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Supplementary Material

Investigating the Effect of Hydrothermal Carbonisation Reaction Times on the Photoluminescence of Bio-Oil-Derived Carbon Polymer Dots

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Table S1: synthesis approaches, size, optical properties, and proposed mechanism of PL for CDs synthesised from chitosan and chitin.

Synthesis	Size (nm)	Proposed PL mechanism	λ_{max} (nm)	Quantum yield (%)	Lifetime (ns)	Reference
Chitosan Microwave, HTC 180 °C, 600W	2.1 1.0 – 3.5	Emission from the carbon core at short wavelengths Emission shifts red upon N and P doing	406 @ 320nm Excitation dependent	-	-	1
Chitosan HTC 190 °C, 15 h	7 4 - 11	Non-uniform size Surface emission sites	408 @ 330 nm Excitation dependent	16.61	-	2
Chitosan & p-phenylenediamine HTC 220 °C, 18 h	1.2 – 2.6	Surface emissive sites Emission from carbon core	520 @ 390 nm Excitation independent	54	-	3
Chitosan HTC 200 °C, 10 h	2.13 0.5 - 4	C=O/C=N is the luminescence centre of CD Phosphorescence when immobilized in PVA	533 @ 457 nm Excitation dependent	38	CDs 1.24 (τ1) 15.69 (τ2) CDs-PVA 0.03 s (59.25%) 0.45 s (40.75%	4
Chitosan HTC	2 1 – 4	Non-uniform size Surface emission sites	410 @ 330 nm Excitation	_	_	5

180 °C, 24 h			dependent			
Chitosan and κ-carrageenan HTC 220 ◦C, 18 h	8 4 – 20	Surface emission sites	420 @ 365 nm Excitation dependent	59	3.75 (τ1) 11.39 (τ2)	6
Chitosan HTC 180°C, 5h	2 - 4	-	430 @ 330 nm Excitation dependent	18.9	-	7
Chitosan HTC 180 °C 12 h	5 4 – 7	Surface emissive states	400 @ 280 nm Excitation dependent	-	-	8
Chitosan Chitin HTC EtOH 200 °C, 6h	8.31 ± 0.3 14.1 ± 2.4	Emission from the hybridised carbon core Surface emissive sites	≈440 @ 360 nm ≈450 @ 380 nm Excitation dependent	13.4 11.6	-	9
Chitosan HTC 200 °C, 12 h	4.68 ± 1.09	Non-uniform size Surface emissive sites	400 @ 320 nm Excitation dependent	13	3.2 (τ1) 7.87 (τ2) 0.48 (τ3)	10
Chitin HTC 240°C, 10h	4.21 1 - 7	Surface emissive sites	430 @ 360 nm Excitation dependent	54	-	11
Chitin Microwave HTC 180°C ,1000 W	2 - 12	-	480 @ 370 nm Excitation dependent	5.1	-	12
Chitin HTC 200°C, 8h	2 - 8	-	405 @ 330 nm Excitation dependent	25.8	-	13

Table S2: Yields of products from the pyrolysis of chitin.

Temperature (°C)	**Bio-char (wt %)**	**Bio-oil (wt %)**	**Gas (wt %)**
450 °C	31.3	36.4	32.3
700 °C	34.5	50.1	15.4

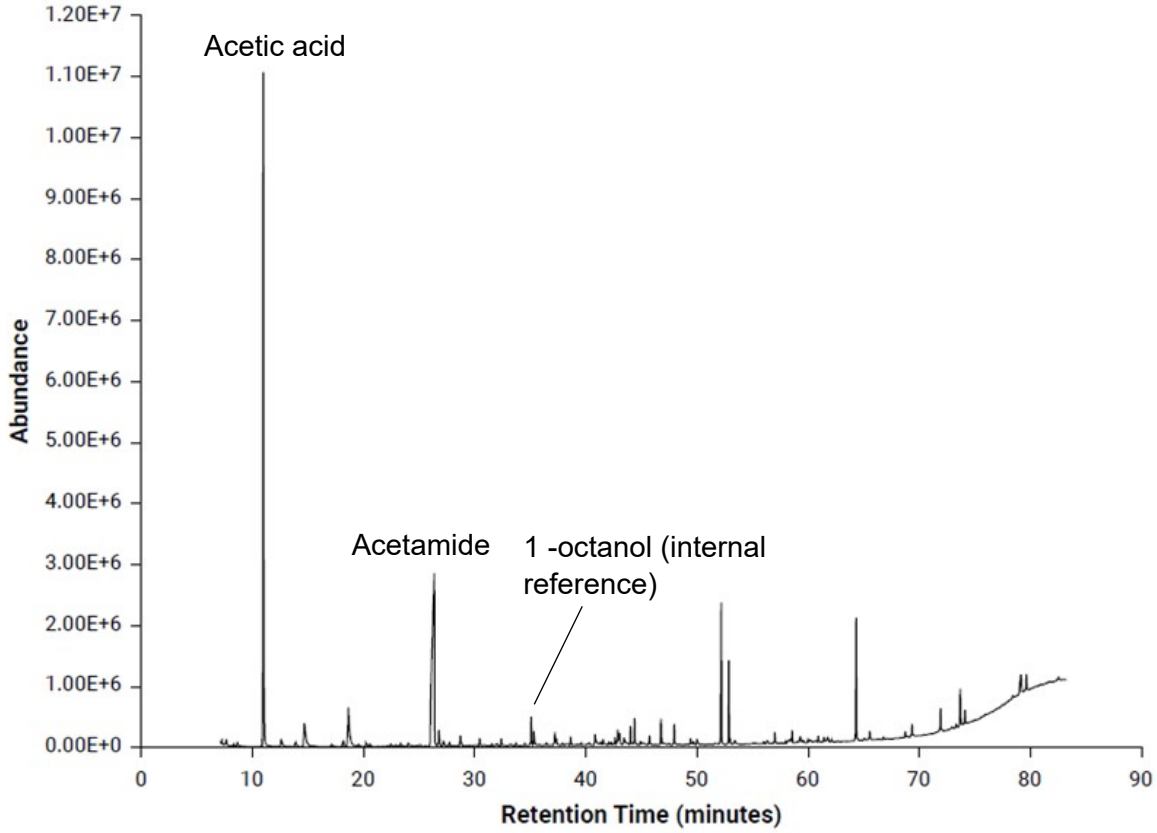

Figure S1: a) GC-MS Analysis (Single Quadrupole) of bio-oil from pyrolysis at 700 °C with a heating rate of with a heating rate of 10 °C/ min in acetyl nitrile with 1-octaonol as an internal reference.

Table S3: Composition of of bio-oil obtained from pyrolysis of chitin at 700 °C with a heating rate of with a heating rate of 10 °C/ min in an inert environment.

Name	**Retention time (min)**	**Quantifier ion (*m/z*)**	**Qualifier ion (*m/z)***
Propane nitrile	8.3	54	28
Acetic acid	10.8	43	60
Oxazole,2,4-dimethyl	12.6	97	42
Pyrazine	13.9	80	53
Pyridine	14.7	79	52
Propanoic acid	17.1	74	73
2-methyl pyridine	18.8	93	66
2,6-Lutidine	22.4	107	32
Acetamide	26.4	59	44
2-Acetylfuran	27.7	95	110
N-Methylacetamide	28.7	43	73
1-octanol (*internal reference*)	35.1	56	70
1,2-Cyclopentanedione, 3-methyl-	35.3	112	55
2-Methylbenzoxazole	37.2	133	64
2-Acetyl pyrrole	38.6	94	109
4-methylphenol	41.3	108	107
4-amino pyridine	42.9	94	67
Piconol	44.0	108	109
Ethanone, 1-(1-methyl-1H-pyrrol-2-yl)-	44.4	108	123
3-Hydroxy-2-methylpyridine	45.7	109	80
5- Hydroxy-2-methylpyridine	47.9	109	80
2-Acetamidophenol	49.4	109	151
3-Acetamidopyridine	64.3	94	136

Table S4: GC-MS analysis of products identified in the organic phase during the purification of nitrogen-doped carbon polymer dots (N-CPDs). Following hydrothermal carbonization (HTC) at 200°C for 2 hours (2H-CPD), the N-CPDs were filtered, centrifuged, and washed with ether. The resulting organic phase was then analysed by GC-MS. The sample was prepared in acetonitrile, with isoamyl ether and methyl laurate used as internal standards.

Name	**Retention time (min)**	**Quantifier ion (*m/z*)**	**Qualifier ion (*m/z*)**
Isoamyl ether (internal standard)	13.9	70	43
3-Methyl-2-cyclopenten-1-one	20.0	96	67
3-Methyl-2-cyclopenten-1-one	23.4	112	55
Phenol	23.4	94	66
3-Aminopyridine	30.9	94	67
3-Pyridinol, 2-methyl-	34.5	109	80
3-Hydroxypyridine	35.6	96	41
2(1H)-Pyridinone, 3,6-dimethyl-	35.7	123	94
Phenol, 4-amino-	36.7	109	80
2,6-Dimethoxyphenol	39.5	154	139
Methyl Laurate (internal standard)	41.7	74	87
3-Acetamidopyridine	52.1	94	136
1,2,3-Benzenetriol	55.6	126	52
2-Acetamidophenol	56.2	109	151
3-Deoxy-D-gluconic acid	61.1	44	54

Table S5: GC-MS analysis of products identified in the organic phase during the purification of N-CPDs. Following hydrothermal carbonization (HTC) at 200°C for 4 hours (4H-CPD), the N-CPDs were filtered, centrifuged, and washed with ether. The resulting organic phase was then analysed by GC-MS. The sample was prepared in acetonitrile, with isoamyl ether and methyl laurate used as internal standards.

Name	**Retention time (min)**	**Quantifier ion (*m/z*)**	**Qualifier ion (*m/z*)**
Propanoic acid	5.4	74	73
2-methyl Pyridine	5.9	93	66
Isoamyl ether (internal standard)	13.8	43	70
Acetamide	14.1	59	44
2,3-Dimethylpyridine	14.5	107	106
2-Acetylfuran	15.2	95	110
N-Methylacetamide	16.9	43	73
2-Ethyl-6-methylpyrazine	17.4	121	122
2,3,5-Trimethylpyrazine	17.6	122	42
2,4,6-Trimethylpyridine	17.8	121	120
2,3-Dimethyl-2-cyclopenten-1-one	19.6	67	110
3-Methyl-2-cyclopenten-1-one	19.9	112	55
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	23.4	112	69
Phenol	26.0	94	66
3-Aminopyridine	30.8	94	67
3-methyl-2(1H)-Pyridinone,	34.5	80	109
6-methyl-3-Pyridinol	36.7	109	80
Methyl Laurate (internal standard)	41.7	74	87
3-Acetamidopyridine	51.9	94	136
2-Methylbenzimidazole	52.5	132	131
2-acetamidophenol	52.6	109	151

Table S6: GC-MS analysis of products identified in the organic phase during the purification of N-CPDs. Following hydrothermal carbonization (HTC) at 200°C for 8 hours (8H-CPD), the N-CPDs were filtered, centrifuged, and washed with ether. The resulting organic phase was then analysed by GC-MS. The sample was prepared in acetonitrile, with isoamyl ether and methyl laurate used as internal standards.

Name	**Retention time (min)**	**Quantifier ion (*m/z*)**	**Qualifier ion (*m/z*)**
2-methyl-Pyridine	5.9	93	66
Isoamyl ether (internal standard)	13.9	43	70
3-Methyl-2-cyclopenten-1-one	19.9	96	67
2,3-dimethyl-2-Cyclopenten-1-one,	23.1	67	110
Phenol	26.0	94	66
2-Methyl-5-(1-propenyl)pyrazine	28.9	133	134
3-Aminopyridine	30.8	94	67
Benzenamine, 4-methoxy-	32.4	108	123
3-amino phenol	34.4	109	80
3-Pyridinol	35.2	95	32
4-amino phenol	36.6	109	80
Methyl Laurate (internal standard)	41.6	74	87
2-Acetylpyrrole	43.3	94	109
Hydroquinone	44.5	110	81
3-Acetamidopyridine	51.9	94	136
2-acetamidophenol	56.2	109	151

Table S7: Yields of bio-char and N-CPDs at different HTC holding times

Time (h)	Bio-char (wt %)	N-CPD (wt %)	Overall yield from chitin (wt %)
2	3.3	3.5	1.8
4	4.4	2.2	1.1
8	12.2	8.8	4.5

Quantum yield calculation:

The quantum yield was calculated at an excitation wavelength of 320 nm relative to quinine sulphate in 0.5 M H_2SO_4 which has a quantum yield of 0.54.

$$\Phi_X = \Phi_R * \frac{I}{I_R} * \frac{OD_R}{OD} * \frac{n^2}{n_R^2}$$

ϕ = quantum yield of sample (X) or reference (R)

I = integrated fluorescence

n = refractive index of solvent

OD = absorbance at excitation wavelength

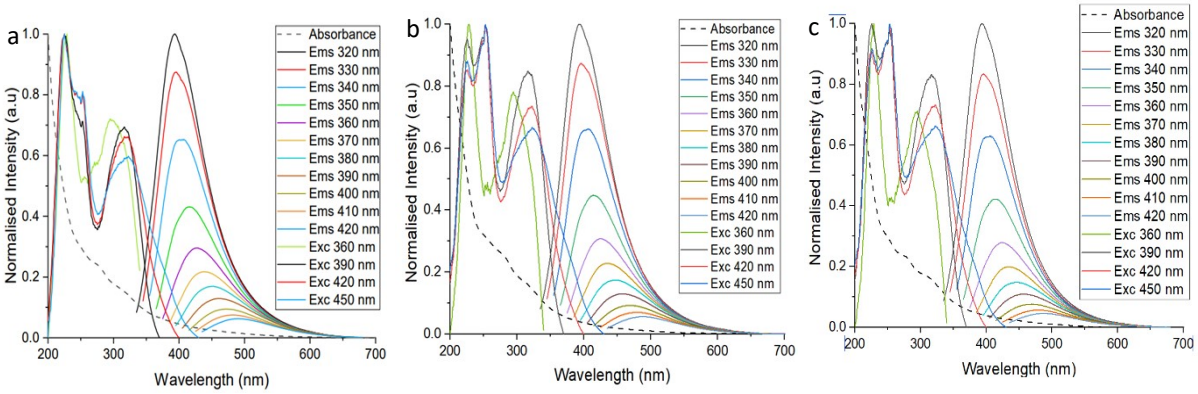

Figure S2: Optical properties of N-CPD dispersed in deionised water and sonicated for 20 minutes. a) 2H-CPD absorbance (dashed line), excitation (left) and emission (right). b) 4H-CPD c) 8H-CPD.

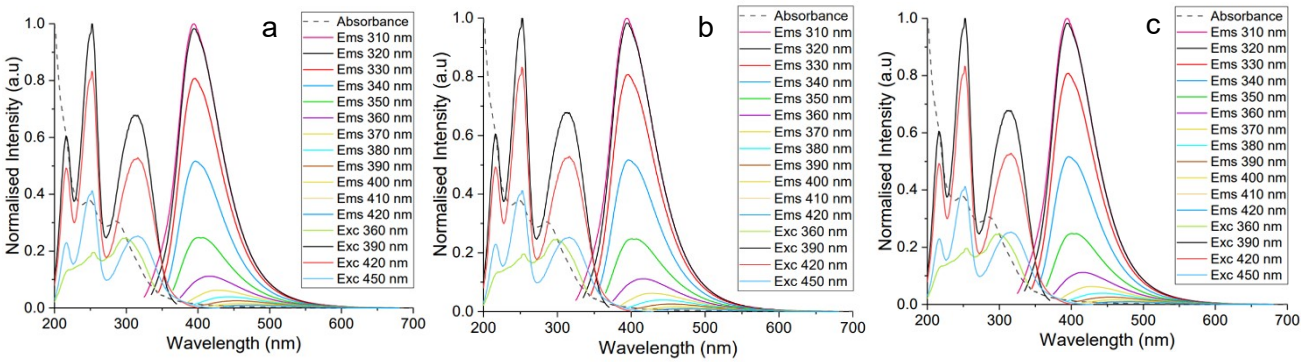

Figure S3 Optical properties of the impurity fraction isolated after the 2-hour HTC dispersed in deionised water and sonicated for 20 minutes. a) 2H-CPD isolated impurity absorbance (dashed line), excitation (left) and emission (right). b) 4H-CPD isolated impurity c) 8H-CPD isolated impurity.

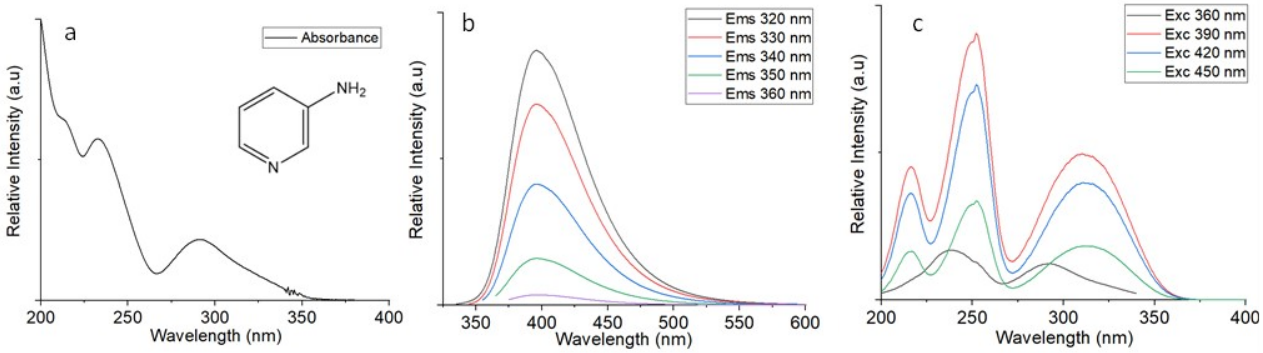

Figure S4: 3-aminopyridene was dissolved in deionised water a) absorbance, b) excitation-photoluminescence and c) excitation spectra.

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