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Phosphorus(V)corrole- Porphyrin Based Hetero Trimers: Synthesis, Spectroscopy and Photochemistry

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Abstract 'Axial-bonding'-type hetero trimers have been constructed by employing a simple 'inorganic' reaction such as axial bond formation of main group element containing phosphorus corrole. The approach is simple and modular in nature. The architecture of these hetero trimers such that, while a phosphorus(V)corrole forms the basal scaffolding unit, either two free-base porphyrins [$(H_2)_2$–PCor] or Zn^{II} porphyrins [$(Zn)_2$–PCor] occupy the two axial sites via an aryloxy bridge. Both hetero trimeric species have been completely characterized by mass (FAB), UV/Vis, proton nuclear magnetic resonance spectroscopies and also by the differential pulse voltammetric method. Comparison of their spectroscopic and electrochemical data of these trimers with those of the corresponding reference compounds reveal that there is no apparent ring-to-ring interactions in these 'vertically' linked hetero trimers. Reduced fluorescence quantum yields were observed for [$(H_2)_2$–PCor] and [$(Zn)_2$–PCor] when compared to corresponding monomeric chromophores. Finally, a comparison is made between the presently reported phosphorus(V)corrole based hetero arrays and the previously reported analogous arrays based on Ge(IV)corrole with regard to their spectroscopic properties and photochemical activities.

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Introduction

Photoinduced electron and energy transfer play a key role in light-driven chemical, physical and biological processes. Photosynthesis represents a remarkable and ubiquitous model that has motivated design of many elaborate assemblies to convert light energy into chemical potential [1–6]. Although research done in this area has explained many phenomena and answered many questions, unsolved problems provide rationale to search for new systems differing from the previous ones for photoactive unit, linker, position of donor or acceptor to the chromophore, etc. [7–11]. During past decades covalently linked arrays of various chromophores and various complexes have been reported in order to mimic the natural photosynthetic events [12–16]. Although a great variety of organic and inorganic photoactive unit have been investigated, in this regard porphyrins are still the most often used. In many of such oligomeric arrays, the monomeric porphyrin subunits have been fixed at their peripheral -*meso* or pyrrole-β carbon position(s) thus necessitating extensive, and often cumbersome, synthetic efforts. In contrast, utilization of 'axial-bonding' concept by conducting simple 'inorganic' reaction at axial position of resident metal ion of porphyrin was employed in the construction of porphyrin based homo oligomeric arrays [17–20]. The concept extends to other tetrapyrrolic compounds such as phthalocyanines, and reported hetero oligomeric trimers by us earlier and studied the excited state properties by change of metal ion of central phthalocyanine cavity of these hetero trimers [21, 22].

On the other hand, corrole-one carbon short analogue of porphyrin have not explored as their counter parts. Nevertheless, investigations of corroles have recently increased with the
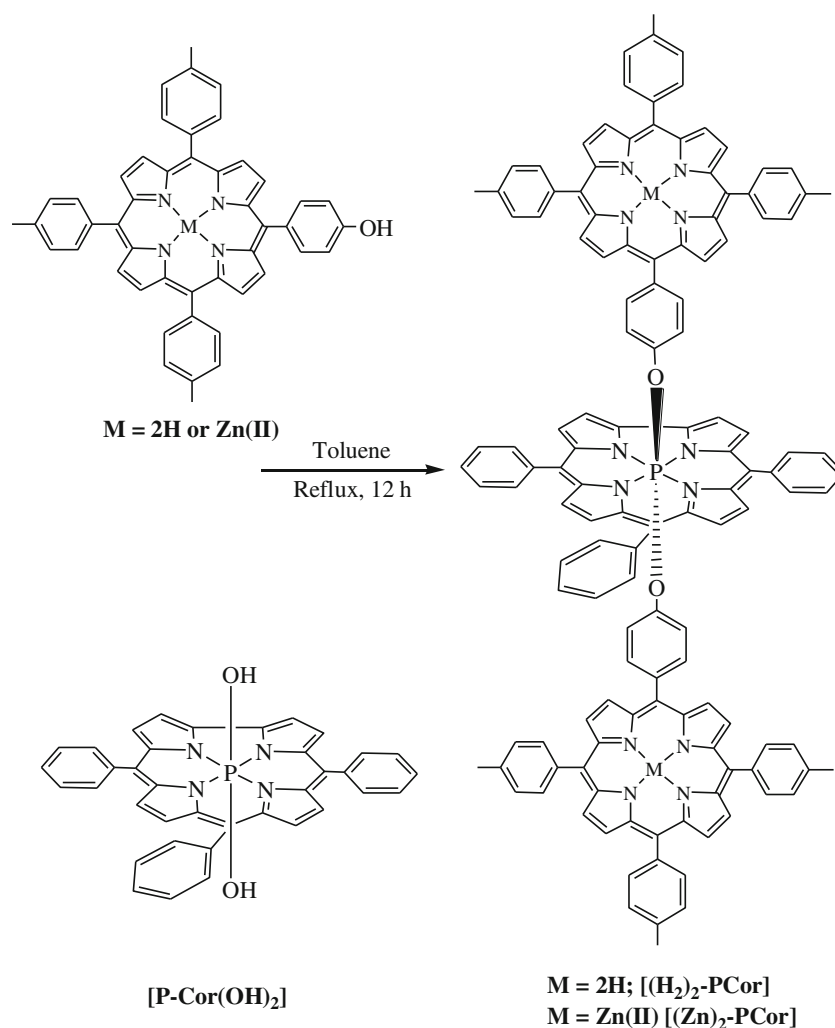
Scheme 1 Synthetic scheme of P(V)corrole-Porphyrin hetero trimers

synthetic work of the groups of Paolesse and Gross, with each of the respective groups reporting a one-pot synthesis of triaryl corroles [23, 24]. These compounds exhibit some interesting properties when compared to porphyrins: higher fluorescence quantum yields, larger stokes shift, more intense absorption of red light and *tri*-anionic ligands that stabilize unusual high oxidation states of metal ions. Moreover, corroles are easy to oxidize and reasonable ease of reduction when compared to porphyrins. Donor-acceptor systems based on corrole-porphyrin by using peripherial position/s have been reported in the literature [25, 26]. During the course of our investigation for the construction of hetero arrays by using 'axial-bonding' concept, recently, we have constructed hetero dimers based on Ge(IV)corrole-porphyrin by using axial position of Ge(IV)corrole [27]. Both excitational energy transfer (EET) and photoinduced electron transfer (PET) reactions were studied in these hetero dimers. Here in the present manuscript, we extended the 'axial-bonding' concept to P(V)corroles and constructed hetero trimers in which P(V)corrole as basal scaffolding unit and either two free-base porphyrins or zinc porphyrins at the axial positions. The molecular structures of both free-base

$[(H_2)_2$-PCor] and zinc hetero trimers $[(Zn)_2$-PCor] are shown in Scheme 1. The excited state properties of both the hetero trimers were studied and compared with our previously reported results. In addition, P(V)corroles are limited to their hydroxyl and methoxy compounds only in the literature so far [28].

Experimental Section

All chemicals were obtained from Aldrich Chemicals (USA). Analytical reagent grade solvents and reagents were used for synthesis, and distilled laboratory grade solvents were used for chromatography. Dry chloroform and dichloromethane were prepared by argon-degassed solvent through activated alumina columns. N_2 (oxygen-free) was passed through a KOH drying column to remove moisture. ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F$_{254}$ plates. All reactions were carried out under nitrogen or argon atmosphere using dry degassed solvents, and the apparatus was shielded from ambient light.

Table 1 Absorption and redox potential data

| Compound | Absorption, λ_{max}, nm (log ε, M^{-1} cm^{-1})[a] | Potential V, vs. SCE[b] | | E_{CT} (P^-PCor^+) | E_{CT} (P^+PCor^-) |
		Reduction	Oxidation		
H_2L^1	418 (5.30), 515 (4.17), 551 (3.92), 594 (3.70), 648 (3.60)	−1.24, −1.64	0.94, 1.30	–	–
ZnL^1	420 (5.21), 510 (3.40), 549 (4.09), 588 (3.61)	−1.40, −1.71	0.72, 1.05	–	–
[P-Cor(OH)$_2$]	408 (5.34), 408 (sh), 522 (3.97), 561 (4.19), 598 (4.50)	−1.48, −1.69	0.64, 1.14	–	–
[(H$_2$)$_2$-PCor]	419 (5.44), 516 (4.40), 553 (4.30), 597 (4.50), 649 (3.95)	−1.25, −1.45 −1.60	0.80, 0.95 1.12, 1.34	2.05	2.40
[(Zn)$_2$-PCor]	420 (5.48), 523 (4.28), 552 (4.52), 597 (4.55), 650 (3.92)	−1.38, −1.53 −1.82	0.70, 1.01 1.19, 1.46	2.23	2.08

[a] Solvent CH$_2$Cl$_2$, Error limits: λ_{max}, ± 1 nm, log ε, ± 10 %

[b] CH$_2$Cl$_2$, 0.1 M TBAP; Glassy carbon working electrode, Pt electrode auxillary electrode. Error limits, $E_{1/2}$±0.03 V

Synthesis

The compounds 5,10,15,20-tetraphenyl porphyrin (**H$_2$L^1**), 5, 10,15,20-tetraphenyl porphyrinato zinc(II) (**ZnL^1**), *meso*-5-(4-hydroxyphenyl)-10,15,20-(4-methyl phenyl)-porphyrin[**H$_2$L^2**], *meso*-5-(4-hydroxyphenyl)-10,15,20-(4-methyl phenyl)-porphyrinato zinc(II) [**ZnL^2**] and 5,10,15-triphenyl-corrole [**H$_2$-Cor**] were synthesized as per the procedures reported in the literature [23, 24, 29].

Synthesis of [**P-Cor(OH)$_2$**]

[**H$_2$-Cor**] (100 mg, 0.19 mmol) and POCl$_3$ (600 µL, 6.45 mmol) were dissolved in 20 ml of dry pyridine. The resulting reaction mixture was refluxed under inert atmosphere until the Q-bands of corrole have changed. Then the solvent pyridine was removed under reduced pressure and obtained residue was dissolved in CH$_2$Cl$_2$ and filtered. The filtrate was washed with dil. HCl, dried and evaporated. The residue was subjected to basic alumina column and eluted with CH$_2$Cl$_2$. The greenish pink colour band was collected and recrystallized from CH$_2$Cl$_2$/hexane to get the desired compound. Elemental analysis calcd for C$_{37}$H$_{25}$N$_4$O$_2$P (588.59): C 75.50, H 4.28, N 9.52; found: C 75.40, H 4.34, N 9.48. ESI-MS: (C$_{37}$H$_{25}$N$_4$O$_2$P) *m/z*: 586 (M^{2+}). ^{1}H NMR (300 MHz, CDCl$_3$): d=9.21 (dd, $^3J_{H,H}$=4.2 Hz, 2H), 9.03 (dd, $^3J_{H,H}$=4.8 Hz, 2H), 8.90 (dd, $^3J_{H,H}$=4.4 Hz, 2H), 8.80 (dd, $^3J_{H,H}$=4.9 Hz, 2H), 8.25 (m, 4H), 8.15 (m, 2H), 7.80 ppm (m, 9H).

Synthesis of [**(H$_2$)$_2$-PCor**]

[**P-Cor(OH)$_2$**] (100 mg, 0.16 mmol) and (**H$_2$L^2**) (220 mg, 0.30 mmol) were dissolved in 50 ml of dry toluene. The resultant reaction mixture was refluxed under nitrogen atmosphere for 12 h. The solvent was evaporated and dried under vacuum. The obtained residue was subjected to silica gel column chromatography and eluted with CH$_2$Cl$_2$ solvent.

The solvent front running brown colour band was collected and evaporated under reduced pressure. The desired product was obtained after recrystallization form CH$_2$Cl$_2$/hexane solvent mixture. Elemental analysis calcd for C$_{131}$H$_{93}$N$_{12}$O$_2$P (1898.19): C 82.89, H 4.94, N 8.85; found: C 82.95, H 4.90, N 8.80. MALDI-MS: C$_{131}$H$_{93}$N$_{12}$O$_2$P (1898.19): [C$_{131}$H$_{93}$N$_{12}$O$_2$P-C$_{48}$H$_{38}$N$_4$O]$^-$ 1227 (30 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ=9.58 (dd, $^3J_{H,H}$=4.0 Hz, 2H), 9.26 (dd, $^3J_{H,H}$=4.6 Hz, 2H), 9.15 (dd, $^3J_{H,H}$=4.6 Hz, 2H), 9.05 (dd, $^3J_{H,H}$=4.0 Hz, 2H), 8.80 (s, 8H), 8.65 (d, $^3J_{H,H}$=4.2 Hz, 4H), 8.30 (d, $^3J_{H,H}$=4.6 Hz, 4H) 8.15 (m, 18H), 7.80 ppm (m, 21H), 6.65 (d, $^3J_{H,H}$=6.2 Hz, 4H), 2.75 (s, 18H), 2.70 (d, $^3J_{H,H}$=6.2 Hz, 4H), −3.0 (s, 4H).

Synthesis of [**(Zn)$_2$-PCor**]

This compound was synthesized by an analogous manner to the above compound by the condensation of **ZnL^2** and [**P-Cor(OH)$_2$**]. Elemental analysis calcd.for C$_{131}$H$_{89}$N$_{12}$O$_2$PZn
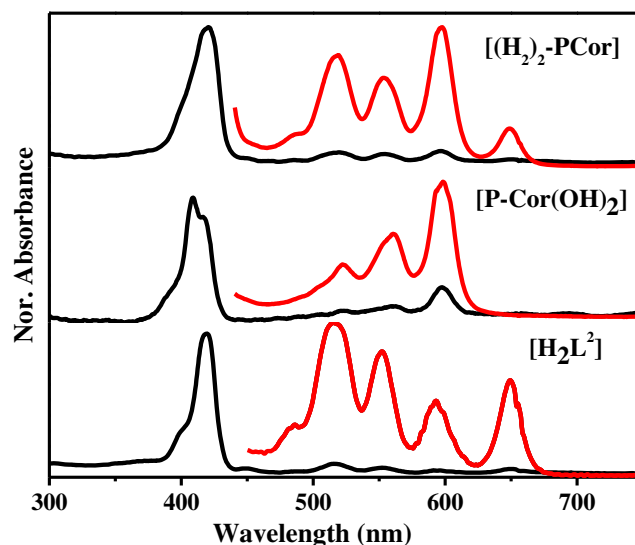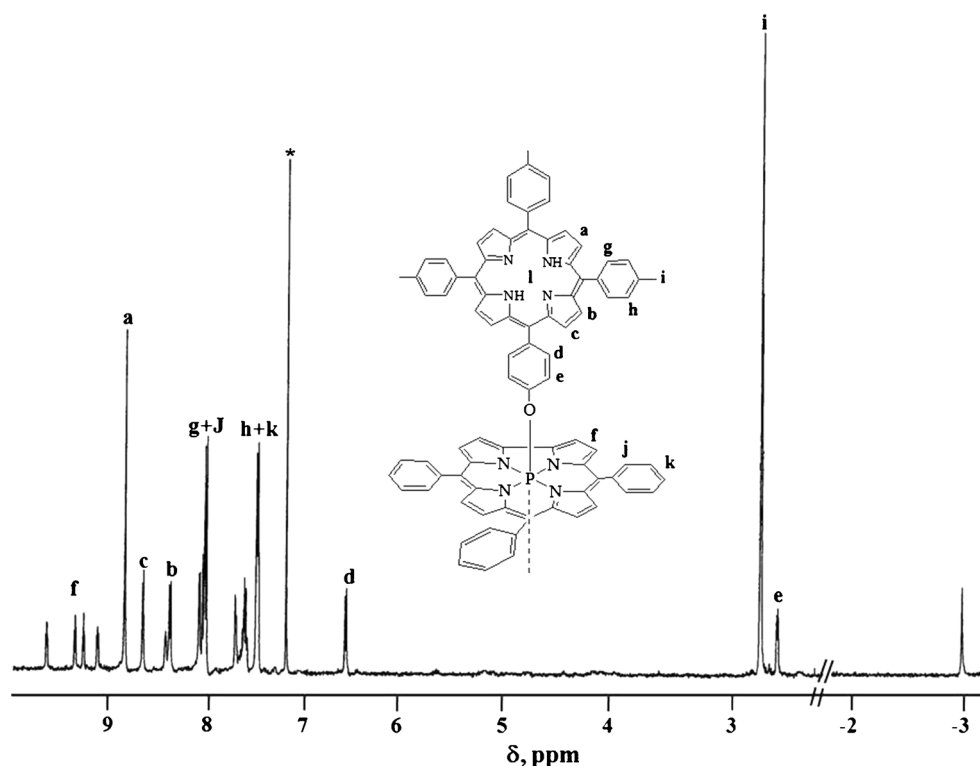

Fig. 1 UV-visible absorption spectra of **H$_2$L^2**, [**P-Cor(OH)$_2$**] and [**(H$_2$)$_2$-PCor**] in CH$_2$Cl$_2$

Fig. 2 ^{1}H NMR spectrum of [$(\mathbf{H_2})_2$-**PCor**] in CDCl$_3$

(2024.94): C 77.70, H 4.43, N 8.30; found: C 77.79, H 4.40, N 8.25. MALDI-MS: $C_{131}H_{89}N_{12}O_2PZn$ (2024.94): [$C_{131}H_{89}N_{12}O_2PZn$-$C_{48}H_{36}N_4OZn$]$^-$ 1290 (35 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ =9.50 (dd, $^3J_{H,H}$=4.0 Hz, 2H), 9.22 (dd, $^3J_{H,H}$=4.6 Hz, 2H), 9.15 (dd, $^3J_{H,H}$=4.6 Hz, 2H), 9.00 (dd, $^3J_{H,H}$=4.0 Hz, 2H), 8.85 (s, 8H), 8.65 (d, $^3J_{H,H}$=4.2 Hz, 4H), 8.32 (d, $^3J_{H,H}$=4.6 Hz, 4H) 8.15 (m, 18H), 7.80 ppm (m, 21H), 6.60 (d, $^3J_{H,H}$=5.8 Hz, 4H), 2.75 (s, 18H), 2.65 (d, $^3J_{H,H}$=5.8 Hz, 4H).

Methods

The UV-visible spectra were recorded on a Shimadzu (UV-3600) spectrophotometer by using 1×10^{-6} M (porphyrin and corrole Soret band) and 5×10^{-5} M (corrole and porphyrin Q-bands) solutions. Steady state fluorescence spectra were recorded using Spex Fluorolog-3 spectrofluorometer (Horiba JobinYvon). For absorption measurements, optical density of the solutions at Soret and Q-bands were maintained≈0.11. For the fluorescence quantum yield measurements, the solutions were optically matched ($\approx$ 0.05) at the excitation wavelengths (λ_{ex}=405 nm and 420 nm) and then the quantum yields were calculated by comparing the integrated areas under the fluorescence emission curves. $\mathbf{H_2L}^1$ (ϕ =0.13 in CH$_2$Cl$_2$), $\mathbf{ZnL}^1$ (ϕ =0.036 in CH$_2$Cl$_2$) and $\mathbf{H_2}$-**Cor** (ϕ =0.37 in benzene) were used as reference compounds [30–32]. 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. ^{1}H NMR spectra were measured on a Bruker 300 MHz Avance NMR spectrometer using personal computer based 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.

Differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI620C electrochemical analyzer. The 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 [33, 34].

Results and Discussion

The synthetic scheme of phosphorous corrole based hetero trimers were exemplified in Scheme 1. The dihydroxy phosphorus corrole was synthesized by refluxing the POCl$_3$ with corresponding free-base corrole in pyridine solvent. Both the hetero trimers [$(\mathbf{H_2})_2$-**PCor**] and [$(\mathbf{Zn})_2$-**Pcor**] were obtained by the condensation of [**P-Cor(OH)$_2$**] with an excess of [$\mathbf{H_2L}^2$] and [$\mathbf{ZnL}^2$], respectively, in toluene under reflux for 16 h. The desired composite was obtained after column chromatographic purification and recrystallization yields in both the hetero trimers with 50 %. Preliminary characterization of these new arrays was carried out by FAB-MS and UV-visible spectroscopic methods. Mass spectral fragmentation pattern
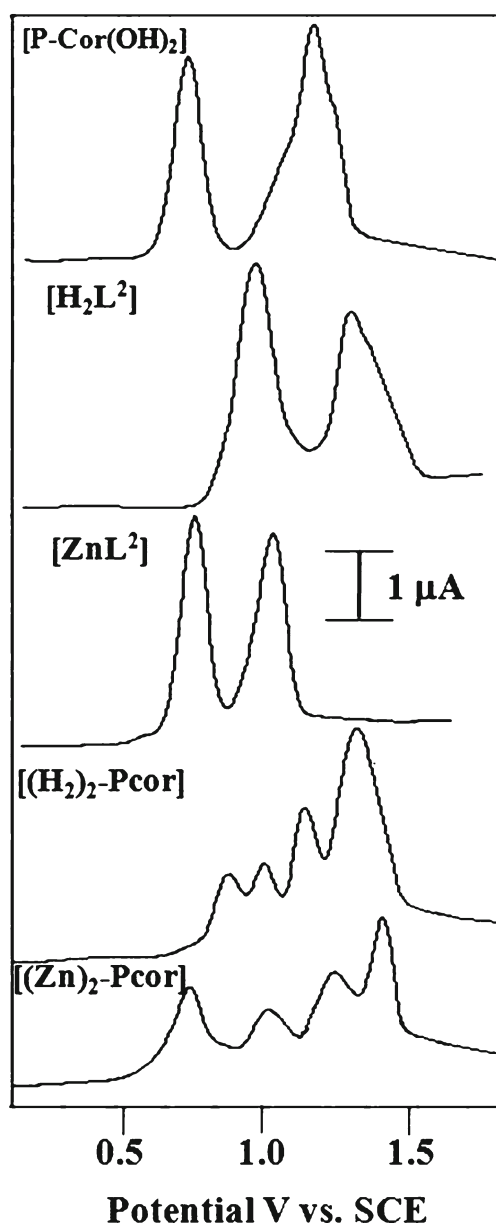
Fig. 3 Differential pulse voltammograms in CH₂Cl₂ and 0.1 M TBAP (scan rate 10 mV s⁻¹)

of the arrays investigated here are characteristic of this class of compounds. The mass spectrum of [(**H₂**)₂-**PCor**] showed a peak at m/z=1227([M]⁺ − C₄₈H₃₈N₄O) ascribable to the detachment of one porphyrin unit from the free-base heterotrimer. A similar type of fragmentation was also observed in the case of [(**Zn**)₂-**PCor**].

Ground State Properties

Electronic absorption characteristics of newly synthesized hetero trimers were studied in dichloromethane (CH₂Cl₂). Wavelengths at maximum absorbance (λ_max) and molar

extinction coefficient (ε) values of both hetero trimers and corresponding monomeric species are summarized in Table 1. Figure 1 illustrates absorption spectra of the free-base hetero trimer along with its reference compounds i.e., [**P-Cor(OH)₂**]&[**H₂L²**]. Comparison UV-visible spectra of each trimer with the spectra of corresponding monomeric units suggested that the λ_max values of the trimers are in the same range as those of the reference compounds. In addition, ε values of the trimer absorption bands are nearly equal to the sum of the ε values of the constituent monomer absorption bands. Thus, the spectrum of each heterotrimer is more or less similar to the spectrum resulting from a combination (1:2 mol/mol) of the corresponding individual precursors [**P-Cor(OH)₂**] and [**H₂L¹**] or [**ZnL²**]. From the absorption properties, it is clear that the both hetero trimers retain their independent absorption features with minimum π-π interactions between the macrocyclic units of hetero trimers.

The ¹H NMR spectrum of heterotrimer [(**H₂**)₂-**PCor**] is illustrated in Fig. 2 along with the proton assignments. It is worthwhile to look into the chemical shifts of *meta* (type-*d*) and *ortho* (type-*e*) protons of the phenoxo groups of the free-base porphyrin that are bound to the phosphorous center. These protons, being affected by both the inherent deshielding effect of the axial porphyrin and the shielding effect of the basal corrole [35], resonate at 6.65 (d, 4H, *J*=6.2 Hz) and 2.70 (d, 4H, *J*=6.2 Hz) ppm, respectively. The inner imino protons of the axial free-base porphyrins (type l) of [(**H₂**)₂-**PCor**] are seen to experience the "long-range" shielding effect due to the ring current of the basal P(V)corrole and resonate at-3.00 ppm (s, 4H) compared to the corresponding -NH protons of **H₂L²** that appear at −2.74 ppm. In addition to this the pyrrole-β protons of axial porphyrins are differently experience the shielding effect of basal P(V)corroles and appeared as a singlet at 8.82 ppm (8H) and two doublets at 8.60 (4H) and 8.42 ppm (4H). This type of shielding and deshielding effects of these hetero arrays suggesting that the porphyrin π plane is "vertical" align to the corrole π-plane, certainly not of a face-to-face (parallel) type in which case an additive shielding effects as in other homo porphyrin arrays, and other hetero arryas such as porphyrin-phthalocyanine hetero trimers and porphyrin-corrole hetero dimers reported by us earlier [19–22]. A similar shielding effect was also observed in alkoxy P(V)corroles [28]. The protons on the basal P(V)corrole are not much effected by axial porphyrins and appeared at the same position as appeared in isolated [**P-Cor(OH)₂**].

The electrochemical properties which are investigated by using differential pulse voltammetric technique also indicated the absence of π-π interactions of macrocyclic units of hetero trimers and retain their individual characteristic features. Figure 3 shows differential pulse voltammograms of both hetero trimers along with its reference compounds and the corresponding redox data
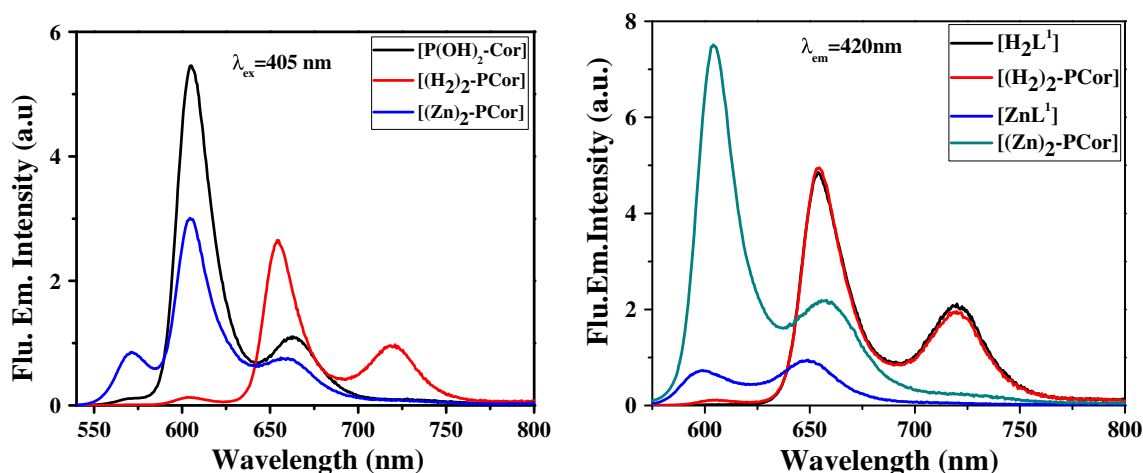
Fig. 4 Emission spectra of hetero trimers **a** $\lambda_{ex}=405$ nm **b** $\lambda_{ex}=420$ nm in CH_2Cl_2

were presented in Table 1. Each hetero trimer undergoes three reduction steps and four oxidation steps in CH_2Cl_2 and 0.1 M tetrabutyl ammonium perchlorate (TBAP). Wave analysis suggested that, in general, while the first two reduction steps and first two oxidation steps are reversible ($i_{pc}/i_{pa}=0.9$–1.0) and diffusion-controlled ($i_{pc}/\nu^{1/2}=$constant in the scan rate (ν) range 50–500 mV/s) one-electron transfer ($\Delta E_p=60$–70 mV; $\Delta E_p=65\pm3$ mV for ferrocenium/ferrocene couple) reactions, the subsequent steps are, in general, are quasi-reversible ($E_{pa}-E_{pc}=90$–200 mV and $i_{pc}/i_{pa}=0.5$–0.8 in the scan rate (ν) range 100–500 mV s^{-1}). Nonetheless, on the basis of the redox data of the individual monomers, we have attempted to assign the peaks to basal P(V)corrole and axial porphyrins separately. Analysis of the data given in Table 1 reveals that the redox potentials of the hetero trimers are in the same range as those of their corresponding monomeric reference compounds. The possible charge transfer states of heterotrimers (i.e., $E_{CT}(P^+PCor^-)$ and $E_{CT}(P^-PCor^+)$ where P = H$_2$ or Zn), as

evaluated from the redox potential data, testify to this conjecture.

Collectively, ^{1}H NMR, UV–Vis, and redox potential data indicate that there exists a symmetric disposition of the two axial H$_2$/Zn porphyrins with respect to the plane of the corresponding basal P(V)corrole and there exists a minimum π-π interaction between the macrocyclic units of these hetero arrays. In general, if there exists π-π interaction between the both covalently or non-covalently linked porphyrin, corrole, phthalocyanine dimers (e.g. face-to-face, slipped etc.) and as well as aggregates, the situation would have been different than the present case [36–38].

Singlet Properties

Figure 4 depicts the fluorescence emission spectra of the trimers compared with individual monomeric units. As shown in the Fig. 4, shapes of the fluorescence emission bands and E_{0-0} values of these arrays are not

Table 2 Fluorescence data

Compound	λ_{em}, nm (ϕ, %Q)[a]					
	Hexane		CH$_2$Cl$_2$		ACN	
	$\lambda_{ex}=405$ nm	$\lambda_{ex}=420$ nm	$\lambda_{ex}=405$ nm	$\lambda_{ex}=420$ nm	$\lambda_{ex}=405$ nm	$\lambda_{ex}=420$ nm
H$_2$L^1	–	653, 720 (0.110)	–	654, 720 (0.110)	–	653, 720 (0.120)
ZnL^1	–	593, 641 (0.032)	–	599, 649 (0.036)	–	607, 660(0.033)
[P-Cor(OH)$_2$]	603, 662 (0.41)	–	605, 664 (0.32)	–	604, 663 (0.38)	–
[(H$_2$)$_2$-P-Cor]	602, 653, 720(0.009,98 %)	603, 653, 720 (0.093)	605, 655,719 (0.009, 97 %)	603, 654, 720 (0.11)	603, 653, 719 (0.009, 98 %)	603, 653, 719 (0.075)
[(Zn)$_2$-P-Cor]	570, 603, 659 (0.35)	603, 658 (0.22)	571, 605, 660 (0.30)	605, 658 (0.12)	570, 604, 660 (0.26)	604, 659 (0.081)

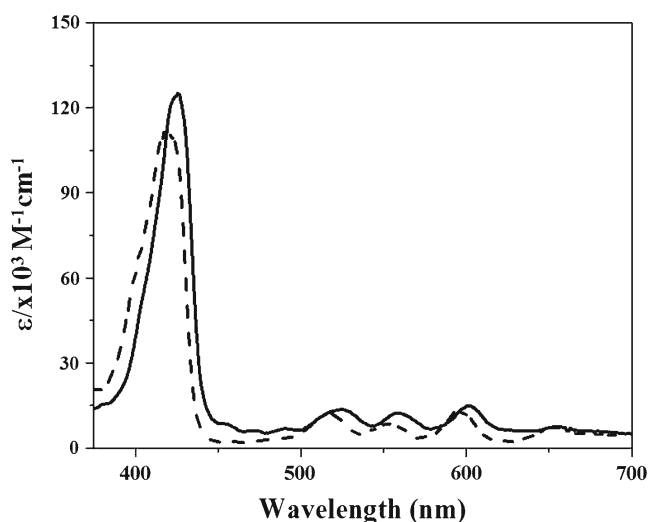Error limits:λ_{ex},±2 nm; ϕ, ±10 %

[a] Q is defined in Eq. 1

Fig. 5 Overlay of excitation (- - - - -) and absorption (——) spectra of [(H$_2$)$_2$-GeCor] in CH$_2$Cl$_2$ (λ_{em}=720 nm). The excitation spectrum was corrected for the instrument response function and was normalized with respect to the absorption spectrum

so different from those of the unlinked monomeric porphyrins. As a result, one can deduce that the electronic structures of the excited states of the individual subunits in these trimers are similar to those of the corresponding monomers.[1] However, fluorescence due to the central P(V)corrole is considerably quenched with respect to the monomeric chromophores (Fig. 4a) when excited at 405 nm where the corrole absorbs predominantly. In contrast, the emission intensity of axial free-base porphyrin/metalloporphyrin units of the trimeric units is not quenched when excited at 420 nm where the absorption majorly due to the porphyrin (Fig. 4b) and more over emission intensity is enhanced in case of [(Zn)$_2$-PCor]. Perhaps this might be due to the corrole excitation along with the porphyrin at 420 nm. Similar fluorescence emission spectra are observed when free-base hetero trimer [(H$_2$)$_2$-PCor] excited at 645 nm, where porphyrin is the only absorber (*See* supporting information). This is not possible in case of [(Zn)$_2$-PCor] because both Q-bands of porphyrin and corrole are overlapped (*See* supporting information). The quenching efficiency values (%Q) have been evaluated using the quantum-yield data Eq. 1

$$Q = [\phi(\text{ref}) - \phi(\text{trimer})/\phi(\text{ref})] \times 100 \quad (1)$$

Where ϕ(trimer) and ϕ(ref) refer to the quantum yield of a given trimer and corresponding reference compound,

respectively. **H$_2$L**[1] and **ZnL**[1] have been chosen as common reference compounds for calculating the poprphyrin (420 nm) fluorescence emission quenching efficiencies of the trimers. Similarly, the [**P-Cor(OH)$_2$**] monomer has conceived as the appropriate reference compound for quenching studies carried out with 405 nm excitation of these hetero trimers. The %Q calculated from Eq. 1 of the hetero-trimers are found to ~98 % (Table 2), indicating the participation of additional pathway(s) for the singlet state decay of the individual subunits of these trimers.

The quenching of emission intensity is probably either due to the intramolecular excitational energy trasnfer (EET) or photoinduced electron transfer (PET) processes. The intramolecular EET is a thermodynamically favored process in these hetero arrays when excited at 405 nm; the singlet-state energy of the P(V)corrole is higher (2.07 ev) than that of the axial free-base porphyrin (1.96 eV) & zinc porphyrin (2.05 eV) in both the hetero trimers. Additionally, there is a considerable overlap of the fluorescence emission of P(V)corrole and the absorption of the free-base porphyrin/zinc porphyrin in the 600–700 nm region (*See* supporting information). Apart from this, the spectra obtained when hetero trimers excited at 405 nm show fluorescence originated from the axial porphyrins indicating an intramolecular EET in these arrays. Further supporting information of intramolecular EET is being the quenching mechanism comes from the excitation spectral measurements. Overlap of the normalized excitation spectrum (emission collected at 720 nm, where the emission is exclusively due to the free-base porphyrin) with its absorption spectrum revealed that the efficiency of the intramolecular EET from the central P(V)corrole to the axial free-base porphyrins is ~85 ±10 % (Fig. 5). Similar quenching efficiency calculations of the zinc porphyrins as axial ligands of trimer arrays was not possible because of absorption overlap of the bands due to the donor P(V)corrole and acceptor zinc
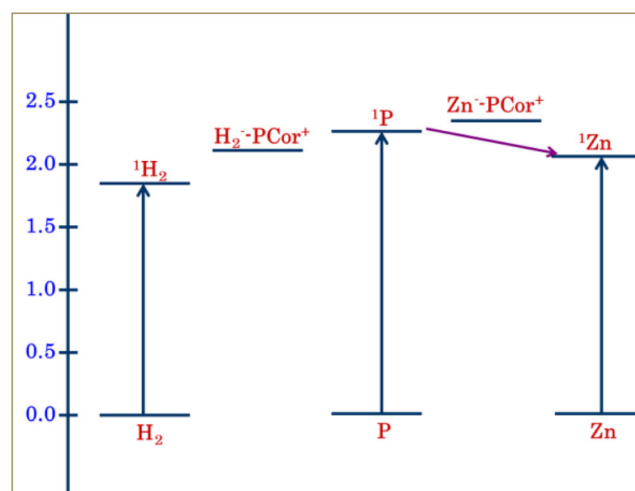

Fig. 6 Energies of singlet and charge-transfer states of the hetero dimers investigated in this study

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[1] E_{0-0} values of **H$_2$L**[1], **ZnL**[1] and [**P(OH)$_2$-Cor**] are 1.96, 2.05 and 2.07 eV (±0.03 eV), respectively.

porphyrin. However, the PET reaction from the singlet-state of central P(V)corrole to the axial free-base porphyrins can not be ruled out based on thermodynamic considerations, when excited at 405 nm. The change in free energy when PET occurs from the singlet-state of central P(V)corroles to the axial porphyrin can be calculated from the following equation.

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

ΔG was found to be −0.02 and 0.18 eV for $[(H_2)_2\text{-Pcor}]$ and $[(Zn)_2\text{-Pcor}]$, respectively (Table 1 & Fig. 6). Thus, the low ϕ values observed upon excitation of these systems at 405 nm can be rationalized in terms of intramolecular EET reaction competing with PET reaction from singlet state of central P(V)corrole to the ground state of axial free-base porphyrin whereas in case of $[(Zn)_2\text{-Pcor}]$ the low ϕ are exclusively due to intramolecular EET as PET in this case thermodynamically not feasible.[2]

In contrast, fluorescence emission quenching was not observed when excited at 420 nm. In fact in case of $[(Zn)_2\text{-PCor}]$, the emission intensity is enhanced when compared to its reference compound i.e., ZnL^1 (Fig. 4b). This is not only due to the corrole absorption but it is also having high fluorescence quantum yiled when compared to ZnL^1 (see Table 1). Based on thermodynamic consideration, one can conclude that neither the intramolecular EET nor PET processes is responsible for inefficient fluorescence emission quenching in these hetero arrays. As we can see from Figs. 1, 2, 3 and 4, the emission spectrum of porphyrin is not overlapping with the absorption of P(V)corrole which straight away rule out the possibility of intramolecular EET. The change in free energy when PET occurs from the singlet-state of axial of H_2/Zn porphyrin to ground state of central P(V)corroles can be calculated from the following equation.

$$\Delta G(^1Por \rightarrow PCor) = E_{CT}(PCor^-Por^+) - E_{0-0}(H_2/Zn) \quad (3)$$

ΔG was found 0.44 and 0.03 eV for $[(H_2)_2\text{-Pcor}]$ and $[(Zn)_2\text{-Pcor}]$, respectively. Therefore, both intramolecular PET and EET reactions are not possible when excited at 420 nm.

The results obtained in the present study were compared with the literature reported corroles dyads and a rationale has

been deduced as follows [27, 39]. In case of previously reported Ge(IV)corrole-porphyrin hetero dyads, the fluorescence emission was quenched when excited at 400 nm (λ_{max} where corrole absorbs predominantly). This is due to predominant PET from corrole to porphyrin than energy transfer pathway as ΔG is more negative in the case of Ge(IV)corrole (−0.57 eV) than in P(V)corrole (−0.02 eV) with free-base porphyrin is the axial ligand. In contrast, fluorescence emission quenched in Ge(IV)corrole-porphyrin hetero dimer, when excited at 420 nm (λ_{max} where porphyrin absorbs predominantly) is due to the PET from excited state of axial porphyrin to the ground state of corrole. This is mainly due to the fact that Ge(IV)corrole is easy to reduce (−0.65 V vs. SCE) than the P(V)corrole (−1.48 V vs. SCE). Gryko, Flamigni and co-workers reported meso-substituted corrole-porphyrin dyads and observed both intramolecular EET from corrole to porphyrin and porphyrin to corrole. Interestingly, they observed an equilibrium between the two lowest singlet excited states localized one on porphyrin and one on corrole which are nearly iso-energitic (ΔG=−0.01 eV). Hence, in the present case also one can expect such equilibrium between the lowest singlet excited states of porphyrin and corrole because of their nearly iso-energitic lowest singlet states (ΔG=−0.02 eV). However, the meso-substituted corrole-porphyrin dimer synthesis includes several steps and tricky purification steps. But our synthetic strategy, 'axial bonding donor-acceptor system' is much better and easy for constructing the new hetero-trimers based on corroles and porphyrins and more over the excited state properties of these hetero arrays can be tune easily by change of metal ion of corrole as was the case in our previously reported homo arrays based on porphyrins and hetero arrays based on porphyrin-phthalocyanines.

Conclusions

In summary, new 'vertically-aligned' hetero trimeric arrays based on the P(V)corrole scaffold have been synthesized and characterized by spectroscopic and electrochemical methods. In addition, their photophysical properties have also been investigated systematically and the results were interpreted in terms of intramolecular electron and energy transfer mechanisms. A rationale has been deduced from present P(V)corroles and the past axial-bonding Ge(IV)corroles and then from a meso-substituted corrole-porphyrin dyads reported in the literature. The extent of fluorescence quenching efficiencies were interpretted in terms of reduction potentials of Ge(IV) and P(V)corroles.

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[2] We have performed time-resolved fluorescent decay measurements in order to justify the EET and PET processes of the trimeric compounds. But unfortunately we did not get supporting information presumably due to instability of the trimeric compounds towards laser light originated from sensitive/weak P-O bond.

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