Ultrafast Singlet-Singlet Energy Transfer in Self-Assembled via Metal-Ligand Axial Coordination of Free-Base Porphyrin-Zinc Phthalocyanine and Free-Base Porphyrin-Zinc Naphthalocyanine Dyads

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Singlet-singlet energy transfer in self-assembled via axial coordination of imidazole-appended (at different positions of one of the *meso*-phenyl entities) free-base tetraphenylporphyrin, H₂PIm, to either zinc phthalocyanine, ZnPc, or zinc naphthalocyanine, ZnNc, dyads is investigated in noncoordinating solvents, o-dichlorobenzene and toluene, using both steady-state and time-resolved transient absorption techniques. The newly formed supramolecular dyads were fully characterized by spectroscopic, computational, and electrochemical methods. The binding constants measured from optical absorption spectral data were found to be in the range of $10^4 - 10^5 \text{ M}^{-1}$ for the 1:1 dyads, suggesting fairly stable complex formation. Electrochemical and computational studies suggested that photoinduced electron transfer is a thermodynamically unfavorable process when free-base porphyrin is excited in these dyads. Selective excitation of the donor free-base porphyrin entity was possible in both types of dyads formed by either of the ZnPc or ZnNc energy acceptors. Efficient singlet-singlet energy transfer was observed in these dyads, and the position of imidazole linkage on the free-base porphyrin entity, although flexible, seems to have some control over the overall efficiency of excited energy transfer process. Kinetics of energy transfer was monitored by performing transient absorption measurements using both up-conversion and pump-probe techniques. Such studies revealed ultrafast singlet-singlet energy transfer in the studied dyads with time constants on the order of 2-25 ps depending upon the type of the dyad.

Introduction

The amazing features of Nature to tap available resources for the benefit of living organisms have intrigued mankind over centuries. One such classic example is photosynthesis which harvests solar energy and converts it to chemical energy in the form of transmembrane charge separation via a multistep electron transfer reaction.¹ Chlorophylls and carotenoids are the primary pigments of natural light harvesting systems responsible for converting the energy of an absorbed photon into an electron excitation. The supramolecular organization of these pigments (antenna) allows the unidirectional excitation energy transfer toward a reaction center, the final destination of the collected energy.^{1,2} Inspired by this natural phenomenon, researchers have been attempting to mimic such complex processes with the help of synthetic molecular architectures, often termed as artificial photosynthesis.^{3–11} Research in this area holds promise not only to improve the fundamental understanding but also to advance technologically in building light energy harvesting photovoltaic devices, to construct molecular optoelectronics and to develop photocatalysts capable of producing hydrogen.¹²

In artificial photosynthesis, two photoinduced events are mainly targeted, viz., excitation energy transfer to mimic the antenna functionality, and electron transfer to mimic reaction center functionality.^{3–11} Several strategies have been employed

to mimic the natural energy transfer process, including covalently linked dyads and polyads,^{13–16} polymers,¹⁷ dendrimers,¹⁸ and selfassembled systems.¹⁹ In these model compounds, successful excitation energy transfer from donor to the acceptor entities has been demonstrated. In the majority of these studies, porphyrins²⁰ and phthalocyanines²¹ have been used as a energy/electron donor/ acceptor due to their close resemblance to the photosynthetic pigment, chlorophyll, and the established synthetic methodologies. Both macrocycles are ideal photoactive units with outstanding electronic properties, namely, strong absorption in the visible region and the possibility of fine-tuning the redox potentials. Further, their absorption can easily be extended into near-IR region by increasing macrocycle π -conjugation.^{20,21}

Self-assembly via metal—ligand axial coordination is one of the successful approaches developed to study photoinduced electron transfer in donor—acceptor dyads.¹¹ However, utilization of this strategy to build dyads composed of different donor and acceptor fluorophores to mimic the natural energy transfer process has not been fully explored. This has been accomplished in the present study by constructing donor—acceptor dyads using free-base porphyrin as energy donor and zinc phthalocyanine as energy acceptor via axial ligand coordination.²² Further, zinc naphthalocyanine, a phthalocyanine structural analogue, having absorption and emission well into the near-IR region, has been utilized to verify energy transfer from singlet excited porphyrin to a near-IR emitting fluorophore. To achieve axial coordination, free-base porphyrin has been functionalized with an imidazole entity at the ortho, meta, or para positions of one of the *meso*-

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CHART 1: Structure of the Donors and Acceptors Employed in the Present Study To Probe Excitation Energy Transfer



aryl groups (see Chart 1). The different substitutions are expected to result in dyads of different orientations. Photochemical studies using both steady-state and time-resolved transient absorption techniques have been performed to probe efficiency and kinetics of excitation energy transfer in the newly formed dyads.

Results and Discussion

Optical Absorption and Binding Constant Studies. Figure 1 shows the optical absorption spectra of H_2P_0Im , ZnPc, and ZnNc derivatives in *o*-dichlorobenzene (DCB), normalized to their most intense absorption bands. The absorption spectrum of H_2P_mIm and H_2P_pIm were found to be similar to that of H_2P_0Im with an intense Soret at 424 and four visible bands at 518, 553, 594, and 652 nm. The spectrum of ZnPc exhibited bands at 348, 614, 653, and 681 nm while the spectrum of ZnNc revealed peaks at 335, 690, 737, and 777 nm, respectively; that is, the spectrum of ZnNc is stretched well into the near-IR region. Importantly, the H_2PIm band at 518 nm had no overlap with the absorption bands of either ZnPc or ZnNc, providing the possibility for selective excitation of the donor, free-base porphyrin.



Figure 1. Absorption spectra of (i) H_2P_0Im , (ii) ZnPc, and (iii) ZnNc in DCB, normalized to their most intense bands. The concentrations are in the range of $5-10 \ \mu M$.

Figure 2a and 2b show absorption spectral changes recorded during increasing addition of H₂P_pIm to the solutions of ZnPc and ZnNc, respectively. Similar spectral changes were observed for H₂P₀Im and H₂P_mIm binding to the acceptor zinc macrocycles (see Supporting Information Figures S1 and S2). The binding of H₂P_pIm to ZnPc was characterized by diminished intensity of 614 and 681 nm bands with isosbestic points at 609, 663, and 672 nm, indicating existence of only one equilibrium process in solution. Similarly the binding of H₂P_pIm to ZnNc was characterized by diminished intensity of 690, 737, and 777 nm bands with 2-4 nm blue shifts (Figure 2b). Isosbestic points were also observed at 665, 686, 731, and 750 nm, indicating existence of only one equilibrium process in solution. Plots of method of continuous variation confirmed 1:1 complex formation between the donor and acceptor entities. The formation constants, K, for H₂PIm binding to ZnPc and ZnNc were obtained from the absorption spectral data using the Benesi-Hildebrand method²³ (Figure 2a and 2b insets) and are listed in Table 1. The magnitude of the K values suggests stable complex formation. The K values follow the trend: para \sim meta > ortho of imidazole substitution on the phenyl ring of porphyrin macrocycle for a given zinc macrocycle binding, a trend that could be easily attributed to the steric constraints of the orthosubstituted porphyrin derivative. Additionally, binding constants for ZnNc were found to be 2-3 times higher than that obtained for the corresponding ZnPc binding. This could be attributed to the electron-rich ZnNc macrocycle compared to ZnPc macrocycle as revealed by their electrochemical oxidation potentials, discussed in the next section.

Electrochemical Studies. Differential pulse voltammetric studies (DPV) were performed to evaluate the oxidation and reduction potential of the investigated donor-acceptor entities. The first reversible oxidation and first two reversible reductions of H_2P_oIm were located at 0.55 V, and -1.67 and -2.02 V vs Fc/Fc⁺ in 0.1 (TBA)ClO₄, respectively. For H_2P_mIm and H_2P_pIm , the first reduction was shifted in the negative direction by 50–60 mV while the first oxidation was anodically shifted by 40 mV (see Figure 3). The first oxidation of ZnPc and ZnNc were overlapping two one-electron processes. The peak potential were located at -0.05 V vs -0.38 V vs Fc/Fc⁺, respectively, for ZnPc and ZnNc. That is, these compounds revealed easier oxidations compared to the free-base porphyrins used in the



Figure 2. UV-visible-near IR spectral changes observed during increasing addition of H_2P_pIm (0.1 equiv) to a solution of (a) ZnPc (0.11 mM) and (b) ZnNc (0.11 mM) in DCB. The figure insets show Benesi-Hildebrand plots constructed to obtain the binding constants. The absorption changes of the 681 nm band of ZnPc and 776 nm band of ZnNc were utilized.

 TABLE 1: Binding Constants, K, and B3LYP/3-21G(*) Computed Results for Dyads Formed by Binding Imidazole-Appended

 Free-Base Porphyrin to Zinc Phthalocyanine or Zinc Naphthalocyanine

dyad ^a	K, mol ^{-1 b}	center-to-center distance, Å	edge-to-edge distance, Å	angle between rings, deg	HOMO-LUMO gap, eV
H ₂ P _o Im:ZnPc	4.20×10^{4}	7.4	5.75	46	2.09
H ₂ P _m Im:ZnPc	3.50×10^{4}	10.7	6.11	35	2.11
H ₂ P _p Im:ZnPc	8.23×10^{4}	13.0	8.83	56	2.08
H ₂ P _o Im:ZnNc	6.60×10^{4}	8.06	5.75	35	1.79
H ₂ P _m Im:ZnNc	1.48×10^{5}	12.1	9.96	55	1.78
H ₂ P _p Im:ZnNc	1.53×10^{5}	13.0	9.22	55	1.82

^{*a*} See Chart 1 for the structure of different donor and acceptor entities; in DCB at room temperature. ^{*b*} Error = $\pm 10\%$.



Figure 3. Differential pulse voltammograms of the investigated compounds ($\sim 0.5 \text{ mM}$) in DCB 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.

present study. The first reduction peaks of ZnPc and ZnNc were located at -1.65 and -1.70 V vs Fc/Fc⁺, indicating these to be poor electron acceptors (vide infra).

Energy Optimization by DFT Calculations. Since the relative orientation of the donor and acceptor dipoles in the dyads is crucial for energy transfer efficiency, the structures of

the supramolecular dyads were visualized by performing computational studies at the B3LYP/3-21G(*) level.^{24,25} Figure 4 shows the structures of the dyad optimized on a Born-Oppenheimer potential energy surface. The two macrocyclic rings of the H₂P₀Im:ZnPc and H₂P₀Im:ZnNc dyads were found to be in a skipped coplanar arrangement while for the meta and para imidazole derivatized dyads, H₂PIm:ZnPc and H₂PIm: ZnNc, they were positioned at an angle less than 90°. The edgeto-edge distances, center-to-center distances, and angles between the two macrocycle planes of the donor-acceptor entities are listed in Table 1. Generally, the distances varied as follows: ortho < meta < para imidazole-substituted porphyrins. That is, a closer distance and skipped coplanar configuration for the ortho derivatives, and a relatively longer distance and near-orthogonal configuration for the meta and para substituted derivatives, were observed.

The frontier orbitals, HOMO and LUMO, were also evaluated for both types of dyads, and the representative orbitals for selected dyads are shown in Figure 4. It is important to note that the HOMO for all of the studied dyads was fully localized on the ZnPc or ZnNc macrocycles while the LUMO was located on the porphyrin macrocycle. In conjunction with the earlier discussed electrochemical results, these results point out that electron transfer from the excited free-base porphyrin to either the coordinated ZnPc or ZnNc is less likely to take place. The gas-phase HOMO–LUMO gap is found to be smaller by \sim 300 mV for the H₂PIm:ZnNc series of dyads compared to the H₂PImZnPc series of dyads, a result that readily agrees with the electrochemical results.



Figure 4. B3LYP/3-21G(*) optimized structures of the dyads formed via axial coordination of H_2PIm (ortho, meta, or para) to (a) ZnPc and (b) ZnNc. The HOMO and LUMO of H_2P_mIm bound to ZnPc and ZnNc are shown in the lower panels.

Using the electrochemical, computational, and excited energy data, the free energies of charge-separation (ΔG_{CS}) were calculated using eq 1 by Weller's approach.²⁶

$$-\Delta G_{\rm CS} = \Delta E_{0-0} - e(E_{\rm ox} - E_{\rm red}) + \Delta G_{\rm S}$$
(1)

where ΔE_{0-0} is the energy of the lowest excited state of H₂P (1.89 eV), $\Delta G_{\rm S} = -e^2/(4\pi\varepsilon_0\varepsilon_{\rm R}R_{\rm Ct-Ct})$, and ε_0 and $\varepsilon_{\rm R}$ refer to vacuum permittivity and dielectric constant of DCB.

The calculations revealed ΔG_{CS} values to be endothermic by 0.1–0.2 eV for electron transfer from the singlet excited freebase porphyrin to either ZnPc or ZnNc, suggesting the less likely occurrence of such reactions in the studied dyads.

Steady-State Fluorescence Studies: Singlet–Singlet Energy Transfer. As pointed out earlier, excitation of the donor, H₂PIm, at 518 nm to a large extent selectively excites the freebase porphyrin, thus allowing us to monitor energy transfer to the acceptor, ZnPc or ZnNc entities, without them being directly getting excited. Figure 5a and 5b show the spectral changes observed for H₂P_pIm emission during increasing addition of ZnPc and ZnNc in DCB. The emission band of H₂P_pIm located at 655 nm revealed quenching with simultaneous appearance of new emission bands at 694 and 758 nm corresponding to ZnPc (Figure 5a), and 782 and 820 nm corresponding to ZnNc (Figure 5b). Similar results were obtained when H₂P_mIm and H₂P_oIm were titrated with either ZnPc or ZnNc (see Supporting

Information for the spectral data, Figures S3–S6). Further, the excitation spectra of the dyads were recorded by holding the excitation wavelength at 758 for ZnPc and 782 for ZnNc. Such spectra revealed absorption bands corresponding to both donor and acceptor entities (see Supporting Information for the spectral data, Figures S7). In a control experiment, free-base *meso*-tetraphenylporphyrin, H₂TPP, was also titrated with the acceptor molecules. Under these conditions, only a slight increase of the acceptor emission in the near-IR region was observed. These results confirm occurrence of singlet–singlet energy transfer in the self-assembled dyads.

Figure 5c and 5d shows the extent of energy transfer for each of the porphyrin derivatives upon increasing addition of ZnPc and ZnNc, respectively. It is clear from these plots that after addition of about 3–4 equiv of the acceptor entities, the energy transfer has attained its maximum value. Further, the extent of energy transfer followed the order: $H_2P_pIm > H_2P_mIm > H_2P_0Im > H_2TPP$ according to their binding constants. The latter plots for H_2TPP interactions being virtually horizontal imply occurrence of little or no energy transfer.

Excited Energy Transfer: Theoretical Considerations. The observed excitation energy transfer (EET) could occur either via Dexter's exchange mechanism or Forster's dipole–dipole mechanism. The former mechanism requires the presence of electronic communication between the donor and acceptor species (via orbital overlap).²⁷ However, the frontier orbitals from the DFT studies (Figure 4) in conjunction with the



Figure 5. Steady-state fluorescence spectra of H_2P_pIm (1.2×10^{-4} M) upon increasing addition of (a) ZnPc and (b) ZnNc, respectively, in DCB, excited at 518 nm. (c and d) Emission intensities of ZnPc monitored at 758 nm and of ZnNc monitored at 781 nm for the titration involving (i) H_2P_pIm , (ii) H_2P_nIm , (iii) H_2P_oIm , and (iv) H_2TPP , demonstrating the extent of energy transfer efficiency.

spectroscopic studies reveal that such intramolecular interactions are almost nonexistent. Therefore, the results of the present study have been analyzed according to Forster's mechanism. According to this mechanism, the rate of excitation energy transfer, k_{Forster} , is given by eq 2.

$$k_{\rm Forster} = [8.8 \times 10^{-25} \kappa^2 \Phi_{\rm D} J_{\rm Forster}] / [n^4 \tau_{\rm D} R^6]$$
(2)

where *n* is the solvent refractive index, Φ_D and τ_D are the fluorescence quantum yield (= 0.12) and the fluorescence lifetime of the isolated donor (free-base porphyrin), J_{Forster} is the Forster overlap integral representing the emission of the donor and absorption of the acceptor ZnPc or ZnNc, and *R* is the donor-acceptor center-to-center distance (Table 1). The τ values measured using a strobe technique were found to be 11.50, 9.95, and 9.45 ns, respectively, for the ortho, meta, and para imidazole-derivatized free-base porphyrins, values close to those reported for free-base tetraphenylporphyrins in the literature.¹¹ In eq 2, κ^2 is the orientation factor as described in eq 3, often playing a key role in determining the directionality of excitation energy transfer.

$$\kappa^2 = \left[\cos\nu - 3\cos\alpha\cos\beta\right]^2 \tag{3}$$

where α and β are the angles made by the transition dipoles of the donor and acceptor entities with the line joining the centers of the transitions, and ν is the angle between the two transition

dipoles. The transition dipoles of tetrapyrroles are known to lie along a line joining two opposing pyrrole nitrogens.²⁸ Depending upon the relative orientation of the donor and acceptor, the value of κ^2 could range from 0 to 4. For head-to-tail parallel transition dipoles, $\kappa^2 = 4$, for parallel dipoles, $\kappa^2 = 1$, and for dipoles oriented perpendicular to each other, $\kappa^2 = 0$. An analysis of the results presented in Figure 4 shows different orientations for the ortho, meta, and para substituted derivatives. However, considering the flexible nature of the connecting axial bond, a value of $\kappa^2 = 2/3$, generally used for randomly oriented dipoles, is employed.

The J_{Forster} spectral overlap integral representing the emission of the donor and absorption of the acceptor is given by eq 4.

$$J_{\text{Forster}} = \int F_{\text{D}}(\lambda) \varepsilon_{\text{A}}(\lambda) \lambda^4 d\lambda \qquad (4)$$

where $F_{\rm D}(\lambda)$ is the fluorescence intensity of the donor with total intensity normalized to unity, and $\varepsilon_{\rm A}(\lambda)$ is the molar extinction coefficient of the acceptor expressed in units of M^{-1} cm⁻¹ and λ in nanometers. Figure 6 shows the spectral overlap of the donor and acceptor absorption and emission bands for both types of dyads. Analysis of the data according to eq 4 resulted in *J* values of $3.52 \times 10^{-12} \text{ M}^{-1} \text{ cm}^3$ and $4.21 \times 10^{-12} \text{ M}^{-1} \text{ cm}^3$, respectively, for the H₂PIm:ZnPc and H₂PIm:ZnNc dyads.

Equation 1 can be further simplified in terms of Forster distance, R_0 , where half the donor molecules decay by energy transfer and half decay by the usual radiative and nonradiative mechanisms.

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$$k_{\rm Forster} = 1/\tau_{\rm D} (R_{\rm o}/R)^{\rm 6} \tag{5}$$

Further, the EET efficiency can be measured by using relative fluorescence intensity or lifetime of the donor in the absence and presence of acceptor, according to eq 6.

efficiency,
$$E = 1 - I_{DA}/I_D = 1 - \tau_{DA}/\tau_D$$
 (6)

From the steady-state data, values of *E* obtained were found to be 0.55, 0.70, and 0.74, for the H₂PIm:ZnPc (o, m, and p) dyads, and 0.40, 0.50, and 0.56 for the H₂PIm:ZnNc (o, m, and p) dyads by monitoring the emission intensity of H₂PIm at 656 nm. The efficiency for ortho derivatives is found to be generally smaller, a trend that readily follows their *K* values. It is interesting to note that both of the acceptors have good spectral overlap and transfer efficiency in the studied series of dyads.

The k_{Forster} values were estimated by using the parameters described in eqs 1– 5 and found to be on the order of $10^{10}-10^{11}$ s⁻¹, revealing ultrafast energy transfer (Table 2). As explained in the subsequent paragraphs, the rate of energy transfer



Figure 6. Spectral overlap (highlighted area) for (a) $H_2PIm:ZnPc$ and (b) $H_2PIm:ZnNc$ type dyads. The donor absorption and emission, and acceptor absorption and emission (all normalized), on an increasing wavelength scale. The schematic above each spectrum shows the energy transfer path for each type of dyad.

TABLE 2: Estimated (k_{Forster}) and Experimentally Determined (k_{ENT}) Rates of Energy Transfer for the Dyads Formed by Coordination of Imidazole-Appended Free-Base Porphyrin to Zinc Phthalocyanine or Zinc Naphthalocyanine in DCB

dyad ^a	k_{Forster} , s ⁻¹ b	$k_{\rm ENT}$, s ⁻¹ ^c
H ₂ P _o Im:ZnPc	3.94×10^{11}	1.4×10^{11}
H ₂ P _m Im:ZnPc	1.32×10^{11}	1.7×10^{10}
H ₂ P _p Im:ZnPc	2.30×10^{11}	3.3×10^{10}
H ₂ P _o Im:ZnNc	3.88×10^{11}	2.0×10^{11}
H ₂ P _m Im:ZnNc	1.41×10^{11}	9.0×10^{10}
H ₂ P _p Im:ZnNc	1.50×10^{11}	4.0×10^{10}

^{*a*} See Chart 1 for the structure of different donor and acceptor entities. ^{*b*} Estimated according to eqs 1–5; error = $\pm 10\%$ ^{*c*} Determined from the pump-probe technique.

measured using pump-probe and up-conversion techniques agree well with the predictions of ultrafast energy transfer in the dyads.

Pump-Probe and Up-Conversion Spectral Studies. The photodynamics of the energy transfer of the newly formed dyads was studied by transient spectroscopy techniques. Transient absorption spectrum of H2PmIm in toluene obtained from the pump-probe technique is shown in Figure S8, Supporting Information. At the excitation wavelength of 410 nm, the internal conversion $(S_2 \rightarrow S_1)$ was faster than the time resolution of the pump-probe instrument, 200 fs; hence, the signal showed instant formation of the lowest excited state. The transient absorption response of ZnPc was relatively more complex and at least biexponential fit had to be used to achieve a reasonable fit of the results as presented in Figure S9, Supporting Information. Similar results indicating the presence of a minor transient absorption perturbation in 2-20 ps time domain have been already reported,^{20d,e} and a few explanations were proposed, but the origin of this signal remains unclear. However, after instant formation of a typical transient absorption spectrum of the singlet excited ZnPc after an excitation pulse at 410 nm, there was a minor (<20%) increase in Q-band bleaching with a relatively slow time constant (15 ps). Apparently this slow component had something to do with photodynamics of the ZnPc, although it had only a minor effect on the transient absorption spectrum of the compound. A similar component was then observed for the porphyrin-phthlocyanine dyads. To distinguish this component from the energy transfer processes taking place in the dyad, one can notice that it has virtually zero intensity in 500-650 nm wavelength range (Figure S9), whereas the porphyrin excited-state specific feature are well pronounced in this range (Figure S8).

Figure 7a shows transient absorption decay component spectra of the H₂P_pIm:ZnPc dyad together with the time-resolved spectrum just after excitation (at 0 ps delay time), while Figure 7b reveals the decay profiles of the 455 and 680 nm bands. The spectrum of the dyad immediately after excitation (at 0 ps) had features typical of the excited singlet state of the porphyrin except for a band around 680 nm which was due to a small portion of directly excited zinc phthalocyanine. This band increased in intensity with a time constant of 30 ps. Additionally, the 30 ps component showed the disappearance of the porphyrin excited-state features and conversion of the spectrum to one corresponding to the excited singlet state of ZnPc. Thus, the 30 ps time constant has been attributed to the energy transfer from H₂P_pIm to ZnPc. The minor component with a 0.5 ps lifetime was similar to the one observed for reference ZnPc and can be attributed to photodynamics of directly excited phthalocyanines.



Figure 7. (a) Transient absorption decay component spectra of the $H_2P_pIm:ZnPc$ dyad in toluene. The dashed line shows the differential absorption spectrum just after excitation (at 0 ps delay time). (b) Transient absorption decays of the dyad monitored at 680 and 455 nm. The solid lines represent the global fits at these wavelengths.



Figure 8. Time profiles showing (a) the porphyrin emission decay monitored at 656 nm and (b) rise of fluorescence of the phthalocyanine entity at 690 nm of the $H_2P_0Im:ZnPc$ dyad in toluene.

The transient absorption spectra of the $H_2P_0Im:ZnPc$ dyad shown in Figure S10 (Supporting Information) revealed similar spectral features. The component corresponding to energy transfer had a 7 ps time constant. The free-base porphyrin features were also observed for the $H_2P_mIm:ZnPc$ dyad (Figure S11, Supporting Information) even at the longest available delay time of 1 ns. However, the 600 ps component had a shape similar to the energy transfer component of the ortho and para derivatives. From these studies, the energy transfer time constant was found to follows the order: ortho > para > meta substitution of the free-base porphyrin.

The dyads were also investigated using a complementary upconversion technique. Figure 8 shows the fluorescence decay of the free-base porphyrin emission at 650 nm and the rise of the zinc phthalocyanine emission at 690 nm for the H₂P_pIm:ZnPc dyad in toluene. The time constant for the fast decay at 650 nm was 80 ± 100 ps while for the rising component at 690 nm it was 18 ± 5 ps. These values are slightly higher than that observed from the pump-probe measurements. Among these three time constants, the one from the pump-probe experiments is the most reliable because of less spectral interference; hence, the energy transfer time constant for this dyad was concluded to be 30 ps.

As shown in Figure S12, the fast decay and rise in fluorescence can also be seen for the H_2P_0 Im:ZnPc dyad. For this sample, a common fit of emission at two wavelengths gave a time constant of 2.2 \pm 0.5 ps for the energy transfer which agreed well with the corresponding value from the pump-probe measurements of 7 ps. As pointed out earlier, because the interference of the photodynamics of phthalocyanine to some extent makes the pump-probe results less reliable, an energy transfer time constant of 2 ps from the pump-probe technique

was assigned for this dyad. No reliable results were obtained for the H_2P_m Im:ZnPc dyad from the up conversion technique.

The transient absorption component spectra for ZnNc from the pump-probe technique are shown in Figure S13, Supporting Information. The results are essentially the same as for the ZnPc reference compound shown in Figure S9. There is some photodynamics of the excited state with a time constant of 2.3 ps. Otherwise the transient spectrum (longer-lived component) showed bleaching of the ground-state absorption bands at 770 and 685 nm and broadband absorption through the visible part of the spectrum.

The transient absorption component spectra of $H_2P_pIm:ZnNc$ dyad in toluene are presented in Figure 9. The spectrum of the dyad just after excitation (at 0 ps) had features typical for the excited singlet state of the porphyrin except for a band around 770 nm which was due to a small portion of directly excited ZnNc. This band increased in intensity with a time constant of 25 ps. Additionally, the 25 ps component showed a disappearance of the porphyrin excited-state features and conversion of the spectrum to the one corresponding to excited singlet state of ZnNc.

Similar results were also obtained for the $H_2P_0Im:ZnNc$ dyad (Figure S14, Supporting Information). The energy transfer time constant was 5 ps (±1.6 ps), somewhat faster than that obtained for the $H_2P_pIm:ZnPc$ dyad of 25 ps. As shown in Figure S15, Supporting Information, somewhat uncertain results were obtained for the $H_2P_mIm:ZnNc$ dyad. The component with a lifetime of 11 ps (±4 ps) seems to be one coming from the energy transfer (there are few deeps corresponding to porphyrin Q-bands), which did not agree with the results for the $H_2P_mIm:$ ZnPc dyad. However, for both dyads formed with H_2P_mIm , the



Figure 9. Transient absorption component spectra of the $H_2P_pIm:ZnNc$ dyad in toluene. The dashed line shows the differential absorption spectrum just after excitation (at 0 ps delay time).

interpretation of the pump-probe spectra is rather speculative, as the intensity of the component responsible for the energy transfer was found to be not well-defined.

The data from the transient spectroscopic studies confirm the occurrence of ultrafast excitation energy transfer in the studied dyads. The magnitude of measured rates of energy transfer agrees well with the estimated rate based on Forster's mechanism. Further, the energy transfer rates for dyads originated from ortho imidazole-substituted free-base porphyrin are generally higher compared to meta and para imidazole-substituted porphyrin likely because of closer proximity and favorable orientations.

Conclusions

Supramolecular free-base porphyrin-zinc phthalocyanine and free-base porphyrin-zinc naphthalocyanine dyads via a metalligand axial coordination approach have been formed in noncoordinating solvents and characterized by spectroscopic, computational, and electrochemical methods. The formation of a 1:1 complex was evident from an analysis of spectral data, and the measured binding constants were found to be on the order of $10^4 - 10^5 \text{ mol}^{-1}$ depending upon the nature of the freebase porphyrin and zinc macrocycle, suggesting moderate-tostable complex formation. The structures of the dyads were deduced from computational studies using the B3LYP/3-21G(*) method, and such studies, although highly flexible, revealed structures depending upon the nature of imidazole-appended free-base porphyrins. The redox potential of the donor and acceptor entities were measured using differential pulse technique, and the performed free-energy calculations suggested electron transfer to be an inefficient process when the free-base porphyrin is selectively excited in these dyads. Selective excitation of the donor free-base porphyrin entity was possible in both types of dyads formed by either of the ZnPc or ZnNc energy acceptors. Efficient singlet-singlet energy transfer was observed in the studied dyads, and the position of imidazole linkage on the free-base porphyrin entity seems to have little control over the overall efficiency, perhaps because of the flexible nature of the single-point axial linkage. Kinetics of energy transfer was monitored by performing transient absorption measurements using both up-conversion and pump-probe techniques. Such studies revealed ultrafast excitation energy transfer in the studied dyads with time constants on the order of 2-25 ps depending upon the type of the dyad.

Experimental Section

Chemicals. Zinc 2,11,20,29-tetra-*tert*-butylphthalocyanine, zinc 2,11,20,29-tetra-*tert*-butyl-2,3-naphthalocyanine, *o*-dichlorobenzene, and toluene (in sure seal bottles under nitrogen) were 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 Imidazole-Appended Free-Base Porphyrins. 2-[3-(1H-Imidazol-1-yl)phenyl]-1,3-dioxolane (1a). Imidazole (0.01 mol) was added to a suspension of sodium hydride (0.01 mol) in 10 mL of DMF. The resulting solution was stirred at room temperature for 20 min. Next, 2-(3-bromophenyl)-1,3dioxolane (0.01 mol) and copper powder (0.001 mol) were added to the reaction mixture which was refluxed for 5 h. The mixture was cooled to room temperature, chloroform and water were added, and the mixture was stirred for 2 h and filtered. The filtrate was washed with water and dried over sodium sulfate. The solvent was evaporated under reduced pressure. The compound was purified over a flash silica gel column using CH₂Cl₂/MeOH (95:5 v/v) as eluent. ¹H NMR (400 MHz, CDCl₃): δ 3.80–4.05 (m, 4 H), 5.68 (s, 1H), 7.05–7.38 (m, 6 H), 7.72 (s, 1H). Mass (APCI mode in CH₂Cl₂): calcd, 184.3; found [M + 1] 185.1.

3-(1*H***-Imidazol-1-yl)benzaldehyde (1b).** 2-[3-(1*H*-Imidazol-1-yl)phenyl-1,3-dioxolane was stirred at room temperature for 3 h in 20 mL of 1 M HCl. Aqueous NaHCO₃ was added to the reaction and extracted with ethyl acetate. The organic layer was washed with aqueous NaCl, dried over Na₂SO₄, and evaporated under reduced pressure to obtain the product as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.25 (s, 1H), 7.36 (s, 1H), 7.67–7.72 (m, 2H), 7.87–7.97 (m, 3H), 10.08 (s, 1H). Mass (APCI mode in CH₂Cl₂): calcd, 172.18; found 173.0.

5-[3'-(1*H***-Imidazol-1-yl)phenyl]-10,15,20-tritolylporphyrin (1c).** Compound 1c was synthesized by reacting 1b (450 mg, 2.6 mmol), tolualdehyde (7.8 mmol), and pyrrole (10.5 mmol) in refluxing propionic acid. The crude product was purified on a basic alumina column with chloroform/methanol (95:5 v/v) as eluent. ¹H NMR (400 MHz, CDCl₃): δ –2.79 (s, 2H), 2.78 (s, 9H), 7.05 (d, 1H), 7.37 (s, 1H), 7.55 (d, 6H), 7.78–7.85 (m, 3H), 8.15 (d, 6H), 8.18 (s, 1H), 8.30 (d, 1H), 8.80–8.91 (m, 8H). Mass (APCI mode in CH₂Cl₂): calcd, 722.88; found [M + 1] 723.6.

2-[2-(1*H***-Imidazol-1-yl)phenyl]-1,3-dioxolane (2a).** Imidazole (0.01 mol) was added to a suspension of sodium hydride (0.01 mol) in 10 mL of DMF. The resulting solution was stirred at room temperature for 20 min. Next, 2-(3-bromophenyl)-1,3-dioxolane (0.01 mol) and copper powder (0.001 mol) were added to the reaction mixture which was refluxed for 4 h. The mixture was cooled to room temperature, chloroform and water were added, and the mixture was stirred for 2 h and filtered. The filtrate was washed with water and dried over sodium sulfate. The solvent was evaporated under reduced pressure. The compound was purified over flash silica gel column using CH₂Cl₂/MeOH (96:4 v/v) as eluent. ¹H NMR (400 MHz, CDCl₃): δ 3.75–4.00 (m, 4 H), 5.35 (s, 1H), 7.01 (s, 1 H), 7.10–7.60 (m, 6H). Mass (APCI mode in CH₂Cl₂): calcd, 184.3; found [M + 1] 185.1.

2-(1*H***-Imidazol-1-yl)benzaldehyde (2b).²⁹ 2-[3-(1***H***-Imidazol-1-yl)phenyl-1,3-dioxolane was stirred at room temperature for 3 h in 20 mL of 1 M HCl. Aqueous NaHCO₃ was added to the reaction and extracted with ethyl acetate. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, and evaporated under reduced pressure to obtain the product as a**

pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.00–7.45 (m, 3H), 7.55 (m, 2H), 7.81 (dd, 1H), 9.58 (s, 1H). Mass (APCI mode in CH₂Cl₂): calcd, 172.18; found [M + 1] 173.1.

5-[2'-(1*H***-Imidazol-1-yl)phenyl]-10,15,20-tritolylporphyrin (2c).** Compound **2c** was synthesized by reacting **2b** (452 mg, 2.6 mmol), tolualdehyde (7.8 mmol), and pyrrole (10.5 mmol) in refluxing propionic acid. The crude product was purified on a basic alumina column with chloroform/methanol (95:5 v/v) as eluent. ¹H NMR (400 MHz, CDCl₃): δ –2.79 (s, 2H), 2.72 (s, 9H), 7.01 (d, 1H), 7.55 (d, 6H), 7.70–7.89 (m, 4H), 8.15 (d, 6H), 8.18 (s, 1H), 8.30 (d, 1H), 8.80–8.91 (m, 8H). Mass (APCI mode in CH₂Cl₂): calcd, 722.8; found [M + 1] 723.8.

5-[4'-(1*H*-Imidazol-1-yl)phenyl]-10,15,20-tritolylporphyrin (3c). Compound 3c was synthesized by reacting 4-(1*H*-imidazol-1-yl)benzaldehyde (450 mg, 2.6 mmol), tolualdehyde (7.8 mmol), and pyrrole (10.5 mmol) in refluxing propionic acid. The crude product was purified on a basic alumina column with chloroform/methanol (95:5 v/v) as eluent. ¹H NMR (400 MHz, CDCl₃): δ -2.79 (s, 2H), 2.75 (s, 9H), 7.01 (d, 1H), 7.38 (d, 2H), 7.55 (d, 6H), 7.78 (d, 2H), 8.15 (d, 6H), 8.18 (s, 1H), 8.30 (d, 1H), 8.80-8.91 (m, 8H). Mass (APCI mode in CH₂Cl₂): calcd, 722.8; found [M + 1] 723.8.

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. Cyclic voltammograms were recorded on a EG&G PARSTAT 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 a Ag/AgCl electrode was used as the reference electrode. A 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^{24} software package on high speed PCs. The mass spectra were recorded on a Varian 1200 L Quadrupole MS using APCI mode in dry CH₂Cl₂. Fluorescence lifetime measurements were carried out using the EasyLife V time resolved fluorimeter of Optical Building Block Corp. (Birmingham, NJ) with a 410-nm pulsed LED excitation source, and a stroboscopic detection system. Fluorescence decay curves were analyzed using the EasyLife II software.

Transient Absorption Measurements.³⁰ 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 primary Ti:sapphire generator (TiF-50, CDP Corp.) was pumped by Nd CW laser (Verdi-6, Coherent Inc.), and a second harmonic (~410 nm) was used to excite the sample solution in a rotating cuvette. 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 pulses 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. The emission decay curve of the sample was detected by scanning through the delay line.

Pump-probe and up-conversion techniques for time-resolved absorption and fluorescence, respectively, were used to detect the fast processes with a time resolution shorter than 0.2 ps. The instrument and the used data analysis procedure have been described earlier. $^{\rm 30}$

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Supporting Information Available: Absorption and fluorescence changes observed during the formation of dyads, Benesi-Hildebrand plots constructed to evaluate the binding constants, excitation spectra of the dyads, transient absorptions spectra of the donor, acceptor, and dyads in DCB. This material is available free of charge via the Internet at http://pubs.acs.org.

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