Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2024

#### **Supplementary Material**

# Carbon Dots on Laponite Hybrid Nanocomposites: Solid-state emission and Inter-aggregate Energy Transfer

Bruno S. D. Onishi,<sup>1,2</sup> Albano N. Carneiro Neto,<sup>1</sup> Ricardo Bortolleto-Santos,<sup>3</sup> Valmor R. Masterlaro,<sup>4</sup> Luís D. Carlos,<sup>1</sup> Rute A. S. Ferreira,<sup>1,\*</sup> Sidney J. L. Ribeiro<sup>2,\*</sup>

<sup>1</sup> Department of Physics and CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>2</sup> Institute of Chemistry, São Paulo State University–UNESP, São Paulo, Araraquara, 14800-060, Brazil

<sup>3</sup>Postgraduate Program in Environmental Technology, University of Ribeirão Preto–UNAERP, São Paulo, Ribeirão Preto, 14096-900, Brazil

<sup>4</sup>São Carlos Institute of Chemistry, University of São Paulo–USP, São Paulo, São Carlos, 13566-590, Brazil.

\* Corresponding authors: rferreira@ua.pt (Rute A. S. Ferreira); sidney.jl.ribeiro@unesp.br (Sidney J. L. Ribeiro)

#### Contents

Table S1	3
Figure S1	4
Figure S2	5
Figure S3	6
Table S2	7
Figure S4	8
Figure S5	9
Figure S6	9
Figure S7	10
Figure S8	10
Figure S9	11
Figure S10	12

12
13
13
14
14
15
16
16
17
- -

Samples	2 <sup>θ</sup> (degree)	d (Å)
CDLP-A	6.75	$13.08 \pm 0.08$
CDLP-B	6.70	$13.18 \pm 0.08$
CDLP-C	6.70	$13.18 \pm 0.08$
CDLP-D	6.67	$13.18 \pm 0.08$
Lap	6.96	$12.69 \pm 0.07$
<b>Pristine Laponite</b>	6.92	$12.76 \pm 0.07$

Table S1 - Data of angle 2 $\theta$  diffracted planes and interlayer distance (d) calculated by Bragg's Law.



**Figure S1.** Powder X-Ray Diffraction (PXRD) patterns of CDLP without pH adjustment (pH = 5) and pristine Laponite.



**Figure S2**. Scanning Transmission Electron Microscopy (STEM) (a) images of CDLP-D (b) with size distribution in (c); STEM images of CD (d) and (e) with size distribution in (f). The histogram of nanoparticle's size distribution was generated by counting at least 150 nanoparticles from several images obtained. The red solid line represents the fitted log-normal distribution, providing an average particle size of  $2.8 \pm 0.5$  nm for CDLP-D and  $15.8 \pm 2.3$  nm.



**Figure S3**. EDX mapping using SEM microscope coupled with EDX spectrometer for CDLP-A (a), CDLP-D (c) and Lap (e); with the respective EDX spectrum (b), (d) and (f). The alluminum content is from the substrate used.

Wavenumber (cm <sup>-1</sup> )	Assignment	Refs
3690	v(Mg <sub>3</sub> OH)	[37]
3720 - 3000	v(OH)/v(NH)	[38,39]
2934	$v_{\rm (CH)}$	[38,39]
1774	v(C=O) – conjugation with oxygen	[38,39]
1704	v(C=O) – amide	[38,39]
1656	δ( <sub>NH)</sub>	[38,39]
1632	$\delta(\text{OH})$ – adsorbed water	[38,39]
1596	v(COO) – carboxylate asymmetric	[40-42]
1552	v(C=C)/v(C=N) – aromatic ring	[38,39]
1440	$\delta( m CH)$	[38,39]
1392	$v(\text{COO})$ – carboxylate symmetric/ $\delta$ (C–N)	[40-42]
1296	$\delta(\text{COH})$	[38,39]
1172	<i>ν</i> (CO)	[38,39]
966	$v_{(SiO)}$	[37]
643	$\delta_{ m (MgO)}$	[37]
430	$\delta_{ m (Si-O-Si)}$	[37]

**Table S2** - FTIR band assignments for the bonds vibrations of the samples in the region of 4000 - 410 cm-1; v represents stretching, and  $\delta$  deformation



**Figure S4.** X-Ray Photoelectron Spectroscopy survey spectrum of CDLP-D (a); high-resolution XPS spectrum of O 1s (b), N 1s (c), C 1s (d), Si 2p (e) and Mg 2p (f) of CDLP-D sample.



**Figure S5.** XPS survey spectrum of CD (a); high-resolution XPS spectrum of O 1s (b), N 1s (c) and C 1s (d) of CD sample.



**Figure S6.** XPS survey spectrum of Lap (a); high-resolution XPS spectrum of O 1s (b), Si 2p (c) and Mg 2p (d) of Lap sample.



Figure S7. UV-Vis spectrum in the 200 - 800 nm range of  $1.0 \text{ mg} \cdot \text{mL}^{-1}$  water suspension of CD, CDLP-A, and CDLP-D samples.



**Figure S8.** Room temperature (298 K) (a) emission and (b) excitation spectra of CD in water suspension. (c) Room temperature emission decay of CD suspension using a 388 nm nano-LED monitoring emission at 450 and 517 nm. (d) Residual plots of the monoexponential fitting on the decay curves presented in (c). For suspension, the quantum yield ( $\phi$ ) at excitation wavelengths of 360, 400, and 500 was  $0.06 \pm 0.01$ ,  $0.03 \pm 0.01$  and  $0.01 \pm 0.01$  respectively; for solid sample in all excitation wavelengths, the  $\phi$  was below 0.01. The lifetime obtained by monoexponential fitting in the emission decay curve for suspension was  $12.0 \pm 1.2$  and  $9.4 \pm 0.9$  ns for 450 and 517 nm wavelength emission, respectively.



**Figure S9.** Room temperature excitation spectra of CDLP-A in (a) powder and (c) water suspension and CDLP-D in (b) powder and (d) water suspension, respectively.



Figure S10. Low temperature (13 K) excitation spectrum of (a) CDLP-A and (b) CDLP-D.



**Figure S11.** Photographs of powder (a) and water suspension (b) samples, with UV lamp ( $\lambda_{exc} = 365 \text{ nm}$ ) above and room light below. From left to right: CD, CDLP-A and CDLP-D.



Figure S12. Room and low temperature emission comparison of CDLP-A.



**Figure S13.** Room and low temperature decay curves of CDLP-D monitored at 450 nm and excited at 375 nm using a nano-LED. IRF is the instrumental response function. The model used was  $y = y_0 + \sum_n A_n exp^{\text{EC}}(-(t_n - x_0)/\tau_n)$ 

n, where y is the PL intensity,  $y_0$  is a constant,  $A_n$  the amplitude of the *n* component of the decay,  $t_n$  is the experimental decay data, and  $x_0 = 6.96$  ns is obtained by the instrument response function. The best fitting was achieved by applying

one component. Lifetime obtained at 298 K was  $\tau_{450}^{298} = 7.0 \pm 0.1$  ns and at 13 K was  $\tau_{450}^{13} = 10.0 \pm 0.1$  ns.



**Figure S14.** Residual plots of the monoexponential fits of the room temperature emission decay curves at 450 nm of CDLP-A (a) powder and (c) suspension and CDLP-D (b) powder and (d) suspension. A 388 nm nano-LED was used as the excitation source.



Figure S15. Residual plots of the monoexponential fits of the (a) room and (b) low temperature emission decay curves at 575 nm of CDLP-D. A 388 nm nano-LED was used as the excitation



source.

Figure S16. Residual plots of the monoexponential fits of the (a) room and (b) low temperature emission decay curves at 450 nm of CDLP-D. A 375 nm nano-LED was used as the excitation source.



Figure S17. Deconvolution of CDLP-D emission band with respective barycenter.  $\sigma_D = 17,873$  cm<sup>-1</sup> with  $\gamma_D = 5,194$  cm<sup>-1</sup> and  $\sigma_A = 23,112$  cm<sup>-1</sup> with  $\gamma_A = 3,232$  cm<sup>-1</sup>.



Figure S18. Estimated energy transfer rate between CDs aggregates as a function of their average distance. The black point corresponds to the experimental rate  $W = 4.7 \times 10^7 \text{ s}^{-1}$  attributed to the distance of 9.6 nm.



**Figure S19.** Thermogravimmetic curves (TGA) (a) and derivate termogravimetric curves (DTG) (b). The weight loss was determinated by *TGA curve*, using the event *obtained in DTG* of CDs decomposition, which was 326°C for CDLP-D and 411 °C for CDLP-A.

Samples	% C	% H	% N
CDLP-A	8.0 (±0.2)	2.1 (±0.1)	0.4 (±0.1)
CDLP-D	9.0 (±0.2)	1.6 (±0.1)	2.2 (±0.1)

 Table S3 - CHN elemental analysis for CDLP-A and CDLP-D samples