Review of Conjugated Porphyrin Systems

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Porphyrin macromolecules play critical roles in many natural processes. Studies are going on to mimic their role in natural systems and use them in various applications in artificial systems. When a porphyrin moiety is conjugated with carbon nanoallotropes, *viz.*, carbon nanomaterials, carbon nanotubes, carbon nanospheres, *etc.*, the hybrid molecules show optimized properties compared to the pristine molecules. In this review, various mechanisms of conjugating carbon nanoallotropes/carbon nanomaterials and porphyrins through stable chemical bond formation are discussed. The non-covalent interactions which cause their aggregation without disrupting their electronic structures are also discussed. This review also gives vital information on the utilization of conjugated systems effectively for society oriented applications.

1. Introduction

1.1 Porphyrins

Porphyrins are naturally occurring colored compounds ubiquitously found in nature as chlorin in chlorophyll pigments, as heme in hemoglobin, as corrin in vitamin B₁₂, *etc.*¹⁻⁵ Some of the important fundamental biological roles played by these “pigments of life” are oxygen storage and transport in myoglobin and hemoglobin, respectively, electron transfer in cytochromes, and radical generation in photosynthesis.⁶⁻⁹ Chemically, a porphyrin is a tetrapyrrolic aromatic macrocyclic compound with an 18 π -conjugated electronic system.

The pyrrole rings of porphyrins are connected at the α position by methine bridges¹⁰ (Fig. 1). The two other important regions of the porphyrin structure are β and *meso* positions where functionalization can be carried out. A porphyrin's macrocyclic cavity can act as a tetradentate ligand resulting from four pyrrole nitrogen atoms and can host a wide array of metal ions.¹¹ The other members of the porphyrinoid family include the “contracted” and “expanded” versions of porphyrins which have contrasting properties compared to “normal” porphyrins.¹² The replacement of one or more inner pyrrole ring(s) of normal, contracted and expanded porphyrins by heterocycles such as furans, thiophenes, and selenophenes leads to “core-modified” versions of these macrocycles with interesting properties.¹³⁻¹⁵

Fig. 1 Porphyrin structure showing α , β and *meso* positions.

The laboratory synthesis of porphyrins generally involves a condensation reaction between aldehydes and pyrroles based on Adler–Longo's¹⁶ or Lindsey's¹⁷ protocols. Adler–Longo's process makes use of harsh reaction conditions like refluxing starting materials in propionic acid, whereas Lindsey's method is based on the Lewis acid catalyzed reaction of pyrroles and aldehydes in low boiling solvents at room temperature followed by oxidation with DDQ/Chloranil. The striking feature of synthetic porphyrins is their aromatic character which is well evident from ^1H NMR spectra. For example, *meso*-5,10,15,20-(tetratolyl)porphyrin, H_2TTP , obtained by condensation of pyrrole and *p*-tolualdehyde exhibits downfield shifted β -pyrrole proton resonances at ~ 8.8 ppm and highly upfield shifted resonances for core NH protons at ~ -2.7 ppm. These observations indicate the aromatic ring current effect operating due to the planar conjugated electronic system of the porphyrin skeleton.¹⁸ Porphyrins exhibit very attractive absorption and emission characteristics in the UV-vis-NIR region. The typical absorption spectrum of free base porphyrin H_2TTP has strong absorption around 400 nm (Soret band, extinction coefficient value $>2 \times 10^5$) and four absorption bands in the 500–700 nm regions (Q-bands) as explained by the Gouterman Four-Orbital model.²⁰ The free base porphyrin, H_2TTP , also exhibits strong fluorescence around 600–800 nm.²¹ Porphyrins generally are attractive from an electrochemical perspective and their redox properties can be tuned by varying the substituents on the *meso*/ β positions, metallation and core-modification.²²

Porphyrins/metalloporphyrins and their derivatives have been used as excellent photosensitizers in dye-sensitized solar cell (DSSC) applications²³ and photodynamic therapy (PDT);²⁴ as catalysts for chemical transformations including asymmetric synthesis;²⁵ in supramolecular chemistry²⁶ and organic electronics,^{27,28} etc.

1.2 Carbon nanoallotropes (CNAs)

CNAs are structures with sizes <100 nm^{29,30} (0.1 mm) at least in one dimension. Many forms of carbon nanoallotropes (Fig. 2) have been developed in the past few decades. Some of them are tubes, dots, fullerenes, graphene, nanohorns, nanodiamonds, etc.^{31–33} These allotropes exhibit exciting structural and functional properties that can be converted into several intriguing applications. Briefly, carbon nanomaterials exhibit extraordinary electrical,³⁴ thermal, mechanical,^{35,36} chemical,^{37,38} optical,³⁹ nuclear (magnetic)⁴⁰ and biological properties.^{41–43} All these

properties in one material were merely impossible to imagine few years back but now it has become a reality. The major contribution behind this paragon is their high surface area to volume ratios.^{44,45} The other reason can be the hybridization state of the carbon atoms in the structure. Carbon orbitals can undergo sp , sp^2 or sp^3 hybridization based on bonding suitability.

Fig. 2 Different forms of carbon nanostructures.¹⁹

1.2.1 Carbon nanotubes (CNTs). CNTs are 1-dimensional (1D)⁴⁶ cylindrical macromolecules with diameters in the nanoscale; single walled carbon nanotubes (SWCNTs) can have a diameter of 1–2 nm⁴⁷ and multiwalled carbon nanotubes (MWCNTs) which contain multiple numbers of carbon layers can have a diameter between 2 and 100 nm.⁴⁸ The walls of CNTs are made up of sp^2 hybridized⁴⁹ carbon atoms arranged in a hexagonal lattice. The shape can be modified as bent or twisted by incorporating pentagonal or heptagonal rings into their structures.⁵⁰ Researchers have made many successful attempts to functionalize CNTs at their surfaces which not only preserved their original qualities but also added optimized properties.

1.2.2 Carbon dots (CDs). CDs are 0D quasi-spherical⁵¹ shaped nanostructures with diameters between 2 and 10 nm.^{52,53} CDs are usually amorphous in nature containing sp^3 hybridized⁵⁴ carbon atoms. The nano-size and surface modifications impart photoluminescence⁵⁵ properties to CDs significantly.

1.2.3 Fullerenes. Fullerenes, also called buckyballs or buckminsterfullerenes, are ball-like structures made up of a mixture of sp^2 and sp^3 hybridized carbon atoms.⁵⁶ In these 0D structures, carbon atoms are arranged to form either 5-membered or 6-membered rings which then develop like a closed hollow cage.⁵⁷ The size of fullerenes varies depending on the number of carbon atoms (from 60 to 100).⁵⁸ The most abundant and simplest fullerene (C_{60}) has an external diameter of 0.71 nm, and 12 pentagonal and 20 hexagonal rings.⁵⁹ The void in their cage and fullerene surface is suitable for functionalization and thus holds excellent possibilities of applications.

1.2.4 Graphene. Graphene is a 2D, planar sheet of sp^2 carbon atoms that are linked *via* covalent sigma bonds.⁶⁰ The layers of graphene (2–10) can pile, forming thick multilayered graphitic nanosheets. Graphene exhibits an aromatic nature due to the flow of electrons through sideways overlapped unhybridized p-orbitals. Graphene also forms 1D nanoribbons, which appear as

unzipped CNTs, with widths of <50 nm.⁶¹ Their excellent conducting properties can be made use of in varieties of applications.

1.2.5 Carbon nanohorns (CNHs). Nanohorns are another class of carbon nanoallotropes, gaining much attention nowadays. They are horn shaped, which aggregate to form dahlia like structures with an average cone angle of 120°. ^{62,63} Generally, the diameter of these aggregates is in the 50–100 nm range, whereas the diameter of each cone is 2–5 nm. The cone can grow up to a length of 40–50 nm.⁶⁴ Nanohorns are the known purest form of carbon nanomaterials because they are obtained from pure graphite rods by laser ablation or arc discharge methods without any involvement of metal catalysts.⁶⁵

1.2.6 Carbon nanospheres (CNSs). Nanospheres are spherical shaped carbon nanoparticles with a hollow space at their center.⁶⁶ The carbon nanospheres possess randomly arranged carbon layers; their size can vary based on the graphitic nature of the particles. A carbon nanosphere with well graphitized layers has a diameter ranging from 2 nm to 20 nm, whereas a poorly graphitized carbon nanosphere will be bigger in size with a diameter of 50 nm to 1 µm. A carbon bead has distorted layers; therefore it exhibits larger diameters, *i.e.*, more than 1 µm.⁶⁷ The research work done in this field is latent; therefore this provides large opportunities to explore intriguing facts and possibilities of CNSs' applications in various fields.

Several top-down and bottom-up approaches have been developed to synthesize CNAs. A top-down method is a disintegration process where a bulk material is converted into minute particles. It includes pyrolysis,^{68–71} electric discharge,^{72–74} laser ablation,^{75,76} decomposition processes,^{77,78} *etc.*; whereas a bottom-up approach focuses on the formation of materials from the atomic level; like chemical vapor deposition (CVD),^{79,80} physical vapor deposition (PVD),^{81,82} hydrothermal methods,^{83,84} *etc.* Now, scientists are aiming at producing CNs *via* catalyst free, template free procedures that require no chemical reagents or that require their minimum usage.

With exorbitant surface areas, CNAs are amenable to functionalization at their surface and interior doping. The properties of CNAs having modified surfaces are well enhanced in comparison with the pristine materials. These properties have provided a wide platform for innumerable applications.

For many years, researchers have been utilizing these tiny structures in electronic devices;⁸⁵ energy technologies such as solar cells;⁸⁶ energy storage;⁸⁷ biomedical applications like tissue engineering,⁸⁸ bioprobe,⁸⁹ biomarking,⁹⁰ cancer diagnosis,⁹¹ and drug delivery;⁹² and many more. Having gained a unique place in the field of nanoscience, the era of CNAs has been propagated, followed by a tremendous increase of research activity in this field. This review focuses on the recent trends in covalent/non-covalent synthetic approaches towards the creation of porphyrin–CNM hybrids and their application in various fields.

1.3 Porphyrin–carbon nanomaterial hybrids

Porphyrins and CNAs have received great attention in research recently due to their excellent structural and functional properties. As individual materials, they have proved their significance in various fields of applications. Looking at these two materials, it is noticeable that they showcase distinct physical, chemical and biological features. In brief, the dominant character of porphyrins is their photosensitivity, whereas CNAs possess huge surface area. So, it is fascinating to bring together the attractive qualities of these two materials. In this regard, the era of immobilizing porphyrins onto different carbon nanoallotropes has started.

In the past few years, conjugation of porphyrins and carbon nanomaterials has emerged as an interesting topic of research because of their fascinating improved properties compared to the

individual compounds. CNAs are functionalised with porphyrins either covalently or non-covalently, which will be discussed further in this review. Covalent interactions provide thermodynamically stable structures, but the electronic structures of the pristine compounds are disturbed during bond formation; whereas non-covalent functionalization is based on secondary interactions such as π - π interactions, electrostatic interactions, hydrogen bonding, *etc.*, and the advantage here is that the non-covalent approach does not disrupt the intrinsic electronic structure of the nanomaterial but keeps it intact. But the stability is proved to be comparatively low. The type of interaction between a porphyrin and a carbon nanomaterial can be chosen based on certain application requirements.

1.3.1 Porphyrin-carbon nanotube (CNT) hybrids. Porphyrins can be immobilized onto CNTs *via* covalent or noncovalent strategies. In covalent approaches, CNTs are first activated to obtain functional groups at their surfaces; the surface functionalized CNTs are then treated with porphyrins, which results in stable bond formation between them. Both single walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs) can be used for hybrid formation with porphyrins. In one such method, a hybrid of 5-(*p*-hydroxyphenyl)-10,15,20-tritolylporphyrin (Por-OH) and carboxyl group functionalized CNTs is prepared *via* ester linkages.⁹⁴ The CNTs are initially subjected to wet-air oxidation, followed by sulfuric acid and nitric acid in a 3 : 1 ratio. The process causes -COOH groups at the CNT surfaces. The carboxylic group functionalized CNTs are treated with thionyl chloride and then with excess Por-OH in toluene and triethylamine (TEA) at 100 °C for 24 h under a nitrogen atmosphere (Fig. 3). During the reaction, the -COCl on the CNTs and OH on the porphyrin undergo condensation, forming ester linkages between the pristine compounds. The unreacted Por-OH is removed by washing with a series of solvents, *viz.*, methanol, acetic acid, triethylamine and tetrahydrofuran.

Fig. 3 Covalent conjugation between a CNT and a porphyrin *via* an ester linkage.

Another mode of porphyrin attachment onto CNTs is *via* amide linkages (Fig. 4). A supramolecular assembly of carboxylic functional group bearing porphyrins with amine-functionalized CNTs^{95,96} can be structured by a simple condensation method. First, the carboxylic group of the porphyrin in dimethylformamide (DMF) is activated into an active carbodiimide ester group by adding dicyclohexylcarbodiimide (DCC). The amine-functionalized CNTs are then added to the reaction mixture at room temperature, followed by stirring for 48 h. The carboxyl and amine groups undergo condensation resulting in a stable porphyrin-CNT hybrid *via* amide linkages.^{93,97} Any DCC intermediate by-products formed during the reaction are removed by washing the product with DMF. A similar type of hybrid can be formed by interchanging the functional groups. A porphyrin molecule with the amine group^{98,99} can be used to form an amide linkage with an acid treated,^{100,101} -COOH group containing CNT.

Fig. 4 Formation of an amide linkage between a porphyrin and a CNT.⁹³

The surface modification of CNTs is favoured for their efficient covalent conjugation with porphyrins. The recent trend is to link CNTs with axially functionalized porphyrins.¹⁰² In this regard, 1,3-dipolar cycloaddition^{103,104} by a one pot Prato reaction¹⁰⁵ and a stepwise approach leads to the formation of a CNT–porphyrin hybrid (Fig. 5) with improved solubility and processability. In the straightforward method, (5,10,15,20-tetraphenylporphyrinato)tin(IV) (SnTPP) and sarcosine are mixed with CNTs in DMF. The mixture is heated at 130 °C under N₂. A portion of sarcosine and SnTPP is added to the reaction system every 24 hours for six days. The hybrid is formed and is isolated from the solution by pouring it into ice cold water.¹⁰⁶

Fig. 5 Formation of a porphyrin–CNT hybrid by a one step Prato reaction and a stepwise 1,3-dipolar cycloaddition; one pot Prato reaction; method 2: stepwise approach.

The stepwise approach involves functionalization of CNTs with 4-hydroxybenzaldehyde and then 1,3-dipolar cycloaddition with SnTPP. Functionalization of CNTs occurs when 4-hydroxybenzaldehyde is added to CNTs in DMF and heated at 130 °C along with sarcosine. The 4-hydroxybenzaldehyde functionalized CNTs in pyridine are added to SnTPP under N₂. A 1,3-dipolar cycloaddition product is obtained by refluxing the mixture for four days, which is then isolated by filtration.¹⁰⁶ The porphyrins and CNTs are conjugated by the Sonogashira coupling reaction; a reaction between tris-(triphenylamine)porphyrinato zinc(II) and single walled and double walled CNTs with iodobenzene functionalization is carried out under microwave irradiation conditions, which results in C–C bonding between porphyrins and CNTs (Fig. 6).¹⁰⁷ A [3+2] cycloaddition reaction also favours the hybrid formation between porphyrins and CNTs.^{108,109} Pyridyl substituted double walled CNTs form supramolecular assemblies with zinc porphyrins. The pyridyl units are attached to the external walls of the CNTs through isoxazolino linkers and esters of carboxylic groups. At 0 °C, nitrile oxide from 4-pyridylcarboxaldehyde oxime undergoes [3+2] cycloaddition reaction with *N*-chlorosuccinimide *in situ*, in the presence of pyridine. A solution of pentyl ester functionalized CNTs and triethylamine in *o*-dichlorobenzene is added, after removing the solvent, to the reaction mixture followed by microwave radiation treatment at 120 W for 45 min. When the solvent is evaporated, the porphyrin–CNT hybrid is obtained as a solid residue.¹⁰⁹

Fig. 6 Covalent linkage between tris-(triphenylamine)porphyrinato zinc(II) and an iodobenzene functionalized CNT.

The porphyrin can be immobilized onto CNTs *via* S_N2 substitution to achieve zwitterionic functionalization by treating it with an electrophile (dichloroethyl acetylenedicarboxylate) and a nucleophile (4-dimethylaminopyridine (DMAP)) in *p*-dioxane at 95 °C. When a cobalt porphyrin is added to a solution containing CNTs in THF at 90 °C, they undergo substitution reaction forming a hybrid.¹¹⁰

Another interesting type of hybrid structure is a porphyrin polymer wrapped around CNTs. A reaction between metal free CNTs and porphyrins is conducted under hot conditions in DMF at 100 °C. The heating is continued for an extended time, *i.e.*, up to four days, until polymer wrap formation occurs. The formation of a hybrid is tested using absorption and fluorescence spectroscopic techniques. Temperature is found to play a major role in this experiment, as no characteristic results are obtained when the same procedure is followed at 200 °C.¹¹¹

It is clear that the covalent conjugation of porphyrins and CNTs results in stable hybrid structures with increased solubility or dispersion in solvents. But the electronic and/or structural properties of the pristine compounds are disturbed. Therefore, the composite mixtures of porphyrins and CNTs grab the attention which promises to retain the original qualities of the pristine compounds. Here, porphyrin molecules and CNTs assemble *via* non-covalent interactions,^{112–114} such as hydrogen bonding, electrostatic forces, π – π stackings, *etc.*

One beautiful method found suitable to produce non-covalent conjugates of porphyrins and carbon nanotubes is by micelle formation as shown in Fig. 7. Both hydrophilic and hydrophobic porphyrins can be architected with CNTs with the help of surfactants that create micelles. In the case of hydrophilic porphyrins, they themselves act as surfactants; whereas when hydrophobic porphyrins are used for hybrid formation, additional surfactants like sodium cholate have to be added. The hydrophobic porphyrins are first dissolved in suitable organic solvents such as dichloromethane and then mixed with a micellar solution of CNTs. The porphyrin molecules travel to the organic core of the micelle that contains CNTs. The two pristine compounds thus form assemblies *via* π stacking interactions.¹¹⁵

Fig. 7 Sketch of the noncovalent conjugation of porphyrins and CNTs by the micelle formation method.¹¹⁵

Composites of porphyrins and CNTs are possible *via* molecular interactions. Glycyl-substituted 5,10,15,20-tetraphenylporphyrin interacts with single walled CNTs at 85 °C, under a nitrogen atmosphere, in the presence of formaldehyde in DMF. The composite requires seven days to form after which it can be separated from the reaction system using dichloromethane (DCM).^{117,118}

The stability of the porphyrin–CNT hybrid is lowered when conjugated non-covalently, due to the lower affinity of the porphyrin towards the CNT surface. The reason behind the decreased interaction is the spatial distance between the porphyrin and CNT that retards the electronic coupling.^{116,120} The stability of a non-covalent hybrid can be increased by increasing the proximity between the chromophore and CNT.

This is achieved using higher π electronic structures such as porphyrins fused with polycyclic aromatic rings.^{121–123} An experiment conducted with bis-pyrenylporphyrin, mono-fused pyrenyl porphyrin and doubly fused pyrenyl porphyrins (Fig. 8) showed enhanced affinity of porphyrins to CNT sidewalls. The suspensions of the above mentioned porphyrins and CNTs are sonicated to get homogeneous solutions¹²⁴ of hybrids. When checked for stability, a solution of a bis-pyrenyl porphyrin–CNT hybrid showed precipitation upon allowing it to stand for one hour, whereas in mono-fused porphyrin–CNT, the precipitation started after a week, indicating increased stability of the system. The stability of non-covalent conjugation as a function of π interactions is well proved by doubly fused porphyrin–CNT, which remained stable displaying no sign of precipitation even after a week.¹¹⁶

Fig. 8 Schematic representation of non-covalent conjugation between porphyrins with fused aromatic rings and

The allure of non-covalent conjugation is that it can immobilize porphyrins with various substituents on CNTs by simple procedures like sonication or stirring for a specific duration. Even porphyrins with long chain or bulky substituents can be attached to CNTs by these methods. For example, tetraphenylporphyrines with hexadecyloxyls, (10-undecenyl)oxyls having terminal alkenes, and (11-acetylthioundecyl)oxyls having terminal thioesters as substituents at the *para*-position are conjugated with CNTs *via* a simple sonication technique (Fig. 9). Solutions of pristine compounds in a 1 : 1 mass ratio are mixed in chloroform and sonicated at 15 °C constant temperature. The formation of a non-covalent hybrid is accompanied by a change of color from purple to green, with a gradual increase in color due to the efficient dispersion of CNTs in solvent followed by hybridization. The stability of the hybrid is analysed on the basis of the structural regularities of porphyrins bearing different substituents. The porphyrin with a structurally regular saturated alkane side chain is found to arrange in a more orderly manner compared to less regular terminal alkene and thioester bearing porphyrins.¹¹⁹

Fig. 9 Schematic representation of non-covalent assembly of terminal alkene and thioester substituted porphyrins

1.3.2 Porphyrin–fullerene hybrids. Conjugation of porphyrins and fullerenes is an intriguing field to many researchers. Owing to the cage structured ball shape and geodesic π -system of fullerenes, it is fascinating to assemble them with other interesting molecules like porphyrins. Both porphyrins and fullerenes possess extended π systems, capable of interacting with applied electric,¹²⁵ magnetic^{126,127} and electromagnetic fields^{128,129} and also with a wide variety of chemical species. Together, they form an electron donor–acceptor system, with the porphyrin being the electron donor.

Many synthetic procedures have been developed over the decades to produce porphyrin–fullerene supramolecular assemblies.^{132–138}

A more frequently spoken procedure is ‘click chemistry’,^{139,140} where the complex hybrid is formed by a versatile and simple reaction. A 1,3-dipolar cycloaddition reaction (Fig. 10) between a fullerene bearing the acetylene group and an azide^{130,141} functionalized porphyrin (or an azide functionalized fullerene) leads to the formation of a chromophoric hybrid.

Fig. 10 Click reaction showing the formation of a porphyrin–fullerene hybrid.¹³⁰

Porphyrin–fullerene hybrids can also be synthesized *via* [4+2] cycloaddition reaction.¹³¹ Tetraphenylporphine, the starting material, is modified to 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin, followed by reaction with the carbanion of chloromethyl *p*-tolyl sulphone, forming the product with the CH₂SO₂Tol group (Fig. 11).

Fig. 11 Reaction showing the [4+2] cycloaddition of a porphyrin onto a fullerene.¹³¹

The product is alkylated to bear an acetylenic functional group. Rearrangement of the acetylenic group to diene is essential so as to use the latter as the point of attachment to fullerene. The rearrangement mechanism is aided by intermolecular enyne metathesis in the presence of a ruthenium based catalyst. The Diels–Alder cycloaddition reaction is performed by refluxing a porphyrin–fullerene mixture for 5 h in toluene. The dyad can also be prepared using a shorter spacer that links the terminal acetylenic group to the sulphone substituent on the porphyrin.¹⁴²

Porphyrin–fullerene hybrids can be achieved by utilizing various chemical entities which act as linkers (Fig. 12). These linkers bring the two compounds into close proximity that facilitates spatial interactions between porphyrins and fullerenes, further resulting in hybrid formation by covalent bonding. Several types of surface modifications have been demonstrated to obtain

glycol-linked,¹⁴⁴ aza-linked,¹⁴⁵ catechol-linked,¹⁴⁶ naphthalene-linked,¹⁴⁷ and steroid-linked¹⁴⁸ fullerenes; these linkers attach to the chromophore, forming stable covalent hybrids.

Fig. 12 Immobilization of porphyrins onto fullerenes *via* various linkages.¹⁴³

Gervaldo *et al.* in 2010 proposed another procedure to functionalize fullerene C₇₀ with porphyrins.¹⁴⁹ The method involves a reaction between pyridyl group substituted 5-(4-formylphenyl)-10,15,20-tris(4-pyridyl)-porphine (D-TMPyP) and C₇₀ in bromobenzene (Fig. 13). Sarcosine added to the reaction mixture facilitates linkage between the two compounds. Conjugation reaction was facilitated by refluxing the solution containing porphyrin and C₇₀ in an argon atmosphere for 1 h followed by the formation of a porphyrin and fullerene C₇₀ amphiphilic dyad. Sarcosine is also found to assist the conjugation of porphyrins with an aniline substituent and fullerene C₆₀ *via* the Prato reaction. This intriguing method involves the formation of a dyad, whose polymerization^{150,151} causes a hole- and electron-conducting electropolymer. The *meso*-position of 5-(4-formylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin is first brominated, followed by its replacement by the 4-aminophenyl group *via* the Suzuki-type coupling reaction. The hybrid formation occurs through the Prato reaction by mixing C₆₀, sarcosine and porphyrin. The interesting part of this hybrid lies in its polymerization by an electrochemical method where the aminophenyl group attached to the porphyrin forms a linear chain.

Fig. 13 Formation of a porphyrin–fullerene dyad followed by electropolymerization.¹⁴⁹

A porphyrin–fullerene hybrid can be prepared in the form of donor-bridge–acceptor molecules. Urbani *et al.* prepared a conjugate system of triad and tetrad molecules in which one and two porphyrin molecules are immobilized onto fullerene C₆₀, respectively, by covalent linkages through phenylethynyl-oligothienylenevinylene bridges.¹⁵²

Researchers have prepared porphyrin–fullerene assemblies by depositing porphyrin molecules on thin films made of fullerenes as shown in Fig. 14. Initially, a thin film of fullerenes is formed *via* a physical vapour deposition technique (PVD) on a highly-oriented pyrolytic graphite (HOPG) support.¹⁵³ *meso*-Tetraphenylporphine and its Ni(II) and Co(II) complexes are then adsorbed onto the fullerene thin film by 2 min PVD in a vacuum. Porphyrins bearing metal centres form ordered non-covalent structures in comparison with the base.

Fig. 14 Porphyrin moieties deposited on a fullerene thin film.

The C₆₀ fullerene is found to have an excellent multi-electron acceptor system with favourable reduction potentials. Due to its minor reorganization energy requirement in electron-transfer reactions, this fullerene can conjugate easily with porphyrins non-covalently¹⁵⁴ *via* π – π interactions. In this regard, incorporation of fullerenes into self-assembled porphyrin molecules attracts attention due to a simple procedure involved. In aqueous medium (Fig. 15), π – π stacking interactions between amphiphilic porphyrin molecules are enhanced by the hydrophobic effect, resulting in their self-assembly. A similar effect is found when a solution of *meso*-tetrakis-(3,5-di-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-phenyl)-porphyrin in THF is injected into a pool of water. The assembly in water can be isolated by evaporating the solvent at 80 °C. Fullerene C₆₀ can be introduced into the assembly of porphyrin macromolecules by injecting a mixture of equimolar amounts of the porphyrin and fullerene in toluene followed by THF into water. A non-covalent hybrid of the porphyrin and fullerene C₆₀ is obtained by evaporating the solvent.¹⁵⁵

Fig. 15 Porphyrin–fullerene assembly in water.¹⁵⁵

1.3.3 Porphyrin–graphene hybrids. Besides CNTs and fullerenes, graphene is one of the most robust nanoallotropes of carbon. A two-dimensional sheet of hexagonally arranged carbon atoms provides an extended π -electron system which imparts unique electronic properties to the material. Graphene, being an electron acceptor, can be chemically modified covalently or non-covalently with electron donating organic moieties like porphyrins.^{156,157}

Like in CNTs and fullerenes, the Prato 1,3-dipolar cycloaddition^{158,159} reaction has been proven as an effective method to functionalize graphene with porphyrins. In a stepwise reaction, reduced graphene oxide (RGO) reacts with sarcosine and 4-hydroxybenzaldehyde in DMF at 145 °C forming OH-functionalized RGO. This is followed by nucleophilic substitution of 5-[4-(2-bromoethoxy)phenyl]-10,15,20-triphenylporphyrin (TPP 1), resulting in a RGO–porphyrin covalent nanohybrid. This method requires excess amounts of reactants and also has difficulty in controlling the degree of nucleophilic substitution of –OH units. A direct Prato reaction can be followed to overcome these disadvantages. A porphyrin containing the formyl group, 5-[4-(2-(4-formylphenoxy)ethoxy)phenyl]-10,15,20-triphenylporphyrin, is directly integrated into RGO, in DMF, through the formation of an azomethine ylide (**Fig. 16**). A similar procedure can also be conducted in *o*-dichlorobenzene instead of DMF at 160 °C. The ylide functionality formed by condensation of the formyl group and α -amino acid (sarcosine) acts as a linker in the nanohybrid.¹⁶⁰

Fig. 16 1,3-Dipolar addition of a porphyrin onto graphene.¹⁶⁰

Covalent integration of porphyrins onto graphene layers can also be facilitated by amide linkages. A reaction between a porphyrin with the amine group and graphene oxide (GO) results in condensation followed by conjugation of these molecules forming nanohybrids (Fig. 17). The sheet of graphene is converted into graphene oxide that is rich in oxygen containing functionalities obtained by Hummers' method. The derivative obtained by refluxing GO in SOCl_2 and DMF at 70°C under an argon atmosphere for 24 hours is allowed to react with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (TPP- NH_2) in the presence of a base, triethylamine (Et_3N), at 130°C for 72 hours under inert conditions. The carboxyl group of GO and the amine group of TPP undergo condensation reaction forming a TPP-NH-CO-graphene nanohybrid.^{161–166}

Fig. 17 Covalent conjugation of porphyrin molecules and graphene *via* amide linkages.¹⁶¹

Other than these procedures, porphyrins can be conjugated to graphene or to its oxidized/reduced forms by non-covalent means. The structures of the porphyrins are almost planar even with different substituents. The 2D 18 π electrons of the porphyrins interact easily with the 2D layers of graphene and this can be achieved by a solvothermal method. In one such successful attempt, a mixture of graphene oxide and a porphyrin is added to *N*-methyl-2-pyrrolidone (NMP) and tetrabutylammonium hydroxide (TBA). The mixture is stirred at room temperature but under an argon atmosphere at 800 rpm for seven days. Finally, a π – π stacked porphyrin–graphene oxide hybrid is isolated from the solvent by centrifugation at 5000 rpm for 30 min.^{167,168}

The interesting reaction of porphyrins and graphene is also found in thin films.^{169–171} A thin film of graphene, in the form of reduced graphene oxide (RGO) cast on glass, is used for this purpose. The film of RGO is immersed into an aqueous solution of a cationic porphyrin, 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP), which results in the attachment of the porphyrin onto the RGO film. With increase in immersion time, the interaction between the compounds is found to increase. Moreover, it is also found that higher solution concentration facilitates the faster rate of binding onto the film, resulting in non-covalent hybrids.¹⁷²

Non-covalent conjugation of porphyrins and graphene^{173–175} is promoted by different types of interactions, *viz.*, π – π stacking, van der Waals forces and/or electrostatic attraction or repulsion. When water soluble negatively charged and positively charged porphyrins, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine-*p,p',p'',p'''*-tetrasulfonic acid tetrasodium hydrate (TPP-SO₃Na) and 5,10,15,20-tetrakis(4-trimethylammonio)phenylporphyrin tetra(*p*-toluenesulfonate) (TPP-ammonium), respectively, are mixed with GO in aqueous medium, they interact *via* π – π stacking (Fig. 18). A stability study of the nanohybrids formed reveals that the GO/TPP-ammonium suspension is temporarily stable, resulting in precipitation upon storage; whereas TPP-SO₃Na enhances the dispersion of GO in water. The negatively charged TPP-SO₃Na moieties aggregated on the GO surface do not allow close interaction between GO sheets due to anionic electrostatic repulsion, thereby increasing the stability of the suspension.¹⁷⁶

Fig. 18 Schematic representation of porphyrin trapping on a graphene layer.^{177,178}

1.3.4 Porphyrin–carbon nanohorn hybrids. The beauty of carbon nanomaterials is that they can be synthesized in various shapes and morphologies and thus exhibit attractive properties. Besides tubular, ball like and layered structures, carbon can also be derived in the form of nanohorns.^{179,180} These high purity carbon nanostructures obtained by disintegration of graphite (hence no metal impurities) provide an excellent platform to produce tailored assemblies with porphyrins. Extensive work done in this area has revealed many covalent and non-covalent ways to conjugate porphyrins and carbon nanohorns, thereby producing stable nanohybrids.^{181–184}

To obtain stable covalent hybrids of carbon nanohorns (CNHs) and porphyrins, CNH surfaces can be initially modified with different easily tunable substituents that can form bonds with porphyrins. One such functionality on CNH that favours bond formation is the amino group. A free-base porphyrin with tetracarboxylic acids ($\text{H}_2\text{P}(\text{CO}_2\text{H})_4$) is found to conjugate with amino CNH both covalently and non-covalently in aqueous medium. Covalent conjugation occurs through the formation of amide linkages (**Fig. 19**),^{185,186} whereas non-covalent interaction occurs through π – π stacking and effective ionic bonding.^{187,188}

Fig. 19 Covalent and non-covalent nanohybrid formation between a porphyrin and a carbon nanohorn.¹⁸⁵

CNHs are excellent electron acceptors and possess the ability to diffuse the electrons readily along the cone axis with negligible loss of energy. This inspires the formation of electron donor–acceptor nanohybrids of CNHs and porphyrins (Fig. 20). In this regard, amide linkages have proven to be one of the suitable pathways to synthesise these nanohybrids. One such attempt made by mixing an amino-group possessing porphyrin, α -5-(2-aminophenyl)- α -15-(2-nitrophenyl)-10,20-bis(2,4,6-trimethyl-phenyl)-porphyrin, and carboxylic acid bearing CNH produces a stable nanohybrid in organic solvents such as THF and dichloromethane. The pristine CNHs are initially modified to obtain carboxylic group functionalities at the surface by heating at 580 °C. These carboxylic groups are utilized to form amide linkages with porphyrins in later stages.^{189,190}

Fig. 20 Schematic of porphyrin–CNH hybrids.¹⁸⁹

Covalent conjugation of porphyrins onto CNHs takes place on graphitic side walls or at the conical tip. In covalent linkages, there will be perturbation of the continuous π electronic system of CNHs that leads to an enhanced dispersion of the functionalised material and solubilisation. This issue can be overcome by supramolecular approaches by utilizing secondary interactions such as π – π stackings between the CNH sidewalls and porphyrin molecules. This can be brought about by modifying the surfaces of the CNHs. In such research work, the pristine CNH-COOH is treated with *tert*-butyl-*N*-(6-aminoethyl)carbamate in DMF followed by treatment with HCl/dioxane that results in CNH-spacer (sp)-NH₃⁺. The CNHs covalently attached to the ammonium cations through the spacer are rich in the amide group, the ethylene spacer and –NH₃⁺ and are used as substrates to form a supramolecular assembly with a zinc porphyrin linked to a crown ether (crown-ZnP). CNH-sp-NH₃⁺ and crown-ZnP are mixed in DMF at room temperature followed by stirring for 2 min. During the stirring process, the two compounds are brought into close proximity, resulting in interaction between the CNH and porphyrin producing a stable nanohybrid.¹⁸⁹

Non-covalent conjugation between CNHs and porphyrins can also be brought about in aqueous medium using water soluble porphyrins. {5,10,15,20-Tetrakis-(1-methyl-4-

pyridinio)porphine tetra-(*p*-toluenesulfonate)} gets immobilized onto CNH sidewalls by mild sonication for a very short period, 3 min in aqueous solution. The mixture is stirred vigorously for 20 hours that brings interactions between the two entities. The black non-covalent hybrid of the CNH and porphyrin formed is isolated by centrifugation after removing any unbound porphyrin by decantation.¹⁸¹

Researchers have been working on various possibilities to design supramolecular assemblies between porphyrins containing a range of metal centres and substituent groups and CNHs. In this regard, use of metal oxides as bridges between porphyrins and CNHs has attracted attention due to the synergistic effect exhibited by the resulting nanohybrid. Tu *et al.*¹⁹¹ has reported a supramolecular assembly, where titanium oxide acts as bridge between metalloporphyrins and CNHs. Here, the carboxylate groups present on ferriprotoporphyrin and CNHs attach onto titanium oxide (TiO₂) nanoparticles' surface *via* dentate binding. The metal bridged porphyrin-CNH hybrid is found to have enhanced electrocatalytic activity.

2. Applications

CNAs have made a revolution in the fields of nanoscience and nanotechnology due to their excellent structural, optical, mechanical and electronic properties – thanks to their huge surface area and chemical stability, which make their application ubiquitous over a wide range of fields. Yet, their chemical inertness, insolubility in organic matrices and tendency to form aggregates hinder their use. With respect to this, the enhancement of nanocarbon surfaces by functionalization with porphyrins results in increased dispersion quality and solubility. The immobilization of porphyrins onto nanocarbon surfaces can be achieved *via* either covalent or non-covalent interactions. The nanohybrids thus formed exhibit optimized properties compared to the pristine compounds and thus effectively contribute to various fields of applications.

2.1 Porphyrin–CNM hybrids in catalysis

Porphyrin/nanocarbon hybrids are gaining worldwide attention due to their excellent catalytic performances. Their ability to convert raw materials into valuable products even when reused has made them useful for commercial applications.

Metalloporphyrins supported on carbon nanoallotropes build stable, heterogeneous catalysts that can be easily separated from the reaction system. Metalloporphyrin functionalised CNTs proved to be promising catalysts in the oxidation of alkenes to epoxides using hydrogen peroxide (H₂O₂) as an oxidant. The catalytic efficiencies of the nanohybrids are found to increase in protic solvents and with irradiation using ultrasonic waves. When the bubbles formed during sonication explode, they produce an enormous amount of energy that facilitates the reaction to complete in a shorter duration.

The proposed catalytic mechanism ([Fig. 21](#)) explains the initial coordination of H₂O₂ to the metal centre of the porphyrin, forming a penta-coordinated intermediate that can sometimes generate an iron–oxo intermediate. In the later step, the olefin attacks as a nucleophile at the oxygen atom of coordinated H₂O₂ or iron–oxo intermediate forming an epoxide product. Similar reactions can be carried out using molecular oxygen as an oxidant to oxidize olefins and various sulfides such as methyl phenyl sulfide, diphenyl sulfide, benzyl phenyl sulfide, phenyl vinyl sulfide and 4-chlorophenyl methyl sulfide *via* a free radical reaction mechanism.^{192,193}

Fig. 21 Proposed catalytic mechanism exhibited by a porphyrin–CNT hybrid.¹⁹²

Porphyrin/carbon nanomaterial hybrids also catalyse hydrogenation reactions such as transformation of levulinic esters into heterocyclic compounds such as γ -valerolactone and pyrrolidone derivatives. A polymer of a ruthenium porphyrin supported on CNTs *via* π – π stacking is an excellent heterogeneous catalyst which shows a conversion efficiency of more than 99%. Like CNTs, graphene and graphene oxides are also found to support porphyrin

catalysts that convert esters to γ -valerolactone and pyrrolidone with similar conversion capacities.¹⁹⁴

The hybrids are capable of eliminating pollutants from the environment by playing the role of catalysts in their oxidative decomposition.^{195,196} Mercaptans are one class of such toxic and corrosive gaseous compounds, hazardous to the environment. Porphyrins supported on CNTs are efficient catalysts to remove mercaptans from a gas stream by an oxidation reaction.¹⁹⁷ The reaction is accompanied by conversion of mercaptan to disulfide in the presence of potassium hydroxide.

Porphyrin/carbon nanomaterial hybrids also catalyse the oxygen reduction reaction through electrochemical activities. These electrocatalysts possess high electrochemically accessible surface area, stability and tolerance to the methanol crossover effect in the reduction reaction. Moreover, these hybrid catalysts enable a direct four electron pathway to reduce oxygen in alkaline medium. Because of their outstanding catalytic performance, porphyrin/nanocarbon hybrids replace high cost metallic catalysts such as platinum, ruthenium complexes, *etc.*^{198–203}

The hybrids also perform electroreduction of carbon dioxide (CO_2). The resistance at the electrode interface greatly decreases due to the high surface area and excellent electrical conductivity of the CNTs, which allow easy movement of electrons between the porphyrins and CNTs. As a result, the potential for CO_2 reductions decreases, resulting in an increased reaction rate.²⁰⁴ In a similar way, porphyrin–CNT hybrids cause the oxidation of nitric oxide. The mechanism is attributed to the fast transfer of electrons through axial coordination of CNTs and porphyrins.²⁰⁵

2.2 Porphyrin–CNM hybrid based sensors

In recent years, porphyrin immobilized carbon nanomaterials have also been used as sensors. Porphyrin–CNM hybrids can be used as sensors due to their extended catalytic efficiencies as many detection procedures seek catalytic redox reactions.²⁰⁶ These sensors are cost effective and easy to use and exhibit rapid and sensitive response. An anionic porphyrin, *meso*-tetra(4-carboxyphenyl)porphine (TCPP), supported on a chemically converted graphene (CCG) is selective in the detection of dopamine by an electrochemical method. During this phenomenon, the hybrid interacts with positively charged dopamine *via* π – π stackings and electrostatic attraction, thus resulting in higher redox current compared to a bare electrode. The higher redox peak indicates the presence of dopamine and hence the hybrid can be used to detect dopamine^{207,208} in various samples like hydrochloride injections, human serum and urine samples.

An iron–porphyrin ([3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropanoato(2-)]iron(III)) functionalised multi-walled carbon nanotube is found to be capable of determining ascorbic acid, dopamine, uric acid and nitrite, which if present in abnormal levels indicate many disorders such as infertility, Huntington's disease, leukaemia, dopamine levels, and many more respectively. The metallic centre in the porphyrin can undergo rapid electron transfer, resulting in a reversible redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$. This mechanism promotes the preparation of desirable sensors based on porphyrin/nanocarbon conjugates.²⁰⁹

Porphyrin–CCG hybrids produce electrocatalytically active and electrochemically stable sensor systems to detect oxygen and hydrogen peroxide in solution.²¹⁰ With similar electrochemical procedures, porphyrins–GO hybrids can be used as sensors to detect serotonin. Further, a biosensor can also be created out of porphyrin–CNM (graphene quantum dot)

hybrids^{211–214} to detect glucose *via* a fluorescence method as the hybrid exhibits good fluorescence properties.

One of the major utilization of porphyrin–CNM hybrids is found in the detection of ultra-traces of explosives. Explosives are generally made of aromatic nitro compounds. Therefore, the material used to sense and electrochemically detect these compounds should exhibit excellent adsorption capacities. Porphyrin immobilized graphene, due to its high conductivity, chemical and mechanical stability, huge surface-to-volume ratio and easy charge transfer, facilitates the adsorption of explosive compounds.

Different explosive nitro compounds such as 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene and 1,3-dinitrobenzene are identified by the hybrid sensor based on two reduction peaks obtained using electrochemical studies. Out of the two peaks, one corresponds to the reduction of the nitro group to hydroxylamine, which is followed by the reduction of the latter to the amine group.²¹² The mechanism is shown in Fig. 22.

Fig. 22 Scheme showing the electrochemical reduction of the nitro group in an explosive nitroaromatic compound

The porphyrin–carbon nanomaterial hybrids have also proven their efficiency as sensors to detect volatile organic compounds. They work based on a combined effect of electrostatic gating and Schottky barrier modulation. The electrical responses collected are compared with the pattern-recognition analysis tool for the selectivities and sensitivities of the sensors.^{216–219}

2.3 Porphyrin–CNM hybrids in photovoltaics

Porphyrins have emerged as suitable materials for photovoltaic applications due to their high extinction coefficients and photostability. They imitate natural photosynthesis to carry out photovoltaic processes by harvesting light and separation and transport of charges.²²⁰ The hybrids of porphyrins and carbon nanoallotropes provide wonderful electron donor–acceptor²²¹ systems, with carbon nanoallotropes being electron acceptors, which help in envisioning more advanced photovoltaics.²²² Upon photoillumination, charge separation (cs) takes place (Fig. 23) in the nanohybrid forming two ephemeral radical ion species such as porphyrin^{•+} (H₂P^{•+}, where H can be replaced by a metal atom) and CNM^{•−}. The negative value of ΔG_{cs} demonstrates that the charge separation in a porphyrin–CNM hybrid is a thermodynamically favourable process.²²³ The significant number of electrons released during the process can be pooled using an electron mediating agent, like hexyl viologen (HV²⁺), and a hole shift agent like 1-benzyl-1,4-dihydronicotinamide (BNAH). The mediation of electrons from the hybrid to HV²⁺ causes HV^{•+}, creating holes in the hybrid. During this process, the concentration of HV^{•+} increases with increasing quantity of BNAH; as a result, the hole from the hybrid shifts to BNAH, forming BNA^{•+}. These electrons and holes are favourable in photovoltaics.²²⁴

Fig. 23 Pictorial representation of electron transfer in a porphyrin–CNT hybrid photovoltaic cell.²¹⁷

3. Future direction

The structural, physical, mechanical, optical and electronic properties of carbon nanomaterials such as carbon nanotubes, fullerenes, graphenes and nanohorns are favourable to obtain supramolecular assemblies with photosensitive porphyrin molecules. The conglomeration of porphyrins and spherical shaped carbon nanoparticles is a less explored territory and the results obtained with porphyrin–CNA hybrids are encouraging for researchers to explore this area. Carbon nanospheres (CNSs) exhibit similar properties to their allotropic carbon nanomaterials and also have smooth surface morphologies. The property that stands as an advantage to CNSs is their porosity, using which they can hold their counterparts strongly, forming stable structures.

CNSs can be produced by a simple and easy method like pyrolysis under controlled conditions.^{225–230} The synthesis of CNSs from bio-waste materials is an attractive proposition and can be envisioned as a scalable “waste to wealth” approach which will have a strong societal impact. We believe that porphyrin–CNS hybrids will find an array of applications in fields like waste water purification, cleansing technology, *etc.* The synthesis and exploration of such novel porphyrin–carbon nanospheres are currently underway in our laboratory.

4. Conclusion

This review summarizes the attractive properties of porphyrins and CNAs as individual compounds and also the optimized characteristics when these two fascinating entities are brought together by chemical means. There are many covalent and non-covalent approaches available to make such hybrid entities. The thermal and chemical stabilities of the hybrids obtained *via* covalent approaches like click chemistry, 1,3-dipolar cycloaddition, and ester and amide formation supersede the ones produced using non-covalent approaches like electrostatic attractions, π – π stacking, and polymer wrapping of photosensitizers on CNAs, *etc.* This article has also critically listed various applications of porphyrin–CNM hybrids in catalysis, sensors, photovoltaics, biotechnology and water treatment. We are optimistic that this article will further stimulate research and enrich the area of porphyrin–CNA hybrids.

Conflicts of interest

There are no conflicts to declare.

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