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Carbon Dots as Photocatalysts for Organic Synthesis: Metal-Free Methylene-oxygen-bond Photocleavage

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We report for the first time that irradiation of four different citric acid-derived carbon dots (CDs), in the absence of any other redox mediators, promotes an organic reaction. In this proof-of-concept study methylene-oxygen bond reductive photocleavage in Nmethyl-4-picolinium esters is demonstrated. Cyclic voltammetry and UV-Vis spectra of the CDs and of the esters indicate that photocleavage reactivity correlates with the redox properties and the relative energies expressed in the Fermi scale. A photofragmentation mechanism is proposed. This study offers a new possibility to employ inexpensive and readily available CDs to promote photo-organic reactions.

Due to their ability to transfer electrons upon irradiation, photoluminescent carbon nanoparticles, referred to herein as carbon dots (CDs) have been used as photosensitizers for water splitting, CO₂ reduction and degradation of pollutants.^[1] CDs are mainly carbonaceous materials, typically 2-10 nm in diameter, constituted of amorphous organic oligomers together with graphitic nanocrystalline regions. They often display strong photoluminescence and good optical absorption in the UV and near-visible regions, making them candidates for photocatalytic applications, usually in conjunction with other photosensitizers. For example, photocatalysis with CDs had been explored in the presence of redox mediators such as nanocomposites or enzymes, that were necessary to shuttle the electrons from the CDs to the substrate. For example, CDs/SiO₂, CDs/Au, Ag or Cu nanocomposites were developed for the oxidation of ciscyclooctene,^[2] alkanes^[3] and for the reductions of nitrobenzenes^[4] or quinones^{[5].} In another instance, the coupling of

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CDs with fumarate reductase promotes photoenzymatic reduction of fumarate to succinate in a semi-biological photosynthesis. ^[6] Direct photo-organic chemistry using only organic sensitizers akin to CDs is instead still an open field for research. Flavins have been recognized as promising photoredox catalysts, albeit mainly for oxidation reactions;^[7] while graphitic carbon nitride (g-C₃N₄)^[8] has attracted interest as a non-metallic photocatalyst for example for H₂O₂ synthesis^[9], as a polymerization photoinitiator ^[10] and as a metal-free photosensitizer for dithiol-ene click reactions. ^[11] However, up to date the only example of direct photo-organic chemistry using only CDs as photosensitizers seems to be a metal-free photocatalytic oxidation of benzylic alcohols using near infrared radiation. ^[12]

Our interests in green organic syntheses, ^[13] led us to explore light-driven metal-free photocatalytic reactions promoted by CDs with the aim of demonstrating that these nanomaterials can directly promote photo-organic reactions. To this end, we recently described the synthesis and full characterization a set of four amorphous and graphitic CDs derived from citric acid: two purely organic, **a-CDs** and **g-CDs**, and two others as nitrogen-doped systems, **a-N-CDs** and **g-N-CDs**.^[14] These materials are readily obtainable in gram-scale quantity with only minimal isolation and purification procedures (see SI for full synthetic details), they are inexpensive, safe, easily disposable and are constituted by aggregates of fluorophores, heavier aggregates/oligomers and extended graphitic carbon cores.

Our previous study showed that these CDs are able to transfer an electron to methyl viologen; it also demonstrated that the carbon-nitrogen source, the synthetic method and the resulting structural properties strongly affect the photo-reactivity of the CDs. Based on this work, the four CDs are here explored for a photo-organic reaction: the reductive methylene-oxygen bond photocleavage of *N*-Methyl-4-picolinium esters. This reaction was chosen not only as a proof-of-concept transformation, but also for its synthetic relevance since picolinium esters are used as photolabile protecting groups for the carboxyl group.^[15] So

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far, such photo-deprotection has been carried out with $[Ru(II)(bpy)_3]^{2+\ [16]}$ or with organic dyes (such as N,N,N',N'pyrene, tetramethylbenzidine, 9-methylcarbazole, and triphenylamine, pyrromethene and coumarin) ^[17] via a photoinduced electron transfer pathway, rather than by direct photolysis. We here demonstrate that conversion of methylpicolinium esters into the corresponding carboxylic acids can be also carried out using solely a-CDs, g-CDs, a-N-CDs or g-N-CDs as the photo-reductant. Cyclic voltammetry was further used to measure the redox activity of these CDs, allowing to correlate the energy levels of the nanomaterials, and the relative band gap, with the photo-reactivity towards methylene-oxygen bond cleavage.

The photocleavage efficiency of the citric acid-derived **a**-**CDs**, **g-CDs**, **a-N-CDs**, **g-N-CDs**^[14] was first tested in the reduction of the picolinium ester of octanoic acid (**1a**), selected as the model substrate (Table 1). The reaction was carried out in ACN d_3/D_2O (6/4) under nitrogen with EDTA as sacrificial electron source, by irradiating the sample with UV light at 365 nm for 48 hours. The cleavage was monitored by NMR (see SI section for further details and Figure S1), by measuring the conversion of **1a**, and the formation of N-methyl-4-methylpyridinium (**2**) and octanoic acid (**3a**) derived from CH₂-O cleavage, as well as any formation of methyl pyridinium carbinol (**4**) potentially derived from competitive ester hydrolysis.

Table 1. CDs promoted CH₂-O bond photocleavage of 1a

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_N			d ₃ /D ₂ O		+ HO nC7	+ _ N+ СЮ4-
	J ₄	1a		2	3a	4
-	Entry	Sensitizer (mg/mL)	EDTA	Conv (%)	Yield 2/3a/4 (%)	CH ₂ -O Cleavage Selectivity (%) ^a
	1	a-CDs (20)	YES	15	15/15/0	>99
	2	g-N-CDs (20)	YES	25	25/25/0	>99
	3	g-CDs (20)	YES	52	49/52/3	94
	4	a-N-CDs (20)	YES	73	73/73/0	>99
	5	None	YES	0		
	6 ^b	a-N-CDs (20)	YES	0		
	7 ^c	a-N-CDs (20)	NO	49	48/49/1	98
	8 ^d	a-N-CDs (100)	NO	90	90/90/0	>99
	9 ^e	Ru(bpy) ₃ Cl ₂	YES	99	96/99/3	>99
	10 ^f	a-N-CDs (20)	YES	7	7/7/0	>99
	11 ^g	a-N-CDs (100)	YES	99	99/99/0	>99

Standard conditions: [CDs] = 20 mg/mL, substrate (0.06 M), EDTA (0.1 M) in ACNd₃/D₂O (6/4) at pD = 7, hv = 365 nm, 48 h at R.T. under N₂. ^aC-O cleavage selectivity determined by considering the amount of **2**. All reactions carried out under standard conditions except ^{b)} in the absence of light, ^{c)} without EDTA, ^{d)} without EDTA and with 100 mg/ml of **a-N-CDs**. ^{e)} Ru(bpy)₃Cl₂ 5 % mol, substrate (0.06 M), EDTA (0.1 M) in ACN-d₃/D₂O (6/4) at pD = 7, halogen lamp, 48 h at R.T. under N₂. ^{f)} under standard conditions but with halogen lamp irradiation ^{g)} with 100 mg/ml of **a-N-CDs** and EDTA (0.1 M).

Results from Table 1 clearly indicated that eachief Athe four different types of CDs could selectively phමೇocleavetheester 1a with conversions between 15 and 73% (Table 1, entries 1-4 and Figure S2-5). The most active photocatalyst was the a-N-CDs that was also the one shown to most easily reduce methyl viologen.^[14] Control experiments conducted in the absence of either CDs or light showed negligible activity (Table 1, entries 5-6 Figure S6-7) thus indicating that the combination of both a light source and CDs were required for the reaction to take place. Interestingly, the photodeprotection proceeded also without EDTA as sacrificial electron source, albeit with lower conversion (49%; Table 1, entry 7 and Figure S8). This observation indicated that CDs themselves could transfer an electron upon irradiation and that this photo-electron transfer ability is therefore an intrinsic property of these nanomaterials. This was further verified by conducting the reaction in the absence of EDTA and by increasing the CDs loading from 20 mg/mL to 100 mg/mL, whereby photocleavage reached 90% conversion with 100% CH₂-O cleavage selectivity (Table 1, entry 8 and Figure S9). These EDTA-free conditions are ideally suited for synthetic scale-up in view of having cleaner mixtures and avoiding waste-generating work-up and purification protocols. As a control experiment, the reaction carried out with 100 mg/mL of a-N-CDs and EDTA showed quantitative conversion and specificity for CH₂-O cleavage already after 28 h (Table 1, entry 11 and Figure S12).

For comparison, the same photodeprotection reaction was also performed using Ru(bpy)₃Cl₂ (Table 1, entry 9 and Figure S10), the best-known metal photosensitizer for the deprotection of these methylpicolinium esters.^[17] Due to the maximum absorption wavelength at 455 nm, the Ru catalysed reaction was performed under visible light (See SI for further details), conditions where a-N-CDs still exhibited some reactivity (7% conversion and high C-O cleavage selectivity; Table 1, entry 10). Gratifyingly, the photodeprotection with the Ru system was comparable with the one with the CDs in terms of conversion, selectivity and reaction rates (see Figure S11). The fact that these carbon-based nanomaterials are re-useable as already demonstrated,^[14] that they are simple to make and available in gram-quantity at low cost, makes them in our view remarkably competitive compared to semiconductor- or metal-containing systems.

After optimizing the photocleavage conditions, the scope of the reaction was extended to other N-methyl-4-picolinium esters **1a-e**, using the most active **a-N-CDs**, both in the presence and absence of EDTA (Scheme 1). The reactions were monitored by NMR and GC-MS (see SI section for further details).

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Scheme 1. Reductive CH_2 -O photocleavage of N-Methyl-4-picolinium esters **1a-e** promoted by **a-N-CDs**. Scope of the substrate.

electrochemical energy gaps that best correspond to the optical ones are shown in Table 2 and Figure 1. DOI: 10.1039/C9GC03811F



Standard conditions: **a-N-CDs** (20 mg/mL), **1a-e** (0.06 M), EDTA (0.1 M) in ACNd₃/D₂O (6/4) at pD = 7, hv = 365 nm, 48 h at R.T. under N₂. ^a Reactions carried out under standard conditions with 100 mg/mL of **a-N-CDs** and without EDTA. ^b C-O cleavage selectivity determined by considering the amount of **2**.

High methylene-oxygen cleavage selectivity (>99%) was observed for benzoic **1b**, phenylalaninate **1c** and phenylacetic **1d** esters, both with and without EDTA as sacrificial electron source. Phenylacetic methylpicolinium ester **1b** yielded the desired CH₂-O photocleavage product **3b** in 70% yield in the presence of EDTA (Figure S16), and only 43% in its absence (Figure S17). The opposite behaviour was observed for phenylalaninate **1c** (45% and 60%, with or without EDTA, respectively, Figure S19-S20) and **1d** (20% and 88%, with or without EDTA respectively, Figure S22-S23). The *p*-nitrobenzoic ester **1e** showed low CH₂-O photocleavage selectivity (ranging from 11 to 57%, Figure S25-S26). Overall, the photocleavage reactivity of the picolinium esters followed the order **1a** > **1b** > **1c** > **1d** > **1e**.

The different photocleavage activity of the CDs prompted us to investigate their electrochemical properties as well as those of the substrates by cyclic voltammetry (CV, full details in SI). The cyclic voltammograms of the a-CDs, g-CDs, a-N-CDs, and g-N-CDs, exhibited several irreversible redox processes. The scans in the positive and negative potential regions are shown in Figure S30. Each observed process involves an electron transfer (from the electrode to the CDs or vice versa) which causes reduction (in the negative potential window) or oxidation (in the positive potential window) of the different surface moieties present in the CDs. Several waves were observed which correspond to different energy levels, expressed in the Fermi scale.^[18] The energy values were estimated by using the respective positive (Eonset,ox) and negative (Eonset,red) onset potentials of the CV responses (Table S1). The largest energy gap is associated to the maximum oxidation or reduction strength of the CDs. The maximum energy gap of each CD was also extrapolated from the UV-vis spectra (Figure S33 and Table S3) and compared with those calculated by CV. The largest

Table 2. Selected E _{onset} reduction potentials ^a and estimated energy levels for	а
CDs, g-CDs, a-N-CDs, g-N-CDs and 1a-e	

	E _{onset,ox} (V) VS	E _{onset,red} (V) VS	Fermi Energy _{ox} د	Fermi Energy _{red} c	Energy gap ^d
	Ag AgCl ^b	Ag AgCl ^b	(eV)	(eV)	(eV)
g-CDs	1.27	-1.60	-5.9	-3.0	2.9
a-CDs	0.52	-1.83	-5.1	-2.8	2.3
g-N-CDs	0.56	-1.87	-5.2	-2.7	2.5
a-N-CDs	1.12	-1.94	-5.7	-2.7	3.0
1a		-0.97		-3,6	
1b		-0.94		-3,7	
1c		-0.89		-3,7	
1d		-0.93		-3,7	
1e		-0.65		-4,0	

^a Uncertainty of E_{onset} is ± 0.01 V. ^b Cyclic voltammetry measurements: 10 mM for **1a-e** and 25 mg/mL for CDs in DMF_{aq}, scan rate 100mV/s, 0.1 M tetrabutylammonium perchlorate, glassy carbon working electrode, saturated Ag|AgCl|KCl reference, platinum counter electrode, and referred to Fc⁺|Fc as internal standard. ^c See SI section for the energy levels calculations. ^d Calculated by CV, see SI section.

The CVs of **a-CDs**, **g-CDs**, **a-N-CDs**, and **g-N-CDs** are representative of complex electrochemical behaviours, highlighting how the syntheses and composition of the CDs influenced the electrochemical, structural, as well as optical and photoredox properties.^[14] In particular, the electron transfer processes, characterizing the CDs employed here, could depend on the type, density and location of active sites produced during their synthesis.^[14b] Nonetheless, the presence of nitrogen simplified the CV curves that showed fewer redox processes in both the positive and negative potential regions. In general, **a-N-CDs** exhibited the most negative potential (E_{onset red} = -1.94 vs Ag|AgCl) while **g-CDs** possessed the highest positive potential (E_{onset ox} = 1.27 vs Ag|AgCl). This suggested that these CDs have the strongest reducing or oxidizing potential among the investigated CDs, respectively.



Figure 1. Estimated Fermi energy levels of the CDs and of the esters 1a-e.

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CV was also used to investigate the redox properties of the *N*-methylpicolinium esters **1a-e**. Each compound showed several irreversible reduction peaks in the negative potential region between -0.65 and -1.46 V vs Ag|AgCl (see Figure S31) which could be attributed to the reduction of the *N*-methylpicolinium, C=O moiety or of the nitro group in **1e**. ^[15c, 17c, 19] E_{onset,red} – which for the substrates corresponds to the LUMO energy levels – evaluated considering the first observed reduction peak (Table S2, Table 2 and Figure 1), decreased in the order **1a** > **1b** > **1c** > **1d** > **1e** which correlates with the electron-withdrawing ability of the substituent (*i.e.*, **1e** > **1d** > **1c** > **1b** > **1c** > **1d** > **1c** which correlates of the substituent (*i.e.*, **1e** > **1d** > **1c** > **1b** > **1c** > **1d** > **1d**

The combined CV data of the CDs and N-methylpicolinium esters indicate that there is a correlation between the redox properties and the photoreactivity. Based on these data, all the CDs have sufficiently negative potentials to act as reductants and to inject an electron into the substrates, at least into the chemical moiety involved in the less negative reduction process. Among the investigated CDs, the a-NCDs possessed the highest energy gap and the highest energy gaps of the CDs decreased in the same order as their photocleavage activity: **a-N-CDs** > **g-CDs** > g-N-CDs > a-CDs. A greater energy gap of the CDs – attributed to the presence of free molecular-like fluorophores that ensure a high PET efficiency of the CDs - implies a greater energy of the excited electron generated upon irradiation, as already observed previously.^[14] This fact justifies the higher photocleavage efficiency towards the N-methylpicolinium esters. Similar considerations explain the reactivity of substrates 1a-e: the energy of the LUMO reflects the energy of the radical anion formed by photoinduced single electron transfer from CDs into the methylpicolinium ester. A higher LUMO energy of the methylpicolinium ester implies that the transfer of the electron requires more energy and thus that the ester is less prone to be reduced. However, in this case, once the electron is transferred from the CDs, its radical is more reactive. Conversely, easier reduction implies a more stable radical ion and a slower methylene-oxygen bond cleavage. In the present case, the octanoic ester 1a, has a higher energy LUMO and is more difficult to reduce, but once it is reduced it readily undergoes photocleavage. On the other hand, the pnitrobenzoic ester 1e is easily reduced, and thus it is less prone to undergo the bond-scission process.

The results discussed above allowed to propose a CH₂-O photocleavage mechanism (Scheme 2). In an initial step, the CDs and the methylpicolinium esters **1a-1e** approach oneanother by electrostatic interactions forming a ground-state supramolecular complex. Formation of such a complex was previously confirmed by the static quenching occurring between the **a-CDs**, **g-CDs**, **a-N-CDs**, and **g-N-CDs** and methyl viologen, observed by PL quenching data and ζ -potential measurements.^[14] In the second step, the CDs are promoted to the excited state (CDs*) by irradiation, followed by single electron transfer to the methylpicolinium ester *via* an exergonic (E_{onset red} = -1.60 -1.94 V vs Ag|AgCl for CDs and E_{onset red} = -0.65

-0.97 V vs Ag|AgCl for **1a-e**) step. This step is likely to be favoured by the presence of EDTA which might act as reductive

quencher (E⁰ $_{5}$ EDTA/EDTA⁻⁺ = 0.57 0.82 vs SCE^[15]), thus increasing the reduction potential and extending^D the⁰ lifetime of ³ the CDs*.^[20] The electron injected into the methylpicolinium ester forms a pyridinium radical which undergoes reductive C-O bond cleavage to release a carboxylate along with a N-methyl-4methyl pyridinium radical. In the final step, hydrogen

abstraction and abstraction of a proton from either the deuterated solvent (deuterated products have been observed, see Supporting info Figure S13-14) or radical EDTA⁺ - or its decomposition products^[21] yields the desired N-methyl-4-methyl pyridinium and the carboxylic acid.

Scheme 2. Proposed CH₂-O bond photocleavage mechanism with CDs



Conclusions

In summary, we have provided a proof-of-concept for the use of inexpensive and readily available bio-based CDs as sensitizers to trigger a novel photosynthetic protocol for the deprotection of N-methyl-4-picolinium esters. The origin of photo-electron transfer is not fully understood yet and cannot be attributed to any of the single different moieties of the CDs. Nonetheless, these complex systems promote a very efficient reductive methylene-oxygen photocleavage and enable a versatile, inexpensive, robust and highly selective photodeprotection of a series of esters of carboxylic- and amino-acids representing a greener alternative to the currently used metal complexes and organic dyes. We have also demonstrated how the structure and electrochemical properties of CDs can influence the photocleavage efficiency. In general, the presence of nitrogen in the amorphous structure of CDs of CDs makes the reduction potential of the CDs more negative, while the energy gaps increase, thereby improving photogeneration of reactive electrons and photoreduction efficiency. We have also shown how the reduction potential of the substrates determines ease of photocleavage.

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Conflicts of interest

There are no conflicts to declare.

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