gradually the yield of the CS state, but lifetime of CS state formed in air saturated sample remains virtually identical to that in deoxygenated sample.

Apparently the TPA triplet state relaxes faster in **1** than in $(TPA)_4$ -ZnP, which has no clear explanation. Though

in air

= 680 μs

1000

Time, μs

1500

in N2

τ₁ = 54 μs

 $\tau_2 = 300 \ \mu s$

= 790 μs

2000



500



Fig. 8. Suggested reaction scheme for 1

one may argue that presence of quinone at the *meso*position may affect electron density distribution along the porphyrin ring, and thus change electronic interactions of the TPA and porphyrin moieties, which is confirmed indirectly by the difference in steady state absorption and emission of the compounds (see Fig. 1).

Based on the time-resolved absorption measurements, reaction scheme presented in Fig. 8 can be suggested. When exciting the TPA units predominantly (at 355 nm), the intersystem crossing is followed by the triplet-triplet energy transfer to yield the triplet state of TPA substituted Zn porphyrin. The long-living CS state with triplet spin character is then formed from the Zn porphyrin triplet state. Alternatively, if the Zn porphyrin is directly excited (at 410 nm), a rapid ET reaction occurs from the singlet excited state and the formed CS state with singlet spin character relaxes quickly to the ground state. A distinct difference between the charge separated states with singlet and triplet spin characters can be attributed to a short (single carbon bond) linker between the donor, porphyrin, and acceptor, quinone, moieties, in which case some degree of electronic coupling between the donor and acceptor remains after the electron transfer, thus preserving multiplicity of the whole dyad.

EXPERIMENTAL

Chemicals

Benzonitrile (in sure seal bottle under nitrogen) was from Aldrich Chemicals (Milwaukee, WI). Tetra-*n*butylammonium perchlorate, (TBA)ClO₄ was from Fluka Chemicals. All the chromatographic materials and solvents were procured from Fisher Scientific and were used as received.

Synthesis of 1

5-(2,5-dimethoxyphenyl)-10,15,20-tri-*N***,N-diphenylporphyrin.** This compound was synthesized by reacting 2,5-dimethoxybenzaldehyde (12 mmol), 4-formyltriphenylamine (37 mmol), and pyrrole (49 mmol) in refluxing propionic acid. The crude product was purified on a basic

0

0,005

0,004

0,003

0,002

0,001 0,000

 \mathbb{A}

alumina column. ¹H NMR (300 MHz; CDCl₃): $\delta_{\rm H}$, ppm -2.69 (2H, s (br), pyrrole-N*H*), 3.5 (3H, s, 5-OC*H*₃), 3.9 (3H, s, 2-OC*H*₃), 7.0–7.16 (12H, m, *N*-ph), 7.26–7.36 (2H, m, ph), 7.38–7.56 (24H, m, *m*-ph and *N*-ph), 7.61 (1H, m, ph), 8.1 (6H, m, *o*-ph), 8.80–9.0 (8H, m, pyrrole-*H*). MS (ESI): *m/z* 1175.49 (calcd. 1176.41).

5-[phenyl(2,5-dione)]-10,15,20-tri-N,N-diphenyl**porphyrin.** A 9 mL solution of BBr₃ (1 M in CH_2Cl_2) was drop wise added to a solution of 5 - [2,2' - (2,5 - dimethoxy)]10,15,20-tri-N,N-diphenylporphyrin (1.0 mmol) in CH₂Cl₂ at -78 °C. The solution was maintained at this temperature until the addition was completed and stirred at room temperature under oxygen for 12 h in dark. Then the mixture was brought to below 5 °C and 100 mL of cold water was added followed by addition of saturated sodium bicarbonate. After stirring 1 h at room temperature the organic layer was separated using CH₂Cl₂ and dried over anhydrous Na₂SO₄. The solvent was evaporated and the crude product was purified on silica column. ¹H NMR (300 MHz; CDCl₃): $\delta_{\rm H}$, ppm -2.70 (2H, s (br), pyrrole-NH), 7.26–7.31 (12H, m, N-ph), 7.39–7.48 (2H, m, ph), 7.48–7.55 (24H, m, *m*-ph and *N*-ph), 7.60 (1H, m, ph), 8.05-8.15 (6H, m, o-ph), 8.90-9.05 (8H, m, pyrrole-*H*). MS (ESI): *m*/*z* 1145.44 (calcd. 1146.34).

Zinc 5-[phenyl(2,5-dione)]-10,15,20-tri-*N*,*N*-diphenylporphyrin, 1. A 0.0125 mmol of free base porphyrin was dissolved in 30 mL of CHCl₃, and an excess of zinc acetate (50 equiv.) in methanol was added. The course of the reaction was monitored spectroscopically. At the end of the reaction (1 h), the solvent was evaporated and the product was purified on silica gel column. ¹H NMR (300 MHz; CDCl₃): $\delta_{\rm H}$, ppm 7.26–7.31 (12H, m, *N*-ph), 7.39–7.48 (2H, m, ph), 7.48–7.55 (24H, m, *m*-ph and *N*-ph), 7.60 (1H, m, ph), 8.05–8.15 (6H, m, *o*-ph), 8.90– 9.05 (8H, m, pyrrole-*H*). MS (ESI): *m*/*z* 1207.36 (calcd. 1209.73).

Instrumentation

The UV-visible spectral measurements were carried out with a Shimadzu Model 1600 UV-visible spectrophotometer. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. A right angle detection method was used. The ¹H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Differential pulse voltammetry was recorded on a EG&G model 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 a 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 argon gas. The computational calculations were performed by DFT B3LYP/3-21G(*) methods with GAUSSIAN 03[22] software package on high speed PCs while the MEP and frontier orbitals were generated using GaussView program. The mass spectra of the newly synthesized compounds were recorded on a Varian 1200L Quadrupole MS using APCI mode in dry CH_2Cl_2 .

Flash-photolysis method was used to study timeresolved absorption in microsecond time-scale. The experiments were carried out with a modified Luzchem laser flash system (mLFP111 prototype from Luzchem Co.) using the third harmonic of Nd: YAG laser providing 30 ns pulses at 355 nm for excitation. Excitation power density was roughly 6 mJ cm⁻². A continuous Xe-lamp (Oriel Simplesity Arc Source) was used to provide monitoring light and the signal was recorded with a digitizing oscilloscope (Tektronix, TDS3032B, 300 MHz). The system was controlled with a PC computer. The samples were deoxygenated by nitrogen bubbling for 20 min prior to the measurements and a nitrogen flow was maintained on the surface of the solution during the measurements. All measurements were carried out at room temperature.

Pump-probe technique for time-resolved absorption was used to detect the fast processes with a time resolution shorter than 0.2 ps. The fundamental of the Ti:sapphire laser (TiF-50, CDP Corp.) pumped by Nd-YAG CW laser (Verdi-6, Coherent Inc.) was split in two: A part of the beam went through a second harmonic generator to obtain excitation at 410 nm (pump), and the other part was passed through a cuvette filled with water generating a white continuum for monitoring (probe) the changes in absorption. Before focusing on the rotating sample cuvette, the pump beam was passed through an adjustable delay line, which was scanned to obtain transient absorption signals up to approximately 1 ns after the excitation. A CCD camera was used to detect the differential absorption spectra at different delay times, and from these the transient absorption decay curves were drawn at different wavelengths. Exponential fitting of the absorption decay curves was done globally for the measured wavelength range for both pump-probe and flashphotolysis results. The data analysis procedure has been described in more detail earlier [27].

Up-conversion instrument (FOG-100, CDP Corp.) for time-resolved fluorescence was used to detect the fast processes with a time resolution of ~200 fs. The same Ti:sapphire generator used for pump-probe was used to excite (~410 nm) the sample solution in a rotating cuvette [27]. Emission from the sample was collected to a nonlinear crystal (NLC), where it was mixed with the so-called gate pulse, which was the laser fundamental. The signal was measured at a sum frequency of the gate pulse and the selected emission maximum of the sample. The gate pulses were passed through a delay line so that it arrived at NLC at a desired time after sample excitation. Scanning through the delay line the emission decay curve of the sample was detected. Exponential fitting of the fluorescence decay curve was carried out in a similar manner as for the transient absorption decay curves [27].

CONCLUSION

A novel multi-modular donor-acceptor system, 1 composed of three triphenylamine entities, porphyrin and quinone, was designed, synthesized and studied to investigate photoinduced processes by time-resolved spectroscopic techniques including pump probe and upconversion methods. The spectral and computational studies revealed appreciable electronic interactions between porphyrin π -system and the *meso*-substituents. The free-energy change for charge-separation and chargerecombination were evaluated using electrochemical and absorption data. The charge-separation processes were monitored by steady-state and time-resolved emission studies, which revealed occurrence of efficient electron transfer processes in 1. The ET reaction path was found to be dependent on the excitation wavelength, *i.e.* whether the Zn porphyrin was excited directly or via the triphenvlamine moieties. When Zn porphyrin was predominantly excited, a rapid charge separation followed by equally fast charge recombination was observed. Instead, excitation of the TPA substituents lead to an extremely long-living CS state with triplet spin character via the TPA triplet and Zn porphyrin triplet states.

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