Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Composites based on nitroprusside cyano-bridged coordination polymers particles and chitosan for NO delivery

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Modelling

Production of NO$_{(g)}$

The NO is generated by a light irradiation of coordination polymer based on nitroprusside material. The light irradiation produces the following chemical reaction:

$$\left[Fe^{II}(CN)_5NO\right]^{2-}\xrightarrow{h\nu}[Fe^{III}(CN)_5]^{2-}+NO_{(g)} \tag{1}$$

Its kinetic is characterised by the reaction rate constant k_{NO} (s^{-1}) and the $[Fe^{II}(CN)_5NO]$ concentration:

$$\frac{\partial[Fe^{II}(CN)_5NO]}{\partial t}=-k_{NO}\cdot[Fe^{II}(CN)_5NO] \tag{2}$$

The result of this equation is:

$$[Fe^{II}(CN)_5NO]=C_{TOT-NO}\cdot e^{-k_{NO}\cdot t} \tag{3}$$

with C_{TOT-NO} which is the maximal concentration of NO that the starting material can produce (mol.m^{-3}).

The $[NO_{(g)}]$ concentration can be written as a function of $[Fe^{II}(CN)_5NO]$ and C_{TOT-NO}:

$$[NO_{(g)}]=C_{TOT-NO}-[Fe^{II}(CN)_5NO] \tag{4}$$

and

$$[NO_{(g)}]=C_{TOT-NO}\left(1-e^{-k_{NO}\cdot t}\right) \tag{5}$$

Diffusion model

In this model we consider that the concentration of NO$_{(g)}$ represented by c (mol.m^{-3}) follows the diffusion equation:

$$\frac{\partial c}{\partial t}+D\cdot\Delta c=f \tag{6}$$

with f which is a volume source term (mol.(m^{-3}.s^{-1})) corresponding to the quantity of NO produced by the irradiation of the starting material as a function of the time, and D (m^2.s^{-1}) the diffusion coefficient of NO in the volume:

$$f = \frac{\partial [NO_{(g)}]}{\partial t} = C_{TOT-NO} \cdot k_{NO} \cdot e^{-k_{NO} \cdot t} \qquad (7)$$

In order to take into account the evacuation of the $NO_{(g)}$ outside the material after release, we consider that the $NO_{(g)}$ molecules on the surface will be directly desorbed:

$$D \cdot \vec{n} \cdot \vec{\nabla} c = - q_{out} \cdot c \qquad (8)$$

with $q_{out} \gg 1$ μm.days^{-1} (in our case).

Then c_{lib} (mol.m^{-2}) the quantity per unit of surface of $[NO_{(g)}]$ liberated on a point P at a position (x,y) on a surface is counted using the following equation:

$$\frac{\partial c_{lib}(t,x,y)}{\partial t} = q_{out} \cdot c(t,x,y) \qquad (9)$$

The total quantity of liberated $NO_{(g)}$ ($c_{lib,TOT}$) is:

$$c_{lib,TOT}(t) = \iint_S c_{lib}(t,x,y) dS \qquad (10)$$

Now if we make the assumption that the volume concentration c and C_{TOT-NO} are homogeneous in the x and y directions, and that lengths in x and y $\gg$ length in z, then we can deduce from equation (6) an equation of surface concentration as a function of z:

$$\frac{\partial c}{\partial t} + D \cdot \frac{\partial^2 c}{\partial z^2} = \frac{C_{TOT-NO} \cdot k_{NO} \cdot e^{-k_{NO} \cdot t}}{L} \qquad (11)$$

and:

$$\frac{\partial c_{lib}}{\partial t} = q_{out} \cdot c \qquad (12)$$

With now c (in mol.m^{-1}), C_{TOT-NO} (in mol) and where L is the thickness of PBA material in the z direction we obtain the total quantity of liberated $NO_{(g)}$ c_{lib} in mol (or in mol.g^{-1}) if we normalize with the mass of the sample).

Surface effect

The SEM-EDX measurements show that the density of $Ag_2[Fe(CN)_5(NO)]$ particles is higher on the surface of the film in comparison with the Fe^{2+} analogue, indicating a higher amount of $NO_{(g)}$ which can be liberated by the surface. To take into account this phenomenon, the surface conditions are modified as follows:

$$D \cdot \vec{n} \cdot \vec{\nabla} c = C_{S-NO} \cdot k_{NO} \cdot e^{-k_{NO} \cdot t} - q_{out} \cdot c \qquad (13)$$

with C_{S-NO} a surface source term in mol for equation (6) or in mol.g^{-1} (if we normalize with the mass of the sample).

Equation (11) becomes:

$$\frac{\partial c}{\partial t} + D \cdot \frac{\partial^2 c}{\partial z^2} = \frac{(C_{TOT-NO} - C_{S-NO}) \cdot k_{NO} \cdot e^{-k_{NO} \cdot t}}{L} \quad (14)$$

Diffusion flux

The diffusion flux *J* in (mol.m^{-2}.s^{-1}) represents the quantity of molecules which passes through a surface unit in a time unit. It is defined as follows:

$$\vec{J} = -D \cdot \vec{\nabla} c \quad (13)$$

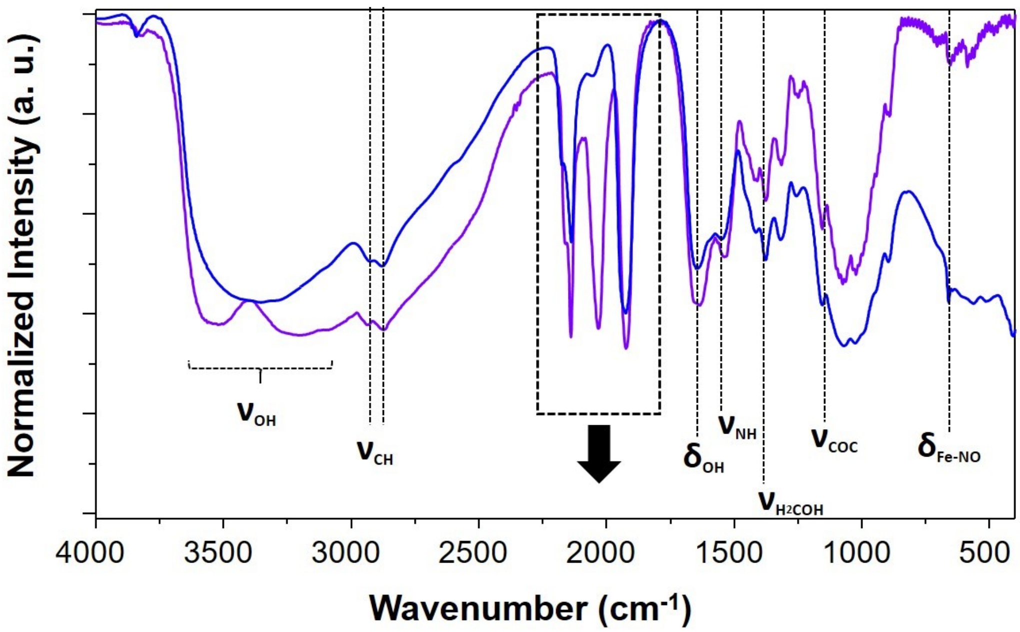
Tables

Table S1. IR characteristic bands' assignment

Pristine chitosane	1@chit	1	2@chit	2	Assignements
-	3838	3844	3844	3854	Overtone ν (NO)
3323	3431	3659	3410	3443	ν (OH)
3291	-	3387	-	-	ν (OH)
2917	2917	-	2920	-	ν_s (CH)
2863	2888	-	2873	-	ν_{as} (CH)
-	2182, 2145 (sh)	2182	2177 (sh), 2141	2177, 2163	ν (CN)
-	2145	2147	2141	2163	ν (CN)
-	1941	1941	1924	1937	ν (NO)
1651	1654		1644	-	ν (CO)
-	-	1616	-	1625	δ (OH)
1558	1525	-	1543	-	δ (NH)
1420	-	-	1422	-	ν (CH-OH)
1375	1378	-	1367	-	ν (CH_2-OH)
1065	1080	-	1053	-	ν (C-O-C)

-	664	666	659	662	δ (Fe-NO)
-	522	520	507	516	ν (Fe-CN)
-	431	443	414	418	δ (Fe-CN)

Figures



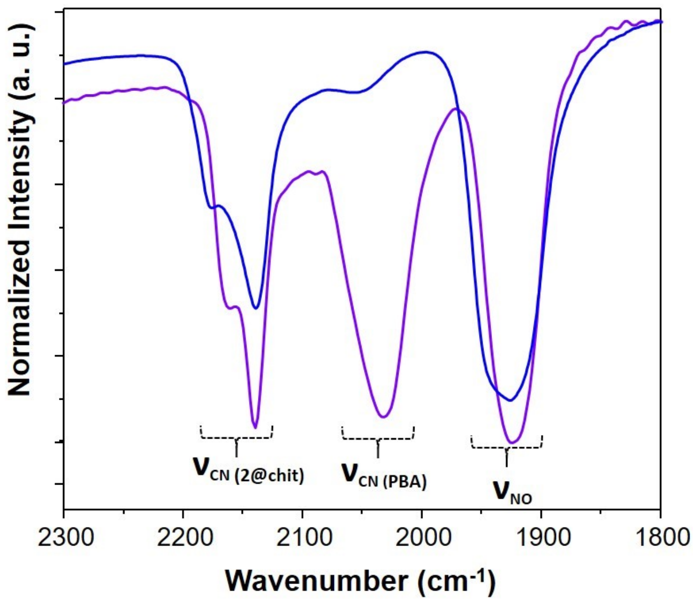


Figure S1. IR spectra f **2@chit** before (blue) and after (purple) NO release; (up) spectral window 4000 - 400 cm^{-1}, (down) spectral window 2300 - 1800 cm^{-1}

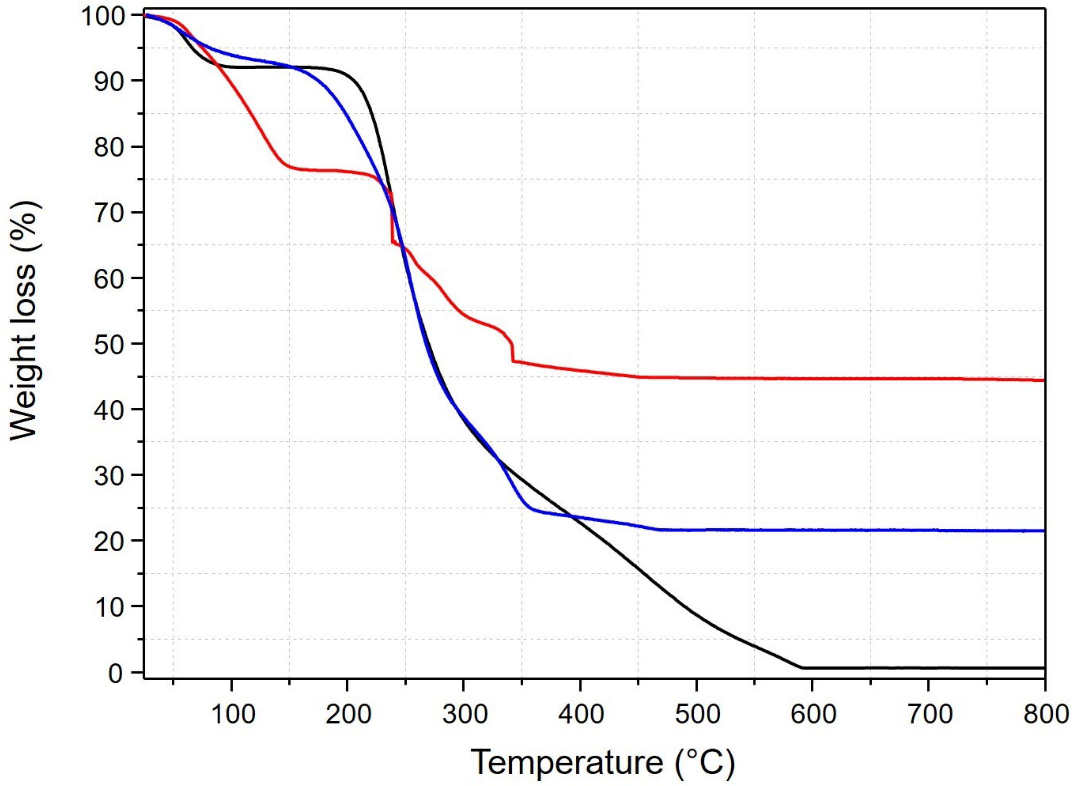


Figure S2. TGA curves of chitosan film (black), **1** (red) and **1@chit** (blue).

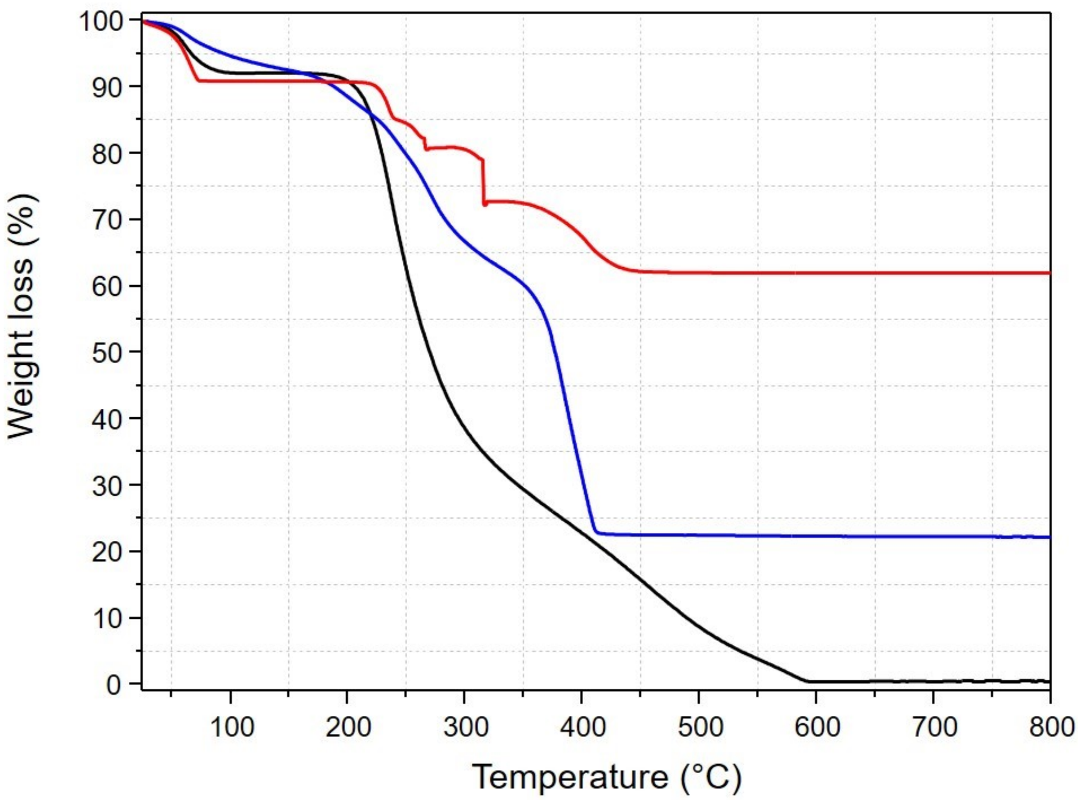


Figure S3. TGA curves of chitosan film (black), **2** (red) and **2@chit** (blue).

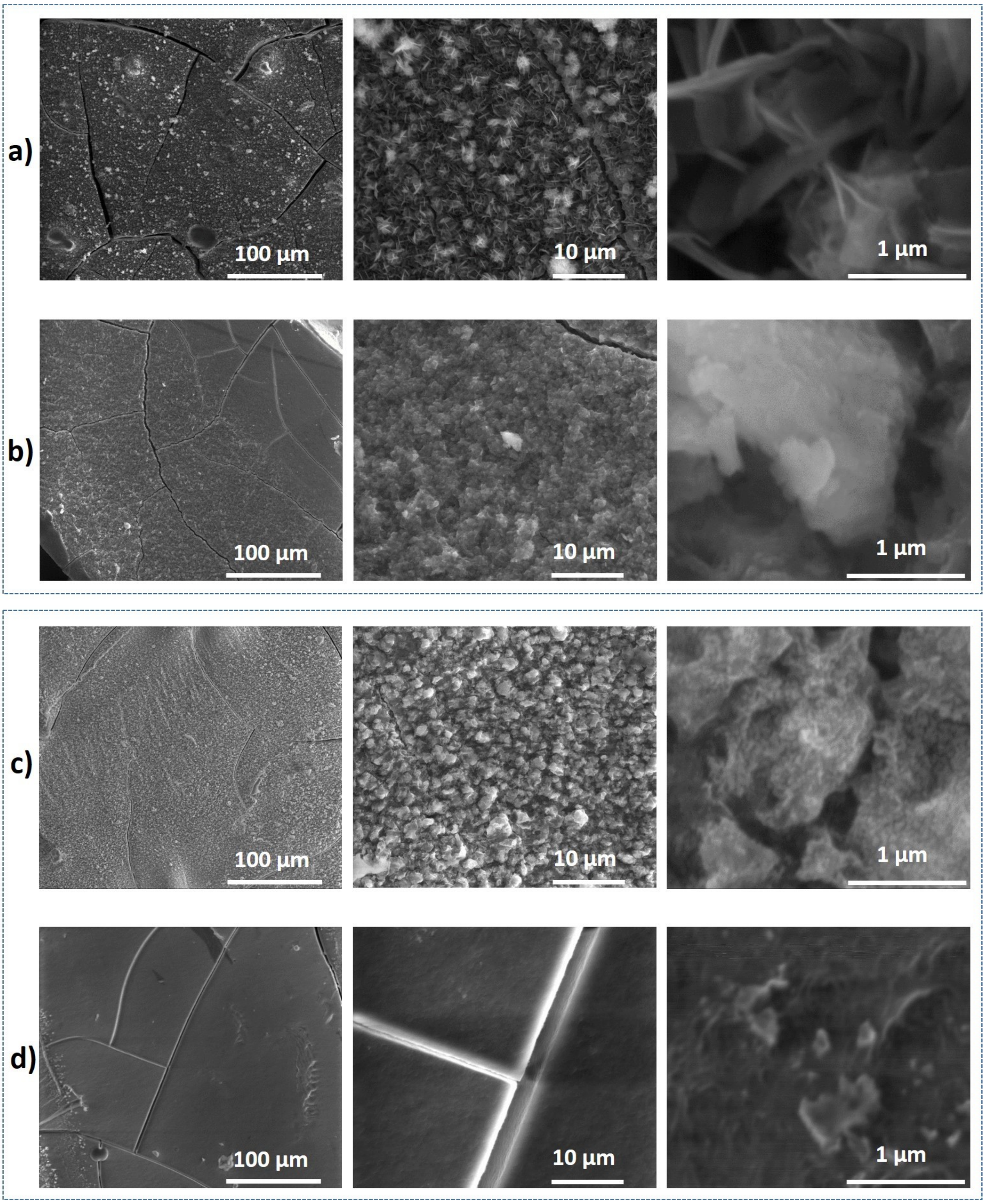


Figure S4. SEM images of the composites (top) **1@chit** : (a) surface and (b) its transversal cut; (bottom) **2@chit :** (c) surface, (d) transversal cut.

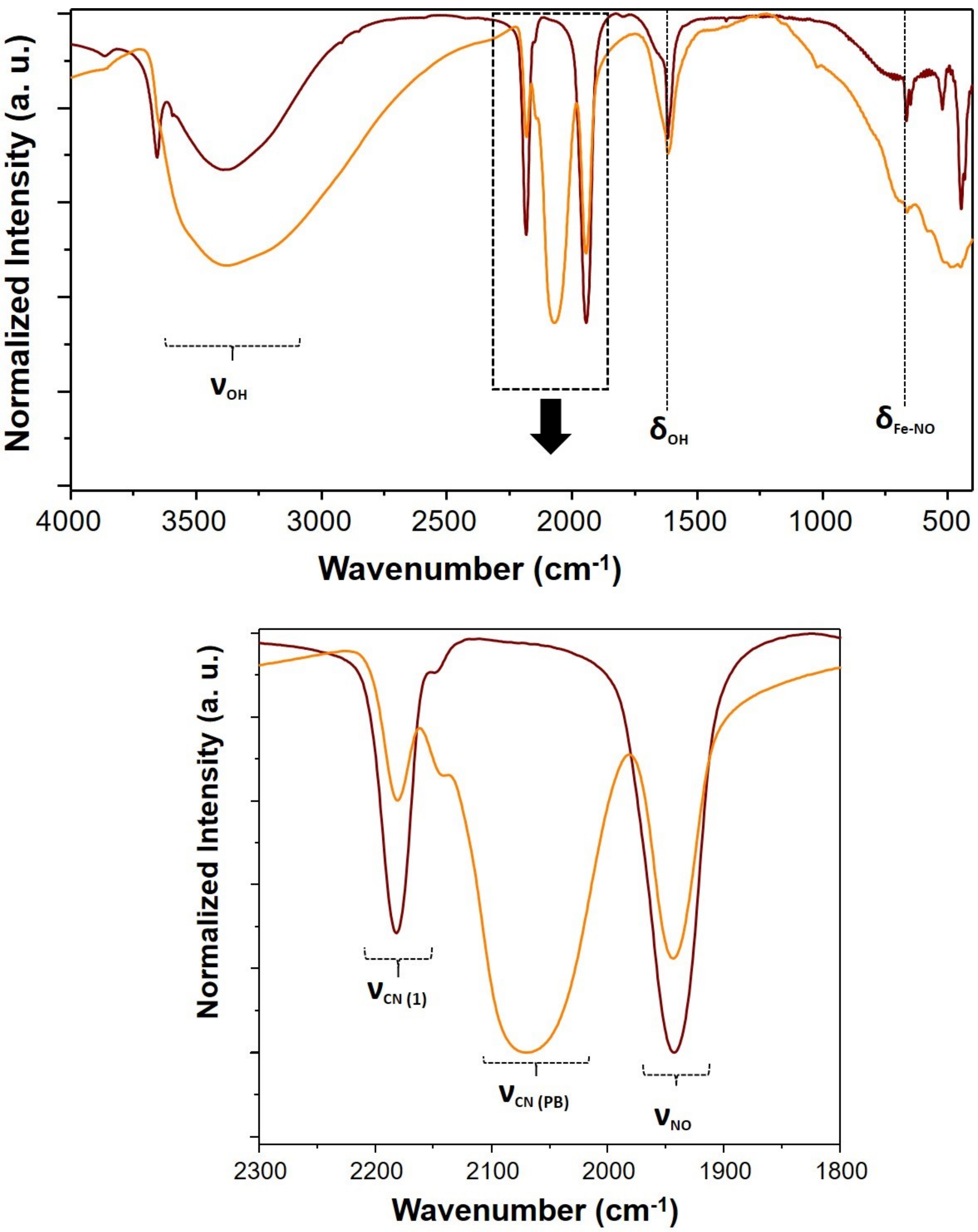


Figure S5. IR spectra f **1** before (brown) and after (orange) NO release; (up) spectral window 4000 - 400 cm^{-1}, (down) spectral window 2300 - 1800 cm^{-1}

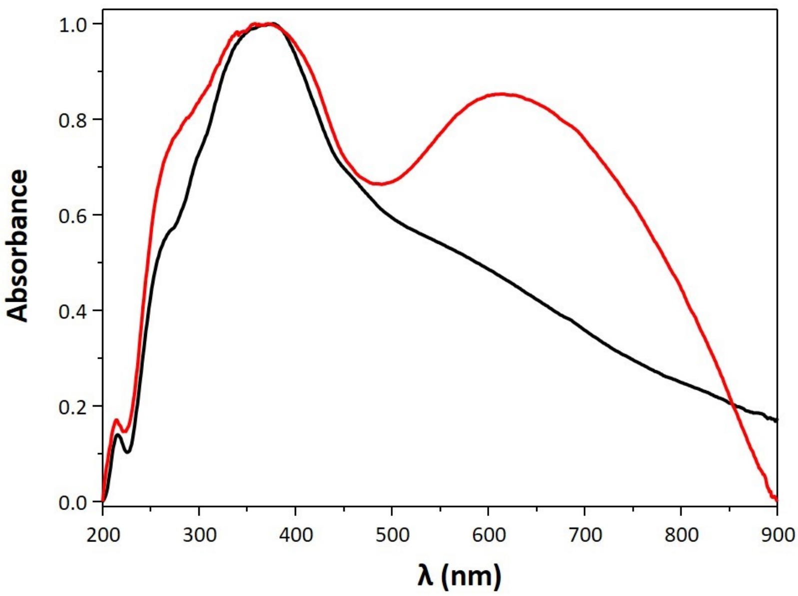


Figure S6. UV-Vis spectra of the nanocomposite **1@chit** before (black) and after (red) irradiation.