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Supramolecular Chemistry of Carbon-Based Dots Offers Widespread Opportunities

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Dedicated to Prof. Maurizio Prato on the occasion of his 70th birthday

Carbon dots are an emerging class of nanomaterials that has recently attracted considerable attention for applications that span from biomedicine to energy. These photoluminescent carbon nanoparticles are defined by characteristic sizes of <10 nm, a carbon-based core and various functional groups at their surface. Although the surface groups are widely used to establish non-covalent bonds (through electrostatic interactions, coordinative bonds, and hydrogen bonds) with various other (bio)molecules and polymers, the carbonaceous core could also establish non-covalent bonds ($\pi-\pi$ stacking or hydrophobic interactions) with π-extended or apolar compounds. The surface functional groups, in addition, can be modified by various post-synthetic chemical procedures to fine-tune the supramolecular interactions. Our contribution categorizes and analyzes the interactions that are commonly used to engineer carbon dots-based materials and discusses how they have allowed preparation of functional assemblies and architectures used for sensing, (bio)imaging, therapeutic applications, catalysis, and devices. Using non-covalent interactions as a bottom-up approach to prepare carbon dots-based assemblies and composites can exploit the unique features of supramolecular chemistry, which include adaptability, tunability, and stimuli-responsiveness due to the dynamic nature of the non-covalent interactions. It is expected that focusing on the various supramolecular possibilities will influence the future development of this class of nanomaterials.

1. Introduction

Carbon dots (CDs) are a class of nanosized carbon particles with typical dimensions below 10 nm. Their carbon-based core typically consists of sp^2/sp^3 domains, and their surface comprises various chemical functional groups. The earliest report of the formation of carbon-based dots was in 2004 and evidenced the serendipitous discovery of a mixture of fluorescent nanoparticles during the electrophoretic purification of single-walled carbon nanotubes.[1] The optical properties of CDs have mostly inspired the subsequent research and made them suitable for a range of applications from biological imaging to photovoltaics.

CDs can be classified as graphene or carbon quantum dots (GQDs or CQDs), carbonized polymer dots (CPDs) and carbon nanodots (CNDs). A comparison of the different types is nicely summarized in recent works,[2–5] although a rigorous classification is not an easy task. They can be broadly classified based on their physicochemical or photophysical properties; for example, GQDs and CQDs usually possess a degree of crystallinity and their fluorescence shows quantum confined effects, while CNDs and CPDs usually possess a carbonized core structure without obvious crystallinity and their fluorescence does not show any quantum confined effects. However, throughout the literature these terms are often used interchangeably and inaccurately. In this Review, we use the term CDs to describe all the types of carbon-based quasi-spherical nanomaterials.

As a new type of photoluminescent nanomaterial, CDs have several advantageous characteristics, enumerated in previous reviews on this subject,[2,6–13] including the following: tunable electronic structure, biocompatibility, good dispersion in water, and photostability. One of the major advantages of this nanomaterial is that it can be prepared by simple top-down or bottom-up approaches using cheap, nontoxic, and abundant materials. The good solubility and easy functionalizable surface without the need of post-synthetic treatments are also advantages of CDs over other carbon nanomaterials. Overall, in the last decade, scientists have made remarkable strides toward preparing tailored CDs for targeted applications. The synthetic versatility of bottom-up procedures enabled the exploration of a vast parameter space that expanded the range of achievable core/surface chemistries and allowed optimization and tuning of properties. Recent work began to elucidate the importance of the rational use of available chemical strategies in dictating the relationship between chemistry and performance.[2] There

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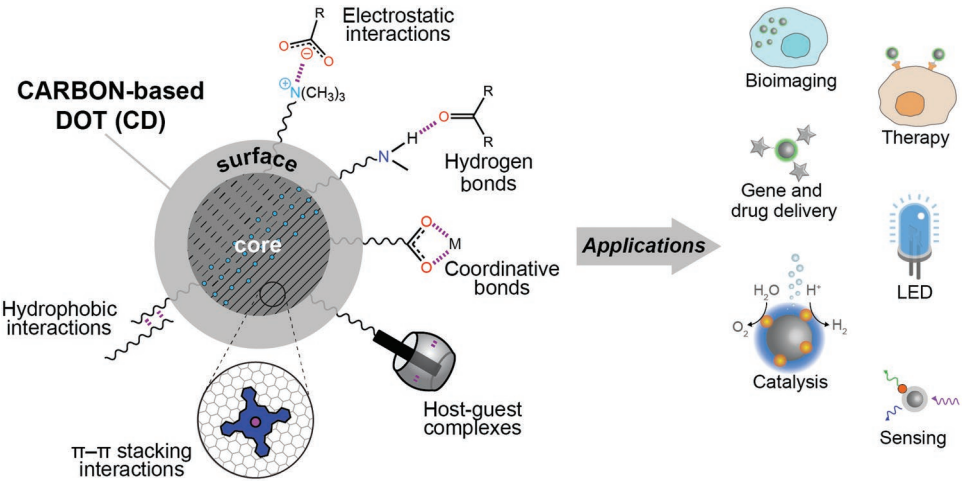

Figure 1. Overview of supramolecular interactions used for exploitation of carbon dots toward applications.

are significant opportunities to afford specific structures and/or properties for further applications, not only by starting with the appropriate reagents, but also by post-functionalization of the as-prepared nanomaterial.[14,15] Especially the choice of the precursors and reaction conditions in the bottom-up syntheses has a profound effect on the final structure and properties of CDs: surface groups,[2,16] optoelectronic and electrochemical properties,[17–27] chirality,[28–30] and so on.

Both core and surface of CDs therefore have their own set of interesting behavior and the advancements in their tuning made possible numerous functional architectures and applications. One promising strategy for creating versatile and functional systems based on CDs is to rely on the use of supramolecular interactions by taking advantage especially of their rich and easily tunable surface chemistry. One can also modulate the structure of the core to create the right combination of properties in hybrid materials or assemblies that integrate multiple functions. The result is that we can synergically combine individual features into more complex systems using non-covalent forces.

Here we discuss strategies to exploit supramolecular interactions for engineering properties and functions of carbon-based dots (**Figure 1**). We first introduce the non-covalent interactions most commonly employed in the field of CDs, providing a brief overview of electrostatic interactions, hydrogen bonding, coordinative bonds, host-guest complexes, and other weak non-covalent interactions. The following sections of the Review then discuss these supramolecular interactions individually by examining the progress in developing functional systems. While self-assembly has been occasionally used as the driving force for the synthesis of CDs,[31] to prepare model CDs for structural investigation,[32,33] to form aggregates useful for studying the fluorescence of CDs,[34,35] we limit our discussion to cases in which supramolecular interactions are used to create hybrid systems and/or impart CDs with novel functionalities. We focus on cases in which features arising from using this set of interactions mediate, influence, and improve biological and energy relevant applications (Figure 1). This Review aims to highlight ways that make supramolecular interactions attractive to expand the range of properties and applications of CDs-based materials.

2. Overview of Supramolecular Interactions and Their Characterization

Before going into detail of applied supramolecular chemistry in contemporary carbon dots research, this brief introduction intends to present some basic concepts to aid with the reading of this Review (**Figure 2**). Of course, it is not possible to give a comprehensive overview of supramolecular bonds and analytical methods to study them and, for a more in-depth discussion, the reader is thus referred to some excellent textbooks.[36,37]

Non-covalent bonds range from electrostatic and coordinative interactions with a strength of several hundreds of kJ mol^{-1} to weak van der Waals interactions of only a few kJ mol^{-1} (Figure 2a).[36,37] Attractive interactions occur when two charges interact with opposite polarity. The strongest bond energies are found for ion–ion interactions (≈100 to 350 kJ mol^{-1}), with the distance between the charges and the extent of delocalization dictating the strength of the attraction and with no particular directionality. Interactions between ions and dipoles (partial charges) are somewhat weaker (≈50 to 200 kJ mol^{-1}), with the orientation of the dipole with respect to the charge being important (eg. crown ether interaction with alkali metals, on occasion used by CDs for sensing purposes). Other strong interactions are found for coordination complexes and transition metal ions, but the covalent contribution of the dative bond blurs the line between supramolecular and molecular chemistry. One of the weakest non-covalent interactions are van der Waals forces (<5 kJ mol^{-1}) that occur between two or more neutral, but polarizable molecules and that can also result in formation of dipoles.

Hydrogen bonding includes a range of binding energies that span from strong (60 to 120 kJ mol^{-1}, with heteroatom to heteroatom distances of 2.2–2.5 Å), to moderate (15–60 kJ mol^{-1}, with heteroatom to heteroatom distances of 2.5–3.2 Å) to weak (≈15 kJ mol^{-1} and up to 4 Å distances). Strong hydrogen bonds are considered to have major covalent contributions, while moderate and weak ones are mainly electrostatic interactions. Strong hydrogen bonds are also highly directional (≈175–180°), while moderate and weak are more flexible (130–180° and 90–150°, respectively).

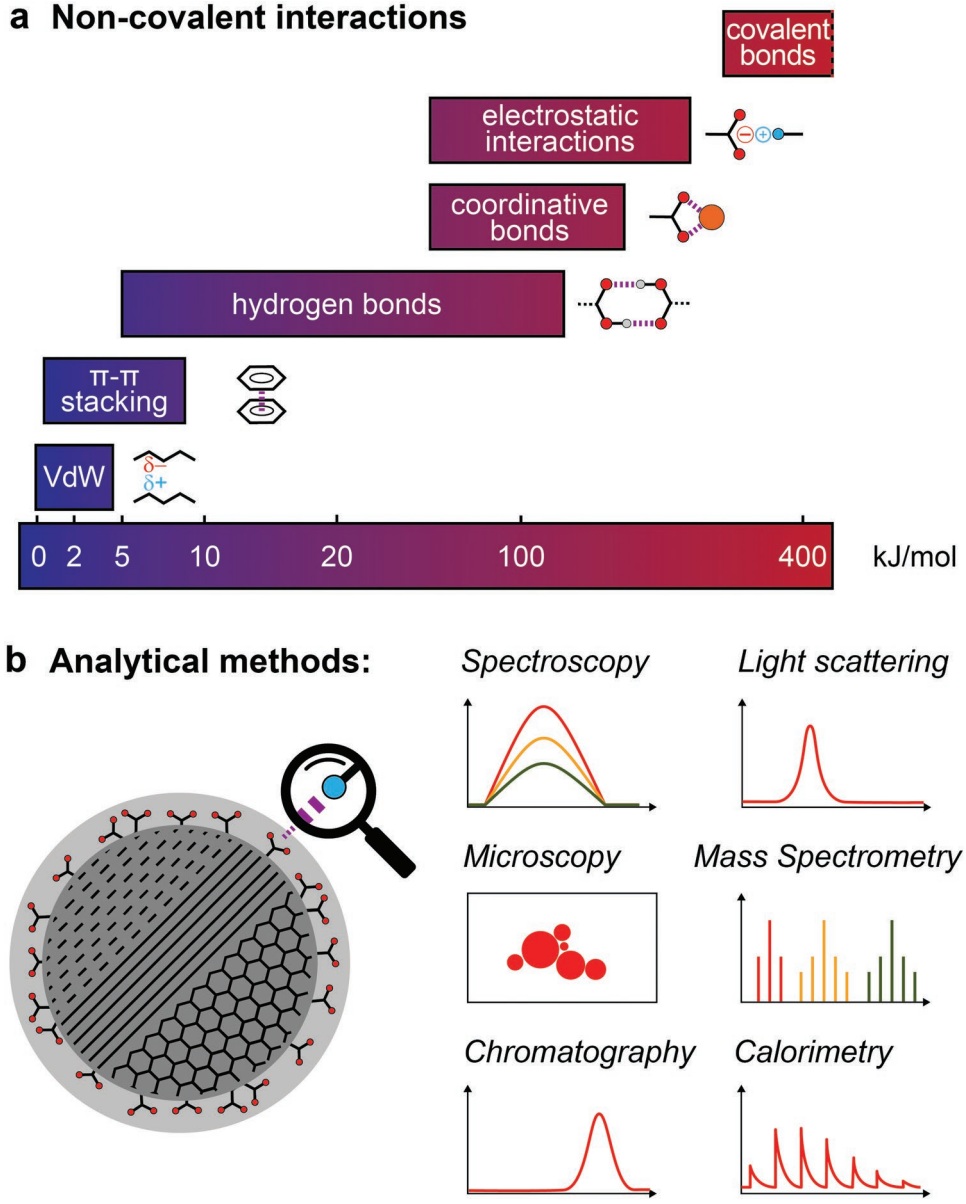

Figure 2. Overview of a) non-covalent interactions used in carbon dots research and b) common methods to characterize them.

Non-covalent interactions also include π-systems that can interact with other π-systems and cations. $\pi-\pi$ interactions, also called π-stacking, can occur either between two similarly electron-rich or -poor π-systems (but to reduce the repulsion between negative π-clouds they either stack in a herringbone orientation or shift sideway in face-to-face orientation) or between electron-rich and electron-deficient π-systems (they can undergo charge-transfer interaction which can be quite strong).

Finally, hydrophobic effects or interactions occur to minimize the surface between polar/protic and apolar/aprotic molecules, which is energetically unfavorable. For example, in host-guest systems there can be both enthalpic and entropic contributions: several water molecules inside an apolar cavity are easily replaced by an apolar guest since their interaction with other water molecules is much greater.

There are several analytical techniques to analyze non-covalent interactions (Figure 2b)[37–40] and some of them have already been discussed as characterization tools for carbon dots.[2] Spectroscopic methods, which include absorption, emission and NMR spectroscopy are frequently used to characterize supramolecular assemblies and CDs. If carbon dots interact through non-covalent bonds with other molecules, there might be changes either to the CDs ground or excited states, and these could be observed by UV–vis and fluorescence spectroscopies. Changes to the optical properties are also observed when CDs form assembly through interparticle interactions (sometimes called "supra-CDs") with spectroscopic methods revealing new photophysical properties that are absent in the individual nanoparticles.[41] Although a powerful technique for solution supramolecular chemistry, nuclear magnetic

resonance is not particularly suited for CDs because it needs either high concentrations of material or ^{13}C-labeled nanomaterials to observe signals (residual signals in diluted solutions are likely from low molecular weight impurities),[42] but it could still be used to observe broadening and signal shifting of the molecules with which CDs interact. Infrared spectroscopy could be particularly useful for studying CD supramolecular bonding as shifting, disappearance and appearance of certain vibrations would allow to discern the non-covalent driving forces between various functional groups.

When forming supramolecular assemblies of CDs or even composites with other materials, microscopy techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) have the potential to provide information about their morphologies. For example, high-resolution TEM images of dispersed and aggregated CDs ("supra-CDs") can be aquired.[43] Furthermore, the emission properties of CDs could be exploited in confocal fluorescence imaging.

Scattering techniques can provide high resolution structural and compositional information of the sample in the bulk solution. Particularly with regard to self-assembly of CDs in larger nanostructures or interaction with (supra)molecular polymers, light scattering and small-angle scattering can provide detailed structural information.

Other techniques that could be particularly useful for the characterization of carbon dots-based supramolecular materials, but are still relatively unexplored, are chromatographic techniques, mass spectrometry and calorimetry. In particular, size exclusion chromatography could enable the determination of representative molar mass or size value of the assemblies.

2.1. Electrostatic Interactions

Carbon dots, compared to other nanomaterials, present a high water solubility, even in as-prepared materials. This is due to abundant surface groups that can easily carry charged groups. For example, a surface rich in amino groups can be protonated in water and carry ammonium charges, which can be exploited to interact with negatively charged molecules, polymers and inorganic nanomaterials. Likewise, CDs with surface carboxylic acids can be deprotonated to carboxylates, which will attract positively charged compounds.

Attraction between opposite charges was found to be very important for electronic communication between CDs and other molecules and materials. In one study, a palette of porphyrin derivatives was used to study their effect on CD photophysical properties (**Figure 3**a).[44] It was found that changing the charge had the most profound effect on donor-acceptor interactions, leading to the conclusion that electrostatic interactions (rather than coordination or $\pi-\pi$ stacking) were the driving force for the formation of donor-acceptor systems. This approach to form donor-acceptor systems was proven versatile and was used to prepare more CDs-porphyrins,[30,54] CDs-perylene diimides,[55] CDs-phthalocyanines,[56] CDs-carbon nanotubes,[57,58] CDs-carbon nitrides,[59] and CDs-polyoxometalate systems.[61–63]

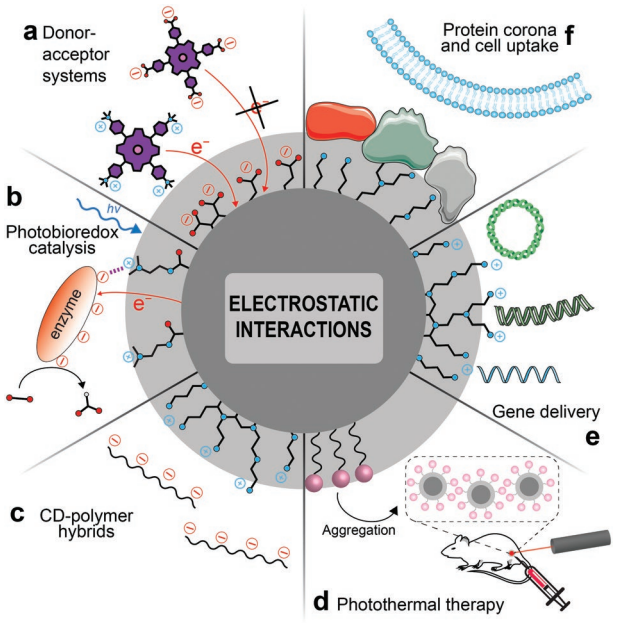

Figure 3. Electrostatic interactions enable carbon dots utilization a) for the development of electron donor-acceptor systems,[44] b) in photo(bio) redox catalysis,[45] c) for interaction with covalent and supramolecular polymers,[46] d) in self-aggregation for photothermal therapy,[47,48] e) for gene delivery,[49–51] and f) for interfacing with proteins and cells.[52,53]

Since electrostatic interactions could improve electronic communication by bringing photosensitizers and catalysts closer together, they were naturally exploited in photo(bio) catalysis (Figure 3b).[64] For example, ammonium-terminated surface functional groups on CDs were found to interact with the negatively charged surface of enzymes, enabling efficient electron transfer from the CD sensitizer to the formate dehydrogenase catalyst for the photocatalytic CO_2 to formate reduction.[45,65] Complementary charges between CD photosensitizers and enzymes,[66] electron mediators,[67] micelles/coacervates,[68–70] and other catalysts[71–73] further proved the importance of this approach in catalysis.

Ionic bonding has also been extensively studied for the formation of CD-polymer composites (Figure 3c). It has been reported that negatively charged CDs interact with cationic covalent polymers such as polypyrrole,[74] chitosan,[75,76] poly(diallyldimethylammonium chloride) (PDDA),[77,78] among others. Interesting is the use of PDDA because it has allowed immobilization of CDs[77] and preparation of coacervates.[78] Likewise, positively charged CDs can form ionic bonds with anionic polymers, such as polystyrene sulfonate.[79] Beside making ionic bonds with covalent polymers, CDs could also interact with supramolecular polymers. In these examples, the co-assembly allowed to tune the CDs emissive properties through interaction of negatively charged nanoparticles with cationic supramolecular polymers[80] and endowed positively charged CDs with circularly polarized luminescence by bonding with anionic chiral peptide hydrogelators.[81]

Some CDs can self-assemble through electrostatic interactions, with the resulting so-called "supra-CDs" featuring absorption into the visible to near-infrared (NIR) range, which

can be exploited for photothermal therapy (Figure 3d).[43,47] Also co-assembly of positively charged CDs with negatively charged amphipathic sodium dodecyl benzene sulfonate has been observed to lead to supra-CDs structures with efficient NIR absorption, which could be utilized for photodynamic therapy through $^1O_2$ photosensitization.[48] For bio-related applications, such as imaging, co-assembly of CDs with other nanomaterials has also been proven as a successful approach.[82–85]

It is also common to co-assemble charged drugs and biomolecules with CDs to prepare drug and gene nanosystems (Figure 3e). The negatively charged backbones of DNA[49,60,86–88] and RNA[50,51,89,90] have been shown to assemble with a variety of positively charged CDs, which allowed not only gene editing, but also bioimaging through the emissive properties of the nanoparticles. The affinity to bind RNA by CDs was exploited with the red emissive properties of the latter, which could be used both for imaging the nucleolus (where RNA transcription occurs) and for photodynamic therapy through photosensitization for $^1O_2$ production.[91]

Various drugs have been reported to load, through complementary charges, on carbon dots-based nanodelivery systems. Although it is still unclear what are the driving supramolecular forces with which drugs bind to CDs (eg. doxorubicin has been reported to load through electrostatic, $\pi-\pi$ stacking and hydrophobic interactions, see also below),[92,93] it is also important to devise treatment strategies that take advantage of the carbon dots emissive properties.[94–97]

The surface charge on CDs was found to influence protein corona formation and cell uptake (Figure 3f).[52,53,98] More specifically it was observed that CDs with high ζ-potential and charge density are much more readily internalized by cells leading to loss of their viability. The surface charge had therefore an impact on the proteins bound to the CD, which in turn drove the cellular uptake and ultimately the toxicity.[52,99]

Ionic bonds between carbon dots and charged inorganic nanomaterials is also an effective approach to prepare organic–inorganic nanocomposites. For example, CDs could be combined with gold nanoclusters to achieve intracellular temperature detection,[100] with 2D transition metal carbides (MXenes) to prepare supercapacitors,[101] or with tungsten disulfide to prepare electrochemical sensors.[102]

2.2. Coordination Bonds

Coordination complexes capitalize on metal-ligand interactions and enable combining metal ions with carbon-based dots. Surface groups on as-prepared CDs, especially amines, can be used to directly coordinate metals, but further post-functionalization of CDs with ligands can aid formation of specific complexes. Both approaches have enabled complexation of numerous metals toward tailored applications.

Most frequently, coordination bonds between CDs and metals were used for sensing of various metal ions. For example, the surface groups of as-prepared CDs were exploited for sensing of Mg^{2+},[109] Fe^{3+},[110–112] Ni^{2+},[113] Cu^{2+},[114–117] Ag^{+},[118] Hg^{2+},[119–121] and Pb^{2+},[122] among others. While as-prepared CDs can show selective metal detection, this is mostly observed through extensive empirical testing. Post-functionalization of the CDs surface can be used to design coordination sites for specific metals and, in this way, bring some rational design to metal sensing by CDs.[123–126] For example, by covalently attaching a quinoline derivative to CDs, a highly specific recognition site for Zn^{2+} was developed (**Figure 4**a).[103] CDs post-functionalized by coordinating metals have also been employed as sensor for various organic analytes.[127,128] Commonly, metal coordination causes CDs fluorescence quenching, which can be restored if the analyte binds to the metal that was causing the quenching (also known as "off-on fluorescence probes").[129–131] One example are CDs with carboxylate groups that can bind Eu^{3+} resulting in fluorescence quenching, but upon addition of phosphate the fluorescence can be restored.[132]

The surface functional groups of CDs were used either directly, after the synthesis, or after post-synthetic functionalization to coordinate metal complexes and, in this way, the use of CDs in catalytic transformations that are dictated by the metal has been enabled (Figure 4b).[133,134] For example, CDs with an amine-rich surface were proposed to coordinate a nickel bipyridine complex, which enabled the use of these hybrids in photoredox-mediated Ni-catalyzed cross-coupling between aryl halides and nucleophiles.[104] It was reported that the photo-excited state of CDs underwent dynamic quenching by the Ni co-catalyst, suggesting that direct coordination to catalysts can be used to overcome the short photoluminescence lifetimes of CD photosensitizers. The surface of CDs could be tailored through pre-synthetic reactions and endow the surface with ligands for specific interactions (Figure 4c). One such example is the pyrolysis of citric acid and histidine, which yielded CDs possessing histidine groups. Inspired by natural peroxidases,

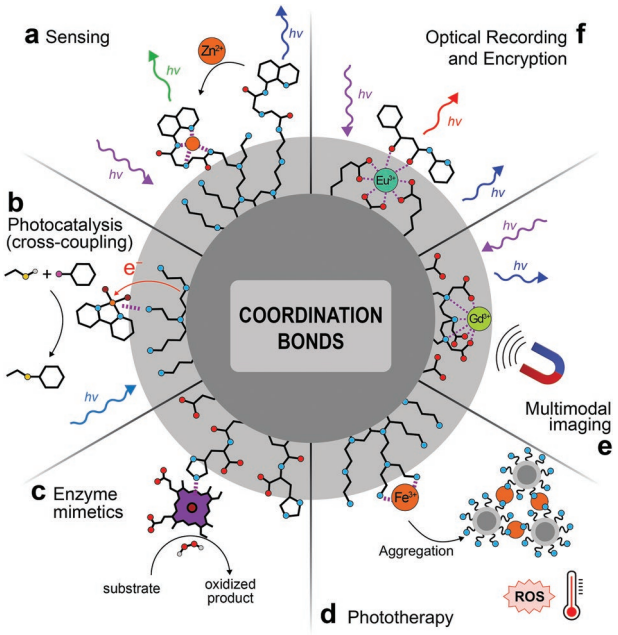

Figure 4. Coordinative bonds have been exploited a) to sense ions,[103] b) in photocatalysis,[104] c) to prepare enzyme mimetics,[105] d) to promote aggregation and reactive oxygen species generation,[106] e) to develop magnetofluorescent imaging agents,[107] and f) to prepare stimuli-responsive composites with lanthanides.[108]

these CDs could coordinate hemin (an iron-containing porphyrin) and the resulting hybrid material showed peroxidase mimetic activity in presence of hydrogen peroxide.[105] The surface of CDs could be used not only to coordinate metal ions, but also to covalently attach nucleic acid for selective binding of certain targets (aptamers).[135] In this way, the substrate can be localized close to the reactive metal center thus improving the reaction rates.

Some metals, like iron and copper, can mediate catalysis for the generation of reactive oxygen species (ROS) and this can be leveraged for therapeutic purposes (Figure 4d). Fe^{3+} can be directly anchored to the carboxylate surface groups of CDs and, in presence of hydrogen peroxide, can catalyze the efficient formation of hydroxyl radicals.[133] In presence of high Fe^{3+} concentrations, the coordination can also lead to aggregation between CDs forming bigger nanostructures (sometimes called "supra-CDs").[106] In addition to the chemodynamic therapy function enabled via the Fe^{3+}-mediated Fenton reaction, the intrinsic photosensitization properties (for photodynamic and photothermal therapy) and fluorescence (for imaging) of CDs, enabled the preparation of multifunctional theranostic nanoplatforms. Coordination sites on amine-rich CDs were also exploited for coordination to Cu^{2+} and to photo-mediate the production of ROS.[136] CDs, in this case, could be used to chelate copper from Cu-aggregated β-amyloid peptides, thought to be the toxic species in the neurodegenerative Alzheimer's disease. Besides hindering the stacking of Aβ peptides, irradiation of the luminescent CDs/Cu composite could cause the photochemical degradation of the peptides through production of ROS.

Combining the fluorescence properties of carbon dots with paramagnetic Gd^{3+} chelates is an interesting opportunity to prepare magnetic resonance/fluorescence multimodal nanomaterials (Figure 4e).[107,137–138] Besides the use of gadolinium, the coordination of lanthanides was also exploited in the modulation of CDs luminescence that can have applications as multidimensional memory and encryption materials (Figure 4f).[108,139] In one example, an europium complex was bridged between CDs surface functional groups and an amide-type β-diketone ligand.[108] Since the ligand energy levels can be modulated by acid/base vapor, resulting in changes to the hybrid fluorescence emission and lifetime, this could be exploited in fabrication of data storage patterns and their encryption.

2.3. Hydrogen Bonding

The abundant hydroxyl, amine and carbonyl surface groups on CDs offer numerous sites for hydrogen bonding, which have been exploited either for aggregation of CDs or preparation of hybrid materials (combining CDs with other organic or even inorganic compounds). Hydrogen bonding between the CDs surface groups and solvent molecules has been observed to change the emission wavelength and intensity for various reasons that are strongly related to the carbon dot structure.[140–143] Similarly, forming hydrogen bonds between nanoparticles toward self-assembly of CDs ("supra-CDs"),[41] as well as with other chromophores,[144,145] polymers,[146–152] biomolecules[153,154] and inorganics has also been studied.[155,156] This allowed changing the CDs photophysical properties and endowing them with new possibilities in energy-related and biological applications.

It is commonly observed that, when CDs undergo self-assembly at high concentrations or even solid state, the fluorescence undergoes quenching.[162] A common approach to avoid the aggregation-induced quenching of CDs emission is to disperse them in matrices, such as polymers.[150–152] Hydrogen bonding between the polymer backbone and CDs has thus allowed preparation of composite materials that not only fluorescence but also improve the mechanical properties.[146–149] The fluorescent polymer hybrids have been employed in anti-counterfeiting,[163] phototherapy,[164] bioimaging,[165] and capacitive sensors[166] applications.

There are, however, some examples where CDs have shown interesting properties without the need of dispersing them in a matrix (**Figure 5**a).[167] In one such example, CDs with boronic acid functionalized edges enabled lateral hydrogen bonding and self-assembly into 2D nanosheets, resulting in interesting optoelectronic properties.[157] The nanosheets, although were embedded in a polystyrene matrix that did not interact with them, could be used to prepare solar concentrators with high power conversion efficiencies. Similarly, CDs with heptazine units were found to undergo lateral hydrogen bonding through the abundant amine and imine surface groups (Figure 5b).[158] In addition to allowing film formation, hydrogen bonding was also proposed to aid the catalytic electroreduction of N_2 to NH_3, by stabilizing reaction intermediates. In another example, CDs have shown matrix-free room temperature phosphorescence in the solid state.[143] The abundant amino and hydroxyl

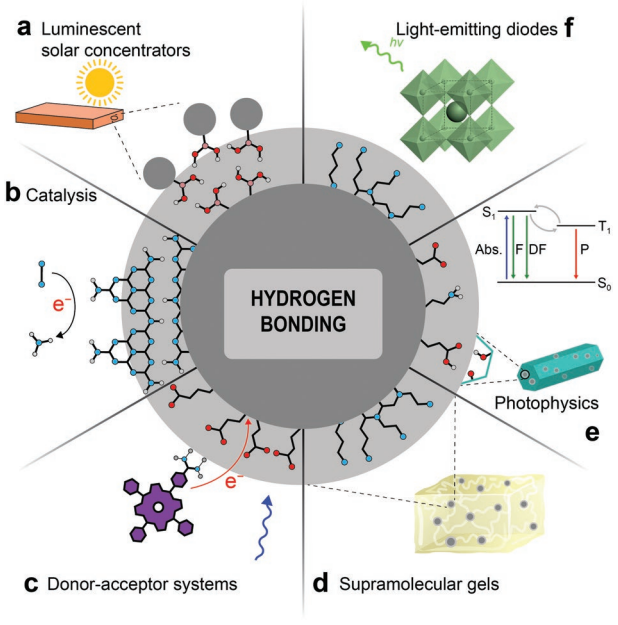

Figure 5. Hydrogen bonding has been useful a) to prepare aggregated CDs for luminescent solar concentrators,[157] b) to develop (electro) catalytic materials,[158] c) to prepare CDs-based electron donor-acceptor systems,[144] d) to assemble supramolecular gels with antioxidant properties,[159] e) to confine CDs in zeolites and generate thermally activated delayed fluorescence materials,[156] and f) to prepare CDs/perovskite hybrids for light-emitting diodes and solar cells.[160,161]

surface groups, resulting in a hydrogen bonded framework in the solid state, were proposed to stabilize the triplet excited state and decrease the non-radiative transitions of triplet excitons, resulting in ultralong afterglow.

The surface groups on CDs can also be used for the co-assembly with other molecules or monomers able to form supramolecular polymers. In one example, the carboxylate CD surface groups were used to form hydrogen bonds with an amidine-functionalized porphyrin (Figure 5c), and the resulting donor-acceptor system featured a charge transfer interaction in the ground state and charge recombination in the excited state.[144] A donor-acceptor hybrid could also be formed through hydrogen bonding between CDs and perylene diimide supramolecular polymers, which helped with photocurrent generation through charge separation.[145] CDs were also incorporated through hydrogen bonding into ionogels (Figure 5d), with their presence improving the mechanical properties of the supramolecular gels and also endowing them with antioxidant properties.[159] The blue emission of CDs could also be utilized with red- or blue-emitting lanthanide monomers to form white-emitting supramolecular materials.[168,169] Co-assembly through hydrogen bonds has been also shown to affect the luminescence properties of CDs, from inducing long-lived room temperature phosphorescence to generating circularly polarized luminescence.[170,171]

Hydrogen bonding has also allowed CDs to interact with inorganic materials (such as perovskites, gold nanoparticles, TiO_2, among others) for the preparation of organic–inorganic composites.[155,156,160,161,172–174] Especially the confinement of CDs within inorganic matrices through hydrogen bonding has been shown as an effective strategy to modify their luminescence properties. In one case, confining CDs in zeolites enabled the stabilization of the triplet states for reverse intersystem crossing processes that yield thermally activated delayed fluorescence (Figure 5e).[156] Enclosing CDs in hydroxy fluorides was also effective in stabilizing the triplet state and promoted room temperature phosphorescence.[155] Hydrogen bonding was also exploited to prepare CDs/perovskites composites (Figure 5f) in which, rather than take advantage of CDs fluorescence, the carbon dots served to improve the stability of the materials and enabled efficient charge transfer between device layers.[160]

2.4. Host-Guest Interactions

Host-guest interactions in the CDs area were mainly used for recognition and sensing of analytes,[175–179] as containers for fluorescent molecules or drugs,[180,181] and to promote photoinduced electron transfer (**Figure 6**a–c).[182,183]

For enabling CDs to participate in host-guest interactions, the surface groups of the nanoparticles are commonly post-functionalized either covalently with crown ethers, cyclodextrins and others[175] or by employing other supramolecular interactions to assemble the CDs with cucurbituril and calixarenes.[179,183] There are also reports on using cyclodextrins, calix[n]arenes, and cucurbit[n]urils as starting materials for the synthesis of carbon dots,[175] but these inevitably lead to chemical modification of the host structure, which could be detrimental for the formation of host-guest complexes.

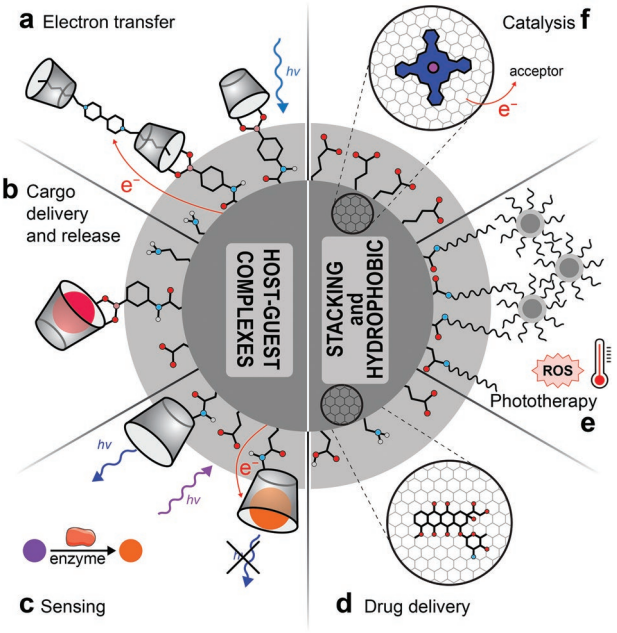

Figure 6. Supramolecular CD-based systems for a) electron transfer,[182] b) cargo delivery,[180] c) sensing,[176] d) drug delivery of polycyclic aromatic compounds,[184] e) phototherapy,[185,186] and f) (photo)catalysis.[187]

For applications in sensing, drug delivery and electron transfer, the CD-host system needs to take advantage of the nanoparticles' fluorescent properties and, once a guest is present, the fluorescence needs to be quenched (Figure 6a,b). For example, CD/α-cyclodextrin hybrids could encapsulate methyl viologen derivatives, which acted as acceptor in the photoinduced electron transfer from CDs and allowed formation of aggregated nanostructures.[182] The fluorescence quenching could also be used to develop more sophisticated systems or assays (Figure 6c). In one such example, CD/β-cyclodextrin prepared through amidation reaction between surface carboxylates and 6-amino-β-cyclodextrin, were used to develop fluorometric glycosidases assay.[176] Glycosidase enzymes cause hydrolysis of *p*-nitrophenol glycoconjugate, with the resulting *p*-nitrophenol now able to act as guest for the CD/β-cyclodextrin hybrid. The formation of the inclusion complex causes quenching of the CDs' fluorescence, which was shown to be selective and could be correlated with the enzymatic activity.

2.5. Other Non-Covalent Interactions

Besides the non-covalent interactions discussed so far, other types of supramolecular interactions are less utilized or, at least, the identification and characterization of $\pi-\pi$ stacking, hydrophobic and dispersion interactions are much more difficult. Part of the difficulty is in the uncertainty of the CDs chemical structure, which also makes discrimination between weak supramolecular forces challenging. These issues, however, have not stopped researchers from developing systems containing CDs that could be potentially applied in various fields (Figure 6d–f).

Similar to other non-covalent interactions mentioned above, $\pi-\pi$ stacking and hydrophobic interactions were exploited for sensing of various analytes. For example, polycyclic aromatic hydrocarbons could interact with CDs and, as a result, cause fluorescence quenching that could be exploited for preparation of sensors.[188] Aptamers (artificial DNA or DNA that can bind selectively to targets) were loaded on CDs, which caused fluorescence quenching of the nanoparticles.[189] In presence of the aptamer target, the fluorescence could be recovered. Similarly, aptamer-functionalized CDs were found to undergo fluorescence quenching only when adsorbed on graphene oxide.[190] Upon presence of the aptamer target, the assembled hybrid is broken down, causing recovery of the fluorescence.

Some hydrophobic drugs, such as doxorubicin and dihydroartemisinin, can be used in chemotherapy and to treat cancer. These drugs are thought to establish $\pi-\pi$ stacking or hydrophobic interactions with the π-structure of CDs (Figure 6d). While difficult to identify these interactions, the approach of combining CDs with these hydrophobic drugs in "nanoassemblies" has shown drug delivery properties and antitumor efficacy.[186,191] To differentiate from other well-studied delivery nanosystems, the CDs-based assemblies should take advantage of nanoparticle properties for the construction of multifunctional nanotherapeutic systems. For example, the surface of CDs can be first functionalized to carry targeting ligands and peptides, and then the drugs (eg. doxorubicin) can be loaded through $\pi-\pi$ stacking or hydrophobic interactions.[192,184] In other examples, the emission properties of CDs could be used for fluorescent imaging,[193] in addition to their gene/drug delivery properties.[191,194] In one case, to promote loading with hydrophobic drugs, the amine surface groups of CDs were functionalized with 2-((dodecyloxy)methyl)oxirane, leading to hydrophobic modification of CDs (Figure 6e).[194] The concept of multifunctional nanotherapeutic systems was taken even further by preparing CDs, starting from a manganese(II) phthalocyanine, which then were assembled through hydrophobic interactions with a phospholipid-PEG conjugate.[195] This nanoassembly could be applied as a dual contrast agent, due to its fluorescence emission and high paramagnetism of Mn(II), as well as to generate efficiently $^1O_2$ for photodynamic therapy.

Catalytically-active molecules and nanomaterials could also interact with carbon-based dots to promote water photoreduction or -oxidation reactions.[187,196] In one example, a supramolecular CDs/copper phthalocyanine hybrid (Figure 6f), was then coupled with bismuth vanadate ($BiVO_4$) for photocatalytic water oxidation.[187] In this hybrid, graphitic-CDs were found to facilitate the electron transfer rate and separation efficiency of photoinduced charge carriers: the electrons are transferred by the CDs to copper phthalocyanines to react with sacrificial electron donors, while the hole on $BiVO_4$ reacted with water to produce O_2. In another example, weak interactions between the CDs surface groups and the substrate (through halogen bonding) were hypothesized to aid carrying out photocatalytic reactions.[197,198]

Interactions like $\pi-\pi$ stacking and hydrophobicity were used also for nanostructuration of CDs into fibers.[192,199–200] To study the effect of edge-functionalization on CDs nanostructuration, the surface carboxylates were functionalized with cholesteryl, naphthyl or pentadecanyl substituents.[199] The CDs with cholesterol were found to self-assemble into bilayer vesicles, while naphthyl substituents were found to form fused vesicular aggregates, and pentadecanyl CDs promoted further fusion of vesicles into fibrillar network. Nanostructuration of CDs into fibers could also be accomplished if they stack on top of each other and elongated into a 1D structure. Especially CDs with extended π-conjugated surfaces, such as CDs made of single layer graphene (or graphene quantum dots), could form $\pi-\pi$ stacking between the graphene planes of the nanomaterial.[192,201] CDs were indeed found to self-assemble into fibers through $\pi-\pi$ stacking interactions, possibly aided by edge-functionalization which could give additional hydrogen bonding and stacking interactions.[192] By leveraging weak supramolecular interactions it was possible to self-assemble CDs also into polymorphic nanocrystals.[202] By carefully tuning the solvent composition and by edge-functionalization of CDs with alkyl chains, attractive van der Waals forces were identified as responsible for the formation of carbon dots crystals.

3. Conclusions and Perspectives

We have covered a set of works to demonstrate advantages and opportunities in exploiting the palette of supramolecular interactions at our disposal to engineer CD-based materials. We have described here the advancements in functional systems that make use of supramolecular interactions and have greatly expanded the range of possible applications of CDs.

The vast scope of synthetic methods for CDs now available permits tuning their core and surface properties. Rational design of the surface functional groups is especially critical to access the set of structural features that can promote supramolecular interactions. There are many demonstrations of using the rich surface chemistry to mediate interactions with other nanomaterials, molecules and polymers, which include, for example, making the surface charged or decorating the surface with coordination sites. The resulting systems could either combine distinct features of the single units into multifunctional platforms or synergistically integrate these features to unravel new and unique properties absent in the individual components. These possibilities have been particularly attractive for applications such as conversion or storage of energy (eg. photocatalysis, electrocatalysis, and supercapacitors), optical sensing and imaging, and theranostics.

Future advances hinge on solving the current and consistent challenges of this fast-evolving area of research. To move this field forward, emphasis should be placed on providing guidelines for the rational design of CDs. While many efforts have been focusing on expanding the synthetic opportunities and properties, the standardization of synthetic and purification protocols is a key area that needs further efforts. To complicate things further, it has become apparent that the application of CDs has progressed more quickly than has the understanding of their structure and formation. Another observation is that more is needed to gain relevant insights into the origin and mechanism of relevant properties of CDs, such as their fluorescence. Accomplishing this is not an easy task and also requires further mechanistic studies. It is now important that scientists

work on these intricacies and unanswered questions and learn how to in-depth characterize the core and surface chemistry. A practical starting point is to plan to perform analytic work, that is, using standard, well-established but also targeted analytical methods, to elucidate structure and composition of CDs and to do so systematically when reporting a new CD material. These studies are critical in developing synthesis able to (re)produce high-quality materials and understanding CD properties. Further understanding of CD structure, composition and properties will enable us to fully exploit CDs for functional architectures. These advances could offer untapped potential to use the unique properties of this attractive class of materials and the unique features of non-covalent interactions for the realization of novel and sophisticated architectures that can enrich current applications and promote new ones.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon dots, nanoparticles, nanotechnology, non-covalent interactions, self-assembly, supramolecular chemistry

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