Synthesis, Structure, Spectroscopic, and Electrochemical Properties of Highly Fluorescent Phosphorus(V)-meso-Triarylcorroles

Avijit Ghosh and Mangalampalli Ravikanth*^[a]

Abstract: The synthesis, spectroscopic, and electrochemical properties of seven new P^{V} -meso-triarylcorroles (1– 7) are reported. Compounds 1–7 were prepared by heating the corresponding free-base corroles with POCl₃ at reflux in pyridine. Hexacoordinate P^{V} complexes of meso-triarylcorroles were isolated that contained two axial hydroxy groups, unlike the P^{V} complex of 8,12diethyl-2,3,7,13,17,18-hexamethylcor-

role, which was pentacoordinate, or the P^{V} complex of *meso*-tetraphenylporphyrin, which was hexacoordinate with two axial chloro groups. ¹H and ³¹P NMR spectroscopy in CDCl₃ indicated that the hexacoordinated P^{V} -

meso-triarylcorroles were prone to axial-ligand dissociation to form pentacoordinated P^{v} -*meso*-triarylcorroles. However, in the presence of strongly coordinating solvents, such as CH₃OH, THF, and DMSO, the P^{v} -*meso*-triarylcorroles preferred to exist in a hexacoordinated geometry in which the corresponding solvent molecules acted as axial ligands. X-ray diffraction of two complexes confirmed the hexacoordination environment for P^{v} -*meso*-triar-

Keywords: corroles • electrochemistry • fluorescence • *meso* compounds • phosphorus ylcorroles. Their absorption spectra in two coordinating solvents revealed that P^V-meso-triarylcorroles showed a strong band at about 600 nm together with other bands, in contrast to P^V-porphyrins, which showed weak bands in the visible region. These compounds were easier to oxidize and more difficult to reduce compared to PV-porphyrins. These compounds were brightly fluorescent, unlike the weakly fluorescent PV-porphyrins, and the quantum yields for selected PV-corroles were as high as Al^{III} and Ga^{III} corroles, which are the best known fluorescent compounds among oligopyrrolic macrocycles.

Introduction

Corroles are tetrapyrrolic macrocycles, like porphyrins, but with one less carbon atom at their periphery and one extra inner NH proton.^[1] They are also 18-π-electron systems and possess aromaticity like porphyrins and other related porphyrinoids. Moreover, like porphyrins, these macrocycles possess very interesting ground- and excited-state properties, and hence can be used as substitutes in the place of porphyrins.^[2] Although corroles have been known for more than three decades, up until 1999, their synthesis was very difficult. In 1999, Gross et al.^[3] and Paolesse et al.^[4] independently published simple procedures to synthesize corroles from commercially available starting materials. These procedures helped to enhance the research into corroles and several new types of corroles and their applications have been reported in recent times.^[5] Because of their -3 charge, these tetrapyrrolic contracted-macrocycles stabilize metals in

 [a] A. Ghosh, Prof. M. Ravikanth Department of Chemistry Indian Institute of Technology, Bombay, Powai Mumbai 400 076 (India) E-mail: ravikanth@chem.iitb.ac.in

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sive and numerous comparisons have been made with porphyrins that contain the same transition-metal ion. In contrast, there are only a few examples of corrole-stabilized main-group ions^[8] and, specifically, to the best of our knowledge, there are only three reports in this regard with PV-corrole complexes.^[9] Paolesse et al.^[9a] reported the synthesis of the first P^{V} -corrole complex (I), a pentacoordinated complex as confirmed by X-ray crystallography, by heating 8,12diethyl-2,3,7,13,17,18-hexamethylcorrole and POCl₃ at reflux in pyridine (Scheme 1). Kadish, Guilard, Vogel, and coworkers^[9b] reported the synthesis of a P^V complex of 2,3,7,8,12,13,17,18-octaethylcorrole and used it as precursor for the synthesis of axially substituted hexacoordinate PV complexes. Gross and co-workers^[9c] reported the synthesis of a hexacoordinated P^V complex of 5,10,15-tris(pentafluorophenyl)corrole (II), which is the only reported P^{V} complex of meso-triarylcorrole (Scheme 1). Here, we report the synthesis, characterization, X-ray structure, electrochemical, and photophysical properties of a series of P^V complexes of meso-triarylcorroles (1-7; Scheme 2). The spectroscopic and electrochemical studies indicated that compounds 1-7 exhibited quite different and interesting properties compared to P^V-meso-tetraarylporphyrins, such as 5,10,15,20tetraphenylporphyrinato(TPP)-phosphorus(V) dihydroxide ([P(TPP)(OH)₂]⁺; III).^[10]

higher oxidation states,^[6] unlike porphyrins which have a -2

charge. The literature on transition-metal corroles^[7] is exten-



Scheme 1. Previously reported P^{V} -corrole complexes (I and II) and a P^{V} complex of a porphyrin analogue (III).



Results and Discussion

The insertion of phosphorus into tetrapyrrolic macrocycles, such as porphyrins^[10] and corroles,^[9] has typically been carried out by heating the free-base macrocycles with various reagents, such as PCl₃, PCl₅, and POCl₃, at reflux in pyridine. However, recently, POCl₃ has become the more-commonly used reagent compared to the other two. We tested the phosphorus-insertion into free-base corroles by taking 5,10,15-triphenylcorrole, [H₃(TPC)], as a reference compound and independently reacting it with all three commonly used reagents in refluxing pyridine. The progress of the reaction was followed by TLC on silica gel and by absorption spectroscopy. Initially, the reaction mixture was green in color but, as the reaction progressed, the color changed

as reported previously.^[10b] Interestingly, spectroscopic analysis (see below) indicated that compounds 1–7 were also hexa-coordinated but contained two axial hydroxy ligands. Thus, we concluded that complexes 1–7, with two axial hydroxy groups, were more stable to isolation than the P^{V} – *meso*-triarylcorroles that contained two axial chloride ligands. Complexes 1–7 were soluble in common organic solvents and were characterized by MS and various other spectroscopic techniques. The HRMS spectra of compounds 1–7 showed molecular-ion peaks that corresponded to hexacoordinate species, as well as $[M-17]^+$ peaks that corresponded to pentacoordinate species, which may have been formed by the loss of one axial OH group (see the Supporting Information, S4–S10).

FULL PAPER

to a bright pink-violet with a slight greenish tint. The absorption data, taken at regular intervals, indicated that absorption bands corresponding to a P^{V} complex of *meso*-triarylcorrole (1) started to appear after 5 min and the reaction was complete within 15-30 min, depending on the reagent. The reaction was very fast when POCl₃ was used as the reagent. Excess reagent and pyridine were removed under reduced pressure and the crude compound was subjected to column chromatography on alumina to afford compound 1 in 78% yield. Compound 1 was also stable to column chromatography on silica gel. Although the reaction proceeded smoothly with all three phosphorus reagents, the six other PV derivatives (2-7) were all prepared by using POCl₃ under similar conditions (Scheme 2). For comparison purposes, we also prepared known P^V-porphyrin complex **III** (Scheme 1) by using POCl₃ in refluxing pyridine.[10b] However, phosphorus-insertion into the porphyrin was very slow and required heating overnight. In this reaction, the hexacoordinated complex [P(TPP)Cl₂]+ initially contained two axial chloride ions, which, on further heating with aqueous pyridine at reflux followed by column chromatography on silica gel, transformed into compound III, with two axial hydroxy groups, **NMR spectroscopy**: The composition of compounds **1–7** was confirmed by detailed NMR spectroscopic studies. ¹H and ³¹P NMR spectroscopic techniques were very useful for judging the coordination number of the phosphorus center. A comparison of the ¹H and ³¹P NMR spectra of compound **1** with those of analogous phosphorus–porphyrin complex **III** recorded is shown in Figure 1. In compound **III**, the



Figure 1. Comparison of ¹H NMR spectra (a,b) and the ³¹P NMR spectra (c) of compounds 1 and III in $CDCl_3$ at room temperature.

eight pyrrole protons appeared as a broad singlet, whereas in compound 1, the eight pyrrole protons appeared as eight sets of doublet of doublets. At first, this result was very confusing. However, we realized that the intensity of the eight sets of pyrrole signals varied when we recorded the ¹H NMR spectra of compounds 1–7 after different lengths of time. For instance, a freshly prepared sample of compound 5 showed four intense sets of signals and four less-intense sets of signals. However, after being left to stand in CDCl₃, the same compound showed eight sets of signals of equal intensity (see the Supporting Information, S22 and S23). Furthermore, the ¹H NMR spectra of compounds 2, 6, and 7 (in $CDCl_3$), which contained electron-withdrawing groups on the meso-phenyl rings, showed predominantly four sets of doublet of doublets, with almost negligible intensity of other four sets of signals (see the Supporting Information, S25). These results indicated that compounds 1-7 may have existed in a hexacoordinate geometry but were prone to ligand-dissociation to form pentacoordinate species. To confirm the presence of penta- and hexacoordinate species in solution, we recorded the ³¹P NMR of compounds 1-7. It is well-established^[11] that the chemical shifts of phosphorus nuclei in ³¹P NMR spectroscopy are sensitive to the coordination number of the phosphorus center, and detailed ³¹P NMR studies on phosphorus derivatives of porphyrins, phthalocyanines, and related macrocycles have indicated that hexacoordinate phosphorus macrocycles typically show signals in the range $\delta = -180$ to -200 ppm, whereas pentacoordinate compounds typically show signals in the range $\delta = -90$ to -110 ppm. In the ³¹P NMR spectra (CDCl₃), compound 1 showed two signals of almost equal intensity at $\delta = -100.7$ and -191.5 ppm, which corresponded to the penta- and hexacoordinate species, respectively. However, compounds 2, 6, and 7, which contained electron-withdrawing substituents on the meso-phenyl groups, showed an intense signal at about $\delta = -200$ ppm and a much less intense signal at about $\delta = -100$ ppm (see the Supporting Information, S25), thus indicating that these complexes were relatively more stable in their hexacoordinate environment, and underwent very slight axial-ligand-dissociation to form pentacoordinate species. Thus, ¹H and ³¹P NMR studies of compounds 1-7 in CDCl₃ indicated that these complexes preferred to exist as hexacoordinated species but were prone to axial-ligand-dissociation. This result suggested that the axial hydroxy groups were weakly bound to the central P^{V} ion and could readily dissociate in solution. At this juncture, it was clear that if we replaced the hydroxy group with any other strongly coordinating group then these P^V-corrole complexes may have preferred to exist in their hexacoordinated geometry. To test this hypothesis, we carried out titrations of compound 1 (in CDCl₃) with increasing amounts of CH₃OH (in CDCl₃); the changes in the ¹H and ³¹P NMR spectra are shown in Figure 2 and Figure 3, respectively. The addition of CH₃OH clearly resulted in the formation of hexacoordinate species by replacing the weakly bound axial OH ligands with more strongly bound OCH₃ ligands. This result was reflected in the reduction of eight sets of β -pyrrole signals to form four sets of signals in the ¹H NMR spectra (Figure 2) and in the disappearance of a signal at $\delta =$ -100.7 ppm in the ³¹P NMR spectra that corresponded to the pentacoordinate species (Figure 3). Thus, the systematic addition of CH₃OH to compound **1** in CDCl₃ resulted in the gradual disappearance of four sets of doublet of doublets $(\delta = 9.38, 9.20, 9.13, \text{ and } 8.88 \text{ ppm})$, which corresponded to the pentacoordinate species, and the simultaneous increase in the intensity of the other four sets of doublet of doublets $(\delta = 9.25, 9.05, 8.96, \text{ and } 8.79 \text{ ppm})$ in the ¹H NMR spectrum (Figure 2). Furthermore, during our systematic ³¹P NMR titration (Figure 3), we noted the possible existence of four intermediate species in solution: one pentacoordinate species, [P(TPC)(OH)]⁺ (type a), and three hexacoordinate species. $[P(TPC)(OH)_2]$ (type b), $[P(TPC)(OH)(OCH_3)]$ (type c), and [P(TPC)(OCH₃)₂] (type d; Scheme 3). As mentioned above, in CDCl₃, compound 1 showed two signals in



Figure 2. ¹H NMR titration of compound 1 with CH_3OH in $CDCl_3$ at room temperature.

the ³¹P NMR spectrum ($\delta = -100.7$ and -191.5 ppm), which corresponded to the type-a and type-b complexes, respectively. On addition of one equivalent of CH₃OH to compound 1 in CDCl₃, a gradual decrease in the intensity of the signal at $\delta = -100.7$ ppm (type a species) as well as a decrease in the intensity of the signal at $\delta = -191.5$ ppm (typeb species) were noted, together with the appearance of a new signal at $\delta = -184.1$ ppm (hexacoordinate type-c species). On addition of two equivalents of CH₃OH, we observed a third hexacoordinate signal at $\delta = -176.9 \text{ ppm}$ (type-d species) in addition to the two signals at $\delta = -184.1$ and -191.5 ppm, which corresponded to other hexacoordinate complexes (type b and type c, respectively). On further increase in the number of equivalents of CH₃OH, the signals that corresponded to the pentacoordinate complex (type a, $\delta \approx -100.7$ ppm) and two of the hexacoordinate complexes (type c and type d, $\delta \approx -184.1$ and -191.5 ppm, respectively) gradually disappeared, whereas the signal that corresponded to the hexacoordinate complex of type d ($\delta \approx -177.1$ ppm) increased in intensity. In the presence of excess CH₃OH, only the signal at $\delta = -177.3$ ppm (type d) was observed, thereby indicating that the complex was now hexacoordinate with two OCH₃ groups as axial ligands. Furthermore, this result was also clearly evident in the gradual disappearance of the signal that corresponded to the axial OH proton ($\delta =$



FULL PAPER

Figure 3. 31 P NMR titration of compound 1 with CH₃OH in CDCl₃ at room temperature.

-4.64 ppm) and the appearance of a doublet at $\delta =$ -2.47 ppm, which corresponded to the axial OCH₃ protons in the ¹H NMR spectra, thus confirming the substitution of the axial OH groups by OCH₃ groups (see the Supporting Information, S11). The existence of complex 1 as a hexacoordinate species in coordinating solvent was further verified by ³¹P NMR spectroscopy in pure CD₃OD, which showed one signal at $\delta = -178.0$ ppm and also by ¹H NMR spectroscopy, which showed four sets of doublet of doublet at $\delta =$ 9.38, 9.03, 8.95, and 8.78 ppm. Similarly, in other strongly coordinating solvents, such as [D₆]DMSO and CD₃CN, complex 1 existed as a hexacoordinate species and showed four sets of pyrrole signals that were more upfield shifted compared to compound 1 in CD_3OD . For example, the four sets of pyrrole signals for compound **1** in CD₃OD (δ = 9.38, 9.03, 8.95, and 8.78 ppm) were shifted upfield to $\delta = 9.30$, 8.96, 8.87, and 8.68 in CD₃CN and to $\delta = 9.19$, 8.80, 8.69, and 8.58 ppm in [D₆]DMSO (see the Supporting Information, S21). The ³¹P NMR spectra also showed only one signal at $\delta \approx -190$ ppm in both of these coordinating solvents, which further supported the hexacoordination of compound 1. We also recorded ¹H and ³¹P NMR spectra of compound 1 in CDCl₃ in the presence of excess amounts of other coordinating solvents, such as THF, which also confirmed the hexa-

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Scheme 3. All of the possible intermediate complexes during the NMR titration of compound 1 with CH_3OH in $CDCl_3$ at room temperature.

coordinate environment of compound **1** (see the Supporting Information S19 and S20). Although the pyrrole signals were very useful for identifying penta- and hexacoordinate species, the *meso*-aryl signals exhibited minimal changes in their chemical shifts between the two environments, and were not helpful in identifying the coordination environment (see the Supporting Information, S12). Thus, our NMR studies clearly indicated that compounds **1–7** preferred to exist in the hexacoordinate geometry with two identical axial ligands in strongly coordinating solvents.

Crystallographic characterization: Further confirmation of the formation of compound $[P(TPC)(OCH_3)_2]$ was provided by single-crystal X-ray crystallography. Figure 4 shows ORTEPs of compound 1. Compound 1 was crystallized by slow diffusion of *n*-hexane into a solution of compound 1 in CH₂Cl₂/benzene (3:1) in the presence of CH₃OH, over a period of one week. Compound 1 crystallized in the ortho-

rhombic space group $P2_1$. The crystal data and data collection parameters are summarized in Table 1. To the best of our knowledge, compound 1 is the first PV-meso-triarylcorrole to be characterized by single-crystal X-ray analysis; the only other reported crystal structure of a phosphorus-corrole complex was that of pentacoordinate compound I (Scheme 1).^[9a] Compound 1 crystallized as a hexacoordinate complex with OCH₃ groups as axial ligands. The central phosphorus atom was almost in the plane defined by the four nitrogen atoms of the pyrrole rings, unlike compounds I and III, respectively. In compound I, the pentacoordinate phosphorus atom lay more than 0.4 Å out of the mean corrole plane towards the oxygen atom of the axial hydroxy ligand. This kind of outof-plane displacement of the central atom of metalloporphyrins^[12] or metallocorroles^[6,13] is commonly observed for pentacoordinate complexes. Similarly, in case of compound III, the hexacoordinate central phosphorus atom was displaced by 0.09 Å from the mean plane of the pyrrole nitrogen atoms. Furthermore, the Р-О bond lengths were inequivalent in compound III, whereas in compound 1, the P–O bond-lengths

(P-O1 1.668 Å, P-O2 1.663 Å) were equivalent and were in the same range as those found in other analogous P^V-mesotetraarylporphyrin complexes.^[10b,c,e] The four P-N distances were inequivalent in compound 1 and the average P-N bond length (1.83 Å) was slightly longer than the average P-N bond length (1.80 Å) in compound I. However, the average P-N distances in both PV-corrole complexes I and **1** were shorter than that in compound **III** $(1.89 \text{ Å})^{[10a,e]}$ as well as the average M-N distance in other metal complexes of *meso*-triarylcorroles reported.^[7,8] Moreover, compound 1 was more planar than its corresponding free-base corrole^[14] and metallocorroles.^[15] In the free-base corrole, the three inner NH protons caused steric crowding, thereby resulting in strain in the corrole macrocycle. On complexation with small P^{V} ions, the strain imposed by the inner NH protons was released and the corrole ring became more planar in compound 1. Furthermore, in compound 1, the opposite

FULL PAPER



Figure 4. Three orthogonal views of the ORTEP of compound 1. Ellipsoids are set at 50% probability.

Table 1. Crystallographic data for compound 1.

Parameters	[P(TPC)(OCH ₃) ₂] (1)
formula	$C_{39}H_{29}N_4O_2P_1$
M _w	616.64
crystal system	orthorhombic
space group	$P2_1$
a [Å]	8.3816(4)
<i>b</i> [Å]	9.5266(6)
<i>c</i> [Å]	37.694(2)
V [Å ³]	3009.8(3)
Ζ	8
$\mu [{ m mm}^{-1}]$	0.136
$ ho_{ m calcd} [m gcm^{-3}]$	1.361
F(000)	1288
2θ range [°]	3.28-25.00
e data (R _{int})	22842/5261
$R_1, wR_2 [I > 2\sigma(I)]$	0.0445, 0.0844
R_1, wR_2 (all data)	0.0684, 0.0895
GOF	0.929
Largest diff. peak/hole, [e Å ⁻³]	0.241/-0.208

meso-phenyl groups were placed in mutually opposite planes compared to the mean corrole plane, with average dihedral angles of 51° and 54°. The other meso-phenyl group was almost perpendicular (dihedral angle $\approx 90^{\circ}$) to the mean plane of corrole ring. Interestingly, a weak hydrogenbonding interaction was observed between the oxygen atoms of the axial OCH3 groups and the hydrogen atoms of one of the meso-phenyl group of another molecule, thereby resulting in the formation of a supramolecular 2D network (see the Supporting Information, S35). Furthermore, we also solved the structure of compound 4, which contained two axial OH groups with slight disorder in one of the meso-substituted phenyl rings (see the Supporting Information, S36 and S37). Because of poor data quality, we could not locate the hydrogen atom of the axial OH group. The P-N and (average 1.83 Å) and P–O bond lengths (average 1.66 Å) were almost in the same range as those observed in compound 1.

Absorption, electrochemical, and fluorescence studies: The absorption spectra of compounds 1-7 and compound III were recorded in two different coordinating solvents: MeOH and THF (Table 2). A comparison of the absorption spectra of compounds 1 and III in THF is shown in Figure 5. In general, P^V-meso-tetraarylporphyrins^[10] show 2-3 weak absorption bands in the Q-band region and one strong sharp Soret band. However, P^V-meso-triarylcorroles exhibited different absorption features compared to PV-meso-tetraarylporphyrins. As shown in Figure 5, compounds 1-7 exhibited strong Soret bands, like compound III, that were either broad or with a small shoulder. However, unlike compound III, compounds 1-7 showed an intense band at about 600 nm along with 3-4 other Q-bands. This band at about 600 nm was much more intense than the Q-band of compound III. Thus, the intense band in the visible region of complexes 1-7 is of potential use in materials and medicinal applications. Furthermore, the absorption bands of compounds 1-7 were blue-shifted compared to compound III. There were also significant changes in the absorption features of compounds 1-7 in terms of their band-position and -intensity depending on the solvent used.

The electrochemical properties of P^V -corroles 1-7 were determined by cyclic voltammetry and by differential pulse voltammetry at a scan rate of 50 mVs⁻¹ with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte in MeCN. The representative first oxidation and reduction waves for compound 1, along with their differential pulse voltammograms, are shown in Figure 6 and the data are given in Table 3. The electrochemical properties of the P^{V} complex of *meso*-triarylcorrole \mathbf{II} (Scheme 1), as studied by Gross and co-workers, showed one oxidation peak at 1.05 V and one reduction peak at -1.05 V.^[9c] However, all of our compounds (1-7) exhibited two oxidation peaks and three reduction peaks. The first oxidation and reduction peaks were reversible in nature whereas the other oxidation and reduction waves were quasi-reversible or irreversible. Compared to compound II, compounds 1-7 were easier to oxi-

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Table 2.	Absorption	data	recorded i	in	THF an	d CH ₃	OH.
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Compound	Absorption data				
	ln '	THE	In C	H ₃ OH	
	Soret band	Q band	Soret band	Q-band	
	[nm] (logs)	[nm]	[nm] (logs)	[nm] (logs)	
	(10g E)	(log e)	(10g 2)	(10g2)	
1	411 (5.34)	508 (sn), 525 (3.07)	407 (5.41)	505 (sn), 521 (3.06)	
	421 (3.21)	525(3.97), 554 (sh)	414 (5.50)	521(5.90), 547(ch)	
		554 (sir), 564 (4 10)		550(4.13)	
		603 (4.59)		594 (4.60)	
ш	A17 (A 7A)	512 (2 71)	121 (5 56)	514 (2.28)	
111	417(4.74)	512(3.71), 556(3.82)	424 (3.30)	514(5.56), 554(4.12)	
	427 (4.92)	507 (3.62),		505(4.12), 505(3.40)	
		597 (5.40)		393 (3.49)	
2	422 (5.31)	510 (3.70),	416 (5.35)	504 (sh),	
		530 (3.90),		525 (3.95),	
		567 (4.03),		550 (sh),	
		604 (4.55)		562 (4.06),	
				596 (4.58)	
3	410 (5.49)	515 (sh),	409 (5.38)	508 (3.75),	
	424 (5.05)	526 (4.09),	417 (5.30)	523 (3.92),	
		555 (sh),	· · · ·	560 (4.08),	
		567 (4.36),		599 (4.62)	
		608 (4.41)			
4	414 (5.36)	509 (sh).	409 (5.48)	503 (sh).	
	422 (5.28)	527 (3.97),	414 (5.44)	522 (4.00),	
	~ /	556 (sh),	× ,	547 (sh),	
		567 (4.16),		560 (4.16),	
		603 (4.83)		594 (4.68)	
5	415 (5.51)	509 (sh).	410 (5.61)	505 (sh).	
	422 (5.45)	527 (4.11),	414 (5.57)	522 (4.12),	
	~ /	555 (sh),	× ,	548 (sh),	
		566 (4.28),		560 (4.27),	
		603 (4.83)		595 (4.80)	
6	422 (5.01)	535 (4.01).	418 (5.17)	529 (4.06).	
	~ /	568 (4.10),	()	563 (4.12),	
		610 (4.59)		601 (4.66)	
7	418 (5 36)	508 (sh)	413 (5 43)	502 (sh)	
	.10 (0.00)	528 (4.04)	115 (5.45)	502(31), 523(4.02)	
		520 (104), 554 (sh)		525 (1.02), 547 (sh)	
		567 (4.19).		561 (4.17).	
		601 (4.69)		593 (4.65)	
				()~)	

dize but more-difficult to reduce (Table 3). For example, compounds 1–7 exhibited a first oxidation in the range 0.6– 0.8 V and a first reduction in the range –1.0 to –1.4 V, depending on the *meso* substituents. Furthermore, it is well established that, for porphyrins^[16] and related macrocycles, the first oxidation and reduction peaks correspond to the removal or addition of an electron from the frontier orbitals of the π -system, and that the potential difference ($\Delta E_{red-ox} = E_{red} - E_{ox}$) between them is very similar for a given series of compounds, thus corresponding to the HOMO–LUMO energy gap. The HOMO–LUMO energy gap, along with other information, gives fundamental information about the redox processes in terms of whether the oxidations and re-



Figure 5. Comparison of the Q-band and Soret-band spectra (inset) of compounds 1 (solid line) and III (dotted line) in THF; the concentrations used for the Soret bands were 10^{-6} M and for the Q bands were 10^{-5} M.



Figure 6. Cyclic voltammogram and differential pulse voltammogram of compound 1 in CH₃CN using tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte at a scan rate of 50 mVs⁻¹.

Table 3. Redox data recorded in CH₃CN.

Compound	Oxidation [V]	Reduction [V]	HOMO–LUMO gap $(\Delta E_{\rm red-ox})$ [V]
1	0.72, 1.22	-1.41, -1.69, -2.07	2.13
2 3	0.77, 1.38 0.57, 1.08	-1.26, -1.66, -1.73 -1.45, -1.74, -2.15	2.03 2.02
4	0.69, 1.26	-1.37, -1.72, -1.99	2.06
5	0.69, 1.26 0.80, 1.38	-1.36, -1.70, -1.96 -1.12, -1.62, -1.90	2.05 1.92
7	0.79, 1.37	-1.11, -1.74	1.90
11	1.05	-1.05	2.10

ductions are metal-centered or macrocycle-centered. The HOMO–LUMO gap has been used to distinguish between metal- and corrole-centered redox processes in many redox-active transition-metal complexes of corroles, and it has been suggested that if the gap is about 2.0 V, the corrole macrocycle is involved in the redox processes but if the gap is significantly less than 2.0 V, then the metal is also involved in the redox processes.^[17] Because the gaps for com-

FULL PAPER

pounds 1–7 were about 2.0 V, we concluded that only the corrole ring was involved in the redox processes of compounds 1–7.

The fluorescence properties of compounds **1–7** and compound **III** were studied by both steady-state and time-resolved fluorescence techniques. In general, it is well-established that main-group metallocorroles are strongly fluorescent with higher quantum yields than their analogous porphyrins derivatives. It is inferred from the photophysical studies of various metallocorroles that Ga^{III} and Al^{III} complexes^[8a,18] are brightly fluorescent and exhibit high quantum yields (Φ =0.37–0.76). A comparison of the fluorescence spectra of compound **1** with its close analogue, compound **III**, in THF at the same concentrations is shown in Figure 7 and the relevant photophysical data are given in



Figure 7. Comparison of fluorescence spectra of compounds 1 (dotted line) and III (solid line) in THF; the compounds were excited at their corresponding absorption maxima and the concentrations of the solutions were about 10^{-7} M.

Table 4. This comparison revealed the following: 1) compounds 1-7 exhibited a very strong fluorescence band at about 600 nm, with shoulder bands that were hypsochromically shifted compared to compound III; 2) compounds 1-7 were brightly fluorescent, with high quantum yields ($\Phi =$ 0.33-0.68), compared to the weakly fluorescent compound III ($\Phi = 0.08$); 3) the quantum yield of compound 5 was notably low, owing to the heavy halogen-atom effect, which increased the intersystem-crossing processes.^[19] The quantum yields of compounds 6 and 7 were lowered because of the nitro group, which is also known to significantly quench fluorescence through a spin-orbit-coupling mechanism that enhances the intersystem-crossing rates.^[19] More-detailed studies are required to understand the photophysical properties of compounds 6 and 7. Thus, the steady-state-fluorescence measurements indicated that P^V-meso-triarylcorroles were as brightly fluorescent as Al^{III}- and Ga^{III}-corroles, which are the best-known fluorescent compounds among oligopyrrolic macrocycles. The high fluorescence yields observed for these P^V-meso-triarylcorroles could be rationalized on the basis that they were structurally rigid hexa-coordinated complexes, which decreased the probability of nonradiative-decay pathways, and also because of their moreplanar structures, which enhanced the radiative-decay path-

Table 4. Em	Table 4. Emission data recorded in THF and CH ₃ OH.						
Compound	λ_{em} [nm]	In THF Quantum yield	τ [ns]	Ι λ _{em} [nm]	n CH ₃ OH Quantum yield	τ [ns]	
1	572 (sh) 610 667 (sh)	0.48	2.92	600 656 (sh)	0.44	3.01	
2	615 670 (sh)	0.62	3.37	605 661 (sh)	0.68	3.69	
3	579 (sh) 618 675 (sh)	0.38	2.10	609 664 (sh)	0.43	2.26	
4	573 (sh) 610 668 (sh)	0.33	1.95	601 656 (sh)	0.40	2.14	
5	573 (sh) 611 669 (sh)	0.06	_	602 658 (sh)	0.07	-	
6	579 (sh) 625 688 (sh)	0.30	-	605 654 (sh)	0.007	-	
7	571 (sh) 606 664 (sh)	0.04	-	600 656 (sh)	0.005	-	

ways, thereby resulting in high fluorescence yields. Time-correlated single-photon-counting measurements of the fluorescence lifetimes (τ) of compounds **1–4** were performed in two different solvents and the data are given in Table 4. The fluorescence decays of compounds **1–4** were fitted to a single exponential in both solvents and the representative fluorescence-decay profile for compound **1** in THF is shown in Figure 8. The singlet-state lifetimes of compounds **1–4** were in the range 1.9–3.7 ns. Compound **2**, which showed the highest quantum yield (Φ =0.68), exhibited the highest singlet-state lifetime of about 3.7 ns. We are currently inves-



Figure 8. Fluorescence-decay profile and the corresponding weighted residual-distribution fit of the fluorescence decay of compound 1 in THF. The excitation wavelength was 406 nm and emissions were detected at the emission-peak maxima of compound 1 in THF.

Chem.	Eur. J.	2012 , 18,	6386 - 6396
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www.chemeurj.org

- 6393

tigating the excited-state dynamics of these P^V complexes of *meso*-triarylcorroles.

Conclusion

We have prepared a series of P^{V} complexes of *meso*-triarylcorroles and characterized them by using various spectroscopic techniques. Detailed NMR spectroscopic studies indicated that the P^{V} -*meso*-triarylcorroles preferentially existed in hexacoordinate environments in coordinating solvents (CH₃OH, THF, DMSO, etc.) and dissociated to their pentacoordinate complexes in non-coordinating solvents, (toluene, CH₂Cl₂, and CHCl₃). X-ray crystal data for two complexes confirmed the hexacoordinate geometry of the P^{V} -*meso*-triarylcorroles. Their optical and electrochemical properties were very interesting and distinct compared to P^{V} -*meso*-tetraarylporphyrins. Unlike P^{V} -*meso*-tetraarylporphyrins, the P^{V} -*meso*-triarylcorroles were very brightly fluorescent with high quantum yields, and will be very useful for various molecular device applications.

Experimental Section

Chemicals: All chemicals and solvents were purchased from S.D. Fine Chemicals (India). Column chromatography was performed on silica gel and basic alumina that were obtained from Sisco Research Laboratories (India). Tetrabutylammonium perchlorate was purchased from Fluka and used without further purification. All NMR solvents were used as received. CH₂Cl₂, THF, and *n*-hexane were purified and distilled according to standard procedures.

Instrumentation: ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for the ¹H NMR spectra (residual proton; $\delta\!=\!7.26~\text{ppm}$ in CDCl3) and 85 % $H_3\text{PO}_4$ was used as an external reference for the ³¹P NMR spectra (CDCl₃ and CD₃OD). HRMS was performed on a Q-Tof micromass spectrometer. Absorption and steady-state fluorescence spectra were obtained on Perkin-Elmer Lambda-35 and ISS (US) PC1 Photon-Counting spectrofluorometers, respectively. The fluorescence quantum yield ($\Phi_{\rm f}$) of P^V meso-triaryl corroles 1–7 were estimated from their emission and absorption spectra by using the comparative method^{\rm [20]} with [H_2(TPP)] as a standard ($\varPhi_{\rm f}{=}0.11).$ Time-resolved fluorescence-decay measurements were carried out at the magic angle by using a picosecond-diode-laser-based time-correlated single-photoncounting (TCSPC) fluorescence spectrometer from IBH (UK). All decay curves were fitted to single exponential functions by using IBH software. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with a BAS electrochemical system by utilizing a threeelectrode configuration that consisted of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The experiments were performed in dry MeCN with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

X-ray crystallography: Single-crystal X-ray analysis of compounds **1** and **4** were performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer that was equipped with an Oxford Instruments low-temperature attachment. Data were collected at 293(2) for compound **1** and at 150(2) K for compound **4** using graphite-monochromated Mo_{Ka} radiation (λ_a =0.71073 Å). The strategy for data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques, and were scaled and reduced by using CrysA-lisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97,

refining on $F^{2,[21]}$ The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, typically $1.2U_{eq}$ of their parent atoms.

CCDC-837991 (1) and CCDC-837992 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General synthesis: Free-base *meso*-triarylcorroles were synthesized according to literature procedures.^[22] Phosphorus derivatives **1–7** were synthesized by heating a solution of the corresponding free-base *meso*-triarylcorrole in pyridine at reflux in the presence of excess $POCl_3$ (about a 100-fold excess).

Synthesis of compound 1: To a solution of 5,10,15-triphenylcorrole (100 mg, 0.189 mmol) in dry pyridine (10 mL) was added POCl₃ (1.8 mL, 19.25 mmol) and the reaction mixture was heated to reflux for 15 min under a nitrogen atmosphere. The solution immediately changed from a deep green color to a purple-violet color with a greenish tint. The progress of reaction was monitored by TLC analysis and its completion was determined by absorption spectroscopy. After completion of reaction, the solvent was evaporated under reduced pressure. The crude solid was subjected to column chromatography on basic alumina and the desired compound was collected from a greenish pink-violet-colored band by eluting with CH₂Cl₂. The solvent was removed on a rotary evaporator to afford a deep purple-violet solid. The compound was recrystallized from CH_2Cl_2/n -hexane (1:3) to afford compound 1 as a purple solid in 78% yield (87 mg, 0.148 mmol). ¹H NMR (400 MHz, CD₃OD): $\delta = 9.38$ (dd, ³J- $(H,H) = 4.4 \text{ Hz}, {}^{4}J(P,H) = 2.6 \text{ Hz}, 2H; \beta$ -pyrrole H), 9.03 (dd, ${}^{3}J(H,H) =$ 4.9 Hz, ${}^{4}J(P,H) = 3.6$ Hz, 2H; β -pyrrole H), 8.95 (dd, ${}^{3}J(H,H) = 4.4$ Hz, ${}^{4}J$ $(P,H) = 3.4 \text{ Hz}, 2 \text{ H}; \beta$ -pyrrole H), 8.78 (dd, ${}^{3}J(H,H) = 4.9 \text{ Hz}, {}^{4}J(P,H) =$ 3.0 Hz, 2H; β-pyrrole H), 8.25-8.28 (m, 4H; Ar H), 8.15-8.17 (m, 2H; Ar H), 7.78–7.87 ppm (m, 9H; Ar H); ³¹P{¹H} NMR (400 MHz, CD₃OD): $\delta = -178.03$ ppm; HRMS: m/z: 571.1697 [M-17]⁺.

Compounds 2–7 were prepared by following the same synthetic route mentioned for compound 1.

Compound 2: Compound **2** was obtained as a pink-violet solid in 80% yield (88 mg, 0.132 mmol). ¹H NMR (400 MHz, CD₃OD): δ =9.43 (dd, ³J-(H,H)=4.4 Hz, ⁴J(P,H)=2.4 Hz, 2H; β -pyrrole H), 9.02 (dd, ³J(H,H)=4.8 Hz, ⁴J(P,H)=3.7 Hz, 2H; β -pyrrole H), 8.96 (dd, ³J(H,H)=4.4 Hz, ⁴J (P,H)=3.4 Hz, 2H; β -pyrrole H), 8.77 (dd, ³J(H,H)=5.0 Hz, ⁴J(P,H)=2.9 Hz, 2H; β -pyrrole H), 8.34–8.46 (m, 5H; Ar H), 8.15–8.21 ppm (m, 7H; Ar H); ³¹P[¹H] NMR (400 MHz, CD₃OD): δ =-184.79 ppm; HRMS: *m*/*z*: 646.1515 [*M*-17]⁺.

Compound 3: Compound **3** was obtained as a dark violet solid in 75% yield (82 mg, 0.121 mmol). ¹H NMR (400 MHz, CD₃OD): δ =9.34 (dd, ³J-(H,H)=4.4 Hz, ⁴J(P,H)=2.6 Hz, 2H; β -pyrrole H), 9.03 (dd, ³J(H,H)=4.8 Hz, ⁴J(P,H)=3.7 Hz, 2H; β -pyrrole H), 8.94 (dd superimposed, J=4.0 Hz, 2H; β -pyrrole H), 8.77 (dd, ³J(H,H)=4.9 Hz, ⁴J(P,H)=3.0 Hz, 2H; β -pyrrole H), 8.52–8.54 (m, 2H; Ar H), 8.16–8.18 (m, 3H; Ar H), 8.04–8.06 (m, 2H; Ar H), 7.78–7.87 (m, 1H; Ar H), 7.33–7.45 (m, 4H; Ar H), 4.06–4.08 ppm (m, 9H, OCH₃); ³¹P[¹H] NMR (400 MHz, CD₃OD): δ = -178.08 ppm; HRMS: *m*/*z*: 679.2129 [*M*]⁺.

Compound 4: Compound **4** was obtained as a dark violet solid in 81% yield (89 mg, 0.128 mmol). ¹H NMR (400 MHz, CD₃OD): δ =9.42 (dd, ³J-(H,H)=4.4 Hz, ⁴J(P,H)=2.6 Hz, 2H; β -pyrrole H), 9.05 (dd, ³J(H,H)=5.0 Hz, ⁴J(P,H)=3.6 Hz, 2H; β -pyrrole H), 8.97 (dd, ³J(H,H)=4.4 Hz, ⁴J-(P,H)=3.5 Hz, 2H; β -pyrrole H), 8.80 (dd, ³J(H,H)=4.9 Hz, ⁴J(P,H)=3.0 Hz, 2H; β -pyrrole H), 8.80 (dd, ³J(H,H)=4.9 Hz, ⁴J(P,H)=3.0 Hz, 2H; β -pyrrole H), 8.52–8.54 (m, 1H; Ar H), 8.12–8.14 (m, 3H; Ar H), 8.23–8.25 (m, 2H; Ar H), 7.80–7.87 (m, 5H; Ar H), 7.42–7.45 ppm (m, 1H; Ar H); ³¹P{¹H} NMR (400 MHz, CD₃OD): δ = -177.89 ppm; HRMS: *m/z*: 692.0707 [*M*+1]⁺.

Compound 5. Compound **5** was obtained as a dark blue-violet solid in 79% yield (85 mg, 0.103 mmol). ¹H NMR (400 MHz, CD₃OD): δ =9.43 (dd, ³*J*(H,H)=4.5 Hz, ⁴*J*(P,H)=2.5 Hz, 2H; β-pyrrole H), 9.06 (dd, ³*J*-(H,H)=5.0 Hz, ⁴*J*(P,H)=3.6 Hz, 2H; β-pyrrole H), 8.99 (dd, ³*J*(H,H)=4.5 Hz, ⁴*J*(P,H)=2.9 Hz, 2H; β-pyrrole H), 8.81 (dd, ³*J*(H,H)=5.0 Hz, ⁴*J*-(H,H)=5.0 Hz, ⁴*J*-(H,H)=5.0

FULL PAPER

(P,H)=3.0 Hz, 2H; β-pyrrole H), 8.52–8.54 (m, 1H; Ar H), 8.17–8.19 (m, 4H; Ar H), 7.89–8.01 (m, 7H; Ar H); ${}^{31}P[{}^{1}H]$ NMR (400 MHz, CD₃OD): δ=-177.88 ppm; HRMS: *m/z*: 823.9159 [*M*+1]⁺.

Compound 6: Compound **6** was obtained as a dark-blue solid in 77% yield (84 mg, 116 mmol). ¹H NMR (400 MHz, CD₃OD): δ =9.46 (dd, ³*J*-(H,H)=4.5 Hz, ⁴*J*(P,H)=2.5 Hz, 2H; β -pyrrole H), 9.07 (dd, ³*J*(H,H)=5.0 Hz, ⁴*J*(P,H)=3.6 Hz, 2H; β -pyrrole H), 9.01 (dd, ³*J*(H,H)=4.4 Hz, ⁴*J*-(P,H)=3.4 Hz, 2H; β -pyrrole H), 8.83 (dd, ³*J*(H,H)=5.0 Hz, ⁴*J*(P,H)=2.9 Hz, 2H; β -pyrrole H), 8.67–8.74 (m, 4H; Ar H), 8.44–8.54 (m, 5H; Ar H), 7.83–7.87 (m, 1H; Ar H), 7.42–7.45 ppm (m, 2H; Ar H); ³¹P{¹H} NMR (400 MHz, CD₃OD): δ =-184.68 ppm; HRMS: *m*/*z*: 706.1262 [*M*-17]⁺.

Compound 7: Compound **7** was obtained as a blue-violet solid in 78% yield (85 mg, 0.117 mmol). ¹H NMR (400 MHz, CD₃OD): δ =9.46 (dd, ³*J*-(H,H)=4.5 Hz, ⁴*J*(P,H)=2.4 Hz, 2H; β -pyrrole H), 9.11 (br s, 2H, β -pyrrole H), 9.04 (dd, ³*J*(H,H)=5.0 Hz, ⁴*J*(P,H)=3.6 Hz, 2H; β -pyrrole H), 8.98 (dd, ³*J*(H,H)=4.4 Hz, ⁴*J*(P,H)=3.5 Hz, 2H; β -pyrrole H), 8.80 (dd, ³*J*(H,H)=5.0 Hz, ⁴*J*(P,H)=2.9 Hz, 2H; β -pyrrole H), 8.62–8.71 (m, 4H; Ar H), 8.51–8.57 (m, 3H; Ar H), 8.04–8.12 (m, 2H; Ar H), 7.83–7.87 (m, 1H; Ar H), 7.41–7.45 ppm (m, 2H; Ar H); ³¹P[¹H] NMR (400 MHz, CD₃OD): δ =-184.76 ppm; HRMS: *m/z*: 724.1371 [M]⁺.

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6396 -