ICT-Driven Ag^+ Detection Using Xylene-spacer integrated Naphthalene Probes as Fluorescent Chemosensors: Selectivity, Practical Monitoring, and Anticounterfeiting

Narmatha Ganesan[a], Kavanya Srinivasan[a], Elizabeth Antony[a], hab. Jan G. Malecki[b], Abisha Nancy Sukumar[c], Abiram Angamuthu[d,*], J. Prabhu [a], Raju Nandhakumar[a,*]

[a]*Fluorensic Materials Lab, Division of Physical Science, Karunya Institute of Technology and Sciences, (Deemed-to-be University), Karunya Nagar, Coimbatore - 641 114, India.*
**E-mail: nandhakumar@karunya.edu*
[b] *Institute of Chemistry, University of Silesia, Szkolna 9 str. 40-006 Katowice.*
[c] *Department of physics, Karpagam College of Engineering, Coimbatore, Tamil Nadu, India*
[d] *Department of physics, Rathinam Technical Campus, Coimbatore- 641021, Tamil Nadu, India*
**E-mail: aabiram@gmail.com*

2. Experimental section

Materials and Instrumentation

2-hydroxy acetonaphthone, dibromo xylene and naphthaldehyde were purchased from sigma-Aldrich. All the chemicals and reagents were purchased from commercially available sources like Himedia, Loba Chem. Ltd and Sigma Aldrich. ^{1}H NMR and ^{13}C NMR Spectra were recorded on a Bruker 300 MHz high-resolution NMR Spectrometer respectively, using $CDCl_3$ solution with TMS as an internal standard. Coupling constants (J) are measured in Hertz. LC-MS were determined on a Shimadzu Lab Solutions Data Report. UV absorption spectra were recorded at ambient temperature using a Shimadzu UV-Vis spectrophotometer using quartz cuvettes. Fluorescence emission spectra were recorded on a Jasco FP-8200 Spectrofluorometer with quartz cuvettes 4.5 cm height of 1 cm path length. The excitation and emission slit widths recorded were 5.0 nm, all absorption and emission spectra at 24±1°C. The stock solution of the probe **ONA** and **MNA** (2×10^{-3} M) and metal salts (4×10^{-6} M) were prepared in MeOH : H_2O (1:1, v/v), HEPES= 50 mM, pH =7.3). The solution of metal ions was prepared from nitrate and chloride salts of K^+, Ca^{2+}, Na^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, Li^+, Bi^{3+}, Sr^{2+}, Ag^+, Ba^{2+}, Zr^{2+}, Pb^{2+} and Fe^{2+}.

Procedure for the extraction of Ag^+

The real samples of barely, millet, sorghum, oats, black rice, radish, turnip, sweet potato, tapioca were soaked overnight in concentrated nitric acid. On the very next day

it was centrifuged to remove the residues. The supernatants layers were used for the detection of Ag^+.

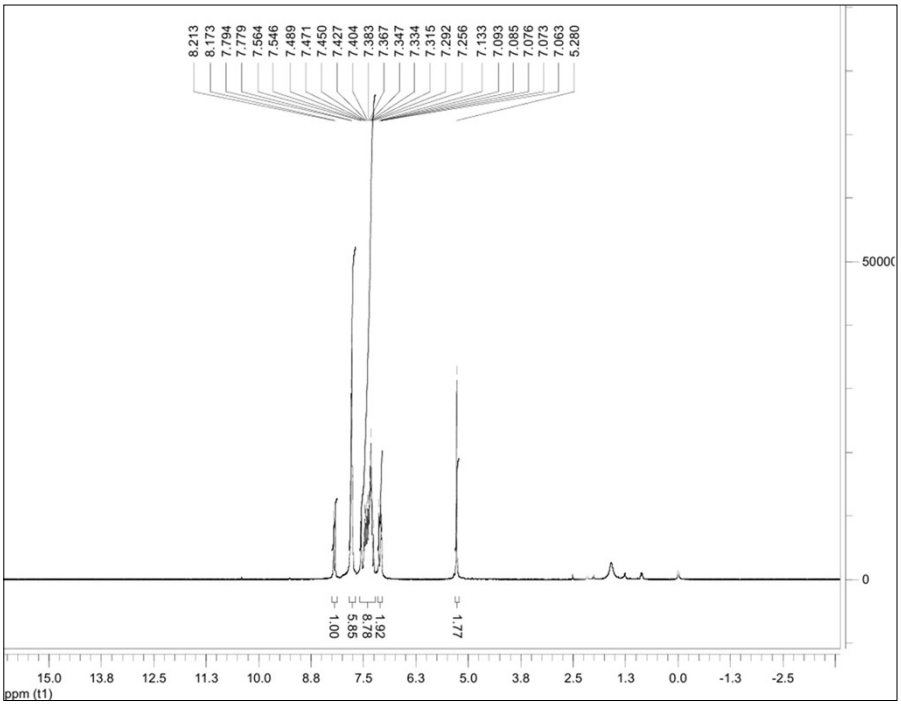

Figure S1. ^{1}H NMR Spectrum of sensor **ONA**

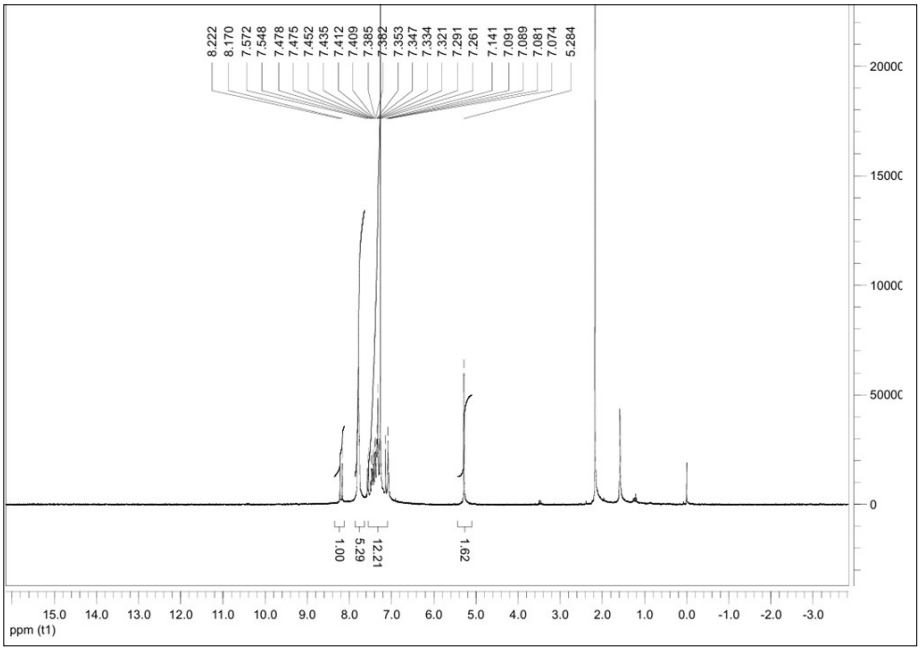

Figure S2. ^{1}H NMR Spectrum of sensor **MNA**

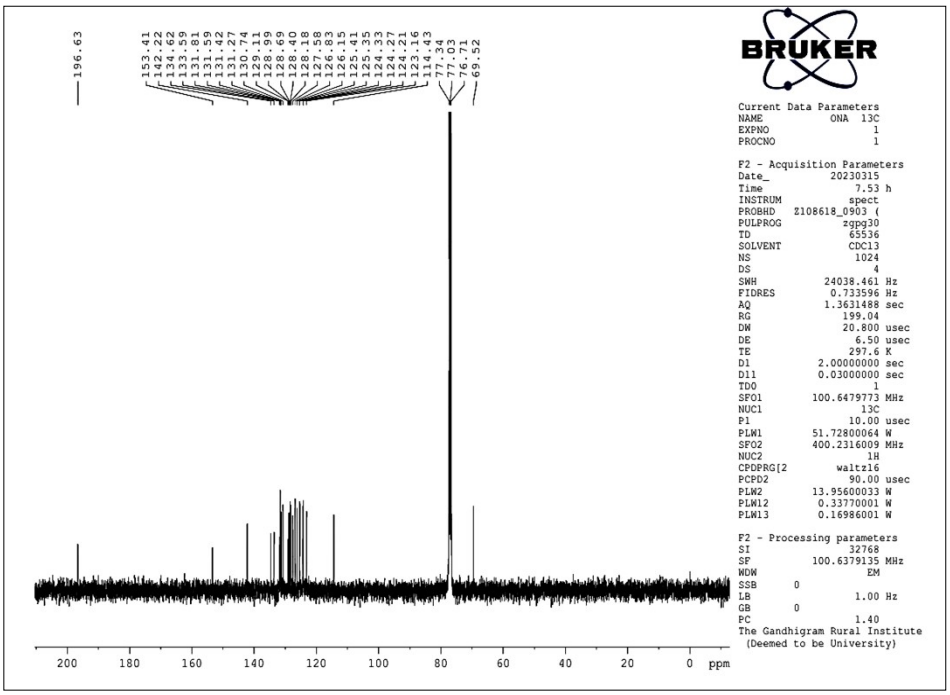

Figure S3. ^{13}C NMR Spectrum of sensor **ONA**

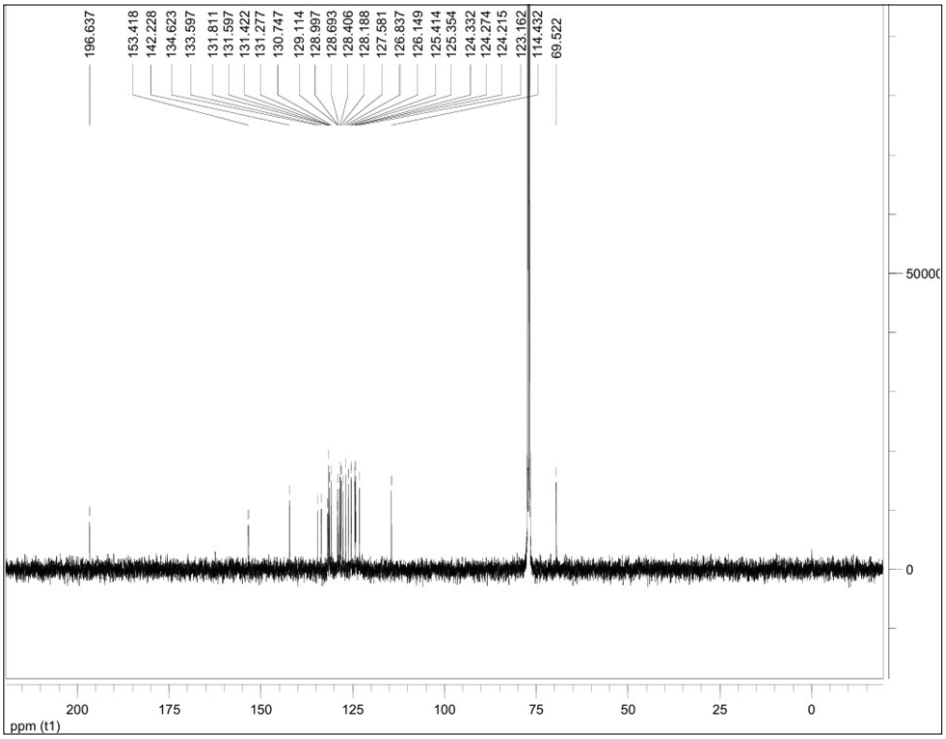

Figure S4. ^{13}C NMR Spectrum of sensor **MNA**

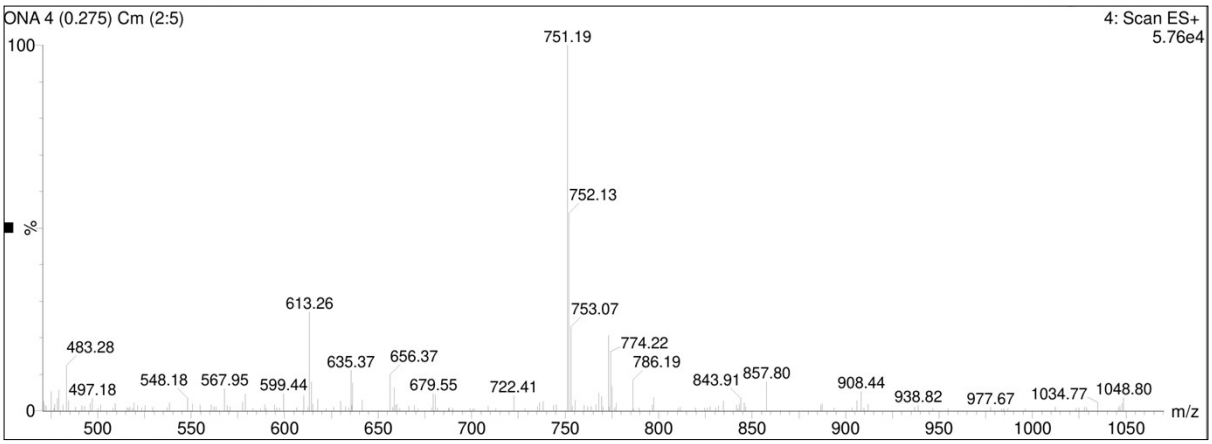

Figure S5. Mass Spectrum of sensor **ONA**

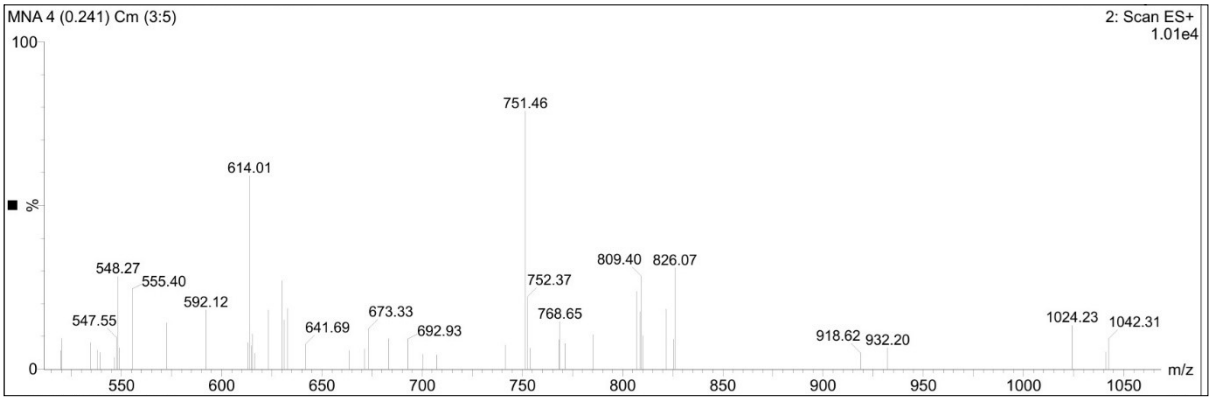

Figure S6. Mass Spectrum of sensor **MNA**

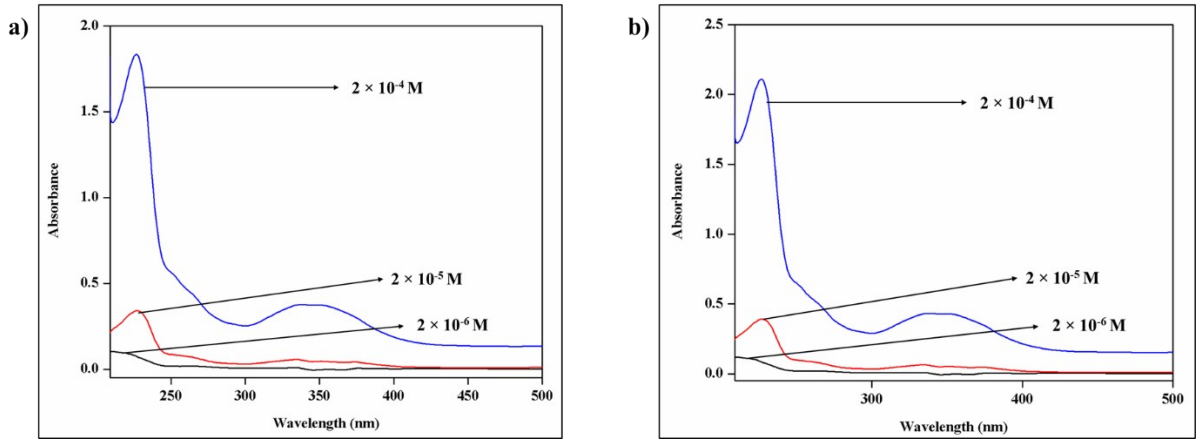

Figure S7. UV-Visible Spectrum of sensor a) **ONA** and b) **MNA** in MeOH solvent

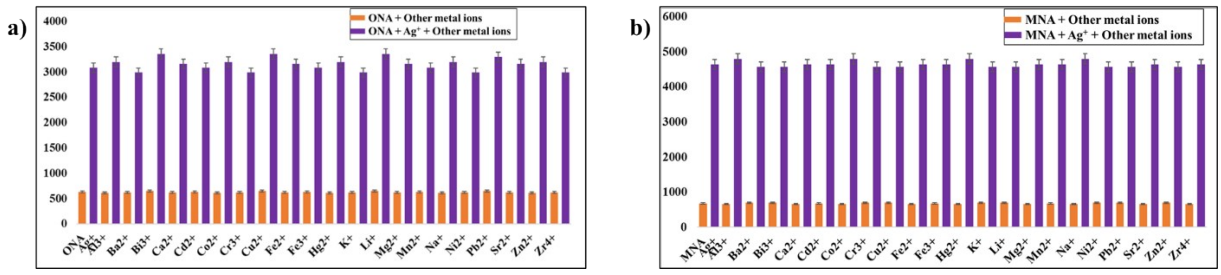

Figure S8. Interference spectra of **ONA** and **MNA** with Ag^+ and other metal ions. Red bar indicates that **ONA**+Ag^+ and **MNA**+Ag^+ with other metal ions and the green bar indicates that **ONA** and **MNA** with other metal ions other than Ag^+ ion. (Error bar, n=3)

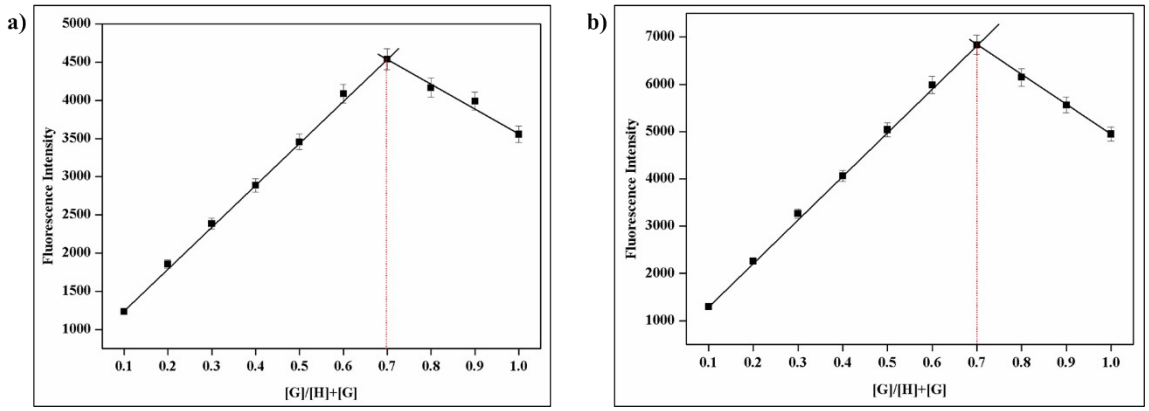

Figure S9. Job's plot of a) **ONA** and b) **MNA** with Ag^+ ion (4×10^{-6} M) in MeOH:H_2O solution (1:1 v/v, HEPES=50 mM, pH=7.3) λ_{ex}=340nm. (Error bar, n=3)

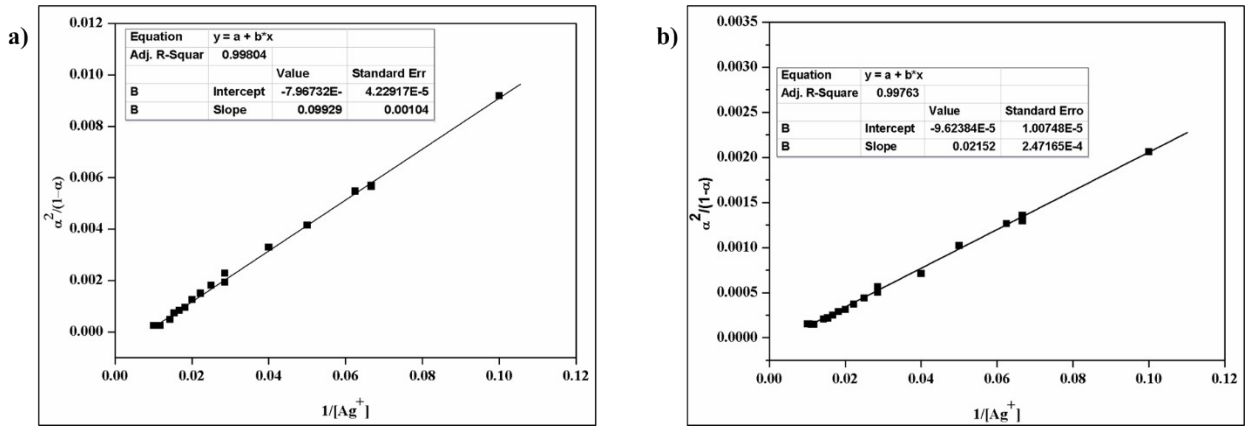

Figure S10. Benesi-hilderband of a) **ONA** and b) **MNA** with Ag^+ ion (4×10^{-6} M) in MeOH:H_2O solution.

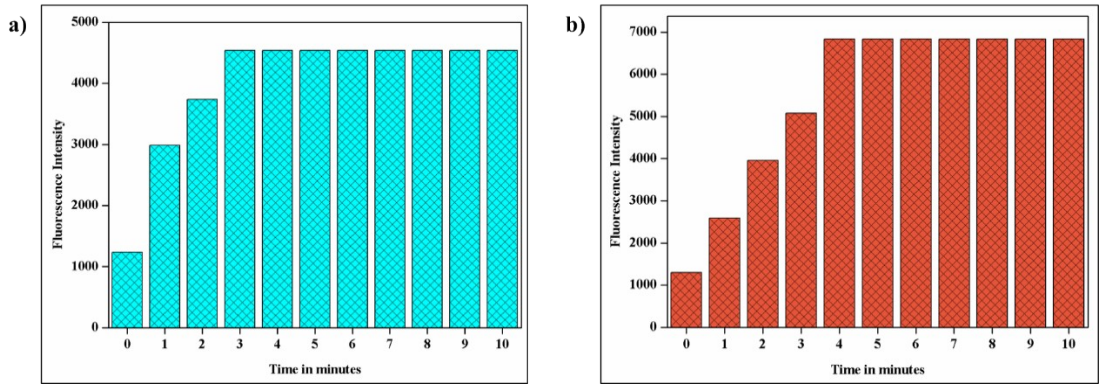

Figure S11. Time effect of a) **ONA** and b) **MNA** with Ag^{+} ion (4×10^{-6} M) in MeOH:H_2O solution (1:1 v/v, HEPES=50 mM, pH=7.3) λ_{ex}=340nm.

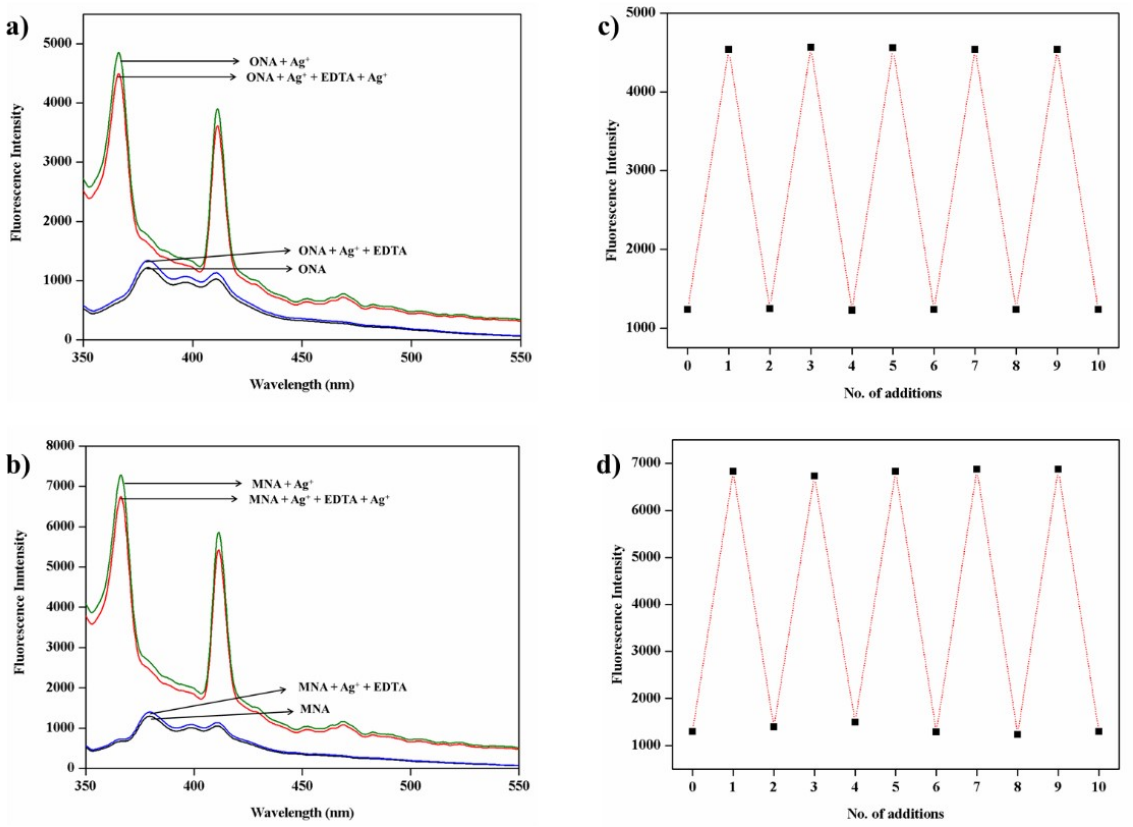

Figure S12. Reversibility experiment was carried out in MeOH:H_2O (1:1) buffer solution in the presence and absence of Ag^{+} with probe a) **ONA** and b) **MNA**. Effective affective addition of c) **ONA** and b) **MNA** with Ag^{+} ion in the presence of EDTA in MeOH:H_2O solution (1:1 v/v HEPES 50Mm, pH=7.3) (λ_{ex}=340nm)

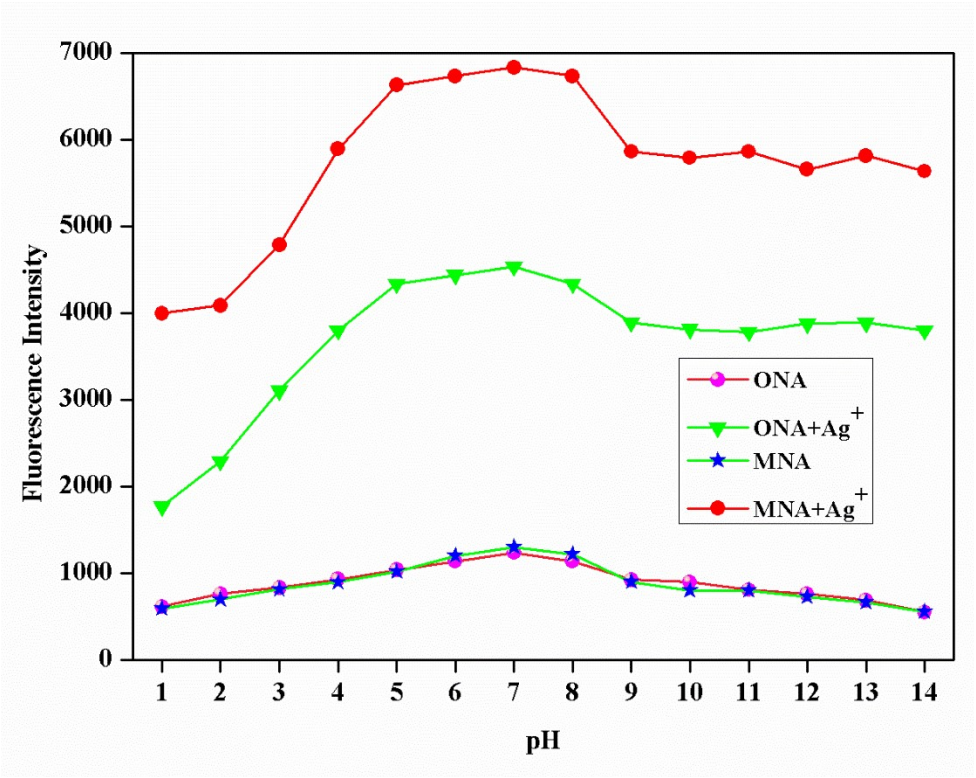

Figure S13. pH effect of **ONA** and **MNA** with Ag^+ in MeOH:H_2O solution (1:1 v/v) (λ_{ex}=340nm).

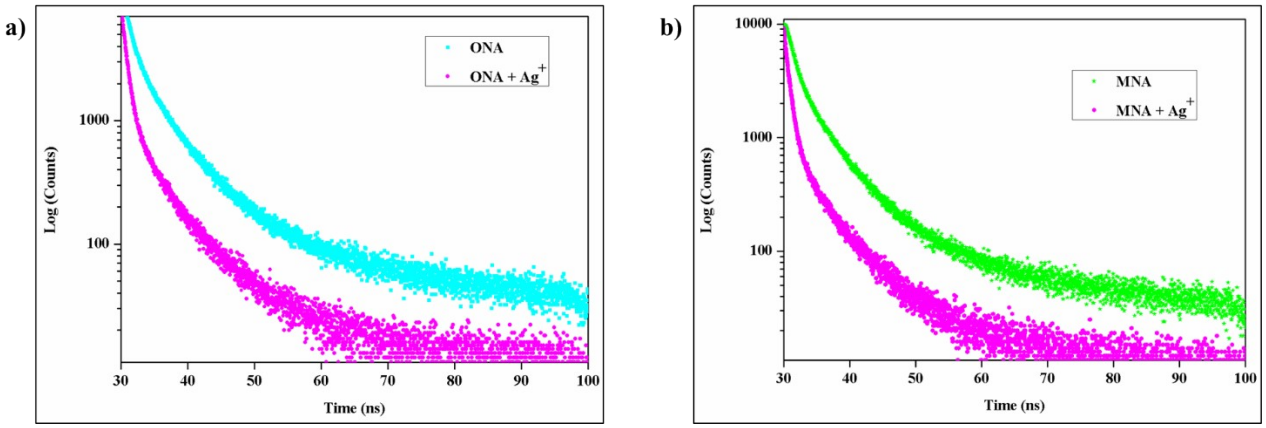

Figure S14. Fluorescence lifetime decay of **ONA** and **MNA** and its complexation with Ag^+ in MeOH:H_2O solution.

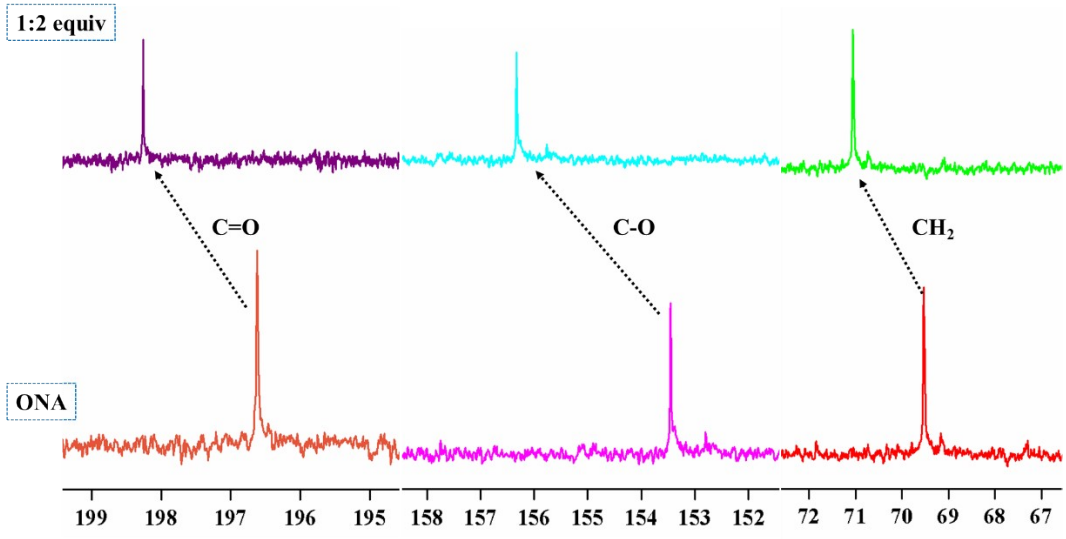

Figure S15. ^{13}C NMR of **ONA** and **ONA**+2Ag^{+}

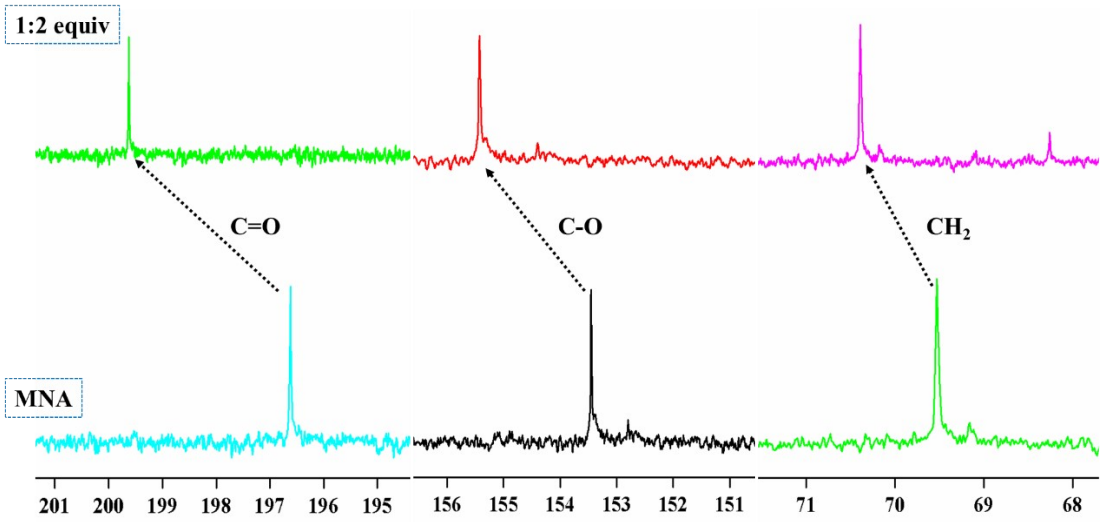

Figure S16. ^{13}C NMR of **MNA** and **MNA**+2Ag^{+}

Table S1. Calculated bond lengths, bond angles and dihedral angles of **ONA, MNA** and its complexes with Ag^{+}

Parameters	**ONA (Å)**	**ONA-Ag^{+} (Å)**	**MNA**	**MNA- Ag^{+} (Å)**
Bond lengths				
C_{18}=C_{19}	1.322	1.323	1.322	1.780
C_{21}=O_{23}	1.215	1.231	1.218	1.337
C_{37}-O_{79}	1.375	1.422	1.382	1.293

C_{88}-C_{81}	1.514	1.514	1.550	1.000
C_{81}-H_{93}	1.078	1.078	1.081	1.000
C_{88}-C_{87}	1.383	1.432	1.380	1.469
C_{87}-C_{86}	-	-	1.383	
C_{86}-C_{82}			1.510	
C_{82}-C_{87}	1.447	1.467	-	-
C_{82}-O_{80}	1.456	1.471	1.466	1.362
C_{60}=O_{62}	1.216	1.311	1.224	1.390
C_{60}-C_{58}	1.479	1.491	1.477	
$Ag^{+}_{97}\cdots O_{23}$	-	2.079	-	-
$Ag^{+}_{97}\cdots O_{79}$	-	1.920	-	-
$Ag^{+}_{98}\cdots O_{62}$	-	1.889	-	-
$Ag^{+}_{98}\cdots O_{80}$		2.263		
$Ag^{+}_{97}\cdots O_{62}$	-	-	-	2.352
$Ag^{+}_{97}\cdots O_{80}$	-	-	-	2.655
$Ag^{+}_{98}\cdots O_{79}$	-	-	-	2.558
$Ag^{+}_{98}\cdots O_{23}$	-	-	-	2.320
Bond angles				
C_{18}=C_{19}-H_{20}	121.72	121.50	121.44	121.87
O_{23}=C_{21}-C_{19}	119.81	120.95	120.48	120
O_{79}-C_{81}-C_{88}	111.10	111.66	111.39	112
C_{88}-C_{87}-C_{86}	-	-	120.57	120.10
C_{88}-C_{87}-C_{86}	-	-	110.08	110.93
C_{88}-C_{87}-H_{95}	122	122.06	-	-
C_{82}-O_{80}-C_{76}	119.99	120.38	120.60	119
O_{62}=C_{60}-C_{58}	120.01	119.69	119.75	120.40
Dihedral angles				
C_{18}=C_{19}-C_{21}=O_{23}	178.03	178.45	-179.59	179.99
C_{37}-O_{79}-C_{81}-H_{93}	-142.24	-129.78	-179.98	-179.9
C_{77}-C_{76}-O_{80}-C_{82}	-71	-61.30	-	-

O_{62}=C_{60}-C_{58}-H_{59}	17.45	13.45	107.99	107.45
C_{27}-N_{39}-C_{28}-C_{29}	126.16	145.57	-179.04	-179.99

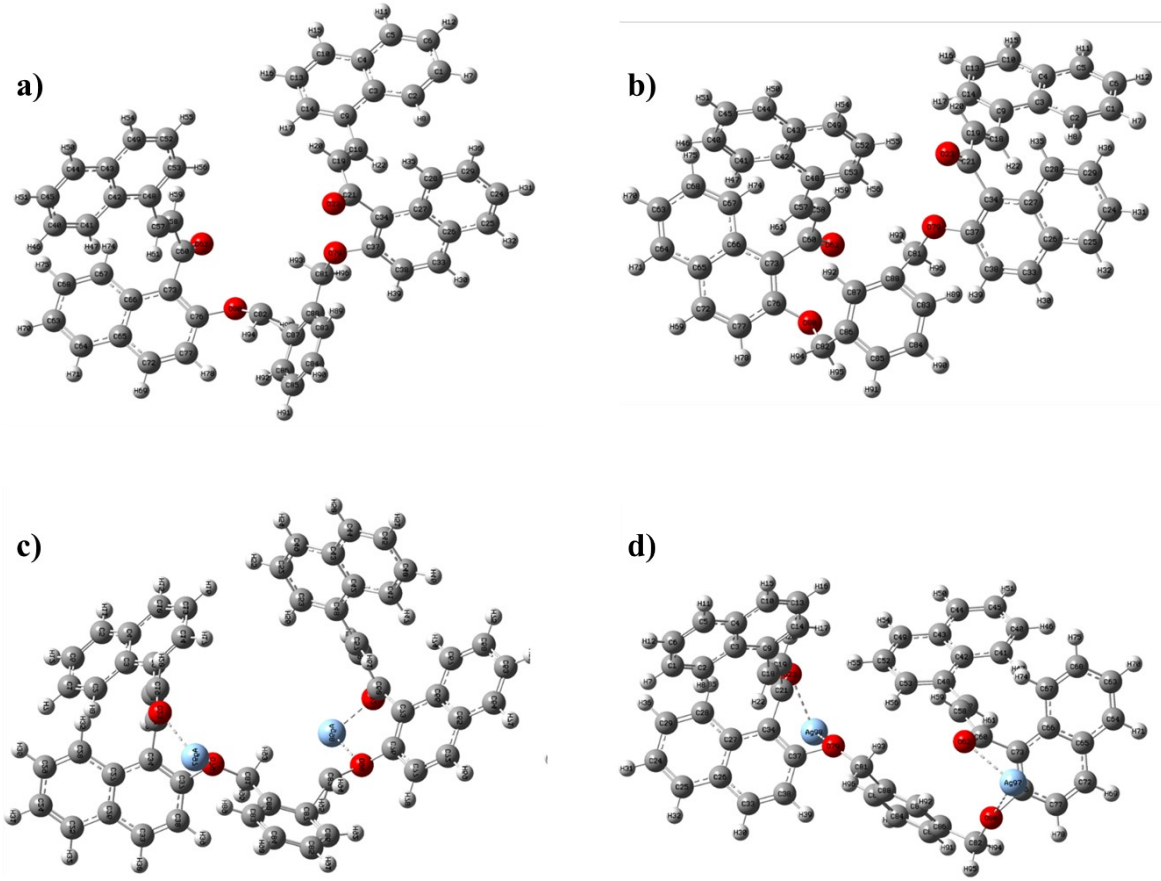

Figure S17. Optimized geometries of (a) **ONA**, (b) **MNA**, (c) **ONA**-Ag^+ and (d) **MNA**-Ag^+

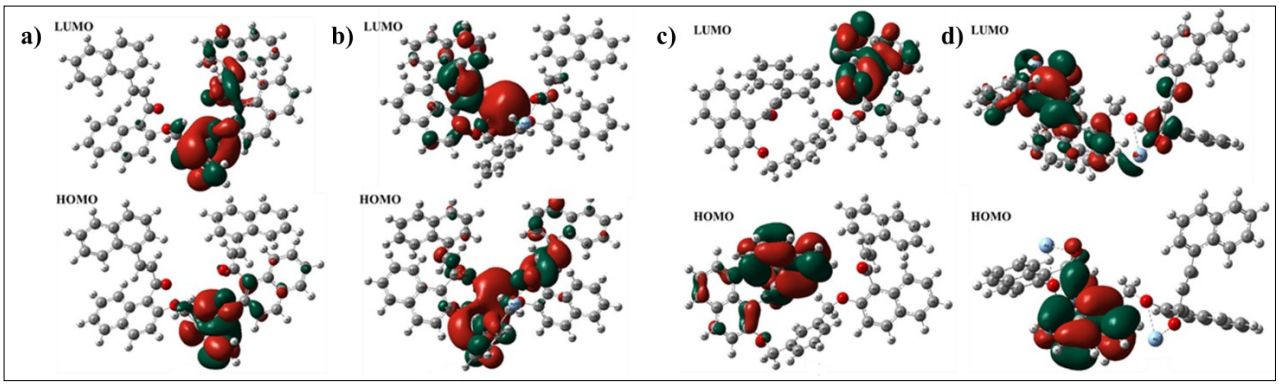

Figure S18. Frontier molecular orbitals of (a) **ONA**, (b) **ONA**-Ag^{+}, (c) **MNA** and (d) **MNA**-Ag^{+}

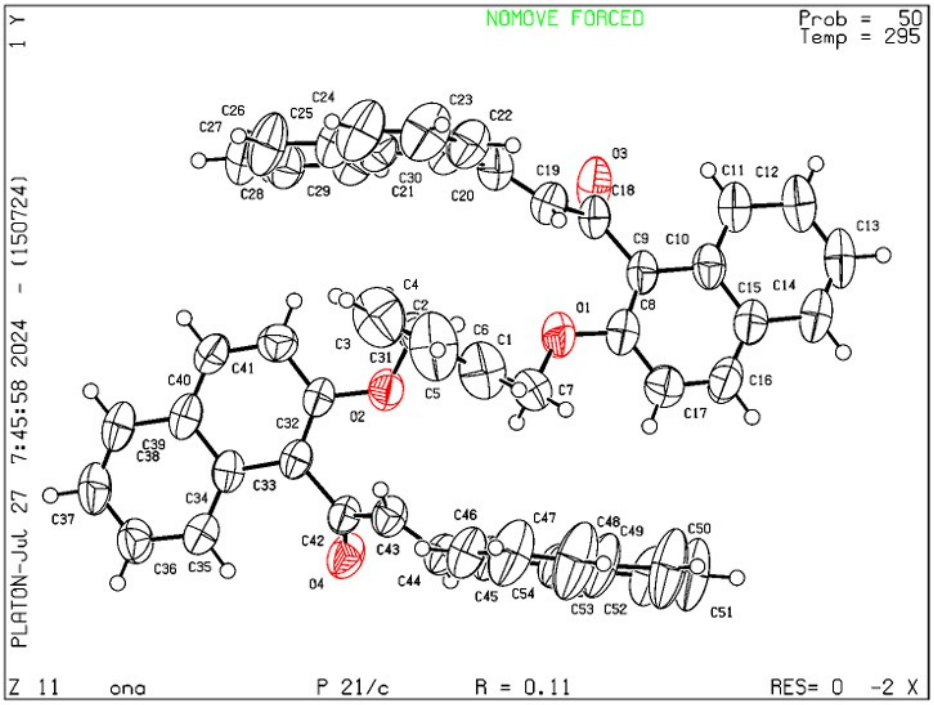

Figure S19. Single crystal XRD of **ONA**

Table S2. Crystal data and structure refinement for **ONA**

Identification code	ONA
Empirical formula	$C_{54}H_{38}O_4$
Formula weight	750.89
Temperature	295 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P 21/ c
Unit cell dimensions	a = 15.5100(12) Å α = 90°. b = 11.3371(15) Å β = 91.122°. c = 21.885(2) Å ν = 90°.
Volume	3847.5(7) Å3
Z	4
Density (calculated)	1.296 Mg/m^3
Absorption coefficient	0.081mm-1
F(000)	1576.0
Crystal size	0.28 x 0.16 x 0.09 mm^3
θ_{max} (◦)	29.541
Index ranges	-19<=h<=21, -10<=k<=15, -29<=l<=30
Reflections collected	9359
Independent reflections	3191
Absorption correction	Multi- scan

Max. and min. transmission	1.000 to 0.432
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F2	1.064
Data / restraints / parameters	1359/ 0 / 523
R indices (all data)	R1 = 0.1093, wR2 = 0.4105
Extinction coefficient	n/a
Largest diff. peak and hole	0.265 and -0.259 e. Å-3

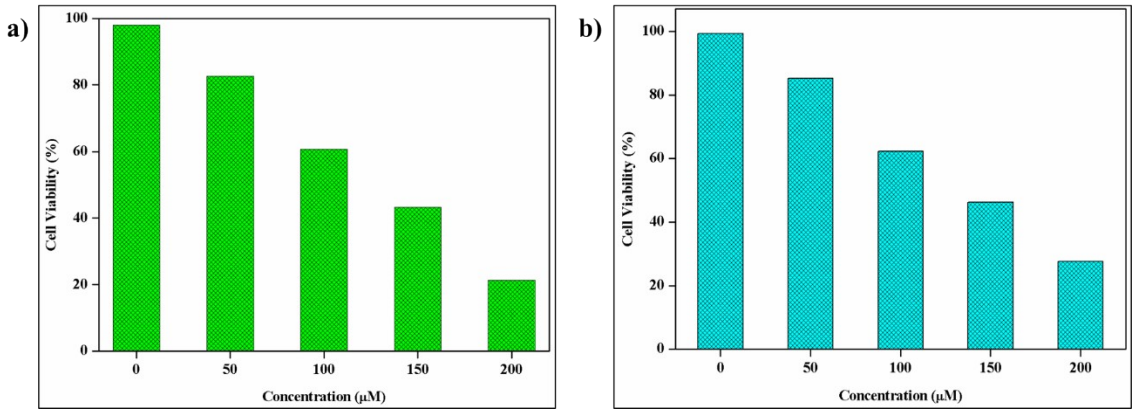

Figure S20. Cytotoxicity of probes **ONA** and **MNA** alone

Table S3. IC_{50} values calculated from MCF-7 cell line

Probes	IC_{50} (μM)
	MCF-7 cell line
ONA	129.04±29.04
MNA	138.75±38.75