**Engaging Copper(III) Corrole as an Electron Acceptor: Photoinduced Charge Separation in Zinc Porphyrin-Copper Corrole Donor-Acceptor Conjugates**

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**Abstract:** An electron deficient copper(III) corrole was utilized for construction of donor-acceptor conjugates with zinc(II) porphyrin as a singlet excited state electron donor, and occurrence of photoinduced charge separation was demonstrated using transient pump-probe spectroscopic techniques. In these conjugates, the number of copper corrole units was varied at 1, 2 and 4 units while maintaining a single ZnP entity to observe the effect of corrole multiplicity in facilitating the charge separation process. The conjugates and control compounds were electrochemically and spectroelectrochemically characterized. Computational studies revealed ground state geometries of the compounds and the electron deficient nature of the copper(III) corrole. An energy level diagram was established to predict the photochemical events using optical, emission, electrochemical and computational data. The occurrence of charge separation from singlet excited zinc porphyrin and charge recombination to yield directly the ground state species were evident from the diagram. Femtosecond transient absorption spectroscopy studies provided spectral evidence of charge separation in the form of the zinc porphyrin radical cation and copper(II) corrole species as products. Rates of charge separation in the conjugates were found to be of the order of 1010 s-1 and increased with increasing multiplicity of copper(III) corrole entities. The present study demonstrates the importance of copper(III) corrole as an electron acceptor in building model photosynthetic systems.

Introduction

Increasing global energy demands and environmental concerns due to burning fossil fuels have given energy research a high priority in recent years.[1] In this regard, energy-harvesting materials, especially those that mimic natural photosynthesis, have attracted much attention due to their potential capabilities for direct conversion of incident light to an electrical current being hence a useful power source.[2] Porphyrins have been commonly used as photosensitizers for the construction of artificial photosynthetic systems because of their resemblance to the naturally occurring chlorophyll pigments.[3] However, other sensitizers, including phthalocyanines,[4] corroles,[5] subphthalocyanines,[6] bodipy,[7] and structural isomers of porphyrins[8] have also been exploited for this purpose. Furthermore, in recent work molecular engineering has been applied in the preparation of elegant multi-modular donor-acceptor systems that are capable of wide-band capture and of generating the long sought after long-lived charge-separated states upon photoexcitation.[9] The utilization of tribasic corroles in the construction of donor-acceptor systems has been a focus of attention in recent years because of their metal cation coordinative properties and other unique features that make them distinct from porphyrins, including easier oxidation.[10] Consequently, there already exist a few reports on donor-acceptor dyads featuring corroles as photosensitizer/electron donor.[5] However, application of corroles as electron acceptors has hardly been studied,[5i,j] primarily due to the lack of a corrole or metallocorrole derivative with an appropriate facile reduction potential. The exception to this generalization is provided by the recently reported copper(III) corroles that are known to undergo facile reduction from copper(III) to copper(II).[11] In the majority of copper(III) corroles, the CuIII/II reduction potential is lower than that of the widely used electron acceptors such as fullerenes[12] and quinones.[13] In the present study, we have exploited this novel property of copper(III) corrole in the construction of covalently linked donor-acceptor dyad, triad and pentad using zinc(II) porphyrin as an electron donor.

Several corrole-porphyrin conjugates have been reported over the past ten years. Multistep sequential syntheses have been described by Paolesse, Smith, Zheng and coworkers to afford directly unsymmetrical corrole-porphyrin dyads or containing spacers with linkage through their *meso*-positions.[14-16] Also, Guilard, Kadish and coworkers have described the electrochemistry, photophysics and catalytic properties of several cofacial corrole-porphyrin hybrids containing different transition metal cations.[17-26] Other synthetic pathways reported in the literature have involved the preparation of individual corrole and porphyrin moieties followed by their intermolecular linkage. Osuka and coworkers[27] reported preparation of *β,β*-linked corrole dimers by using Suzuki–Miyaura cross-coupling (after regioselective Ir-catalyzed direct borylation) while Gryko has disclosed preparation of *meso-meso*-corrole-porphyrin dyad containing an amide and imide spacer.[28-29] In recent years, we have focused on the synthesis and functionalization of corrole.[30-38] One such example involves a high yielding preparation of a bis-porphyrin-corrole triad employing nucleophilic aromatic substitution of pyrimidinyl-substituted corroles involving phenolic porphyrins.[30] The first report of the application of the click reaction in tetrapyrrole chemistry was made by Collman and Chidsey in 2006.[39] Recently, Le Pleux *et. al.* described multiporphyrin arrays with different metal centers constructed by using the click reaction.[40] In this work, we describe an investigation of different corrole-porphyrin conjugates prepared using the click reaction. The structures of the newly prepared donor-acceptor conjugates are shown in Figure 1 together with those of the control compounds.[41] Here we report not only the high yielding synthesis of the porphyrin-corrole dyads but also provide definitive spectroscopic evidence for the occurrence of photo-induced electron transfer within these conjugates. Covalent linkage of the different units was

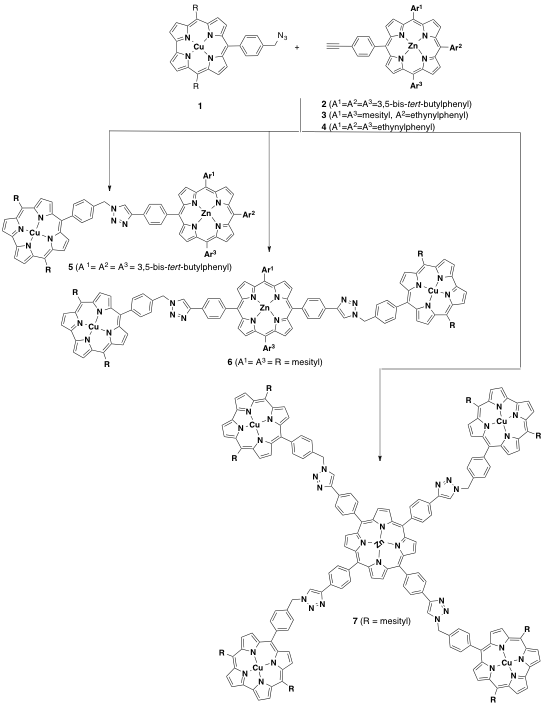


**Figure 1**. Structure of the zinc porphyrin-copper corrole donor-acceptor conjugates, and the control compounds investigated in the present study.

accomplished using the well-known click chemistry involving formation of 1,2,3-triazole moieties.[42] Synthetic details are given in the experimental section and Supporting Information. Purity of the compounds was confirmed by thin layer chromatography while structures were confirmed using 1H and 13C NMR, mass spectrometric, and spectroscopic studies. All compounds were ESR silent indicating that copper corrole, CuC, exists as Cu(III)C. Photoinduced electron transfer in these donor-acceptor conjugates was established and studied using femtosecond transient absorption spectroscopy.

Results and Discussion

**Synthesis.** Four different reaction conditions were investigated in the optimization of the synthetic procedure to the corrole-porphyrin conjugates from azidocorrole **1** and porphyrins **2-4** (Scheme 1, Table 1). The active catalytic species for the coupling is Cu(I), which can be introduced directly using Cu(I) salts or by its *in situ* generation by reduction of Cu(II). Reactions were carried out in the presence of an excess of Cu-corrole **1** with reaction monitored by using thin layer chromatography (t.l.c.).



Scheme 1: Click synthesis of the conjugates **5**, **6** and **7**

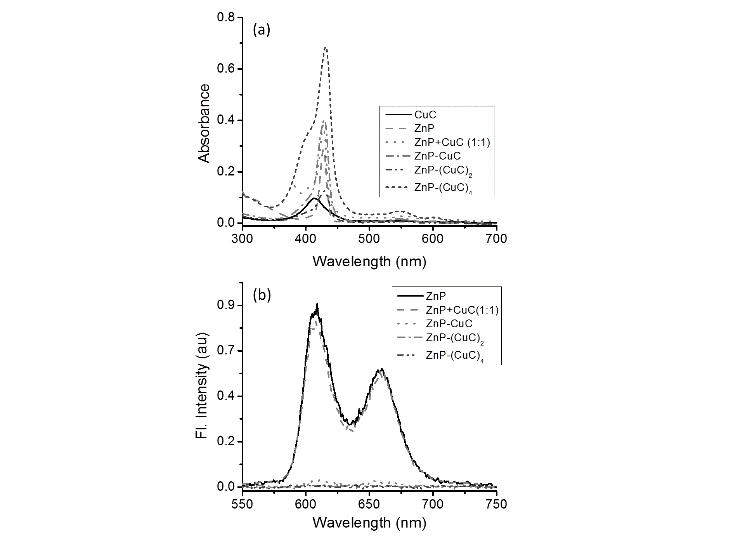
Dyad **5** was obtained in 88% yield if Cu(I) was added directly in the form of CuI while yields as high as 94% could be obtained by employing *in situ* formation of Cu(I) catalyst by reduction of copper(II) sulfate with ascorbic acid. Hu and Wang have described acid and base promoted click reactions.[44,45] By applying this procedure to our system, essentially quantitative yields could be obtained after 24 h. A similar result was obtained if tetrakis(acetonitrile)copper(I) hexafluorophosphate ([Cu(CH3CN)4]PF6) was added as catalyst. For the synthesis of triad **6** and pentad **7**, reaction conditions with the three highest yields for the dyad were selected. The yields for the click reaction of copper corrole **1** and bis-acetylenyl porphyrin **3** leading to triad **6** were slightly lower than for the dyad at 89 and 73% for the *in situ* reduced CuSO4 pentahydrate and acid-base mediated CuI catalyst, respectively. As expected, the yields from the same reaction were reduced further to 79 and 63%, respectively, for the preparation of pentad **7** from tetra-acetylenyl porphyrin **4** and azidocorrole **1**. ([Cu(CH3CN)4]PF6 gave the most satisfying results with no significant reduction in yield observed for **6** and **7.**

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| **Table 1:** Isolated yields (%) of conjugates 5-7 with different copper catalysts. | | | |
|  | Dyad **5** | Triad **6** | Pentad **7** |
| CuI[a] | 88 |  |  |
| CuSO4·5H2O/ascorbic acid[b] | 94 | 89 | 79 |
| CuI/DIPEA/acetic acid[c] | quantitative | 73 | 63 |
| [Cu(CH3CN)4]PF6[d] | quantitative | 99 | 98 |
| [a] acetonitrile, dichloromethane, rt, 3d. [b] DMF, 50 °C, 3d. [c] rt, 1d. [d] dichloromethane, 80 °C, 12-24h. | | | |

**Absorbance and Emission Studies.** Figure 2a shows the absorption spectra of representative compounds in benzonitrile. ZnP exhibits a Soret band at 428 nm, and bands in the visible range at 557 and 598 nm, respectively. The Soret band of CuC appears at 413 nm with broad spectral features in the visible range between 500-660 nm. The spectrum of a mixture of equivalent amounts of ZnP and CuC is similar to that of the ZnP-CuC dyad. The spectra of the triad and pentad were also simple additions of the spectra of the respective stoichiometric amounts of their individual components. These observations suggest a lack of significant intramolecular interactions between the entities. At 400 nm, the excitation wavelength of our femtosecond transient spectrometer, about 75% of the absorbance was due to CuC while about 25% was due to ZnP in the case of the dyad.

Fluorescence spectra of the conjugates and the control compounds are shown in Figure 2b. The emission spectrum of ZnP contains peaks at 608 and 660 nm while CuC was non-fluorescent. ZnP emission was quenched by less than 5% when equimolar CuC was added to the solution suggesting a lack of intermolecular association, which would lead to fluorescence quenching between the entities. Conversely, in the covalently linked conjugates, strong quenching was observed at 96% for ZnP-CuC, and over 99% in the case of ZnP(CuC)2 and ZnP-(CuC)4. Varying the excitation wavelength from 428 nm to 557 nm of ZnP lead to similar spectral and quenching trends. These results suggest the occurrence of intramolecular events from singlet excited state of ZnP (1ZnP\*) to CuC in the conjugates.

**Electrochemical and Spectroelectrochemical Studies.** Differential pulse voltammograms (DPVs) of the ZnP-CuC dyad along with control compounds (CuC and ZnP) are shown in Figure 3. The first reduction of CuIIIC is located at -0.61 V vs. Fc/Fc+ indicating that it is nearly 400 mV easier to reduce than the other popular electron acceptors, C60 and benzoquinone,[12a,13a] signifying its potential as an electron acceptor in building donor-acceptor conjugates.

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**Figure 2**. Electronic absorption and fluorescence spectra of the indicated compounds (and a mixture) in benzonitrile. Concentration was maintained at 2.5 x 10-6 M for all samples. λex = 428 nm.

On the anodic side two oxidations at 0.28 and 0.90 V vs. Fc/Fc+ corresponding to corrole ring oxidations were observed (Figure 3a). ZnP, used as an electron donor in the present study, undergoes two oxidations at 0.32 and 0.67 V *vs.* Fc/Fc+ corresponding to ring oxidations (Figure 3b). The first reduction of ZnP is located at -1.79 V *vs*. Fc/Fc+. In the ZnP-CuC dyad, the first reduction of CuC was found to be at the same potential of -0.61 V while the first oxidation process appears as an overlap of the first oxidations of ZnP and CuC and appeared at 0.30 V. Other anodic processes were at potentials not significantly different from the control compounds. Similar voltammograms were obtained for the triad and pentad although the currents of CuC redox couples were larger as anticipated from the increased number of CuC entities (2 in the case of dyad and 4 in the case of pentad).

Further, spectroelectrochemical studies on the control compounds and donor-acceptor dyad were performed to characterize spectrophotometrically the one-electron oxidized and reduced species, which assists in the spectral interpretation of transient absorption data. The spectral changes observed for CuIIIC reduction are typical of spectral changes associated with metal centered reduction. During reduction, the Soret band located at 414 nm diminished in intensity with the appearance of a new band at 435 nm. In the visible region, new peaks at 577 and 610 nm were observed (see Figure S13a). Isosbestic points at 357 and 462 nm were observed and these spectral changes were found to be fully reversible. During the first oxidation of CuC, the 412 nm peak was diminished and red-shifted as a broad peak centered at 421 nm. Isosbestic points at 381 and 434 nm were observed (Figure S13b).



**Figure 3**. Differential pulse voltammograms of (a) CuC, (b) ZnP and (c) ZnP-CuC dyad in benzonitrile containing 0.1 M (TBA)ClO4. Scan rate = 20 mV/s, pulse width = 50 ms, pulse height = 0.025 V. The ‘\*’ corresponds to the oxidation of ferrocene used as an internal standard.

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**Figure 4.** Spectral changes observed during (a) first reduction and (b) first oxidation of ZnP-CuC dyad in benzonitrile containing 0.1 M (TBA)ClO4.

Reduction of ZnP was accompanied by the appearance of new red-shifted peaks at 438, 574 and 615 nm with these spectral changes being reversible (Figure S13c). During the first oxidation of ZnP, Soret and visible bands were diminished in intensity with the appearance of new peaks at 370, 454(sh), 602 and 674(br) nm. These spectral changes were reversible with isosbestic points at 416, 438 and 543 nm (Figure S13d).

Next, the spectroelectrochemical study on the representative ZnP-CuC dyad was performed. As shown in Figure 4a for the first reduction, new peaks at 575 and 605 nm, that were similar to those observed during reduction of pristine CuC, were observed. This confirms formation of ZnP-CuIIC during the first electroreduction of the dyad. During the first oxidation, typical blue shifted ZnP Soret and broad spectral features in the 600-700 nm range characteristic of ZnP oxidation were observed (Figure 4b). This confirms formation of ZnP•+-CuC during electrooxidation of the dyad. Observation of these peaks during transient spectral studies would confirm photoinduced electron transfer leading to formation of the ZnP•+-CuIIC radical ion-pair in these donor-acceptor conjugates.

**Computational Studies.** The geometry and electronic structures of the conjugates were probed using B3LYP functional and a mixed basis (H and C(6-31G), N and O(6-31G(d), and Cu and Zn(6-31G(df)) as parameterized in the *Gaussian 09* software suite.[43]  The ZnP and CuC entities were constructed using the GaussView program on a local pc. After construction, the structures were uploaded to a supercomputer and then the geometry of both were optimized to a stationary point on the Born-Oppenheimer surface using the model chemistry and software described above. Using the Gaussview program on a local pc, the optimized ZnP and CuC entities were then used to construct the dyad (compound a) the triad (compound b), and the pentad (compound c). Once constructed the geometries of dyad, triad and pentad were uploaded to a supercomputer and optimized to a stationary point on the Born-Oppenheimer surface. Next, using the GaussView program, frontier orbitals were generated for each of the optimized structures as shown in Figure 5. Symmetric disposition of the CuC entities around the central ZnP in the triad and pentad were observed.

The Cu-Zn distance in the optimized geometry of the dyad was approximately 17.6 Å, the edge-to-edge distance was approximately 10.19 Å, the Cu-triazole center was approximately 10.4 Å, and the Zn-triazole center was approximately 10.5 Å. The Cu-Cu distance in the optimized geometry of the triad was approximately 34.9 Å, the edge-to-edge distance is approximately 44.8 Å, the average Cu-Zn distance is approximately 9.86 Å, the average Cu-triazole center is approximately 10.4 Å, and the average Zn-triazole center is approximately 10.4 Å.

The average Cu-Cu distance of the “*cis*” Cu in the optimized geometry of the pentad was approximately 25.0 Å, the average Cu-Cu distance of the “*trans*” Cu is approximately 35.4 Å, the edge-to-edge distance was approximately 10.30 Å, the average Cu-Zn distance was approximately 17.7 Å, the average Cu-triazole center was approximately 10.5 Å, and the average Zn-triazole center was approximately 10.5 Å. Importantly, no steric crowding or constraints were found in these superstructures.

In agreement with the electrochemical and spectroelectrochemical results, the HOMO was found to be on the ZnP entity while the LUMO was on the CuC entity of the conjugates, establishing them to be the electron donor and electron acceptor entities within a given conjugate.

**Figure 5**. Frontier HOMO and LUMO of the optimized structures of (a) ZnP-CuC, (b) ZnP-(CuC)2 and (c) ZnP-(CuC)4 conjugates.

Using the Rehm-Weller approach, free-energy calculations for charge-recombination (∆*G*CR) and charge-separation (∆*G*CS) processes were calculated according to equations 1 and 2,[46]

-∆*G*CR = (*E*ox–*E*red) + ∆*G*S (1)

-∆*G*CS = ∆*E*-∆*G*CR (2)

where ∆*GC*R and ∆*GC*S are respectively the free-energy change for charge recombination and charge separation, and ∆*E* corresponds to the singlet state energy of ZnP (2.04 eV). *E*ox and *E*red are the oxidation potentials of the electron donor ZnP, and the reduction potential of the electron acceptor CuC, respectively. ∆*G*S refers to the static energy, calculated by using the ‘dielectric continuum model’ according to the following equation,

-∆*G*s = *e*2/4**o[(1/2*R*+ + 1/2*R*- - 1/*R*CC) ∆ (1/**s) (3)

where *R*+ and *R*- refer to radii of the radical cation and radical anion species, respectively. *R*CC is the center-to-center distance between the donor and acceptor entities from the optimized structures. Symbols **0 and **R refer to vacuum permittivity and dielectric constant of the solvents, respectively. These calculations lead to ∆*G*CS = -1.20 eV and ∆*G*CR = -0.84 eV in benzonitrile. The large negative ∆*G*CS value suggests that photoinduced electron transfer is thermodynamically possible in these conjugates.

An energy level diagram depicting different photochemical events in the ZnP-CuC dyad is shown in Figure 6. Based on similarities in the energies of different processes, similar diagrams can be envisioned for the triad and pentad. In the diagram, excitation of ZnP produces 1ZnP\* that could undergo intersystem crossing to populate the triplet state of ZnP (3ZnP\*) or, alternatively, could undergo energy or electron transfer involving the covalently linked CuC. Due to the poor spectral overlap between ZnP fluorescence and CuC absorption spectra, singlet energy transfer can be considered a minor process, although this is difficult to confirm due to the non-emissive nature of CuC. Photoinduced electron transfer from 1ZnP\* to CuC is energetically a highly favored process (∆*G*CS = -1.20 eV) that would lead to the formation of ZnP•+-CuIIC species. The energy level of the ZnP•+-CuIIC (-0.84 eV) is much lower than that of 3ZnP\* (1.50 eV). Our attempts to obtain the phosphorescence spectrum of CuC at 77 K in various glass forming solvents was not successful. Based on the 3MC\* and 3MP\* energy levels of corrole and porphyrin systems (1.4-1.6 eV), we assume that the energy level of 3CuC\* is higher than that of the charge separated state (> 1 eV). In that case, the ZnP•+-CuIIC would directly charge recombine to yield ground state ZnP-CuC dyad. In order to verify this mechanism and to evaluate the kinetics of these processes, femtosecond transient spectral studies were systematically performed and are discussed in the next section.



**Figure 6**. Energy level diagram showing the different photochemical events occurring in ZnP-CuC dyad in benzonitrile. Energies of different states were evaluated from spectral and electrochemical studies. Solid arrows indicate major photo-processes, dashed arrow indicates minor photo process. ISC = intersystem crossing, CS = charge separation and CR = charge recombination.

**Femtosecond Transient Absorption Studies.** First, femto-second transient spectral characterization of the control compounds, ZnP and CuC, was performed. As shown in Figure 7a, excitation of ZnP revealed peaks corresponding to S0-Sn transitions with peak maxima at 458, 581, 625, and 1280 nm, and minima at 560, 600 and 663 nm due to ground state depletion. The latter two peaks also contained contributions from stimulated emission. The singlet peaks decayed in intensity over time with the appearance of new transient peaks at 474 and 850 nm corresponding to a triplet state population of ZnP due to intersystem crossing (see Figure inset for time profile of the 850 nm peak). As shown in the figure inset, the 1280 nm peak decayed at a rate of 6.03 x 108 s-1 yielding a time constant of 1.7 ns in agreement with the lifetime of ZnP in benzonitrile. The nanosecond transient absorption spectra of ZnP further revealed peaks due to the anticipated triplet state of ZnP at 474, 750 and 850 nm (Figure 7b). As shown in the figure inset, 3ZnP\* decayed with a lifetime of about 77 s.

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**Figure 7**. (a) Femtosecond transient absorption spectra of ZnP at the indicated delay times (λex = 400 nm) in benzonitrile. Figure inset: (i) time profile of the 1280 nm peak corresponding to singlet excited ZnP and (ii) time profile of the 850 nm peak corresponding to growth of 3ZnP\* via intersystem crossing. (b) Nanosecond transient absorption spectra of ZnP at the indicated delay times (λex = 425 nm) in benzonitrile. Figure inset: time profile of the 474 nm peak. (c) Femtosecond transient spectra of CuC at the indicated delay times (λex = 400 nm) in benzonitrile. Figure inset: time profile of the 667 nm peak.

The femtosecond transient spectra of CuC revealed spectral features of instantaneously formed but short lived singlet excited CuC with peak maxima at 667 and 609 and 753 nm. The 609 nm peak decayed at a rate greater than 1010 s-1 indicating fast intersystem crossing to populate the triplet excited state. This result is consistent with the earlier discussed fluorescence studies where little or no fluorescence from CuC could be detected. The 1CuC\* decays rapidly to populate the 3CuC\* state, which has peaks at 450 and 665 nm. As shown in the Figure inset, the 667 nm peak corresponding to 3CuC\* decayed at a rate of 7.0 x 109 s-1 indicating rapid relaxation of the triplet excited state to the ground state. In summary, both singlet and triplet excited states of CuC are relatively short lived in benzonitrile. Accordingly, nanosecond transient studies on CuC revealed no detectable signal.

The femtosecond transient spectra of ZnP-CuC at different delay times in benzonitrile are shown in Figure 8a. From these data it was possible to confirm charge separation in the dyad leading to formation of the ZnP•+-CuIIC species. On a short time scale, peaks corresponding to the singlet excited state of ZnP decayed without populating the 3ZnP\* triplet state although new transient peaks in the 610 nm region (corresponding to CuIIC) and a broad peak in the 625-700 nm region (corresponding to the formation of ZnPc•+) could clearly be observed, establishing charge separation in the dyad. We observed charge separation from the 1ZnP\* state and not from the fast decaying 1CuC\* state, although at the excitation wavelength of 400 nm both entities can be excited. At higher delay times, decay of the charge separated state did not lead to any peaks corresponding to 3ZnP\* or 3CuC\* indicating that the charge recombination process yields directly the ground state dyad. This is consistent with the energy level diagram in Figure 6 where populating 3ZnP\* from the low-lying charge-separated state is an uphill process. To evaluate the rate of charge separation, *k*CS, the decay profile of the near-IR band at 1280 nm was monitored and is shown in Figure 8b. For comparative purposes, the decay profile of pristine ZnP is also shown revealing the rapid decay of 1ZnP\* in the dyad system. The *k*CS evaluated using a standard procedure was found to be 1.1 x 1010 s-1 revealing fast charge separation. The decay of the 616 nm peak corresponding to charge recombination was found to be biexponential. The faster decay component had a time constant of about 20 ps and the relatively slower decay component had a time constant of 270 ps. These values result in *k*CR values of 5.0 x 1010 s-1 and 3.7 x 109 s-1, respectively. However, at the monitoring wavelength of 610 nm, overlapping peaks of the singlet excited state of are also present. Hence, the values of *k*CR reported here should be treated as estimates.

**Figure 8**. (a) Femtosecond transient absorption spectra of ZnP-CuC dyad at the indicated delay times (ex = 400 nm) in benzonitrile. (b) Time profile of the 1280 nm peak corresponding to singlet excited ZnPin pristine ZnP (curve i) and in the dyad (curve ii). (c) Time profile of the 616 nm peak corresponding to CuIIC.

The transient spectral data for the triad and pentad are shown in Figure 9a and b, respectively. In the case of the triad, spectral features were similar to the dyad discussed earlier with a peak at 610 nm corresponding to CuIIC and in the 625-700 nm range corresponding to ZnP•+, again establishing charge separation in the triad. The *k*CS determined from the time profile of the 1280 nm band was found to be 1.2 x 1010 s-1, slightly faster than that observed in the case of dyad. The decay of the 610 nm peak corresponding to charge recombination is a biexponential process (see Figure 9a inset) with *k*CR estimated from the long component being around 5 x 109 s-1.



**Figure 9**. (a) Femtosecond transient absorption spectra of ZnP-(CuC)2 triad at the indicated delay times (ex = 400 nm) in benzonitrile. Inset: time profile of the 616 nm peak. (b) Transient absorption spectra of ZnP-(CuC)4 pentad at the indicated delay times (ex = 400 nm) in benzonitrile. Inset: time profile of the 616 nm peak

The spectral features observed for the ZnP-(CuC)4 pentad (Figure 9b) are also supportive of charge separation but, owing to the presence of four CuC entities, intensities of the peaks corresponding to the charge separated species were minimal. Also, the 1280 nm peak of 1ZnP\* was too low in intensity for its use in the calculation of *k*CS, so that a rate greater than that calculated in the cases of the dyad and triad is expected. The same could be said for *k*CR (see Figure 9b inset for time profile of the 610 nm peak), where the decay corresponding to CuIIC was very rapid. Hence, although charge separation is evident, values of *k*CR and *k*CR cannot be reported here for the pentad.

Conclusions

In summary, syntheses of a series of donor-acceptor conjugates based on zinc porphyrin as an electron donor and copper(III) corrole as an electron acceptor have been successfully accomplished with outstanding yields. Electrochemical and computational studies revealed the electron deficient nature of copper(III) corrole in the conjugates in terms of facile reduction and the locations of LUMO orbitals. Free energy calculations were suggestive of occurrence of photoinduced electron transfer from the singlet excited zinc porphyrin to copper corrole and, accordingly, steady-state fluorescence studies revealed almost complete quenching of ZnP fluorescence in the conjugates. The oxidized and reduced products of the conjugates were characterized spectroelectrochemically and used in the interpretation of transient spectral data from femtosecond transient measurements. The energy level diagram, established using the spectroscopic, electrochemical and computational data, predicts occurrence of charge separation from 1ZnP\*, and indicates that the charge separated state relaxes directly to the ground state during the charge recombination process. Proof for charge separation was obtained from femtosecond transient spectroscopic studies since it was possible to spectrally characterize the existence of ZnP•+ and CuIIC species. The *k*CS determined for the conjugates were of the order of 1010 s-1 revealing ultrafast charge separation. These studies illustrate the importance of copper(III) corrole as a potent electron acceptor for the construction of energy harvesting model compounds, and constitute the first defintive proof of charge separation in ZnP-CuIIIC systems.

Experimental Section

**General**. Solvents and reagents were obtained from Aldrich Chemicals (Milwaukee, WI), Tokyo Kasei Chemical Co. Ltd. (TCI), Fischer Chemicals (Plano, TX), or Wako Chemical Co. Ltd. Tetra-*n*-butylammonium perchlorate, (*n*-Bu4N)ClO4 used in electrochemical studies was obtained from Fluka Chemicals (Ronkonkoma, NY). NMR spectra were acquired using a JEOL BX300 spectrometer and chemical shifts (*δ*) are reported in parts per million (ppm) relative to tetramethylsilane. ESI mass spectra were measured using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser.  Mass spectra were measured using a Shimadzu Axima *CFR*+ spectrometer using dithranol as matrix. Infrared spectra were measured using a Thermo-Nicolet 760X FTIR spectrophotometer from samples deposited on a barium fluoride disc from dichloromethane solution followed by drying in air. Electron spin resonance spectra were measured at room temperature from solutions of the compounds in dichloromethane using a JEOL JES-FA-200 X-band ESR spectrometer.

**Synthesis of ZnP-CuC Donor-Acceptor Conjugates.** Four different methods were used in the optimization of the synthesis of dyad 5, triad 6 and pentad 7. Typical procedures are given for dyad 5 with corresponding procedures for 6 and 7 given in the Supporting Information.

Method (a): CuI (2 mg, 1.05 × 10−5 mol) was added to a solution of porphyrin 2 (10 mg, 9.63 × 10−6 mol, 1 eq.) and corrole 1 (7 mg, 9.64 × 10−6 mol) in dry dichloromethane (3 mL) and acetonitrile (0.5 mL). The reaction mixture was stirred under argon atmosphere for 3 d at r.t. The crude product was purified by size extrusion chromatography (Biobeads SX-1) eluting with tetrahydrofuran to afford the corrole-porphyrin diconjugate 5 as a brown solid (15 mg, 88%).

Method (b): CuSO4· 5H2O (2 mg, 7.7 × 10−6 mol) and ascorbic acid (1.7 mg, 9.64 × 10−6 mol) were added to a solution of porphyrin 2 (10 mg, 9.63 × 10−6 mol, 1 eq.) and corrole 1 (7 mg, 9.64 × 10−6 mol, 1 eq.) in dry DMF (3 mL) under an argon atmosphere. After stirring for 3 d at 50°C the reaction mixture was partitioned between dichloromethane (20 mL) and H2O (20 mL) and the layers separated. The organic layer was washed with H2O (3 × 20 mL), dried over Na2SO4 and the solvent removed under reduced pressure. The crude product was purified by size extrusion chromatography (Biobeads SX-1) eluting with tetrahydrofuran affording the corrole-porphyrin diconjugate 5 as a brown solid (16 mg, 94%).

Method (c): CuI (1 mg, 5.25 × 10−6 mol, 0.5 eq.), DIPEA (1 mg, 7.74 × 10−6 mol) and acetic acid (1 mg, 1.67 × 10−5 mol) were added to a solution of porphyrin 2 (10 mg, 9.63 × 10−6 mol, 1 eq.) and corrole 1 (7 mg, 9.64 × 10−6 mol) in dry dichloromethane (3 mL). The reaction mixture was stirred for 1d at r.t. The crude product was purified by size extrusion chromatography (Biobeads SX-1) eluting with tetrahydrofuran to afford the corrole-porphyrin diconjugate 5 as a brown solid (17 mg, quant.).

Method (d): A solution of azidocorrole 1 (18.1 mg, 2.72 × 10−5 mol), porphyrin 2 (26 mg, 2.5 × 10−5 mol) and [Cu(CH3CN)4]PF6 (12 mg, 3.26 × 10−5 mol) in 4 mL DCM was stirred at 80 °C under N2 atmosphere. The reaction was monitored using t.l.c. After completion, water (20 mL) was added and the mixture was extracted with dichloromethane (3x 20 mL). The combined organic phases were dried over Na2SO4 and solvent evaporated under reduced pressure. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded 44 mg (quant.) of dyad 5 as a brown solid.

**Dyad 5**. 1H−NMR (300 MHz, CDCl3, 25°C, TMS): δ=9.00 (m, 8H, Hβ′), 8.29 (d, 3*J*(H,H) = 7.7 Hz, 2H, Har), 8.20 (d, 3*J*(H,H) = 7.7 Hz, 2H, Har), 8.09 (s, 6H, HC), 7.98 (sbr, 3H, HD+Hβ′ ), 7.79 (s, 3H, HA), 7.66 (d, 3*J*(H,H) = 7.5 Hz, 2H, Har), 7.53 (d, 3*J*(H,H) = 7.4 Hz, 2H, Har), 7.35 (sbr, 2H, Hβ), 7.25 (sbr, 2H, Hβ), 7.14 (d, 3*J*(H,H) = 4.4 Hz, 2H, Hβ), 7.03 (s, 4H, HG), 5.79 (s, 2H, HE), 2.39 (s, 6H, HH), 2.07 (s, 12H, HF), 1.52 (s, 54H, HB) ppm. 13C−NMR (75 MHz, CDCl3, 25°C, TMS): δ 150.51, 150.44, 149.99, 148.78, 148.56, 148.47, 143.12, 141.85, 137.64, 135.23, 134.85 (CH), 132.25 (CH), 132.24 (CH), 132.16 (CH), 131.54 (CH), 129.64 (CH), 129.59 (CH), 128.19 (CH), 127.68 (CH), 123.97(CH), 122.63 (CH), 122.49, 121.09 (CH), 120.81 (CH), 120.06, 119.98, 77.20, 54.09 (CH2), 35.05, 31.77 (CH3), 29.70, 21.19 (CH3), 19.78 (CH3) ppm. MS (ESI): calc: 1761.77; found: 1761.76

**Triad 6.** 1H−NMR (300 MHz, CDCl3, 25°C, TMS): δ=8.91 (d, 3*J*(H,H) = 4.5 Hz, 4H, Hβ′), 8.78 (d, 3*J*(H,H) = 4.6 Hz, 4H, Hβ′), 8.29 (d, 3*J*(H,H) = 7.7 Hz, 4H, Har), 8.18 (d, 3*J*(H,H) = 7.5 Hz, 4H, Har), 8.02 (sbr, 6H, HE+Hβ), 7.65 (d, 3*J*(H,H) = 7.9 Hz, 4H, Har), 7.51 (d, 3*J*(H,H) = 7.6 Hz, 4H, Har), 7.35 (s, 4H, Hβ), 7.27 (s, 4H, HG), 7.23 (sbr, 4H, Hβ), 7.14 (sbr, 4H, Hβ), 7.02 (sbr, 8H, HB), 5.77 (s, 4H, HD), 2.62 (s, 6H, HH), 2.39 (s, 12H, HA), 2.07 (s, 24H, HC), 1.83 (s, 12H, HF) ppm. 13C−NMR (75 MHz, CDCl3, 25°C, TMS): δ=150.02, 148.79, 148.44, 144.02, 143.68, 142.94, 139.25, 139.00, 137.65, 137.48, 135.26 (CH), 134.96, 132.22 (CH), 131.63 (CH), 130.87, 129.68, 128.19 (CH), 127.67 (CH), 124.01 (CH), 121.06, 120.02 (CH), 77.20 (CH), 54.10 (CH2), 29.71 (CH2), 21.62 (CH3), 21.44 (CH3), 21.18 (CH3), 19.77 (CH3) ppm. MS (ESI): calc.: 2258.72; found: 2259.71

**Pentad 7.** 1H−NMR (300 MHz, CDCl3, 25°C, TMS): δ 8.98 (sbr, 4H, HE ), 8.23 (sbr, 8H, Har), 7.97 (sbr, 8H, Hβ), 7.65 (sbr, 8H, Har), 7.51 (sbr, 8H, Har), 7.34 (sbr, 8H, Hβ), 7.30 (sbr, 8H, Har), 7.26 (sbr, 8H, Har), 7.20 (8H, Hβ), 7.15 (8H, Hβ), 7.00 (s, 16H, HB), 5.78 (s, 8H, HD), 2.37 (s, 24H, HA), 2.05 (s, 48H, HC) ppm. 13C−NMR (75 MHz, CDCl3, 25°C, TMS): δ=150.14, 148.78, 148.26, 144.17, 143.62, 142.72, 138.26 (CH), 137.61, 135.16/135.14 (CH), 134.87, 132.03 (CH), 131.38 (CH), 129.71 (CH), 128.15 (CH), 127.54 (CH), 123.95, 121.14 (CH), 120.71, 120.01, 77.20, 54.00 (CH2), 21.18 (CH3), 19.77 (CH3) ppm. MS (ESI): calc.: 3677.09; found: 3679.12 [M+2H]. MALDI-TOF-MS (dithranol): found 3675.84 [M-H]

**Spectrophotometric and Electrochemical Studies.** Electronic absorption spectra were measured using a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer or a JASCO V-570 UV/Vis/NIR spectrophotometer. Differential pulse voltammograms (DPVs) were recorded using an EG&G Model 263A potentiostat with 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. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon 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.

**Computational Studies.** Computational geometry optimizations were performed using B3LYP functional and a mixed basis (H and C(6-31G), N and O(6-31G(d), and Cu and Zn(6-31G(df)) using GAUSSIAN 09 software package.[43] The copper corrole and zinc porphyrin structures were first optimized and those structures were used to construct the combined conjugates. *GaussView* program of GAUSSIAN was used to generate frontier HOMO and LUMO orbitals.

**Femtosecond Laser Flash Photolysis.** 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 was 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 harmonic generator, which produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of a white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

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

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[41] During this work, Nikolaou and coworkers reported a synthesis (also using the click reaction) of a porphyrin-corrole dyad and some of its photophysical and electrochemical properties.[5i] They assigned the phenomenon of fluorescence quenching in their dyad as a possible symptom of electron transfer from porphyrin to copper corrole although this was not unequivocally demonstrated.

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| **Donor-acceptor conjugates based on zinc porphyrin as an electron donor and copper(III) corrole as an electron acceptor have been successfully prepared with outstanding yields. Electrochemical and computational studies revealed the electron deficient nature of copper(III) corrole leading to phenomena of photoinduced electron transfer from the singlet excited zinc porphyrin to copper corrole, as demonstrated by femtosecond transient spectroscopy.** |  | Thien H. Ngo,\* David Zieba,Whitney A. Webre, Gary N. Lim, Paul A. Karr, Scheghajegh Kord, Shangbin Jin,Katsuhiko Ariga, Marzia Galli, Steve Goldup, Jonathan P. Hill,\* and Francis D’Souza\*  Page No.–Page No.  Engaging Copper(III) Corrole as an Electron Acceptor: Photoinduced Charge Separation in Zinc Porphyrin-Copper Corrole Donor-Acceptor Conjugates |
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