Supporting Information

An Efficient approach to Bis-benzoquinonylmethanes On Water Under Catalysis of the Bio-derived O-Carboxymethyl Chitosan

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The $^1$H NMR spectrum of $O$-cm-chitosan in $D_2O$

*The CH peak of $f$ is overlapping with the solvent HOD signal at 4.72.*
The FT-IR spectrum of fresh and recovered O-cm-chitosan

The FT-IR spectrum shows the basic characteristic absorptions at: 3424 cm\(^{-1}\) (O–H stretch.), 2927 cm\(^{-1}\) (C–H stretch.), 1598 cm\(^{-1}\) (N–H bend), 1727 cm\(^{-1}\) (–COOH), 1076–1143 cm\(^{-1}\) (–C–O stretch.).
The X-ray diffraction (XRD) patterns of chitosan and O-cm-chitosan

The XRD of original chitosan displays two characteristic peaks at $2\theta = 10^\circ$ (weak diffraction peak) and $2\theta = 20^\circ$ (strong diffraction peak) indicating a considerably high degree of crystallinity for chitosan. However, as the XRD of O-cm-chitosan shows, much (but not all) of the crystallinity was lost on O-carboxymethylation of chitosan. Therefore, the synthesized O-cm-chitosan is rather an amorphous bio-derived polymer, very likely due to a large change in intermolecular hydrogen bonding between the individual chains of chitoan on O-carboxymethylation.
The TGA and DSC traces of O-cm-chitosan display a smooth endothermic weight loss at 60-274 °C, presumably due to dehydration and decarboxylation of O-cm-chitosan. The large weight loss at 296 °C in the TGA thermogram of O-cm-chitosan corresponds to a strong exothermic decomposition peak in the DSC trace of this compound. In an earlier study, the maximum thermal decomposition temperature of chitosan was reported to be 302 °C which is slightly greater than the value of 296 °C determined by the present study for O-cm-chitosan. The lower thermal stability of O-cm-chitosan with respect to that of chitosan can be attributed to the less crystallinity and presence of carboxyl groups in this compound.
The scanning electron microscopy (SEM) images of chitosan and O-cm-chitosan

The SEM images showed a smooth surface morphology for chitosan (A1, A2, A3) before being carboxymethylated. Upon O-carboxymethylation (B1, B2, B3), the surface of chitosan was completely changed, indicating that the desired modification was achieved.
S6 The $^1$H NMR spectrum of 3,3′-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3a)

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$H 7.91 (d, $J$ 6.7 Hz, 2H), 7.83 (d, $J$ 6.3 Hz, 2H), 7.71 (br t, 2H), 7.62 (br t, 2H), 7.10-7.01 (m, 7H, Ph), 6.64 (1H, s, Aliph. CH) ppm.
A-Asghari 1H NMR in DMSO at 298 K 93/6/22

Current Data Parameters
NAME: Guest-1
EXPNO: 82
PRGNO: 1

F2 - Acquisition Parameters
B1ax_2: 20140914
Time: 9.34
INSTTRM: spect
POWERS: 5 mm QNP 1/13
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 16
DS: 0
SW: 0.000000 Hz
FIQP: 0.035476 Hz
AQ: 1.630500 s
NS: 574.7
DN: 0.000000 usec
DE: 6.50 usec
TE: 298.10 K
DI: 0.000000000000
NCREST: 0.000000000000
NOEAK: 0.015000000000

-------- CHANNEL f1 --------
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PL1: -3.00 dB
SF10: 500.1300885 MHz

F2 - Processing parameters
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W: 2H
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

2D NMR plot parameters
CX: 20.00 cm
CY: 33.00 cm
F1P: 6.668 ppm
F1: 4305.55 Hz
F2P: 5.668 ppm
F2: 9343.84 Hz
PPM/cm: 0.13914 ppm/cm
Hz/cm: 69.66583 Hz/cm
The $^1$H NMR spectrum of 3,3'-((4-Chlorophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3b)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_{H}$ 16.37 (br s, 2 Enolic OH), 7.99 (d, $J$ 7.2 Hz, 2H), 7.90 (d, $J$ 6.8 Hz, 2H), 7.78 (br t, 2H), 7.69 (br t, 2H), 7.22 (br d, 2H, Ar), 7.15 (br d, 2H, Ar), 6.68 (1H, s, Aliph. CH) ppm.
Sample code: 1 (haji)

![Spectrum Image]

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**Bruker**

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**PTDRES:** 6.125266 Hz  
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**DI:** 4.00000000 usec  
**TDD:** 1  

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**CHANNEL f1**

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**PL1:** 2.00 dB  
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**S1:** 32768  
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**WNR:** FM  
**RSL:** 0  
**LS:** 0.30 Hz  
**C3:** 0  
**PC:** 1.00
The $^1$H NMR spectrum of 3,3'-(4-
Hydroxyphenyl)methylene)bis(2-
hydroxynaphthalene-1,4-dione) in
DMSO-$d_6$ (3c)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$
16.56 (br s, 2 Enolic OH), 7.97 (d, $J$
7.6 Hz, 2H), 7.88 (d, $J$ 7.6 Hz, 2H),
7.77 (t, $J$ 7.6 Hz, 2H), 7.68 (t, $J$ 7.6 Hz,
2H), 6.90 (d, $J$ 8.4 Hz, Ar), 6.58 (s, 1H,
Phenolic OH), 6.56 (d, $J$ 8.4 Hz, Ar),
6.58 (1H, s, Aliph. CH) ppm.
The $^1$H NMR spectrum of 3,3׳-(3-Methoxyphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3d)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$
16.45 (br s, 2 Enolic OH), 7.98 (d, $J$ 7.6 Hz, 2H), 7.89 (d, $J$ 7.6 Hz, 2H), 7.77 (t, $J$ 7.6 Hz, 2H), 7.68 (t, $J$ 7.6 Hz, 2H), 7.09 (t, $J$ 8.0 Hz, 1H, Ar 5-H), 6.72-6.64 (m, 3H, Ar), 3.64 (s, 3H, OCH$_3$), 6.66 (s, 1H, Aliph. CH) ppm.
The $^1$H NMR spectrum of 3,3′-((4-Nitrophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3e)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$

16.18 (br s, 2 Enolic OH), 8.06 (d, $J$ 8.6 Hz, 2H, Ar), 7.99 (d, $J$ 7.2 Hz, 2H), 7.91 (d, $J$ 7.6 Hz, 2H), 7.79 (t, $J$ 7.4 Hz, 2H), 7.71 (t, $J$ 7.2 Hz, 2H), 7.43 (d, $J$ 8.6 Hz, 2H, Ar), 6.79 (s, 1H, Aliph. CH) ppm.
The $^1$H NMR spectrum of 3,3'-(4-Methylphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3f)

$^1$H NMR (400 MHz, DMSO-d6): $\delta_{H}$ 16.45 (br s, 2 Enolic OH), 7.97-6.99 (m, 12H), 6.65 (s, 1H, Aliph. CH), 2.23 (s, 3H, CH$_3$) ppm.
The $^1$H NMR spectrum of 3,3'-((3-Bromophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3g)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$

16.38 (br s, 2 Enolic OH), 7.98-7.70 (m, 8H), 7.30-7.16 (m, 4H, Ar), 6.70 (s, 1H, Aliph. CH) ppm.
Sample code: G (haj1)
The $^1$H NMR spectrum of 3,3′-((4-chlorophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-$d_6$ (3h)

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$
16.43 (br s, 2 Enolic OH), 7.97 (d, $J$ 7.6 Hz, 2H), 7.89 (d, $J$ 7.2 Hz, 2H), 7.77 (t, $J$ 7.4 Hz, 2H), 7.68 (t, $J$ 7.4 Hz, 2H), 7.02 (d, $J$ 8.4 Hz, 2H, Ar), 6.74 (d, $J$ 8.4 Hz, 2H, Ar), 6.62 s, 1H, Aliph. CH), 3.69 (s, 3H, OCH$_3$) ppm.
Sample code: H (haji)