## **Electronic Supplementary Information**

## High-performance liquid chromatographic analysis of as-synthesised N,N'-dimethylformamide-stabilised gold nanoclusters product

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**Fig. S1** Photoluminescence spectra of DMF-AuNCs in aqueous solution at different excitation wavelengths. The blue line displays the strongest fluorescence emission when excited at 350 nm.



**Fig. S2** HPLC chromatograms of the as-prepared DMF-AuNCs product dissolved in (A) MeOH/H<sub>2</sub>O (3:97 v/v) and (B) MeOH/H<sub>2</sub>O (1:4 v/v) which was left to stand for 0, 3, and 12 h respectively. The detection wavelength is 250 nm.



Fig. S3 Photoluminescence spectra of HPLC Fraction 1–12 at different excitation wavelengths.



**Fig. S4** Ion chromatographic separation of (a) a standard mixture of  $Li^+$  (0.50 ppm),  $Na^+$  (5.0 ppm) and  $K^+$  (5.0 ppm) and (b1–b3) HPLC Fraction 1 dissolved in 20.0 mM CH<sub>3</sub>SO<sub>3</sub>H which was left to stand for 0, 3 and 12 h respectively.

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**Fig. S5** (a) MALDI-TOF mass spectra of HPLC Fraction 1. (A) is the expanded mass spectrum of the blue dash rectangle in (a). (A1)–(A3) are the expanded mass spectra of (A).









HPLC fraction	Gold nanocluster species <sup>a</sup>	Quantum yield (%)
As-synthesised product	$Au_x(DMF)_y$ (where $x = 10-14$ and $y = 6-12$ )	0.73
1	$[Au_{10}(DMF)_9]^+$	0.31
2	$Au_{10}(DMF)_9$	0.82
3	$Au_{11}(DMF)_{10}$	0.31
4	$Au_{13}(DMF)_{10}$	4.1
5	Au <sub>13</sub> (DMF) <sub>12</sub>	2.1
6	$Au_{10}(DMF)_7$	0.23
7	$Au_{12}(DMF)_9$	1.7
8	$Au_{14}(DMF)_{10}$	1.4
9	$Au_{10}(DMF)_6$	1.8
10	$Au_{11}(DMF)_6$	0.44
11	Au <sub>12</sub> (DMF) <sub>7</sub>	0.50
12	Au <sub>11</sub> (DMF) <sub>9</sub>	0.54

## **Table S1** Quantum yields of Fraction 1–12

<sup>a</sup> Determined by MALDI-TOF MS.