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doi.org/10.1002/cctc.202300708
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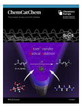

# Nitrogen-doped Carbon Dots as Biobased Catalysts for Visible Light Driven 1,2-Functionalization of Olefins through an Atom Transfer Radical Addition Process

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Amorphous nitrogen-doped carbon dots (a-N-CDs) have been obtained under hydrothermal conditions from citric acid and diethylenetriamine (DETA) as the carbon and nitrogen source, respectively. Such materials exhibit a significant absorption in the visible light region and have been successfully employed as photoredox catalyst under violet LED irradiation for the 1,2-difunctionalization of olefins via an atom transfer radical addition (ATRA) process. The reported approach occurs smoothly under metal-free conditions in an aqueous medium, showcasing the (yet not completely explored) applications of such bio-derived carbon materials in organic synthesis.

## Introduction

Among the different carbon allotropes, carbon dots (CDs) are zero-dimensional carbon-based materials with a diameter below 10 nm, which were first discovered in 2004.[1] Intriguingly, they exhibit an enhanced solubility in water, low toxicity and tunable photophysics.[2] Such nanomaterials can be prepared via two main strategies, namely top-down or bottom-up. The first approach involves the breakdown of larger carbon structures, such as graphite, carbon nanotubes (CNTs) or even candle sooth, which can be degraded via exfoliation, laser ablation or electrochemical etching. On the other hand, in the bottom-up approach, easily accessible organic molecules (indifferently, raw materials or wastes) or polymers undergo thermal decomposition. By adopting such method, multicomponent procedures to form heteroatom-doped CDs can be followed.[3] Recently, several protocols for the production of *N*-doped carbon dots starting from low-value natural sources, including among the others brewing[4] and seafood waste,[5] and vegetables[6], have been reported in the literature. The so-prepared CDs are commonly purified via centrifugation and dialysis.[7] Depending on the nature of their carbogenic cores, CDs can be classified either as graphitic (derived from the physical or chemical modification of graphene materials) or amorphous.[8] In both cases, however, such nanomaterials typically exhibit an enhanced optical absorption in the UV region (280–360 nm), which arises from a variety of $\pi$-$\pi^*$ (C=C) and n-$\pi^*$ (C=O) transitions in the core and on the surface of the particles,[9] along with a tail that extends up to the visible range. The emission is mainly in the blue and green regions, and photoluminescence properties,[10] as well as the (photo)redox behavior[11] can be tuned by doping with nitrogen or sulfur atoms. In view of the peculiar photo-physical properties, CDs have found, in the last decade, wide application in biomedical areas, including their use in bioimaging, biosensing,[12] drug delivery and uptake,[13] and as photosensitizers for singlet oxygen generation.[14] On the other hand, the excellent electron transfer ability upon irradiation[15] makes such derivatives excellent candidates as photocatalysts for depollution processes,[16] hydrogen production[17] and organic synthesis.[18] As for the latter application, different protocols have been developed, including, among the others, solar light-driven aldol condensations,[19] oxirane ring opening,[20] perfluoroalkylation of arenes[21] and C(benzyl)–O bond cleavage.[22] Furthermore, due to the high solubility of CDs in water and aqueous organic solvents, such media are considered as the elective environment for carrying out such processes.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202300708

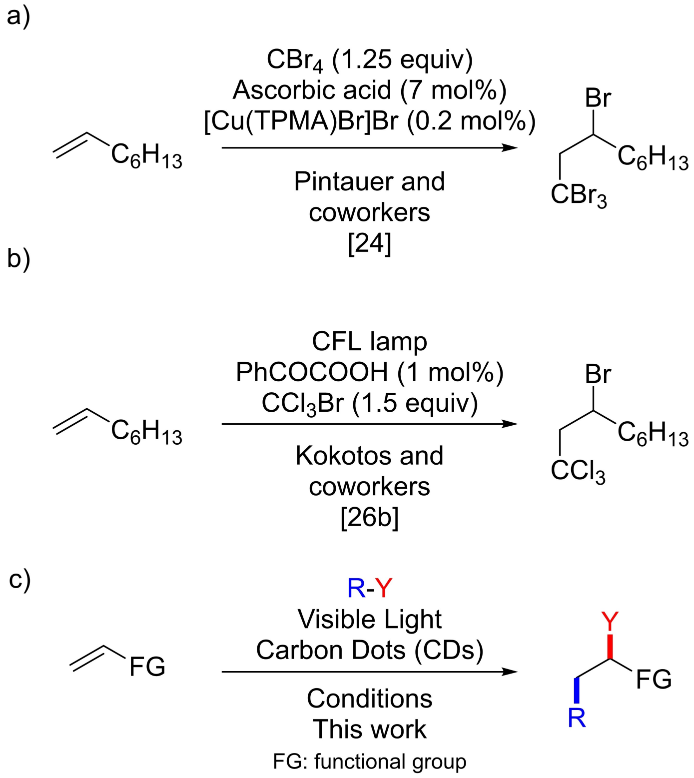
In the last decades, atom transfer radical addition (ATRA) reactions have emerged as a precious tool for the simultaneous introduction of two functional groups across a double bond,[23] which takes place in the presence of a halogenated derivative. In most cases, transition metal-catalyzed thermal (e.g., Cu; see an example in Scheme 1a) and photoinduced conditions have been adopted,[24] but the interests for the development of metal-free ATRA processes occurring under either thermal[25] or photocatalytic/photoinitiated conditions (Scheme 1b)[26] is dramatically increasing. In view of such premises, in this work we focused on the chance of employing carbon dots as bio-derived, organic-based photocatalysts in the 1,2-difunctionalization of alkenes (Scheme 1c) in aqueous media.

## Results and Discussion

### Synthesis and characterization of amorphous nitrogen-doped carbon dots (a-N-CDs)

The nitrogen-doped carbon dots (**a-N-CDs**) examined in the present investigation have been synthesized through the hydrothermal treatment of an aqueous solution of citric acid and diethylenetriamine, as already reported elsewhere.[27–30] The presence of different organic functionalities on the surface of the carbon nanoparticles has been pointed out by means of FT-IR spectroscopy analysis (Figures S1–S2 in the supporting information). In particular, a broad band assigned to the presence of hydroxyl groups can be seen at 3400 $cm^{-1}$, together with another peak at 3300–3000 $cm^{-1}$, due to the stretching of N–H bonds and one at 3000–2800 $cm^{-1}$, reasonably assigned to the presence of ammonium groups. The presence of carboxylic, carbonylic and amidic functionalities has been also pointed out by the presence of strong absorption bands in the 1700–1600 $cm^{-1}$ region, while the multiple signals at 1600–1400 $cm^{-1}$ have been assigned to N–H bending and C=C stretching of both aromatic and conjugated double bonds. The amount of nitrogen doping in the material was evaluated via elemental analysis showing 16.5 % of nitrogen (along with 53.3 % carbon and 5.84 % hydrogen). The presence of the cited functional groups on the surface of the CDs has been also confirmed in our previous studies via X-ray photoelectron spectroscopy: C=C, C–O and C=O moieties were observed together with two bands in the $N_{1s}$ peak due to pyridinic environments or $-NH_2$ groups and to the C–N–C groups.[27] The CDs resulted to have an amorphous core with an average diameter of 13 nm determined via atomic force microscopy.[29] As shown in Figure S2, the CDs showed two main absorptions in the UV region: at 250 nm it is possible to observe the absorption due to the π-π* transitions in the carbogenic core, while at 350 nm the one due to the n-π* transition of the functional groups on the surface. The emission quantum yield (QY) and lifetime of the excited state (τ) of this type of nanoparticles have been investigated in our previous study, highlighting values of 17.3 % of QY and an emission lifetime τ = 13 ns.[29]

**Use of nitrogen-doped carbon dots (a-N-CDs) as photoredox catalysts in ATRA reactions.** In order to test the



**Scheme 1.** Strategies for the 1,2-difunctionalization of alkenes via: a) Cu-catalysis; b) visible light-irradiation and c) CDs-photocatalysis (this work).

feasibility of our proposal, we initially focused on the reaction between alkenoate **1a** and $CCl_3Br$ to form derivative **2** (see Table 1). Early attempts involved the irradiation of a 0.1 M solution of **1a** in a MeCN–$H_2O$ 1:1 mixture, in the presence of $CCl_3Br$ (1 equiv.) and DIPEA (2 equiv.) as the sacrificial electron donor upon irradiation at 427 nm (Kessil LED lamp, 40 W power). Under the described conditions, the desired product **2** was formed in low yield, according to GC analysis (15%). Similar results were observed in different aqueous/organic solvent mixtures (entries 2–5), and the best performance was observed in a THF–$H_2O$ 1:1 mixture, with **2** obtained in 27% yield (entry 4). A decrease in the concentration of CDs (entries 6, 7) as well as a change in the irradiation wavelength (entry 8) resulted in a lowering of the product yield. The simultaneous presence of both CDs and light was required to observe product formation, since no products was observed in the conditions described in entries 9 (no CDs) and 10 (no light). Notably, the formation of **2** is strongly enhanced in the presence of 2 equiv. of $CCl_3Br$ (entry 11), and further improved in the absence of any sacrificial electron donor (entry 12). The conditions shown in the last run led to the formation of **2** in 74% yield (based on GC analysis) and has been adopted throughout the rest of the work.

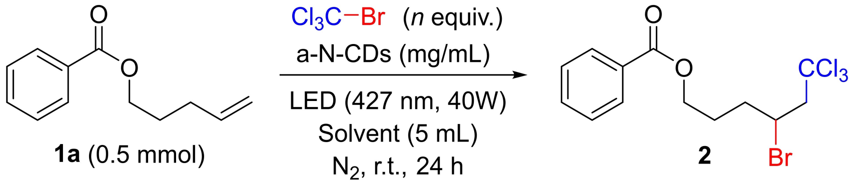
Next, we moved to study the scope of the transformation by subjecting to optimized reaction conditions a set of alkenoates in the presence of different halogenated derivatives. As depicted in Scheme 2, functionalization of both carboxylate and sulfonate esters with $CCl_3Br$ afforded the desired products in high isolated yields, independently from the length of the tethered chain and the substitution pattern at the double bond (compare the results obtained in the preparation of compounds **2**–**4** and **5**–**7**) as well as the nature of the ester moiety (benzoates **1a**–**f**, naphthoate **1g** and benzenesulfonate **1h** derivatives have been all alkylated in good yields by adopting this approach). Less satisfactory results have been obtained when using diethyl bromomalonate as the halogenated reaction partner (to deliver products **10**–**12**), and the desired products have been obtained in moderate yields, with the exception of 4-chlorobenzoyl derivative **11**, which has been isolated in 74% yield. Analogous results have been obtained in the iodoperfluoroalkylation of olefins, that afforded the desired adducts **13**–**16** in 44–53% yield of the isolated products.

We thus shifted to $CBr_4$ as the coupling partner; in this case, however, the observed reaction exhibited a different outcome, and the isolated products **17**–**22** (obtained in the 24–60% yield range) featured a $-CHBr_2$ moiety, instead of the expected $-CBr_3$ group (Scheme 4).

The interaction between the photoexcited CDs and electron acceptors $CCl_3Br$ and $CBr_4$ was evaluated by means of fluorescence analysis (see Figures 1a,b) and the quenching of the emission (located at 448 nm) of **a-N-CDs** was observed to occur with a nearly diffusional rate, along with the formation of a weak exciplex in the 500–520 nm region in both cases, with a stronger effect observed when $CCl_3Br$ was used as the quencher.

As hinted in the introduction section, the potentialities of CDs in photoredox catalysis have been recently pointed out by different research groups.[18,27] In our case, and in accordance with the previous reports in the literature, we considered that the photoexcited state of **a-N-CDs** ($E_{RED\,onset} = -1.94$ V vs SCE)[22] undergoes oxidative quenching by R–Y (Scheme 3a, step *i*, e.g. $E_{RY/RY^{\bullet-}} = -1.46$ V vs SCE for $CBr_4$),[31] thus generating the radical anion $R–Y^{\bullet-}$, which then delivers the radical intermediate $R^{\bullet}$ upon loss of $Y^-$ (step *ii*). It should be noticed that the adsorption of R–Y substrates onto the a-N-CDs surface (as already suggested in the literature for other CDs photocatalyzed processes)[32] cannot be excluded. Trapping of $R^{\bullet}$ by olefins **1a**–**h** resulted in the formation of the radical adduct $\mathbf{I}^{\bullet}$ (step *iii*),

**Table 1.** Optimization of reaction conditions.[a]

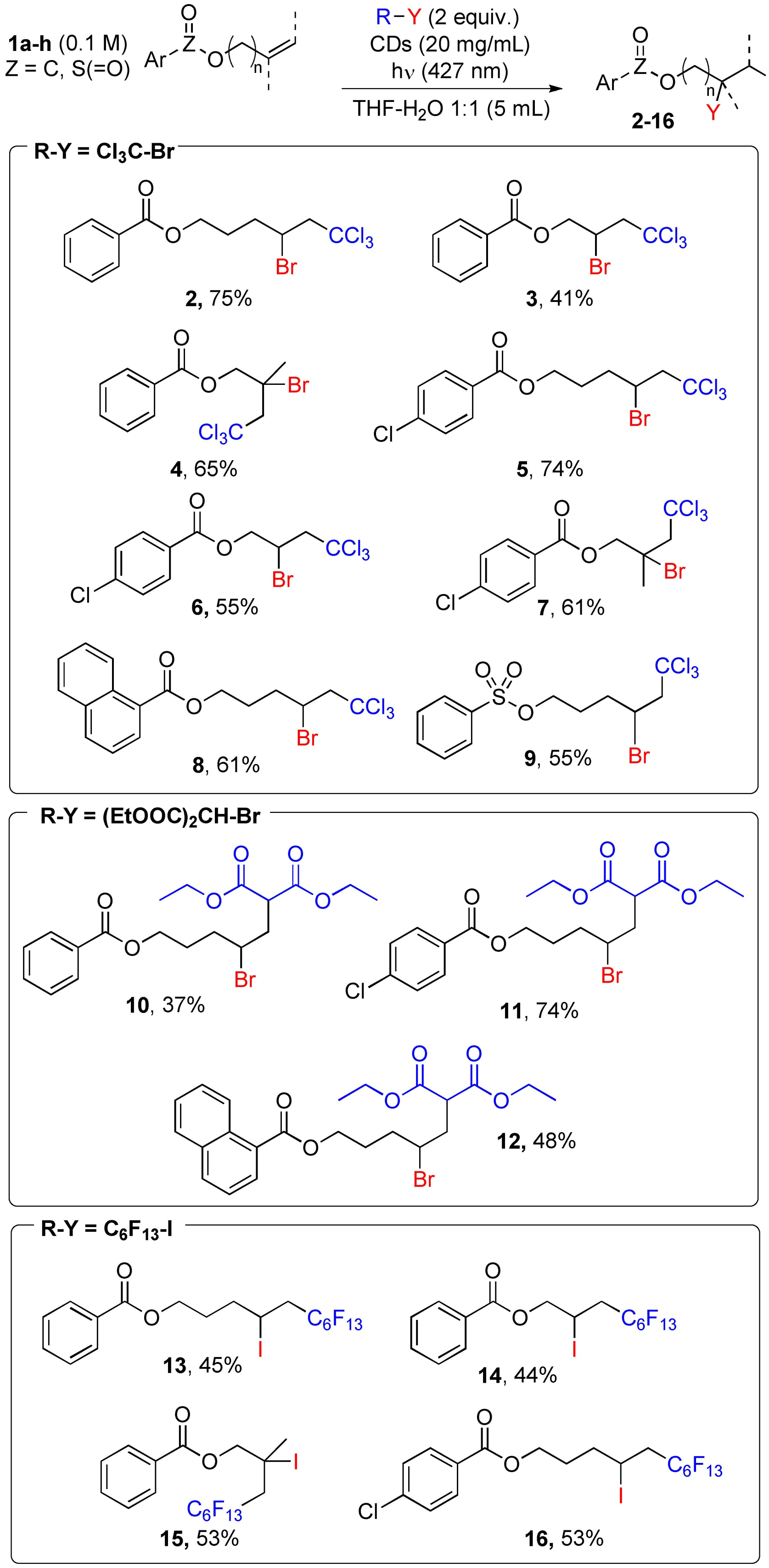


**1a** (0.5 mmol)

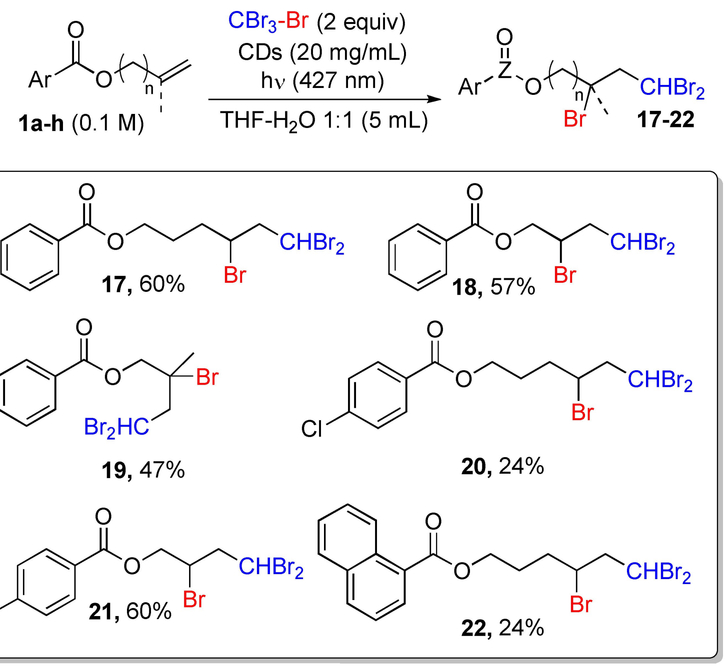
**2**

| Entry | $CCl_3Br$ (equiv.) | Solvent | Additive | CDs (mg mL$^{-1}$) | 2 Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 1 | $CH_3CN/H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | 15 |
| 2 | 1 | $CH_3OH/H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | 18 |
| 3 | 1 | DMSO/$H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | 17 |
| 4 | 1 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | 27 |
| 5 | 1 | THF/$H_2O$ 2:1 | DIPEA (2 equiv.) | 20 | 23 |
| 6 | 1 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | 10 | 14 |
| 7 | 1 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | 5 | 16 |
| 8[c] | 1 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | 24 |
| 9 | 1 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | – | traces |
| 10[d] | 1 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | n.d. |
| 11 | 2 | THF/$H_2O$ 1:1 | DIPEA (2 equiv.) | 20 | 64 |
| 12 | 2 | THF/$H_2O$ 1:1 | – | 20 | 77 |

[a] Reaction conditions: a $N_2$-bubbled MeCN solution (5 mL) containing **1a** (0.5 mmol, 0.1 M), $CCl_3Br$ (1–2 equiv.), and CDs (up to 20 mg mL$^{-1}$) was irradiated with a 427 nm LED lamp (40 W) in a Pyrex vessel for 24 h. [b] Gas chromatography (GC) yields are based on the amount of **2** *vs* *n*-dodecane (1 µL mL$^{-1}$) used as internal standard. [c] Irradiation performed with a 456 nm LED lamp (40 W). [d] Reaction performed in the dark. n.d.: not detected.



**Scheme 2.** CDs-photocatalyzed 1,2-difunctionalyzation of olefins **1 a–h**. Reaction conditions: a $N_2$-bubbled THF-$H_2O$ 1 : 1 mixture solution (5 mL) containing **1 a–h** (0.5 mmol, 0.1 M), R–Y (2 equiv), and CDs (up to 20 mg L$^{-1}$), irradiated with a 427 nm LED lamp (40 W) in a Pyrex vessel for 24 h.



**Scheme 3.** CDs-photocatalyzed 1,2-difunctionalyzation of olefins **1a–h** with $CBr_4$. Reaction conditions: a $N_2$-bubbled THF-$H_2O$ 1:1 solution (5 mL) containing **1a–h** (0.5 mmol, 0.1 M), $CBr_4$ (2 equiv), and CDs (up to 20 mg mL$^{-1}$), irradiated with a 427 nm LED lamp (40 W) in a Pyrex vessel for 24 h.

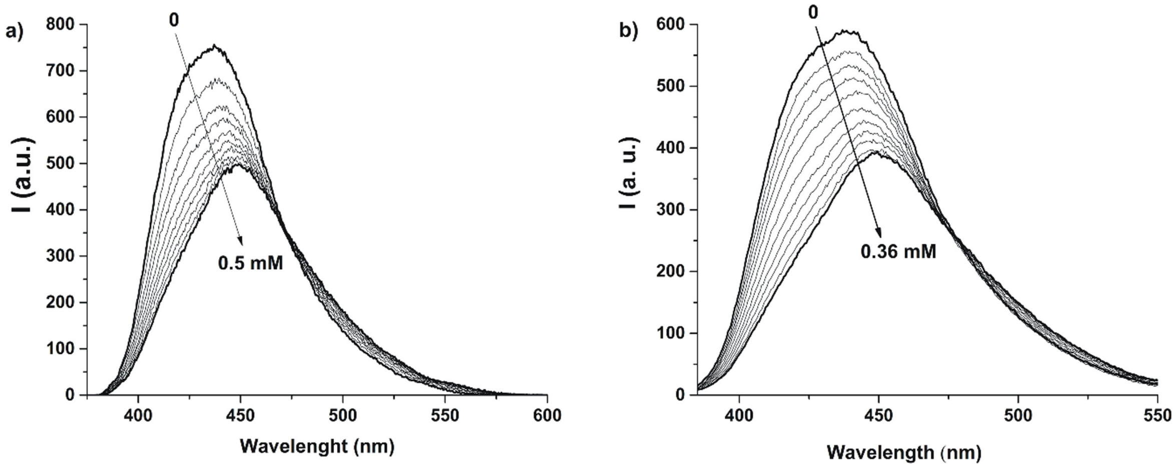
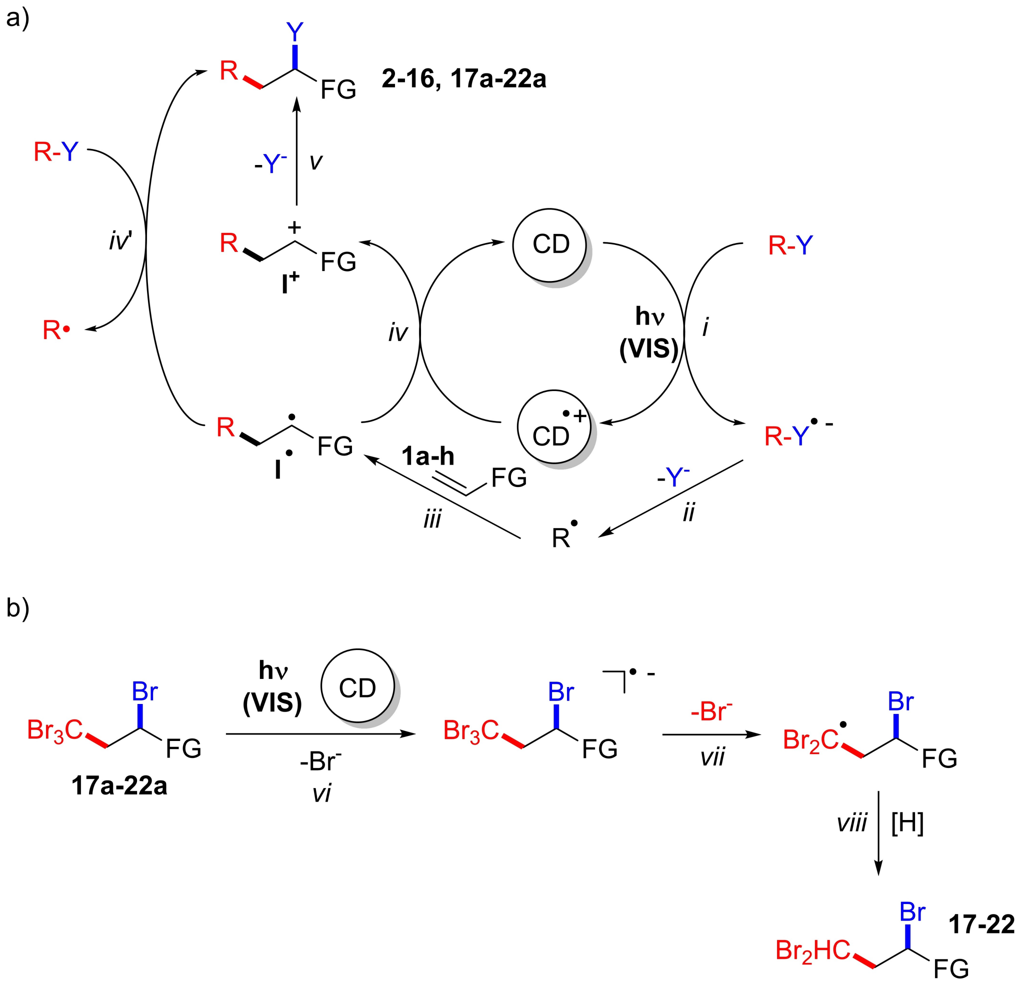


**Figure 1.** Quenching of a-N-CDs in THF-water 1:1 mixture by increasing concentration of: a) $CCl_3Br$ and b) $CBr_4$.

which is in turn oxidized by CDs$^{\bullet+}$ ($E_{OX\,onset}$ = +0.53 V vs SCE) to I$^+$ (path *iv*). The resulting cation in turn reacts with Y$^-$ to form the desired products **2–16** ($E_{I^\bullet/I^+}$ ranging from +0.09 to +0.47 V vs SCE for prototypical tertiary and secondary carbon-based radicals, respectively, path *v*).[33] A radical chain step involving the halide donor substrates (as described in step *iv′*) can compete with the photocatalytic cycle, as also pointed out by the $\Phi_{-1}$ value measured for **1a** during the synthesis of **2** ($\Phi_{-1}=6.7$). On the other hand, when $CBr_4$ is employed as the coupling partner, we propose the initial formation of the expected ATRA products **17a–22a** (Scheme 3b), incorporating four bromine atoms. These initially formed derivatives further undergo single electron transfer (SET) by photoexcited CDs (step *vi*), and ensuing loss of bromide ion (Br$^-$; step *vii*) affords radical **II**$^\bullet$ which abstracts a hydrogen atom from the surrounding medium (step *viii*) to deliver the isolated products **17–22**. In order to demonstrate that the loss of bromine was caused by the photoexcited CDs, we synthesized **17a** (that contains both the –$CBr_3$ and Br moieties), by following a known procedure (see supporting information for further details).[34] **17a** was thus irradiated under the reaction conditions optimized in the present work, and GC-MS analyses showed the quantitative conversion of the substrate to debrominated **17**, thus confirming the photoreducing power of **a-N-CDs** towards **17a–22a**.



**Scheme 4.** Proposed mechanism for the CDs-photocatalyzed 1,2-difunctionalization of olefins **1 a–h**.

## Conclusions

As hinted previously, ATRA reactions are still considered one of the most useful approaches to introduce both carbon- and heteroatom-based functionalities across an alkene moiety.[24] The success of the reported protocol is based on the enhanced reducing power of **a-N-CDs** in the excited state, which can be efficiently applied to the monoelectronic reduction of (electron-poor) alkyl halides (both iodides and bromides). Thus, while most ATRA protocols require the use of transition metal catalysts, a recent trend involves the adoption of metal-free conditions.[26] This work further demonstrates that nitrogen-doped CDs can be adopted in combination with visible light irradiation (a violet LED lamp has been conveniently used) to trigger the desired reactivity, which smoothly takes place in an aqueous organic mixture, without any need of additives. Given the low price, ease of synthesis and the possibility to adopt bio-based (waste) materials for their synthesis, CDs are expected to further contribute to the development of the photoredox catalysis field under sustainable conditions.

## Experimental Part

**Synthesis of nitrogen-doped carbon dots** (**a-N-CDs**). CDs employed in the present investigation were synthesized through hydrothermal treatment, by adapting a protocol already reported in literature [27–30]. An aqueous solution of citric acid (2 g in 20 mL of MilliQ water) and diethylenetriamine (0.67 g) was heated in a sealed autoclave for 6 h at 180 °C. The mixture was then filtered (porosity 8–12 μm) and evaporated to dryness leading to a brown solid ($72\,\%_{wt}$ yield) which was used without any further purifications. The obtained nanoparticles have been characterized via NMR, UV-Vis and CHNS elemental analysis.

### General procedure for the photochemical synthesis of compounds 2–22

A $N_2$-saturated solution of the chosen olefin **1 a–h** (0.5 mmol, 0.1 M, 1.0 equiv), the alkyl halide (0.2 M, 2.0 equiv), CDs (100 mg), in a $THF:H_2O$ 1:1 mixture (5 mL) was irradiated for 24 h by means of a 40 W Kessil lamp (emission centered at 427 nm). The progress of the reaction was monitored by GC-FID and TLC. The photolyzed mixture was then evaporated and the crude residue purified via silica gel column chromatography (cyclohexane:ethyl acetate mixture as eluant).

## *Acknowledgements*

*We gratefully acknowledge the support from Fondazione Cariplo (Photo and Mechano-Chemistry for the Upgrading of Agro- and Sea-food Waste to advanced polymers and nanocarbon materials, CUBWAM, project 2021–0751). S.P. thanks the Hawler Medical University, Erbil, Kurdistan Region (Iraq) for granting A.H. H and financial support. S.P., D.R., L. Q. and V. B. acknowledge support from the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program "Dipartimenti di Eccellenza 2023–2027".*

## *Conflict of Interests*

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

**Keywords:** Visible light photochemistry · Carbon Dots (CDs) · atom transfer radical addition (ATRA) · Metal-free processes · C–C bond formation

[1] X. Xu, R. Ray, Y. Gu, Harry J. Ploehn, L. Gearheart, K. Raker, W. A. Scrivens, *J. Am. Chem. Soc.* **2004**, *126*, 12736–12737.
[2] See for review: M. Tuerhong, X. Yang, Y. Xue-Bo, *Review on Carbon Dots and Their Applications, Chin. J. Anal. Chem.* **2017**, *45*, 139–150; J. Wang, J. Qiu, *J. Mater. Sci.* **2016**, *51*, 4728–4738.
[3] A. Emanuele, S. Cailotto, C. Campalani, L. Branzi, C. Raviola, D. Ravelli, E. Cattaruzza, E. Trave, A. Benedetti, M. Selva, A. Perosa, *Molecules* **2020**, *25*, 101; doi:10.3390/molecules25010101.
[4] S. Cailotto, D. Massari, M. Gigli, C. Campalani, M. Bonini, S. You, A. Vomiero, M. Selva, A. Perosa, C. Crestini, *ACS Omega* **2022**, *7*, 4052–4061.
[5] A. Sharma, R. K. Sharma, Y.-K. Kim, H.-J. Lee, K. M. Tripathi, *J. Env. Chem. Eng.* **2021**, *9*, 106656.
[6] B. De, N. Karak, *RSC Adv.* **2013**, *3*, 8286–8290; X. Niu, G. Liu, L. Lia, Z. Fu, H. Xu, F. Cui, *RSC Adv.* **2015**, *5*, 95223–95229; J. Wanga, Y. H. Ng, Y.-F. Lim, G. W. Ho, *RSC Adv.* **2014**, *4*, 44117–44123.
[7] V. Strauss, J. T. Margraf, C. Dolle, B. Butz, T. J. Nacken, J. Walter, W. Bauer, W. Peukert, E. Spiecker, T. Clark, D. M. Guldi, *J. Am. Chem. Soc.* **2014**, *136*, 17308–17316.
[8] A. Kelarakis, *MRS En. Sust.* **2014**, *1*, E2 DOI: https://doi.org/10.1557/mre.2014.7.
[9] N. Dhenadhayalan, K.-C. Lin, R. Suresh, P. Ramamurthy, *J. Phys. Chem. C* **2016**, *120*, 1252–1261.
[10] S. Bhattacharyya, F. Ehrat, P. Urban, R. Teves, R. Wyrwich, M. Döblinger, J. Feldmann, A. S. Urban, J. K. Stolarczyk, *Nat. Commun.* **2017**, *8*, 1401.
[11] N. Kaushal, A. L. Sharma, A. Saha, *Mater Adv* **2022**, *3*, 355–361.
[12] B. Wang, H. Cai, G. I. N. Waterhouse, X. Qu, B. Yang, S. Lu, *Small Sci.* **2022**, *2*, 2200012.
[13] C. Zhao, X. Song, Y. Liu, Y. Fu, L. Ye, N. Wang, F. Wang, L. Li, M. Mohammadniaei, M Zhang, Q. Zhang, J. Liu, *NanoBiotechnology* **2020**, *18*, 142.
[14] S. Wu, R. Zhou, H. Chen, J. Zhang, P. Wu, *Nanoscale* **2020**, *12*, 5543–5553; H.-Y. Fan, X.-H. Yu, K. Wang, Y.-J. Yin, Y.-J. Tang, Y.-L. Tang, X.-H. Liang, *Eur. J. Med. Chem.* **2019**, *182*, 111620.
[15] X. Wang, L. Cao, F. Lu, M. J. Meziani, H. Li, G. Qi, B. Zhou, B. A. Harruff, F. Kermarre, Y.-P. Sun, *Chem. Commun.* **2009**, 3774–3776; W. Wu, L. Zhan, W. Fan, J. Song, X. Li, Z. Li, R. Wang, J. Zhang, J. Zheng, M. Wu, H. Zeng, *Angew. Chem. Int. Ed.* **2015**, *54*, 6540–6544.
[16] Y. Yao, H. Zhang, K. Hu, G. Nie, Y. Yang, Y. Wang, X. Duan, S. Wang, *J. Env. Chem. Eng.* **2022**, *10*, 107336; M. Han, S. Zhu, S. Lu, Y. Song, T. Feng, S. Tao, J. Liu, B. Yang, *Nano Today* **2018**, *19*, 201–218; K.-W. Chu, S. L. Lee, C.-J. Chang, L. Liu, *Polymer* **2019**, *11*, 689; doi:10.3390/polym11040689.
[17] H. Luo, Q. G. Petra, Á. Szilágyi, A. B. Jorge, M.-M. Titirici, *Trends Chem.* **2020**, *2*, 623–637; F. Li, Y. Liu, B. Mao, L. Li, H. Huang, D. Zhang, W. Dong, Z. Kang, W. Shi, *Appl. Catal. B: Env.* **2021**, *292*, 120154.
[18] H. Yu, R. Shi, Y. Zhao, G. I. N. Waterhouse, L.-Z. Wu, C.-H. Tung, T. Zhang, *Adv. Mater.* **2016**, *28*, 9454–9477; Z. Zeng, S. Chen, T. Thatt, Y. Tan, F.-X. Xiao, *Catal. Today* **2018**, *315*, 171–183.
[19] Y. Han, H. Huang, H. Zhang, Y. Liu, X. Han, R. Liu, H. Li, Z. Kang, *ACS Catal.* **2014**, *4*, 781–787.
[20] H. Li, C. Sun, A. Chenghua, Z. Muataz, Z. X. Fengling, D. R. MacFarlane, *Angew. Chem. Int. Ed.* **2015**, *54*, 8420–8424.
[21] C. Rosso, G. Filippini, M. Prato, *Chem. A Eur. J.* **2019**, *25*, 16032–16036.
[22] S. Cailotto, M. Negrato, S. Daniele, R. Luque, M. Selva, E. Amadio, A. Perosa, *Green Chem.* **2020**, *22*, 1145–1149.
[23] a) S. Engl, O. Reiser, *Chem. Soc. Rev.* **2022**, *51*, 5287–5299:; b) S. Engl, O. Reiser, *ACS Catal.* **2020**, *10*, 9899–9906.
[24] T. Pintauer, W. T. Eckenhoff, C. Ricardo, M. N. C. Balili, A. B. Biernesser, S. J. Noonan, M. J. W. Taylor, *Chem. Eur. J.* **2009**, *15*, 38–41.
[25] R. Dasi, D. Schmidhuber, L. M. Gronbach, J. Rehbein, M. Brasholz, *Org. Biomol. Chem.* **2021**, *19*, 1626–1631.
[26] a) A. Steiner, O. de Frutos, J. A. Rincó, C. Mateos, J. D. Williams, C. O. Kappe, *React. Chem. Eng.* **2021**, *6*, 2434–2441; b) N. F. Nikitas, E. Voutyritsa, P. L. Gkizis, C. G. Kokotos, *Eur. J. Org. Chem.* **2021**, *2021*, 96–101; c) C. T. Constantinou, P. L. Gkizis, O. T. G. Lagopanagiotopoulou, E. Skolia, N. F. Nikitas, I. Triandafillidi, C. G. Kokotos, *Chem. Eur. J.* **2023**, e20230126; d) E. Voutyritsa, I. Triandafillidi, N. V. Tzouras, N. F. Nikitas, E. K. Pefkianakis, G. C. Vougioukalakis, C. G. Kokotos, *Molecules* **2019**, *24*, 1644; doi:10.3390/molecules24091644.
[27] S. Cailotto, R. Mazzaro, F. Enrichi, A. Vomiero, E. Cattaruzza, D. Cristofori, E. Amadio, A. Perosa, *ACS Appl. Mater Interf.* **2018**, *10*, 40560–40567.
[28] S. Cailotto, M. Negrato, S. Daniele, R. Luque, M. Selva, E. Amadio, A. Perosa, *Green Chem.* **2020**, *22*, 1145–1149.
[29] C. Campalani, E. Cattaruzza, S. Zorzi, A. Vomiero, S. You, L. Matthews, M. Capron, C. Mondelli, M. Selva, A. Perosa, *Nanomaterials* **2021**, *11*, 524.
[30] C. Campalani, N. Bragato, A. Morandini, M. Selva, G. Fiorani, A. Perosa, *Catal. Today* **2023**, 114039.
[31] S. M. Bonesi, R. Erra-Balsells, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1583–1595.
[32] a) D. Xu, Y. Huang, Q. Ma, J. Qiao, X. Guo, Y. Wu, *Chem. Eng. J.* **2023**, *456*, 141104; b) Y. Zhou, E. M. Zahran, B. A. Quiroga, J. Perez, K. J. Mintz, Z. Peng, P. Y. Liyanage, R. R. Pandey, C. C. Chusuei, R. M. Leblanc, *Appl. Catal. B* **2017**, *248*, 157–166.
[33] A. K. Vardhaman, P. Barman, S. Kumar, C. V. Sastri, D. Kumar, S. P. De Visser, *Chem. Commun.* **2013**, *49*, 10926–10928.
[34] K. Matsuo, E. Yamaguchi, A. Itoh, *J. Org. Chem.* **2020**, *85*, 10574–10583.

Manuscript received: June 1, 2023
Revised manuscript received: June 16, 2023
Version of record online: July 6, 2023