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# Excitational energy and photoinduced electron transfer reactions in Ge(IV) corrole–porphyrin hetero dimers

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## ABSTRACT

We have constructed hetero dimers by utilizing the axial bonding capabilities as well as known oxophilicity of Germanium(IV) ion of Germanium(IV) corroles as basal scaffolding unit and either free-base or Zn<sup>II</sup> porphyrin at axial position for the first time. Both the hetero dimers have been completely characterized by elemental analysis, UV–visible, proton nuclear magnetic resonance (<sup>1</sup>D and <sup>1</sup>H–<sup>1</sup>H COSY) and fluorescence spectroscopies as well as electrochemical methods. The ground state properties indicate that there exists a minimum  $\pi$ – $\pi$  interactions between the macrocyclic units of these dyads. Excited state properties showed that there is an electronic energy transfer competing photoinduced electron transfer from singlet state of basal metalloid corrole to the axial porphyrin and a photoinduced electron transfer from excited state of axial porphyrin to the ground state of central metalloid corrole are possible.

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## 1. Introduction

Multichromophoric structures with intense complementary absorption properties, in particular, those containing the tetrapyrrolic macrocyclic ligands, are currently receiving much attention in view to impersonate the natural photosynthesis [1–5]. The core function of natural photosynthesis is a cascade of photoinduced energy and electron transfers between donors and acceptors in the antenna complexes and the reaction center [6,7]. A great variety of oligomeric donor–acceptor systems has been reported to explain many phenomena and answered many questions, unsolved problems provide rationale to search for new systems differing from the previous ones for photoactive unit, linker, spatial arrangement, etc. [8–13]. In many of these artificial systems, oligomers based on porphyrins (and/or metalloporphyrins) and closely related compounds such as phthalocyanines (and/or metallophthalocyanines) play a major role as active chromophores. In contrast, oligomers based on corroles are limited in the literature due to the lack synthetic methods for corroles until recently [14,15]. However, investigations of corroles have recently increased with the synthetic work of the groups of Paolesse and Gross, with each of the respective groups reporting a one-pot synthesis of triarylcorroles [16,17]. Corroles are *tri*-anionic ligands that stabilize higher oxidation states of transition metal centers like Fe(IV), Cu(III), Co(IV), Ag(III), Cr(V) etc. [18]. Both porphyrins and corroles exhibit complementary optical transitions. Thus, oligomeric

arrays that contain porphyrin and corrole in the same molecular frame are possible to study the electronic energy transfer (EET) and photoinduced electron transfer (PET) reactions.

Homo oligomers based on either porphyrins (and/or metalloporphyrins) or phthalocyanines (and/or metallophthalocyanines) or corroles are widely reported in the literature [19,20]. On the other hand, hetero oligomers based on either porphyrin–phthalocyanine systems or porphyrin–corrole systems were also widely reported in the literature [21–27]. All these oligomers have been obtained by conducting multistep and tedious organic reaction sequences carried out at the peripheral position/s of porphyrins and corroles (either pyrrole- $\beta$  or *-meso*). In contrast utilization of “inorganic” reactions, which can be readily conducted, either at the corrole central cavity (e.g., metal/non-metal ion insertion) or on the resident metalloid ion therein (e.g., metal–metal covalent bond formation etc.) appears to be an attractive and viable alternative approach for the facile construction of hetero type macrocyclic arrays.

By using axial bonding concept, Maiya and co-workers have reported homo oligomers of metallo/metalloid porphyrin based branched arrays and they studied EET and PET reactions in these oligomers [28–31]. Recently, our group have demonstrated the change in the energy and electron transfer efficiencies by variation of central metal/metalloid ion of phthalocyanine macrocycle in porphyrin–phthalocyanine hetero arrays [32,33]. During the course of our investigation on the construction of hetero oligomers using axial bonding concept, we realized that this concept can be extended to other tetrapyrrolic compounds such as corroles. Here in, we have constructed hetero dimers for the first time by exploiting

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“axial-bonding” strategy as well as oxophilicity of hydroxy germanium(IV) corrole as a basal scaffolding unit and either free-base porphyrin or zinc porphyrin at the axial position for the fabrication of these hetero dimers. In addition, the germanium(IV) corroles are limited to their hydroxyl, methoxy and alkyl compounds only in the literature so far [34–36].

## 2. Experimental section

The chemicals and solvents utilized in this study were purchased from either Sigma-Aldrich Chemical Co. (USA) or Spectrochem (India). The solvents utilized for spectroscopic and electrochemical experiments were further purified using standard procedures [37].

### 2.1. Synthesis

5,10,15,20-tetraphenyl porphyrin [**H<sub>2</sub>-Por**], meso-5-(4-hydroxyphenyl)-10,15,20-(4-methyl phenyl)-porphyrin [**H<sub>2</sub>-Por-OH**], 5,10,15,20-tetraphenyl porphyrinato zinc(II) [**Zn-Por**], and meso-5-(4-hydroxyphenyl)-10,15,20-(4-methyl phenyl)-porphyrinato zinc(II) [**Zn-Por-OH**] were synthesized as per the procedures reported in the literature [38].

**[Ge(OH)-Cor]**: This compound was synthesized by a modified procedure reported in the literature [34–36]. 5,10,15-triphenyl corrole (0.10 g, 0.16 mmol) and GeI<sub>4</sub> (250 mg, 0.43 mmol) were dissolved in 50 ml of DMF solvent. The resulting reaction was heated at 150 °C under nitrogen atmosphere until the Q-bands of UV–visible spectrum was changed. The solvent DMF was removed under reduced pressure. The resultant solid material was subjected to alumina column and eluted with chloroform to get iodogermanium(IV) corrole. The iodo complex was dissolved in chloroform and to this about 50 ml of 10% NaOH solution was added and resulting reaction mixture was stirred at room temperature for 4 h. The organic layer was separated and washed with water twice and dried over anhydrous sodium sulfate. The organic layer was evaporated under reduced pressure and recrystallized from CHCl<sub>3</sub>/Hexane to get [**Ge(OH)-Cor**] in 70% yield. Elemental analysis of [**Ge(OH)-Cor**] C<sub>37</sub>H<sub>24</sub>N<sub>4</sub>OGe (calculated mass % in parentheses): C=72.47 (72.51); H=3.94 (3.91); N=9.14 (9.14). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.38 (d, 2H), 9.20 (d, 2H), 9.05 (d, 2H), 8.84 (d, 2H), 8.42 (d, 2H), 8.35 (m, 1H), 8.24 (m, 2H), 8.10 (m, 1H), 7.80 (m, 9H). UV–visible, (λ<sub>max</sub>, log ε, M<sup>-1</sup> cm<sup>-1</sup>): 410 (5.31), 520 (4.13), 558 (4.31), 588 (4.59).

**[(H<sub>2</sub>)-GeCor]**: [**Ge(OH)-Cor**] (0.1 g, 0.17 mmol) and 5-(4-hydroxy phenyl)-10,15,20-tritolyl porphyrin [**H<sub>2</sub>-Por**] (150 mg, 0.22 mmol) were dissolved in 30 ml of toluene. The resulting reaction mixture was refluxed under nitrogen atmosphere for 16 h. The solvent toluene was removed under reduced pressure. The obtained solid material was subjected to alumina column and eluted with chloroform. The solvent front running band was collected and recrystallized twice from hexane/CH<sub>2</sub>Cl<sub>2</sub> to get the desired compound in 62% yield. Elemental analysis of **[(H<sub>2</sub>)-GeCor]** C<sub>84</sub>H<sub>58</sub>N<sub>8</sub>OGe (calculated mass % in parentheses): C=79.60 (79.56); H=4.58 (4.61); N=8.80 (8.84). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.28 (d, 2H), 9.15 (d, 2H), 9.00 (d, 2H), 8.84 (d, 4H), 8.75 (d, 2H), 8.55 (d, 2H), 8.48 (d, 4H), 8.39 (d, 2H), 8.05 (d, 12H), 8.00 (d, 2H), 7.60 (m, 9H), 6.65 (d, 2H), 2.70 (s, 9H), 2.17 (d, 2H)–2.98 (b, 2H).

**[(Zn)-GeCor]**: This compound was synthesized by an analogous manner to the above compound by the condensation of 5-(4-hydroxy phenyl)-10,15,20-tritolyl porphyrinato zinc(II) [**Zn-Por**] and [**Ge(OH)-Cor**]. **[(Zn)-GeCor]** C<sub>84</sub>H<sub>56</sub>N<sub>8</sub>O<sub>2</sub>GeZn: C=75.75 (75.78); H=4.20 (4.24); N=5.49 (5.46). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.28 (d, 2H), 9.15 (d, 2H), 9.00 (d, 2H), 8.84 (d, 4H), 8.75 (d, 2H), 8.55 (d, 2H), 8.48 (d, 4H), 8.39 (d, 2H), 8.05 (d, 12H), 8.00 (d, 2H), 7.60 (m, 9H), 6.65 (d, 2H), 2.73 (s, 9H), 2.17 (d, 4H).

### 2.2. Methods

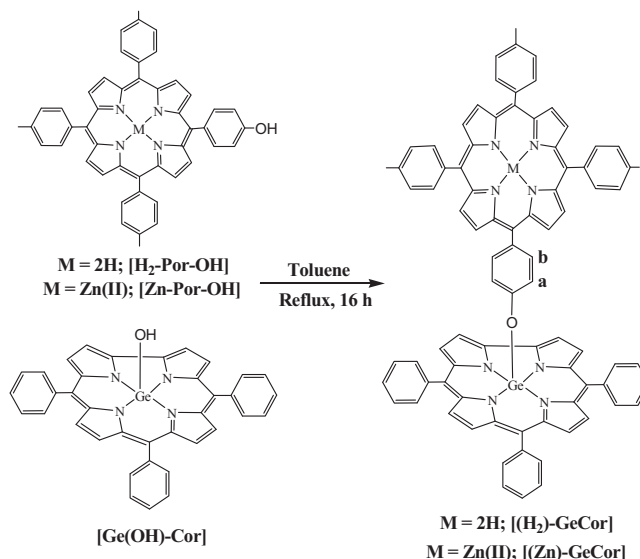
The UV–visible spectra were recorded with a Shimadzu model 170 spectrophotometer for 1 × 10<sup>-6</sup> M (porphyrin and corrole Soret band) and 5 × 10<sup>-5</sup> M (porphyrin and corrole Q-bands) solutions. Steady state fluorescence spectra were recorded using a Spex model Fluorolog-3 spectrofluorometer for solutions having optical density at the wavelength of excitation (λ<sub>ex</sub>) ≈ 0.11. The fluorescence quantum yields (φ) were estimated by integrating the fluorescence bands and by using either [**H<sub>2</sub>-Por**] (φ=0.13 in CH<sub>2</sub>Cl<sub>2</sub>), [**Zn-Por**] (φ=0.036 in CH<sub>2</sub>Cl<sub>2</sub>) [39]. MALDI-MS spectra were recorded on a TO-4X KOMPACT SEQ, KARTOS, UK, mass spectrometer. Major fragmentations are given as percentages relative to the base peak intensity. <sup>1</sup>H NMR spectra were obtained at 300 MHz using a Bruker 300 Avance NMR spectrometer running X-WIN NMR software. The chemical shifts are relative to tetramethylsilane (TMS). The Fourier transform IR (FTIR) spectra of all the samples were measured using a Thermo Nicolet Nexus 670 spectrometer.

Cyclic and differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI620C electrochemical analyzer. Cyclic voltammetric experiments were performed with 1 mM concentration of compounds in dichloromethane at a scan rate of 100 mV/s using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte as detailed in our previous studies [40,41].

## 3. Results and discussion

### 3.1. Ground state properties

Both hetero dimers **[(H<sub>2</sub>)-GeCor]** and **[(Zn)-GeCor]** were synthesized according to Scheme 1. Hydroxy germanium(IV) corrole (**[Ge(OH)-Cor]**) was synthesized by a modified procedure reported in the literature (see Section 2) [34–36]. The free-base hybrid dimer **[(H<sub>2</sub>)-GeCor]** was synthesized by condensation of **[Ge(OH)-Cor]** with excess of [**H<sub>2</sub>-Por-OH**] in toluene by refluxing at 120 °C for 16 h. The solvent toluene was evaporated and the solid material was subjected to alumina column by eluting with chloroform. The solvent front running band was collected and recrystallized from CHCl<sub>3</sub>/hexane twice to get **[(H<sub>2</sub>)-GeCor]**. In a similar manner **[(Zn)-GeCor]** was synthesized and only the



Scheme 1. Synthesis of hetero dimers.

**Table 1**  
UV–visible, electrochemical and singlet state data<sup>a</sup>

Compound	Absorption, $\lambda_{\max}$ , nm ( $\log \epsilon$ , M <sup>−1</sup> cm <sup>−1</sup> ) <sup>a</sup>					Potential V vs. SCE <sup>b</sup>		$E_{\text{CT}}$ (P <sup>−</sup> GeCor <sup>+</sup> )	$E_{\text{CT}}$ (P <sup>+</sup> GeCor <sup>−</sup> )
						Reduction	Oxidation		
[H <sub>2</sub> -Por-OH]	418 (5.30)	516 (4.17)	551 (3.90)	592 (3.64)	650 (3.72)	−1.24, −1.64	0.94, 1.30	–	–
[Zn-Por-OH]	419 (5.60)	550 (4.23)	584 (3.84)			−1.40, −1.71	0.72, 1.05	–	–
[Ge(OH)-Cor]	410 (5.31)	520 (4.13)	558 (4.31)	588 (4.59)		−0.65, −1.86	0.57, 1.15,	–	–
[(H <sub>2</sub> )-GeCor]	400 (5.34)	419 (5.50)	520 (4.20)	555 (4.27)	594 (4.30)	648 (3.96)	−0.58, −1.35, −0.60, −1.53,	0.65, 1.25, 0.67, 1.30	2.00 1.52
[(Zn)-GeCor]	400 (5.60)	420 (5.61)	553 (4.23)	595 (4.27)				2.20 1.27	

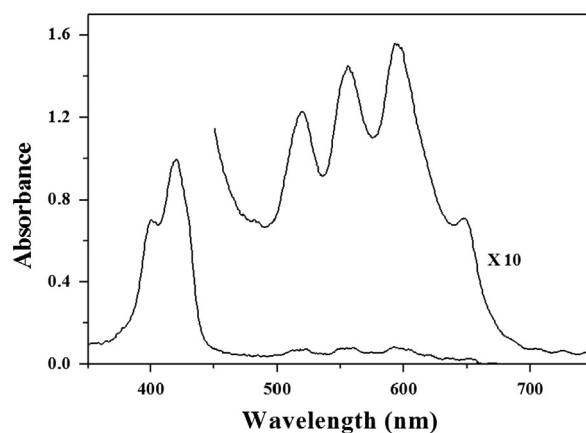
<sup>a</sup> Solvent CH<sub>2</sub>Cl<sub>2</sub>, Error limits:  $\lambda_{\max}$ ,  $\pm 1$  nm,  $\log \epsilon$ ,  $\pm 10\%$ .

<sup>b</sup> 0.1 M TBAP; Glassy carbon working electrode, Standard calomel electrode is reference electrode, Pt electrode is auxiliary electrode. Error limits,  $E_{1/2} \pm 0.03$  V.

difference is that [Zn-Por-OH] was taken instead of [H<sub>2</sub>-Por]. Both the hybrid dimers [(H<sub>2</sub>)-GeCor] and [(Zn)-GeCor] were characterized by elemental analysis, FAB-MS, UV–visible <sup>1</sup>H NMR (one- and two-dimensional), fluorescence spectroscopies and cyclic voltammetry. The MALDI-MS spectrum of [(H<sub>2</sub>)-GeCor] showed a peak at 1268 ([M]<sup>+</sup>, C<sub>84</sub>H<sub>58</sub>N<sub>8</sub>OGe) ascribable to the molecular ion peak.

The absorption spectra of both the dimers along with their individual constituents were measured in dichloromethane solvent and the corresponding  $\lambda_{\max}$  and  $\epsilon$  values are presented in Table 1. [Ge(OH)-Cor] has an intense Soret band at 408 nm, which is  $\pi$ – $\pi^*$  electronic transition, assigned to the second excited state (S<sub>2</sub>) and three less intense Q bands and originated from  $\pi$ – $\pi^*$  electronic transition, attributed to the first excited state (S<sub>1</sub>). The absorption spectra of hetero dimer, [(H<sub>2</sub>)-GeCor] is illustrated in Fig. 1. A comparison of the UV–visible spectrum of a hetero dimer with the spectra of the corresponding precursor units suggest that the  $\lambda_{\max}$  values of the both hetero dimers are found in the same range as those of the reference compounds except a small bathochromic shift of Soret band 400 nm (8 nm) in comparison with its reference compound, [Ge(OH)-Cor]. Whereas Q bands of [Ge(OH)-Cor] has not changed its absorption maxima in hetero dimer, [(H<sub>2</sub>)-GeCor]. This is not the case in corrole dimers by using *meso*–*meso* position reported by Gryko and co-workers, the Soret band is split (42 nm difference), which indicates that the electronic structure has been significantly altered. A similar Soret band split was also observed by Osuka and co-workers but not by Chandrasekhar, for 5,5'-linked oxacorrole dimers [14,15,42]. In addition, the  $\epsilon$  values of the bands due to the hetero dimers are nearly equal to sum of the  $\epsilon$  values of corresponding bands of the constituent monomers. Thus, the spectrum of each hetero dimer is more or less similar to the spectrum resulting from a combination (1:1 mol/mole ratio) of [Ge(OH)-Cor] and [H<sub>2</sub>-Por]/[Zn-Por] of the corresponding individual precursors. The absorption features of these hetero dimers reflect the lack of any  $\pi$ – $\pi$  interactions between the individual macrocyclic units. For instance, as in the case of covalently or noncovalently linked porphyrin, phthalocyanine, corrole dimers (e.g., face-to-face, slipped etc.) and aggregates (e.g., J, H, and nonspecific) shows distinct UV–visible properties than their corresponding monomeric species [43–48].

On the other hand, the <sup>1</sup>H NMR investigations of these hetero dimers revealed that certain specific spectral features observed for the protons on axial porphyrin/metalloporphyrin are quite different from those observed for the same protons in the spectrum of [H<sub>2</sub>-Por-OH] or [Zn-Por-OH]. Fig. 2 gives the <sup>1</sup>H NMR (2D <sup>1</sup>H–<sup>1</sup>H COZY Inset) spectrum of [(H<sub>2</sub>)-GeCor] and a similar spectrum has been observed in the case of [(Zn)-GeCor]. Spectra were analyzed on the basis of the resonance position and integrated intensity data as well as the proton-to-proton connectivity information



**Fig. 1.** UV–visible absorption spectra of [(H<sub>2</sub>)-GeCor] in CH<sub>2</sub>Cl<sub>2</sub>.

revealed in the COSY spectra to arrive at the structures of these new hetero dimers. Of specific interest in this regard are the ortho (type 'a') and meta (type 'b') protons of the phenoxy group of the free-base porphyrin that are bound to the Ge(IV) corrole. These protons, being affected by both the inherent deshielding effect of the axial porphyrin and the shielding effect of the basal Ge(IV) corrole, resonate at 6.65 (d, 2H,  $J_{\text{H,H}} = 7.6$  Hz) and 2.17 (d, 2H,  $J_{\text{H,H}} = 7.6$  Hz) ppm, respectively. The inner imino protons of the axial free-base porphyrins of [(H<sub>2</sub>)-GeCor] are seen to experience the "long-range" shielding effect due to the ring current of the basal Ge(IV) corrole and resonate at −2.98 ppm (s, 2H) compared to the corresponding −NH protons of [H<sub>2</sub>-Por] that appear at −2.73 ppm. Similar shielding and deshielding effects were also observed in the case of [(Zn)-GeCor]; the only difference is the absence of inner imino protons. This type of shielding and deshielding effects of these hetero arrays suggesting that the porphyrin  $\pi$  plane is "vertical" align to the corrole  $\pi$ -plane, certainly not of a face-to-face (parallel) type in which case an additive shielding effects as reported for the axial protons of the 'wheel-and-axle' type porphyrins as well as 'face-to-face' phthalocyanines would be expected [49,50]. A similar shielding effect was also observed in alkoxy or alkyl Ge(IV) corroles [36–36].

The electrochemical redox potentials, as measured from the cyclic and differential pulse voltammetric measurements, also reveal the absence of electronic interaction between the macrocyclic units of the both hetero dimers. Fig. 3 illustrates the cyclic and differential pulse voltammograms of both the hetero dimers and Table 1 provides redox potential data of hetero dimers and the corresponding monomeric species. Each dimer, up to four reduction steps and three or four oxidation steps in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M TBAP.

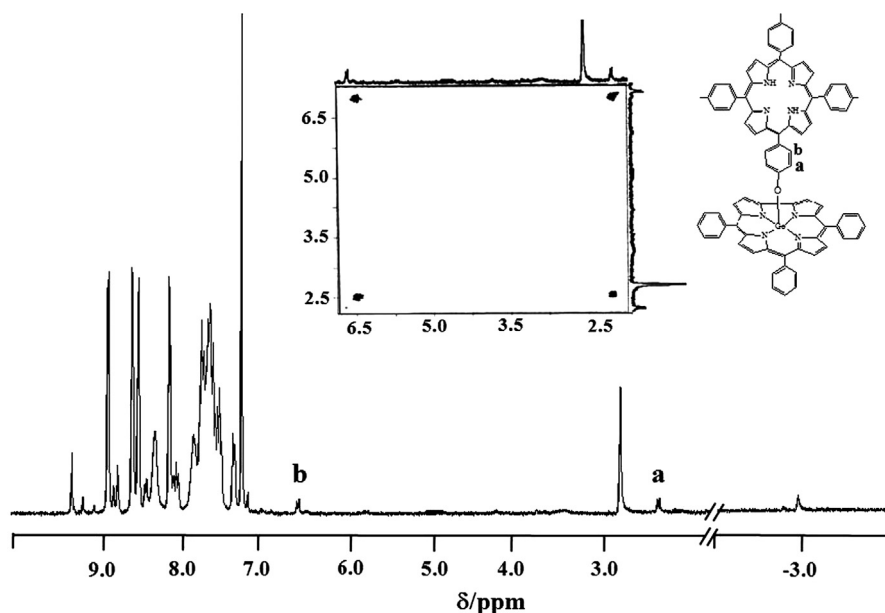


Fig. 2.  $^1\text{H}$  NMR spectrum of  $[(\text{H}_2)\text{-GeCor}]$  in  $\text{CDCl}_3$ . Inset:  $^1\text{H}\text{-}^1\text{H}$  COSY spectrum of  $[(\text{H}_2)\text{-GeCor}]$ .

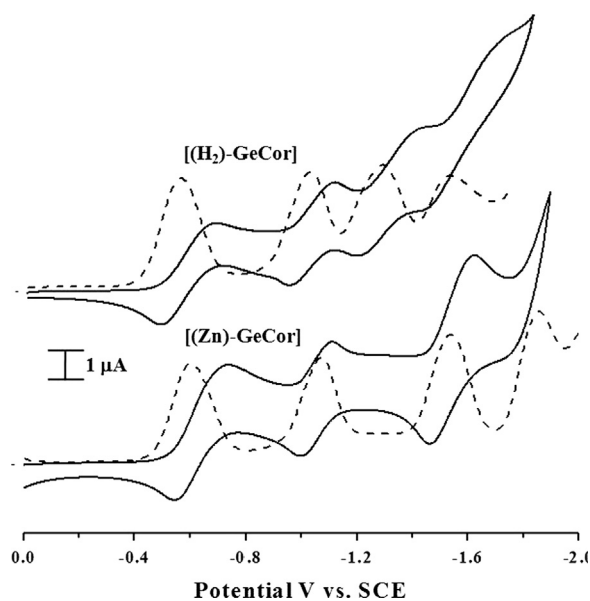


Fig. 3. Cyclic and differential pulse voltammograms of  $[(\text{H}_2)\text{-GeCor}]$  and  $[(\text{Zn})\text{-GeCor}]$  in  $\text{CH}_2\text{Cl}_2$  and 0.1 M TBAP (scan rate  $100\text{ mV s}^{-1}$ ).

Wave analysis suggested that, in general, while the first three reduction steps and first two oxidation steps are reversible ( $i_{\text{pc}}/i_{\text{pa}}=0.9\text{--}1.0$ ) and diffusion-controlled ( $i_{\text{pc}}/\nu_{1/2}=\text{constant}$  in the scan rate ( $\nu$ ) range  $50\text{--}500\text{ mV/s}$ ) one-electron transfer ( $\Delta E_{\text{p}}=60\text{--}70\text{ mV}$ ;  $\Delta E_{\text{p}}=65 \pm 3\text{ mV}$  for ferrocenium/ferrocene couple) reactions, the subsequent steps are, in general, either quasi-reversible ( $E_{\text{pa}}-E_{\text{pc}}=90\text{--}200\text{ mV}$  and  $i_{\text{pc}}/i_{\text{pa}}=0.5\text{--}0.8$  in the scan rate ( $\nu$ ) range  $100\text{--}500\text{ mV s}^{-1}$ ) or totally irreversible. On the basis of the redox potential data of the individual monomers (i.e.,  $[\text{Ge}(\text{OH})\text{-Cor}]$ ,  $[\text{H}_2\text{-Por}]$  and  $[\text{Zn-Por}]$ ), we have attempted to assign the midpoint potentials to basal  $\text{Ge}(\text{IV})$  corrole and axial porphyrin separately. Analysis of the data reveals that the redox potentials of the dimers are in the same range as those of their corresponding monomeric analogs, which were the case in other hetero arrays, reported by us earlier [28–31].

Collectively, the ground state properties (UV–visible,  $^1\text{H}$  NMR and redox data) indicate that there exist ‘vertical’ disposition of the axial porphyrin with respect to the plane of the corresponding basal  $\text{Ge}(\text{IV})$  corrole in these hetero dimers. The data also indicate that there exist a minimum  $\pi\text{-}\pi$  interactions between the macrocyclic species of these dimers. A similar condition was also observed in other homo oligomers based on porphyrins and hetero oligomers based on porphyrins–phthalocyanine systems reported by us earlier [28–31].

### 3.2. Singlet state properties

In contrast to the ground state properties, the excited state properties of hetero dimers showed remarkable differences when compared with their individual constituents. After careful examination of the UV–visible data (Fig. 1, see Section 2) of hetero dimers and their constituent monomers investigated in this study indicate that it is possible to inquire into the individual photochemical activities of the basal  $\text{Ge}(\text{IV})$  corrole and axial porphyrin by excitation in the Soret band region of the spectra. Thus, we chose to excite the basal  $\text{Ge}(\text{IV})$  corrole at  $400\text{ nm}$  (wavelength at which the axial porphyrin shows minimum absorption) and the axial free-base/ $\text{Zn}^{\text{II}}$  porphyrin at  $425\text{ nm}$  (wavelength at which basal  $\text{Ge}(\text{IV})$  corrole shows minimum absorption) during the steady state fluorescence experiments. Representative spectra thus obtained for both the hetero dimers along with the corresponding reference compounds are given in Fig. 4. As seen, excitation at either  $400$  or  $425\text{ nm}$  results in quenching of fluorescence for both the hetero dimers in comparison with fluorescence from the corresponding individual, unlinked chromophores. It should be noted here while there exists a reduction of emission intensity for each subunit, the spectral shapes and wavelengths of maximum emission for the individual chromophores of these systems remain close to those the corresponding monomeric entities. Thus, the  $E_{0-0}$  (i.e., singlet state energy) values of individual components of these dimers are assumed to be essentially similar to those of constituent monomers [51]. Singlet state data of both the hetero dimers investigated in the present study are summarized in Table 2. The quenching efficiency values (%Q) have been evaluated



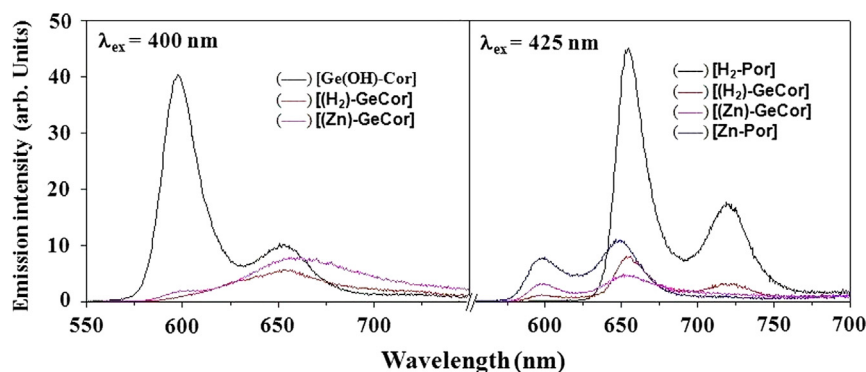


Fig. 4. Emission spectra of heterodimers along with those of corresponding monomers in  $\text{CH}_2\text{Cl}_2$ .

Table 2

Fluorescence data in different solvents <sup>a</sup>.

Compound	$\lambda_{\text{em}}$ , nm ( $\phi$ , %Q) <sup>b</sup>					
	Hexane		$\text{CH}_2\text{Cl}_2$		$\text{CH}_3\text{CN}$	
	$\lambda_{\text{ex}}=400$ nm	$\lambda_{\text{ex}}=425$ nm	$\lambda_{\text{ex}}=400$ nm	$\lambda_{\text{ex}}=425$ nm	$\lambda_{\text{ex}}=400$ nm	$\lambda_{\text{ex}}=425$ nm
[H <sub>2</sub> -Por]	–	653, 720 (0.110)	–	655, 720 (0.110)	–	653, 719 (0.11)
[Zn-Por]	–	642, 594 (0.037)	–	603, 649 (0.036)	–	606, 659 (0.042)
[Ge(OH)-Cor]	603, 662 (0.26)	–	598, 652 (0.24)	–	597, 652 (0.23)	–
[(H <sub>2</sub> )-GeCor]	654, 597, 721 (0.067, 74%)	653, 597, 722 (0.030, 72%)	508, 655, 713 (0.050, 79%)	598, 655, 721 (0.03, 73%)	653, 597, 718 (0.063, 73%)	653, 598, 720 (0.024, 78%)
[(Zn)-GeCor]	650, 595 (0.080, 69%)	596, 648 (0.01, 73%)	508, 656 (0.048, 80%)	598, 659 (0.010, 72%)	656, 601 (0.073, 68%)	658, 600 (0.009, 78%)

<sup>a</sup> Error limits:  $\lambda_{\text{ex}}$ ,  $\pm 2$  nm;  $\phi$ ,  $\pm 10\%$ .

<sup>b</sup> %Q is defined in Eq. (1) (see text).

using the quantum yield data

$$Q = \frac{(\phi(\text{ref}) - \phi(\text{dimer}))}{\phi(\text{ref})} \quad (1)$$

where  $\phi(\text{dimer})$  and  $\phi(\text{ref})$  refer to the quantum yield of a given dimer and appropriate reference compound, respectively. It was found that %Q in these heterodimers is in between 70 and 80%.

Various radiative and non-radiative intramolecular processes can be conceived to participate in the excited state decay of these novel, hybrid-type donor–acceptor (D–A) systems. Among these, an electronic energy transfer (EET) from basal Ge(IV) corrole to the axial H<sub>2</sub>/Zn and photoinduced electron transfer (PET) from ground state of axial H<sub>2</sub>/Zn to the excited state of basal metalloid corrole seem to be more probable as revealed by the thermodynamic considerations based on the singlet state energy ( $E_{0-0}$ ) and redox potential ( $E_{\text{CT}}$ ) data (Table 1 and Fig. 5) [51]. There exists a strong overlap between the emission of corrole and the absorption of porphyrin in these dyads and, this suggests that the quenching of the fluorescence of these dyads can be due to an intramolecular EET from singlet state of basal metalloid corrole to the axial porphyrin. In addition, overlap of the corrected and normalized excitation spectra (emission collected at the porphyrin emission maximum, 720 nm) with the corresponding absorption spectra reveals that the fluorescence quenching is due to the energy transfer in these dyads from the central metalloid corrole to the axial H<sub>2</sub>/Zn, when excited at 400 nm. The energy transfer efficiency was found to be 72 and 60% ( $\pm 10\%$ ) in [(H<sub>2</sub>)-GeCor] and [(Zn)-GeCor], respectively (Fig. 6) [52]. However, the PET reaction from ground state of axial H<sub>2</sub>/Zn to the excited state of basal metalloid corrole cannot be ruled out on thermodynamic considerations when excited at 400 nm. The change of free-energy

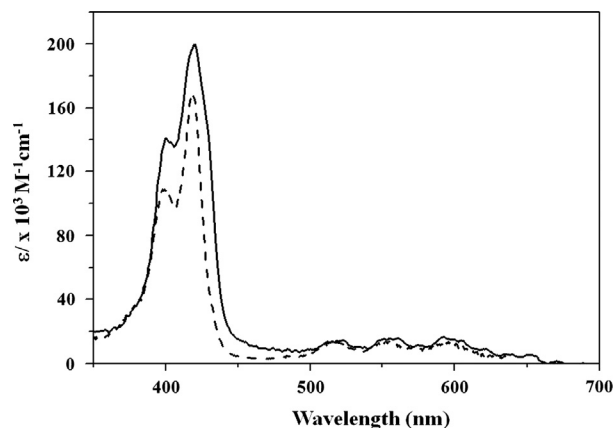


Fig. 5. Overlay of excitation (---) and absorption (—) spectra of [(H<sub>2</sub>)-GeCor] in  $\text{CH}_2\text{Cl}_2$  ( $\lambda_{\text{em}} = 715$  nm). The excitation spectrum was corrected for the instrument response function and was normalized with respect to the absorption spectrum [53].

when a PET occurred from ground state of axial H<sub>2</sub>/Zn porphyrins to the excited state of basal metalloid corrole is calculated by

$$\Delta G(^1\text{GeCor} \rightarrow \text{Por}) = E_{\text{CT}}(\text{Por}^+ \text{GeCor}^-) - E_{0-0}(\text{GeCor}) \quad (2)$$

$\Delta G$  was found  $-0.57$  and  $-0.82$  eV for [(H<sub>2</sub>)-GeCor] and [(Zn)-GeCor], respectively. Thus, the low  $\phi$  values observed upon excitation of these systems at 400 nm can be rationalized in terms of intramolecular EET reaction competing with PET reaction from singlet state of basal Ge(IV) corrole to the axial H<sub>2</sub>/Zn.

In contrast, the quenched emission was observed when excited at 425 nm is purely due to intramolecular PET from excited state of

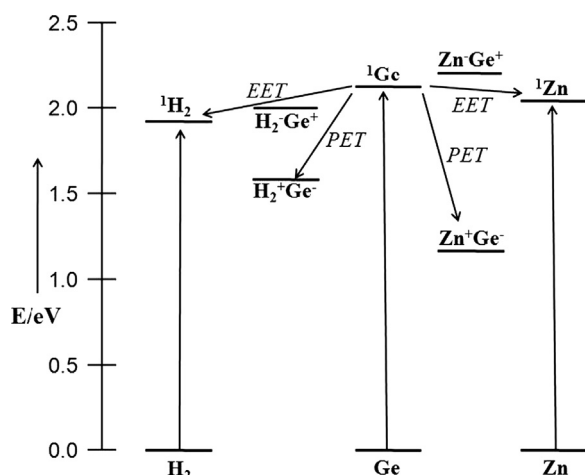


Fig. 6. Energies of singlet and charge-transfer states of the hetero dimers investigated in this study.

axial  $\text{H}_2/\text{Zn}$  to the ground state of basal metalloid corrole. This is because the energy transfer from axial porphyrin to the basal metalloid corrole is neither thermodynamically feasible nor was it experimentally detected in this study. The free-energy change for this electron transfer process,  $\Delta G(^1\text{Por} \rightarrow \text{GeCor})$  is calculated by

$$\Delta G(^1\text{Por} \rightarrow \text{GeCor}) = E_{\text{CT}}(\text{Por}^+ \text{GeCor}^-) - E_{0-0}(\text{H}_2/\text{Zn}) \quad (3)$$

$\Delta G$  was found  $-0.43$  and  $-0.78$  eV for  $[(\text{H}_2)\text{-GeCor}]$  and  $[(\text{Zn})\text{-GeCor}]$ , respectively. Thus, the low  $\phi$  values observed upon excitation of these systems at 425 nm can be rationalized in terms of PET reaction from excited state of axial  $\text{H}_2/\text{Zn}$  to the ground state of Ge(IV) corrole. The general dependence of  $\phi$  values when excited at 425 nm is somewhat on the solvent polarity (see Table 2). This suggests that this might indeed be the case where as low  $\phi$  values obtained when excited at 400 nm is due to the intramolecular EET competing with PET from excited state of basal metalloid corrole to the ground state of axial porphyrins.

In contrast, hetero dimers reported by using *meso-meso* positions, a different phenomenon was observed. For instance, Flamigni, Gryko and coworkers have reported a *meso*-substituted free-base porphyrin–corrole dyad in which, there is an energy transfer from corrole to porphyrin and porphyrin to corrole and interestingly, an equilibrium existed between the two lowest singlet excited states of the dyad in which one localized on the corrole and the other on the porphyrin unit, which are nearly *iso*-energetic ( $\Delta G = -0.01$  eV) [25]. However, in the present study we observed relatively high energy gap between Ge(IV)-corrole and porphyrin ( $\Delta G = -0.11$  eV). Hence, one cannot expect such equilibrium as it was observed in previously reported corrole–porphyrin dyad. We have observed energy transfer and electron transfer from Ge(IV)-corrole to porphyrin and electron transfer from porphyrin to Ge(IV)-corrole were observed. Axial bonding of both monomers perhaps could be another reason for such energy and electron transfer processes.

### 3.3. Conclusions

In conclusion, we have constructed hetero dimers by exploiting ‘axial’ bonding capabilities of Ge(IV) corroles for the first time. The ground state properties indicates that there is minimum  $\pi$ – $\pi$  interactions between the macrocyclic units of these hetero dimers.  $^1\text{H}$  NMR spectra indicates that the disposition of porphyrin unit in these hetero dimers is of ‘vertical’ type. Quenched emission observed due to an intramolecular EET from Ge(IV) corrole to the axial porphyrin compete with a PET from ground state of axial porphyrin to the excited state of Ge(IV) corrole, when excited at 400 nm in both the hetero dimers. The quenched emission was

observed, when excited at 425 nm was due to intramolecular PET from axial excited porphyrin to the ground state of Ge(IV) corrole. The energy transfer and electron transfer efficiency of these hetero dimers can be tuned by change of central metal ion of corrole macrocycle.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlumin.2013.08.009>.

### References

- [1] G. Bottari, O. Trukhina, M. Ince, T. Torres, *Coord. Chem. Rev.* 256 (2012) 2453.
- [2] F. D'Souza, O. Ito, *Chem. Soc. Rev.* 41 (2012) 86.
- [3] D. Bai, A.C. Benniston, J. Hagon, H. Lemmetyinen, N.V. Tkachenko, W. Clegg, R.W. Harrington, *Phys. Chem. Chem. Phys.* 14 (2012) 4447.
- [4] M.R. Wasielewski, *Acc. Chem. Res.* 42 (2009) 1910.
- [5] D. Gust, T.A. Moore, A.L. Moore, *Acc. Chem. Res.* 42 (2009) 1890.
- [6] I. McConnell, G. Li, G.W. Brudvig, *Chem. Biol.* 17 (2010) 434.
- [7] I. Grotjohann, P. Gromme, *Photosynth. Res.* 85 (2005) 51.
- [8] V.S. Shetti, M. Ravikanth, *Inorg. Chem.* 50 (2011) 1713.
- [9] B. Basic, J.C. McMurtrie, D.P. Arnold, *Eur. J. Org. Chem.* (2010) 4381.
- [10] J.J. Cid, C. Ehli, C. Atienza-Castellanos, A. Gouloumis, E.M. Maya, P. Vazquez, T. Torres, D.M. Guldi, *Dalton Trans.* (2009) 3955.
- [11] D.P. Arnold, J. Blok, *Coord. Chem. Rev.* 248 (2004) 299.
- [12] N. Kobayashi, *Coord. Chem. Rev.* 227 (2002) 129.
- [13] M. Graca, H. Vicente, L. Jaquinod, K.M. Smith, *Chem. Commun.* (1998) 1771.
- [14] B. Koszarna, D.T. Gryko, *Chem. Commun.* (2007) 2994.
- [15] J. Sankar, H. Rath, V. Prabhuraja, S. Gokulnath, T.K. Chandrasekhar, C.S. Purohit, S. Verma, *Chem. Eur. J.* 13 (2007) 105.
- [16] R. Paoless, L. Jaquinod, D.J. Nurco, S. Mini, F. Sagone, T. Boschi, K.M. Smith, *Chem. Commun.* (1999) 1307.
- [17] Z. Gross, N. Galili, I. Saltsman, *Angew. Chem. Int. Ed.* 38 (1999) 1427.
- [18] Z. Gross, *J. Biol. Inorg. Chem.* 6 (2001) 733.
- [19] C.S. Classens, U. Hahn, T. Torres, *The Chem. Rec.* 8 (2008) 75.
- [20] K. Kadish, L. Fremont, J. Shen, P. Chen, K. Ohkubo, S. Fukuzumi, M.E. Ojaimi, C.P. Gros, J.M. Barbe, R. Guillard, *Inorg. Chem.* 48 (2009) 2571.
- [21] H. Wang, K. Wang, Y. Bian, N. Kobayashi, *Chem. Commun.* 47 (2011) 6879.
- [22] P. Chen, M.E. Ojaimi, C.P. Gross, P. Richard, J.M. Barbe, R. Guillard, J. Shen, K.M. Kadish, *Inorg. Chem.* 50 (2011) 3479.
- [23] A. Harasat, E.L. Johan, *Tetrahedron Lett.* 50 (2009) 1113.
- [24] P.C. Lo, X. Leng, D.K.P. Ng, *Coord. Chem. Rev.* 251 (2007) 2334.
- [25] L. Flamigni, B. Ventura, M. Tasior, D.T. Gryko, *Inorg. Chim. Acta* 360 (2007) 803.
- [26] R. Paoless, F. Sagone, A. Macagnano, T. Boschi, L. Prodi, M. Montalti, N. Zaccaroni, F. Bolletta, K.V. Smith, *J. Porphyrins Phthalocyanines* 3 (1999) 364.
- [27] P.P. Kumar, B.G. Maiya, *New J. Chem.* 27 (2003) 619.
- [28] A.A. Kumar, L. Giribabu, D.R. Reddy, B.G. Maiya, *Inorg. Chem.* 40 (2001) 6757.
- [29] L. Giribabu, A.A. Kumar, V. Neeraja, B.G. Maiya, *Angew. Chem. Int. Ed.* 40 (2001) 3621.
- [30] L. Giribabu, T.A. Rao, B.G. Maiya, *Inorg. Chem.* 38 (1999) 4971.
- [31] J. Kandhadi, R.K. Kanaparthi, L. Giribabu, *J. Porphyrins Phthalocyanines* 16 (2012) 282.
- [32] L. Giribabu, Ch. Vijaykumar, P.Y. Reddy, *Chem. Aisan J.* 2 (2007) 1574.
- [33] H. Fang, Z. Ling, P.J. Brothers, X. Fu, *Chem. Commun.* 47 (2011) 11677.
- [34] S. Nardis, F. Mandoj, R. Paoless, F.R. Fronczek, K.M. Smith, L. Prodi, M. Montalti, G. Battistini, *Eur. J. Inorg. Chem.* (2007) 2345.
- [35] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, *Chem. Eur. J.* 7 (2001) 1041.
- [36] H. Fang, Z. Ling, P.J. Brothers, X. Fu, *Chem. Commun.* 47 (2011) 11677.
- [37] W.L.F. Armarego, C.L.L. Chai, *Purification of Laboratory Chemicals*, Elsevier, Amsterdam, 2003.
- [38] J.-H. Fuhrhop, K.M. Smith, in: K.M. Smith (Ed.), *Porphyrins Metalloporphyrins*, Elsevier, Amsterdam, 1975, p. 769.
- [39] D.J. Quimby, F.R. Longo, *J. Am. Chem. Soc.* 97 (1975) 5111.
- [40] L. Giribabu, C.V. Kumar, P.Y. Reddy, *J. Porphyrins Phthalocyanines* 10 (2006) 1007.
- [41] L. Giribabu, C.V. Kumar, V.G. Reddy, P.Y. Reddy, Ch.S. Rao, S.-R. Jang, J.-H. Hum, M.K. Nazeeruddin, M. Gratzel, *Solar Energy Mater. Solar Cells* 91 (2007) 1611.
- [42] A. Osuka, H. Shimadzu, *Angew. Chem. Int. Ed.* 36 (1997) 135.
- [43] S. Cho, J.M. Lim, S. Hiroto, P. Kim, H. Shinokubo, A. Osuka, D. Kim, *J. Am. Chem. Soc.* 131 (2009) 6412.

- [44] S. Hiroto, K. Furukawa, H. Shinokubo, A. Osuka, J. Am. Chem. Soc. 128 (2006) 12380.
- [45] J.F.B. Barata, A.M.G. Silva, M.G.P.M.S. Neves, A.C. Tome, A.M.S. Silva, J.A. S. Cavaleiro, Tetrahedron Lett. 47 (2006) 8171.
- [46] K. Kameyama, A. Satake, Y. Kobuke, Tetrahedron Lett. 45 (2004) 7617.
- [47] N. Kobayashi, Coord. Chem. Rev. 227 (2002) 129.
- [48] H.L. Anderson, Chem. Commun. (1999) 2323.
- [49] Y. Yang, B. Sama, V.O. Kennedy, D. Macikenas, B.L. Chaloux, J.A. Miller, R.L. Speer, J. Protasiewicz, A.A. Pinkerton, M.E. Kenney, J. Phys. Chem. A 115 (2011) 12474.
- [50] N.C. Maiti, S. Mazumdar, N. Periasamy, J. Phys. Chem. B 102 (1998) 1528.
- [51] Excited state singlet state energy levels ( $E_{0-0}$ ) of [**H<sub>2</sub>-Por**], [**Zn-Por**] and [**Ge (OH)-Cor**] are 1.96, 2.05 and 2.09 eV, respectively.
- [52] We have performed time-resolved fluorescent decay measurements in order to justify the EET and PET processes of the dimer compounds. But unfortunately we did not get supporting information presumably due to instability of the dimer compounds towards laser light originated from sensitive/weak Ge–O bond.
- [53] L. Giribabu, B.G. Maiya, Res. Chem. Intermediates 25 (1999) 769.