

## One-step microwave-assisted green synthesis of luminescent N-doped carbon dots from sesame seeds for selective sensing of Fe(III)

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The present study focuses on the green synthesis of nitrogen-doped carbon dots (C.dots) from sesame seeds using microwave pyrolysis method. The C.dots obtained were characterized and extensively studied using transmission electron microscopy (TEM), UV/visible spectroscopy, fluorescence spectroscopy and Fourier transform infra-red spectroscopy (FTIR) techniques. The results indicated the presence of highly fluorescent, aqueous soluble and significantly photostable C.dots with a quantum yield of 8.02%. The average size distributions of C.dots were found to be 5 nm. These C.dots were effectively applied as a selective sensor for Fe(III) as the fluorescence intensity was significantly quenched with increasing metal concentrations. The limit of detection (LOD) was found to be 2.56  $\mu\text{M}$  of Fe(III). This study demonstrates a low cost, environmental friendly and waste recyclable synthetic method for preparation of C.dots and its application as a selective Fe(III) sensor.

**Keywords:** Carbon dots, fluorescence, sesame seeds, microwave pyrolysis, metal ions, quenching.

CARBON DOTS (C.dots) are gaining increasing attention within the carbon nanomaterial family due to their varied applications in biological, sensing, optical and electrical fields<sup>1-3</sup>. They are swiftly replacing the conventional semiconductor nanoparticles (Q.dots) which have raised serious health and environmental concerns because of the presence of heavy metals in it<sup>4</sup>. C.dots are spherical, oxygenous carbon nanoparticles with size below 10 nm. C.dots akin to Q.dots show several interesting properties such as excitation-dependent emission, chemical and photostability, enhanced fluorescence quantum yields and the possibility of fine-tuning the sensing properties by surface modification<sup>5-11</sup>. It can be synthesized from non-toxic, cheap and environmental friendly molecular precursors<sup>12</sup>. Peng *et al.*<sup>13</sup> used glucose, Yang *et al.* used sucrose and citric acid<sup>14</sup>, Sun *et al.* used pomelo peel<sup>15</sup> and willow bark<sup>16</sup>, Zhou *et al.* used milk<sup>17</sup>, etc. to synthesize C.dots. Several strategies have been demonstrated for the synthesis of C.dots, of which laser ablation, electrochemical oxidation, chemical oxidation, thermolysis, microwave, ultrasonication methods, etc. are some of the widely used methods<sup>18-24</sup>.

In order to improve the photophysical and photochemical properties of C.dots, hetero-atom doped C.dots are synthesized by different ways. Among them, nitrogen-doped C.dots received much attention because of their good biocompatibility and the related broad applications in the areas of bio-imaging, electrocatalysis and sensors<sup>25,26</sup>. However, most of the synthesis methods reported so far have either a long reaction time or a need of extra chemicals for doping. Thus, synthesizing N-doped C.dots in a cost effective and ecofriendly manner and using them for sensing applications, especially for biologically active and environmentally hazardous metal ions will be highly beneficial.

Iron is an essential element for many biological processes<sup>27</sup>. The presence of iron in body either at higher levels or at lower levels can lead to several problems which eventually disturbs the lipid metabolism and glucose levels<sup>28</sup>. Therefore, quantitative determination of bioactive iron is an important health care challenge. Some studies have already been reported in this direction; Qian *et al.*<sup>29</sup> used the N-doped C.dots for detection of Fe(III). Wang *et al.*<sup>30</sup> used a wide variety of green carbonaceous precursors like milk, silk, honey, hair, lemon, etc. to detect Fe(III).

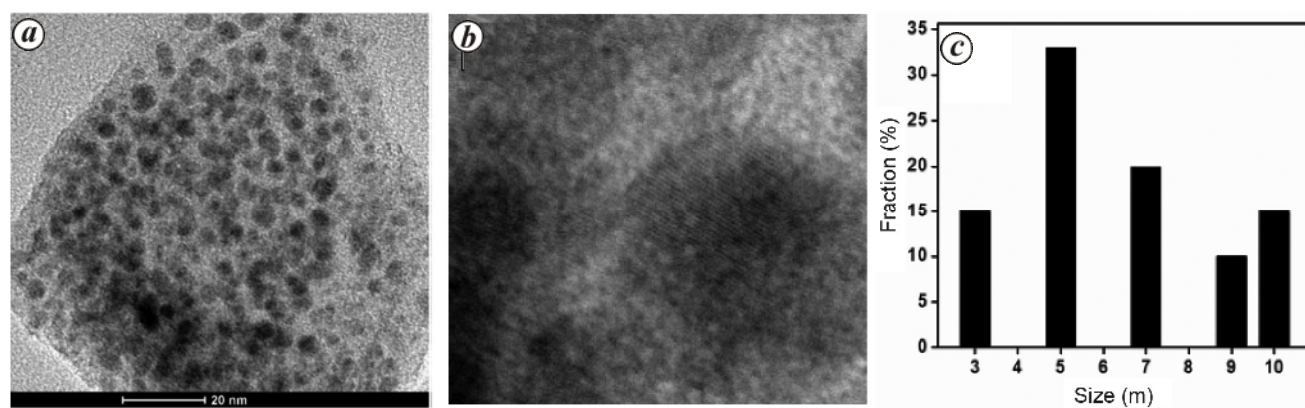
The present study demonstrates a green approach towards synthesis of N-doped C.dots from sesame seeds using low-cost and energy-efficient microwave-assisted pyrolysis. The fluorescence properties and photostability of C.dots are evaluated. These C.dots will be used to understand the metal sensing properties especially for Fe<sup>3+</sup>.

Sesame seeds, without any preservatives, are used as the molecular precursor. A.R. grade cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ ), calcium sulphate ( $\text{CaSO}_4$ ), cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), magnesium sulphate ( $\text{MgSO}_4$ ), nickel nitrate ( $\text{Ni}(\text{NO}_3)_2$ ), ferrous sulphate ( $\text{FeSO}_4$ ), ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3$ ), manganese sulphate ( $\text{MnSO}_4$ ), zinc sulphate ( $\text{ZnSO}_4$ ), sodium chloride ( $\text{NaCl}$ ),  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  were bought from S.D. Fine Chemicals. Water distilled thrice was used for all experiments (conductance  $\sim 0.18 \mu\Omega$ ). Phosphate buffer solutions of different pH were prepared using different combinations of 1 M  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and 1 M  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ . Quinine sulphate procured from SDFCL (suitable for fluorescence) was used for quantum yield measurement.



**Figure 1.** Digital image of sesame seeds before microwave irradiation and the photograph of C.dots dispersed in water on excitation at 364 nm under UV light.

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**Figure 2.** (a) TEM, (b) HR-TEM and (c) size distribution of C.dots produced by microwave irradiation of sesame seeds.

For the synthesis of C.dots, sesame seeds were irradiated with microwave radiation using a domestic microwave oven (800 W) (LG-MS-2029UW). UV-visible spectrophotometer (Shimadzu) and spectrofluorimeter (Jasco FP-8300 with 150 W Xe lamp) were used to record the absorbance and fluorescence respectively. The absorbance of C.dots was recorded from 200 to 600 nm. C.dots have excitation wavelength at 365 nm and emission in the range of 375 to 650 nm. Slit width was kept constant at 2.5 nm for both excitation and emission scans and the scan rate was maintained at 1000 nm/min. Absorbance of all the solutions was kept below 0.1 at excitation wavelength to reduce errors due to inner filter effects. Functional groups on C.dots were characterized using infrared spectrometer (FTIR-8400, Shimadzu). For physical characterization of the synthesized C.dots, a transmission electron microscope (TEM, model TECNAI G2-20 U-Twin) of 200 kV was used. TEM samples were prepared by drop-casting the aqueous solution on a carbon coated copper grid. FL-TCSPC fluorescence spectrometer (Horiba Jobin Yvon Inc. France) with picosecond laser diodes as excitation source was used to record the fluorescence lifetime measurements. IBH-DAS6 software was used for decay fitting. The energy-dispersive X-ray spectroscopy (EDS) (EDAX-FP 9761/72, RTEM-2SUTW, 200kV UT) was employed for elemental composition analysis on C.dots.

Sesame seed is one of the oldest oil seed crops known with a high oil content and rich source of carbohydrate and protein. Luminescent C.dots are synthesized from sesame residue, which usually is a waste product and is discarded after removing the sesame oil from sesame seeds. Cost-effective, time-saving and green synthesis of C.dots was performed by microwave irradiation method on the sesame seeds.

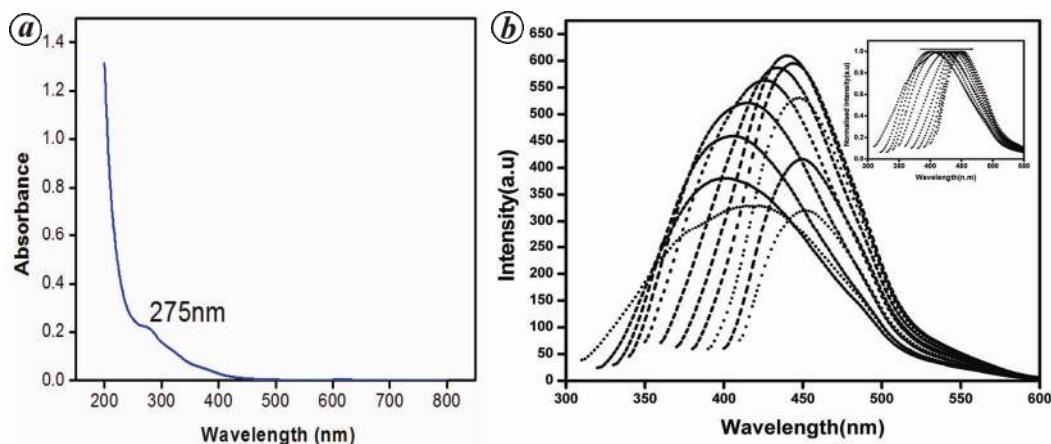
In a typical process, one gram of sesame seeds was washed thoroughly with water and air-dried. These were then kept for microwave treatment for about 10–15 min. The microwave irradiation results in efficient and uniform heating thereby higher temperature is easily

obtained to initiate the synthesis<sup>23</sup>. This results in carbonization of sesame seeds (Figure 1). The sesame oil separated during the process and a carbonized residue was left behind. This residue was ground well and dissolved in water and centrifuged at 8000 rpm for 15 min to get highly fluorescent supernatant liquid with large agglomerated particles which was discarded. This lyophilized sample is highly dispersible in water and shows deep blue fluorescence on irradiation with UV light. Finally, the test solution was prepared with a concentration of 10 mg/ml for further characterization and application.

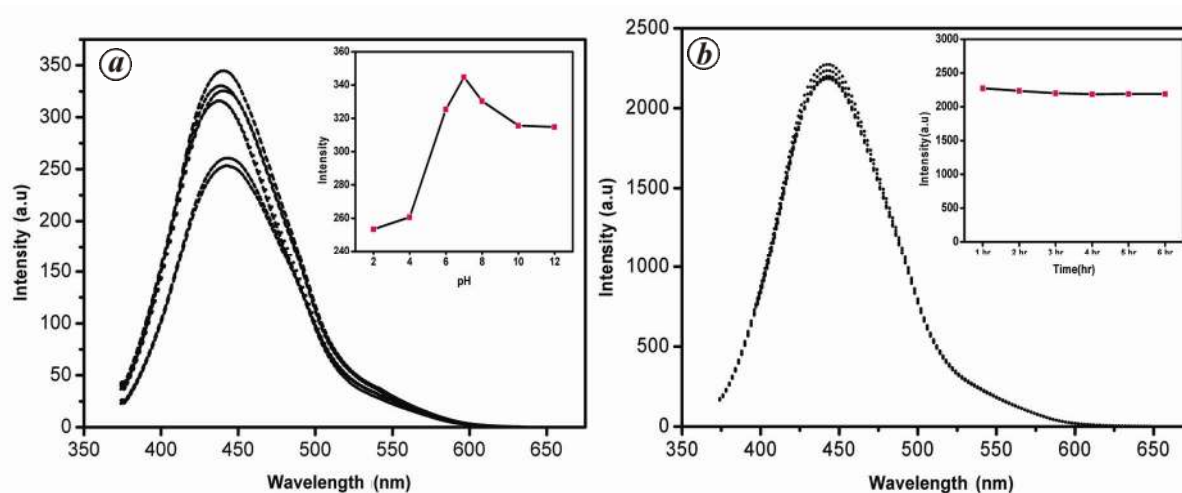
Figure 2a and b shows the TEM and HRTEM images of C.dots obtained from sesame seeds which contain nanodots with spherical morphology. Figure 2c shows the histogram of particle size distribution of C.dots. It is obvious that C.dots size distribution falls in the range 3–10 nm.

The elemental composition of the carbon dots was determined. The C.dots obtained were found to contain C, N, O and S with relative percentage composition of 96.37, 2.05, 1.54 and 0.03 respectively. In order to identify various possible functional groups on the C.dots, FT-IR spectroscopy (see Supporting Information online, Figure S1) was employed. O–H or N–H stretching vibrations are observed at 3335  $\text{cm}^{-1}$ . The C–H stretching vibration is shown by the peak at 2956  $\text{cm}^{-1}$ . The other peaks observed at 1668  $\text{cm}^{-1}$  and 1417  $\text{cm}^{-1}$  are due to C–O and C–N stretching vibrations respectively. The above mentioned data indicates the presence of alcoholic, amine and carbonyl groups in the carbon core structure.

UV-Visible absorption spectrum of carbon dots with a very broad UV absorption band ranging from 230 to 350 nm and a tail extending up to the visible region is shown in Figure 3a. Absorption edge at around 275 nm could be due to the  $\pi-\pi^*$  transition of aromatic  $sp^2$  domains which confirms the existence of aromatic  $\pi$ -system in the C.dots<sup>31</sup>. The emission spectra (Figure 3b) of C.dots show a Stokes shift starting from 398 to 454 nm on exciting the sample from 300 to 400 nm. The maximum emission intensity when excited at 365 nm is



**Figure 3.** (a) UV/Vis absorption spectra and (b) emission spectra of C.dots when excited with wavelengths ranging from 300 to 400 nm. Inset: Normalized emission spectra of C.dots.



**Figure 4.** a, Fluorescence spectra of C.dots in different pH conditions. Inset: graphical representation of pH spectra. b, Fluorescence intensity of C.dots with respect to time on continuous irradiation for 6 h. Inset: Graphical representation of time-dependent spectra.

obtained at 440 nm. This excitation-dependent emission spectrum is one of the important properties of C.dots. The photoluminescence mechanism of C.dots is still not clear but there are reports about the role of quantum confinement and existence of surface energy traps on the C.dots surface<sup>32</sup>. It was found earlier that the dependence of C.dot fluorescence on its size is limited, ruling out C.dot fluorescence as size-dependent phenomenon<sup>33</sup>.

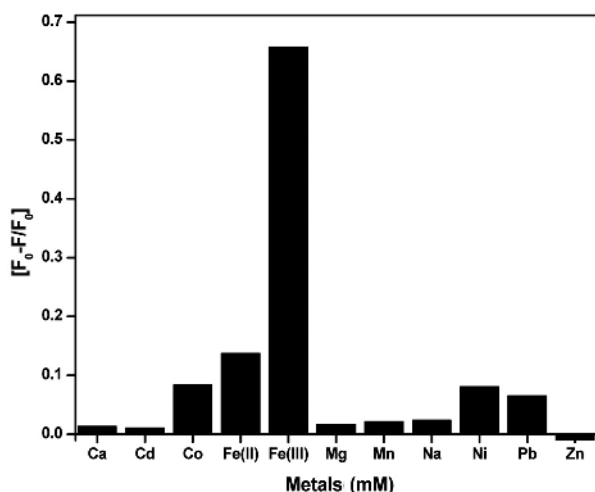
Fluorescence emission of C.dots is recorded at different pH medium (Figure 4 a). The fluorescent intensity of C.dots has been quenched both in basic and acidic pH and has been enhanced to maximum intensity at the neutral pH. This could be due to the protonation and deprotonation of functional groups on the carbon structure in acidic and basic environments respectively<sup>34</sup>. Since there is no change in emission intensity at the neutral pH, C.dots can be successfully applied as an optical sensor in various

biological applications. The photostability of the carbon dots prepared was tested by irradiating the sample by a UV lamp at a wavelength of 365 nm for 6 h continuously (Figure 4 b). The fluorescence intensity of C-dots did not change appreciably and is retained at 95% of the initial fluorescence intensity, indicating good photostability.

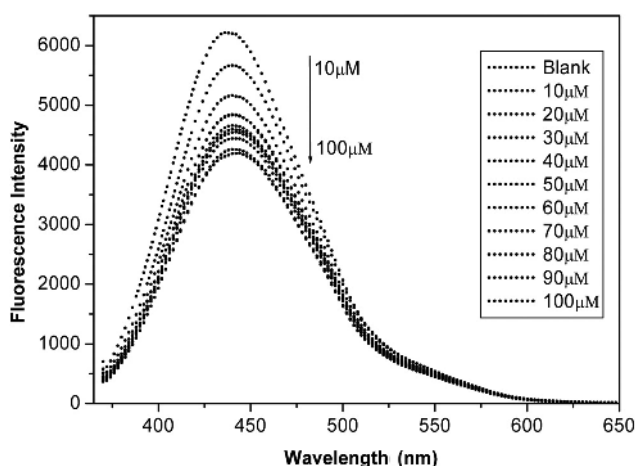
The fluorescence quantum yield of photoluminescent C.dots was estimated to be 8.02% (see Supplementary Information online, Figure S2) which was higher or comparable with most of the nitrogen containing naturally occurring carbon dots reported so far<sup>17,35,36</sup>. The presence of nitrogen in the carbon core structure stabilizes the excitons and it plays a significant role in the photoluminescent properties of carbon dots<sup>37</sup>. The lifetime measurement (see Supplementary Information online, Figure S3) using a TCSPC instrument indicates an average lifetime of 3.36 ns.

From the present results it is evident that C.dots obtained from sesame seeds are characterized by zero toxicity, high photoluminescence, good aqueous solubility and has an appreciable photostability. It also shows that hydrophilic functional groups are present on the carbon core structure. These superior qualities make them a strong candidate for optical sensing applications.

Since carbon dots show high sensitivity and selectivity towards metal ions, the fields of sensor application using carbon dots have been significantly expanding. Carbon dots, which are considered as novel and environmentally friendly fluorescent probes, can be effectively employed for detection of environmentally hazardous metal ions. Many research groups have reported the sensing application of C.dots<sup>38,39</sup>. Fe(III), one of the biologically important metal ions, has a peculiar quenching tendency towards the luminescence of C.dots. This fluorescence quenching may be attributed to a particular type of



**Figure 5.** Effect of different metal ions on the emission intensity of C.dots (excitation wavelength 360 nm).



**Figure 6.** Fluorescence quenching of C.dots in the presence of Fe(III) of concentration varying from 10 to 100 μM.

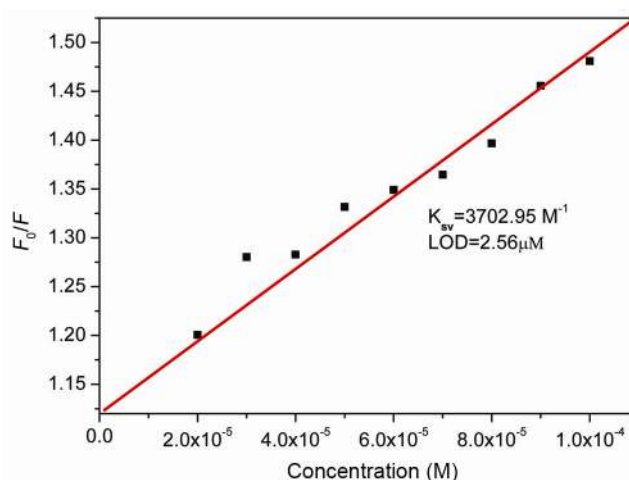
binding interaction between the carbon dot structure and Fe(III) which results in the formation of certain complexes. The possible mechanism of quenching is assumed to be non-radiative electron transfer from the excited state of carbon dots to the d-orbital of Fe(III)<sup>40</sup>. Along with that, the nitrogen-doped carbon dots play a role in quenching mechanism according to the hypothesis put forward in various studies. The nitrogen-doped carbon dots must be having some co-ordination interaction with Fe(III) because of the occurrence of electron-rich nitrogen atom in the structure. This could result in non-radiative electron transfer between them which can cause a substantial quenching of photoluminescence of carbon dots<sup>41,42</sup>. This electron transfer process plays a major role for the significant quenching of C.dots fluorescence.

To investigate the selectivity of the prepared carbon dots towards Fe(III) a thorough study was followed in which a series of environmentally important metal ions were selected and its interaction with the carbon dots studied. Metal ions like, Pb(II), Ni(II), Co(II), Cd(II), Zn(II), Mn(II), Mg(II), Na(I), Ca(II), Fe(II) and Fe(III) were employed for the sensing study. The concentration of all metal ions in the solution was kept at 1 mM. From Figure 5 it is evident that a significant fluorescent quenching effect was observed for Fe(III) and the influence of other metal ions was found negligible. This indicates that nitrogen-doped carbon dots obtained from sesame seeds are selective for Fe(III) detection.

Figure 6 shows quenching of C.dots fluorescence at different concentrations of Fe(III) from 10 to 100 μM. On increasing metal ion concentration, a gradual decrease in fluorescence intensity was observed. Based on this, a Stern-Volmer plot was generated (Figure 7).

The photoluminescence quenching can be analysed by Stern-Volmer equation

$$F_0/F = 1 + K_{SV}[Q], \quad (1)$$



**Figure 7.** Stern-Volmer plot of fluorescence quenching ( $K_{SV}$  value 3702.95  $M^{-1}$  and LOD 2.56  $\mu M$ ).

where  $F_0$  and  $F$  represent the fluorescence intensities of carbon dots in the absence and presence of metal ions,  $[Q]$  is the metal ion concentration, and  $K_{SV}$  is the Stern-Volmer quenching constant. The plot of  $F_0/F$  against concentration of metal ion ( $Q$ ) is a straight line with a correlation coefficient ( $r$ ) of 0.97. Slope of the line gives  $K_{SV}$  value, which was  $3702.95 \text{ M}^{-1}$ . LOD was found out using the ( $3\sigma$ ) rule and its value was  $2.56 \mu\text{M}$ .

Green, economical as well as waste recycling synthesis of C.dots was carried out from sesame seeds by energy-efficient and time-saving microwave heating. The carbon dots obtained had an average size of 5 nm with good aqueous dispersibility. The fluorescent quantum yield of carbon dots was 8.02%. These carbon dots without any modification were then used for metal sensing studies. The fluorescence of C.dots gets appreciably quenched only in the presence of Fe(III). Hence, detailed studies were performed with different concentrations of Fe(III). LOD was found to be  $2.56 \mu\text{M}$ .

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## Biocompatibility of synthetic and bio-material fusion

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**This communication proposes methods to improve the biocompatibility performance of synthetic materials for biological and biological material for synthetic applications.  $\pi$ -cloud extension by suitable ligand–ligand/metal–ligand interactions can make the synthetic–biological fusion suitable for such applications. The judicious use of ligands for  $\pi$ -cloud extension can be applied to carbon transformations and target-oriented drug delivery systems. Embedded metal-centre catalysts for synthetic–biological fusion include: (i) axial coordination via bridging ligands; (ii) ligands with weak to intermediate field strength and multidentities; (iii) design of inert complexes, and (iv) development of multi-nuclear complexes.**

**Keywords:** Biocompatibility, carbon transformation, drug delivery, sequestration, synthetic–natural fusion.

SYNTHETIC and biological materials can be used for many complex transformations in carbon management and target-oriented drug delivery systems. Carboxylation and reduction are two important reactions responsible for carbon management in nature. Eight biological pathways are known for converting inorganic carbon to organic material in cell biomass: (i) reductive pentose phosphate; (ii) Hatch–Slack cycle; (iii) Crassulacean acid metabolism; (iv) reductive citric acid; (v) 3-hydroxypropionate; (vi) dicarboxylate/4-hydroxybutyrate; (vii) 3-hydroxypropionate/4-hydroxybutyrate pathway and, (viii) reductive acetyl-CoA cycle. The first three are present in plant and some prokaryotes, 4th and 5th in bacteria, 6th and 7th in archaea and 8th in bacteria and archaea.

The choice of a carrier molecule is important in targeted drug delivery because it significantly affects pharmacodynamics and pharmacokinetics of drugs. Materials like lipids, natural and synthetic polymers, carbohydrates, surfactants and dendrimers are used as drug carriers<sup>1–3</sup>. The drug conjugate can be designed for improving its potential for complex  $\pi$ – $\pi$  interactions towards the target moiety and drug<sup>4–7</sup>.

Biological materials are eco-friendly, but they have limitation with regard to the proposed application as they are less durable in terms of mechanical strength and resistance to corrosion. Synthetic materials, on the other hand, have issues related to environment and biocompatibility in complex transformations. Metal complexes can serve

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