Supporting Information

Facile Decoration of Multiwalled Carbon Nanotubes with Hetero-oligophenylene Stabilized-Gold Nanoparticles: Visible Light Photocatalytic Degradation of Rhodamine B Dye

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S-16 Pseudo-first-order kinetic for the photodegradation of RhB over AuNPs@MWCNTs and dye adsorption efficiency and photocatalytic efficiency of the recycled AuNPs@MWCNTs nanocatalyst to RhB.

S-17 TEM images of the AuNPs@MWCNTs nanohybrid catalyst after three runs of photocatalytic degradation of RhB and table showing fluorescence lifetime of derivative **3** in absence and presence of Au^{3+}ions (15 equiv) in H_2O/CH_3CN (6:4, v/v).

S-18 Comparison of present method over other reported procedure in literature for the preparation of AuNPs@MWCNTs nanohybrid materials.

S-19 Comparison of catalytic efficiency of AuNPs@MWCNTs nanohybrid materials for photocatalytic degradation of RhB reported in present manuscript with other catalytic systems in the literature.

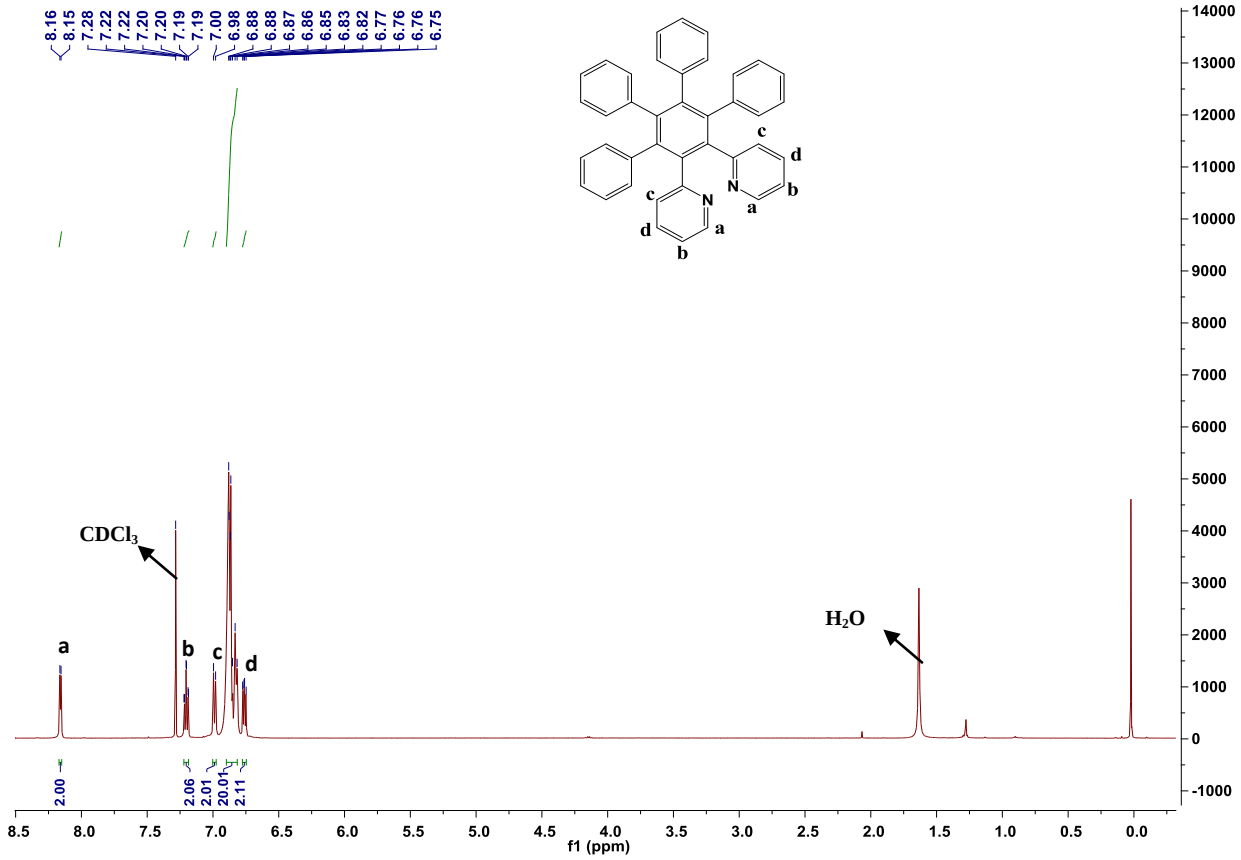

Fig. S1 ^{1}H NMR spectrum of derivative **3** (500 MHz, $CDCl_3$)

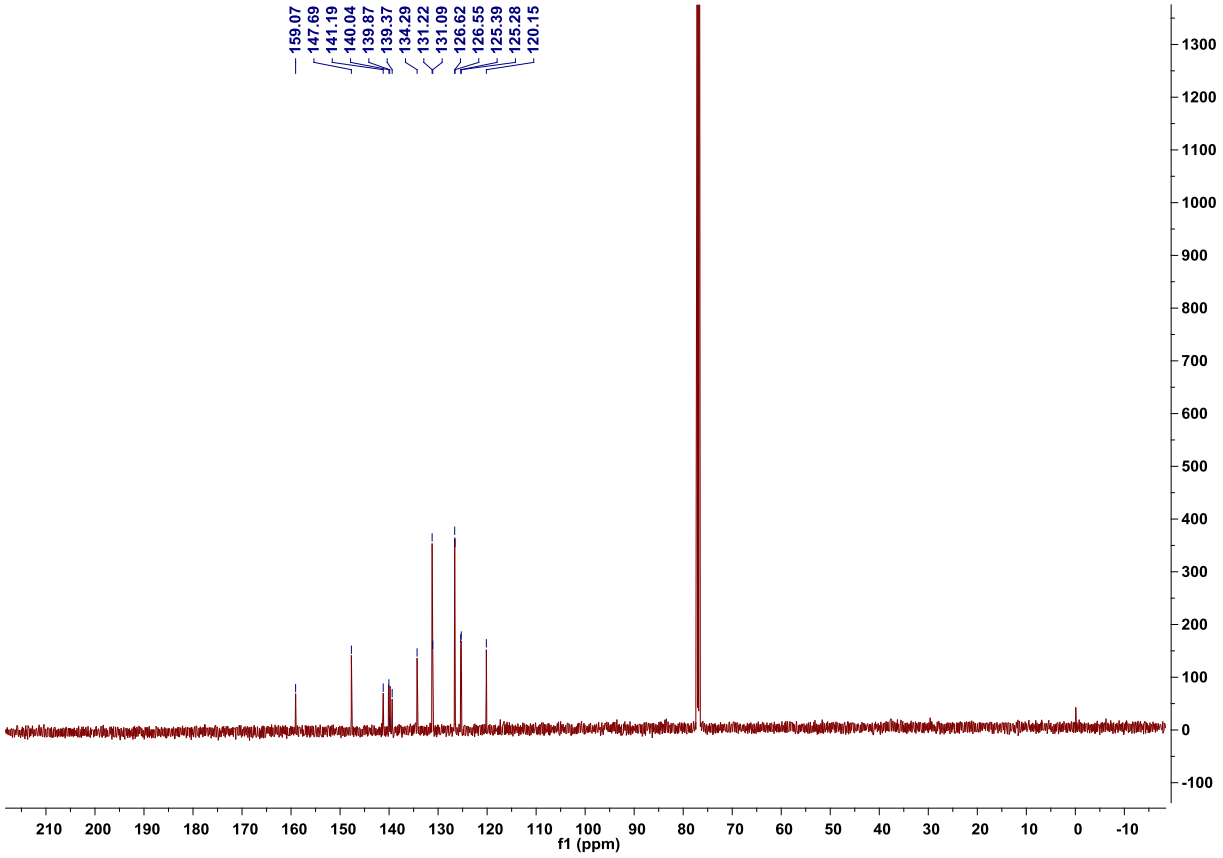

Fig. S2 ^{13}C NMR spectrum of derivative **3** (75 MHz, $CDCl_3$)

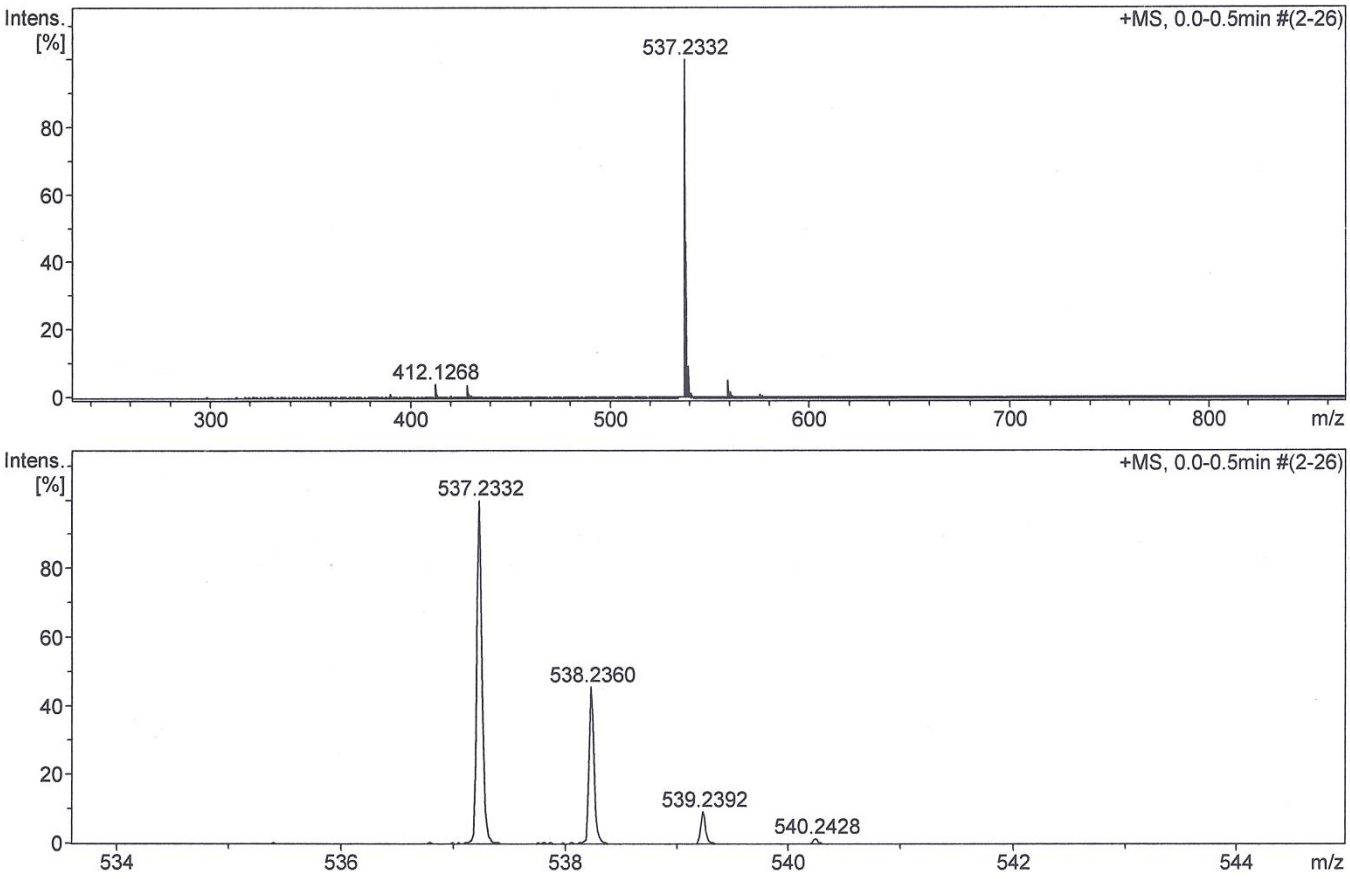

Figure S3 Mass spectrum of derivative **3**.

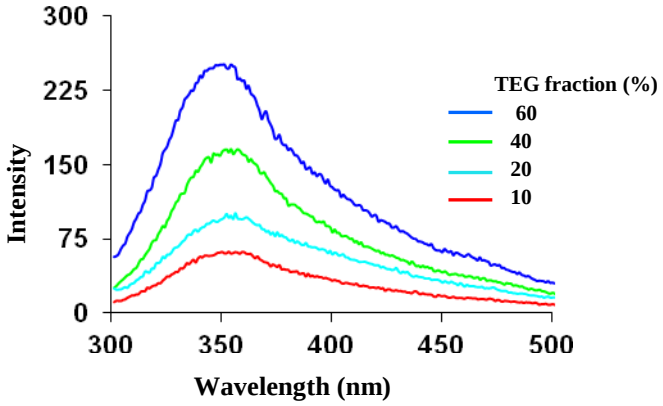

Fig. 4 Fluorescence spectra of compound **3** (5 μM) showing the variation of fluorescence intensity in TEG/CH_3CN mixture (0 to 60% volume fraction of TEG in acetonitrile); λ_{ex}= 290 nm.

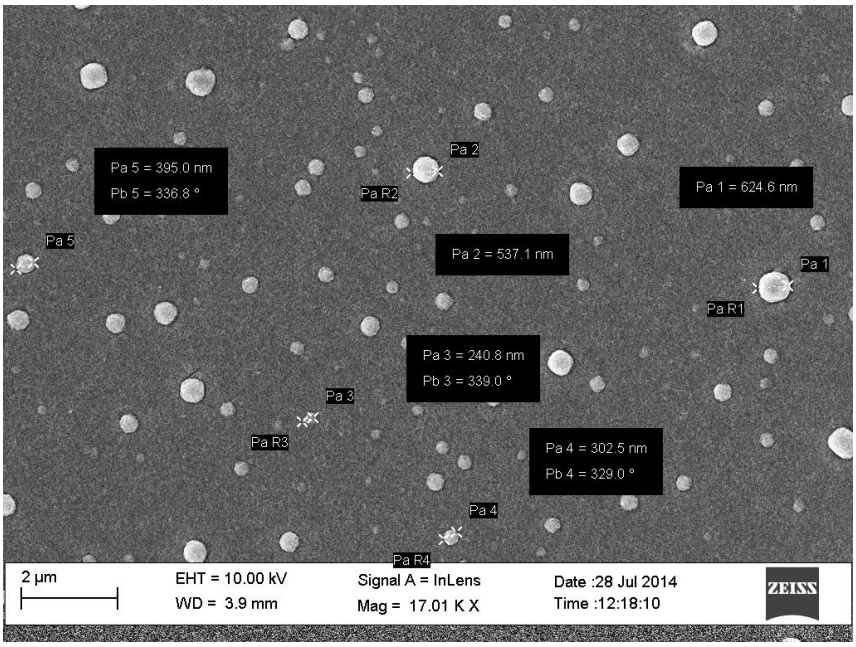

Fig. S5 SEM image of aggregates of compound **3** in H_2O/CH_3CN (6:4) mixture.

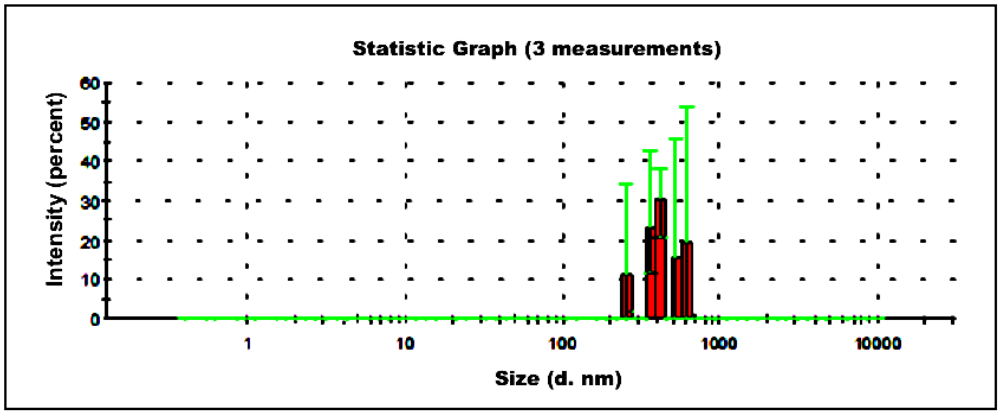

Fig. S6 The dynamic light scattering (DLS) studies derivative **3** showing the average diameter of aggregates is in the range of 500 nm in H_2O/CH_3CN (6/4).

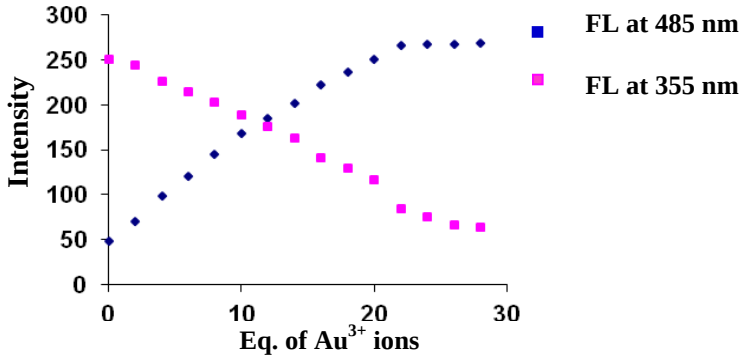

Fig. S7 Ratiometric combinational curve I_{485} (blue) and I_{355} (pink) as a function of [Au^{3+}] increased.

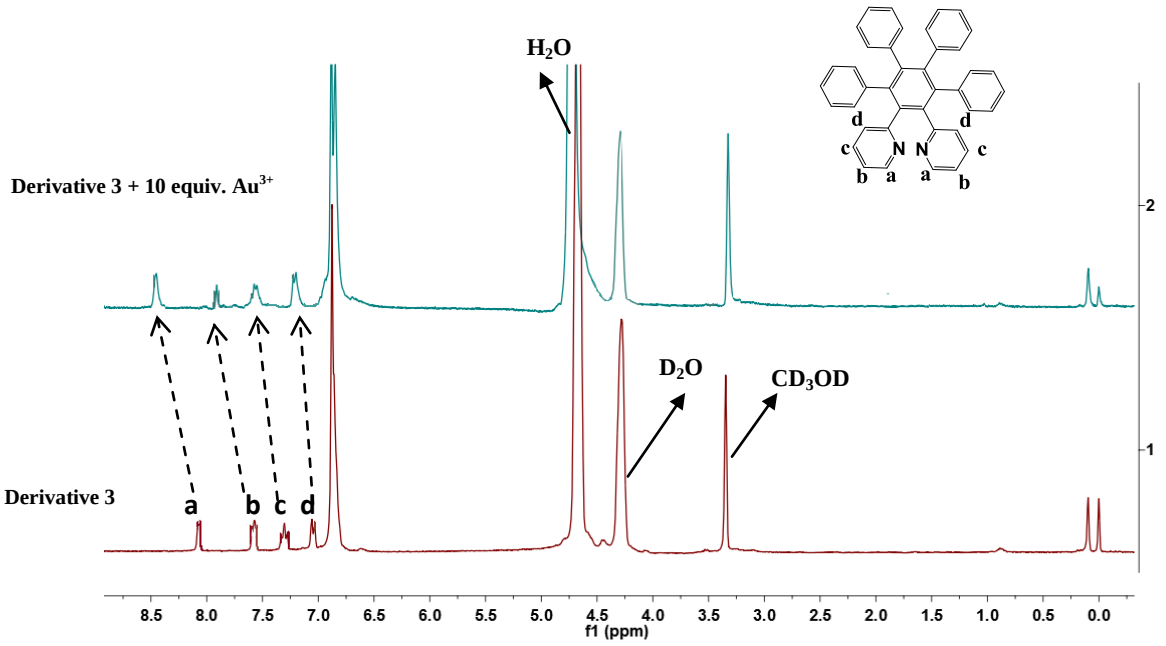

Fig. S8a ^{1}H NMR titration of compound **3** with Au^{3+} ions in $CDCl_3/CD_3OD/D_2O$ (1:6:3).

Derivative 3 (δ_1 ppm)	3 + 10 equiv. Au^{3+} (δ_2 ppm)	$\Delta\delta = \delta1 - \delta2$
8,1 (d, 2H, ArH) (a)	8.5 (d)	0.4
7.52-7.6 (m, 2H, ArH) (b)	7.7-7.78 (m)	0.18
7.3-7.39 (m, 2H, ArH) (c)	7.49-755 (m)	0.19
7.12 (d, 2H, ArH) (d)	7.23 (d)	0.11

Fig. S8b Change in chemical shift (δ) value of compound **3** before and after addition of Au^{3+} ions in $CDCl_3/CD_3OD/D_2O$ (1:6:3).

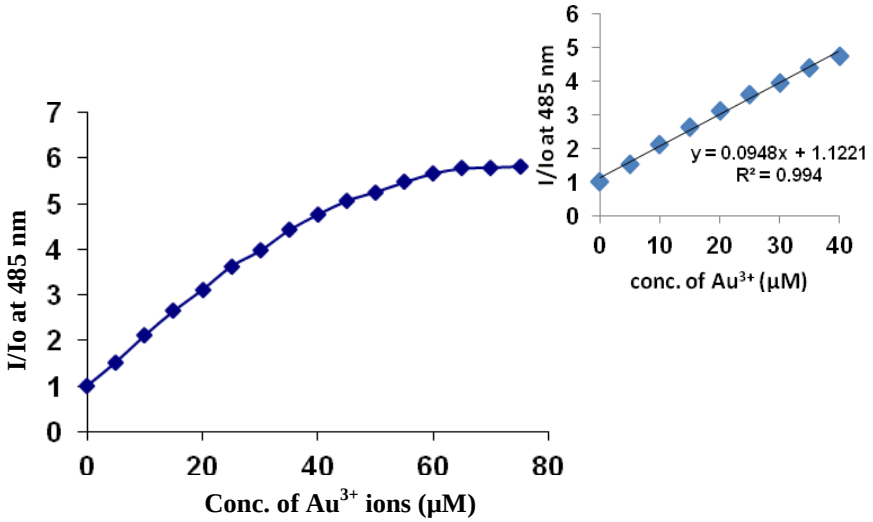

Fig. S9 Calibration curve for Au^{3+} (µM) over the range of 0 – 75 µM of Au^{3+}. Inset the fluorescence intensity of derivative **3** at 485 nm showed a linear response to Au^{3+} in the concentration range of 0 to 40 µM.

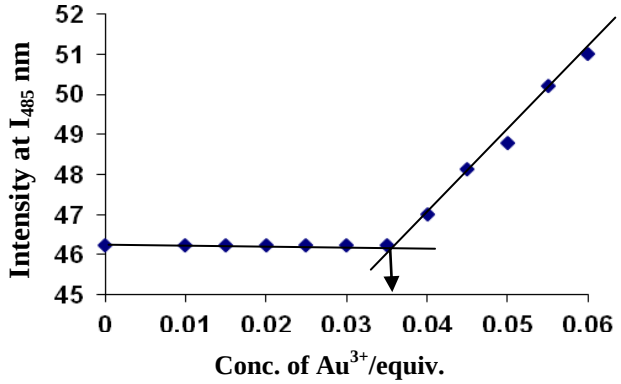

Fig. S10 Showing the fluorescence intensity of derivative **3** at 485 nm as a function of Au^{3+} ions concentration (equiv.) in H_2O/CH_3CN (6:4, v/v), λ_{ex}= 300 nm.

To determine the detection limit, fluorescence titration of compound **3** with Au^{3+} ions was carried out by adding aliquots of gold solution (in equiv.) and the fluorescence intensity as a function of Au^{3+} ions added was then plotted. From this graph the concentration at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor **3** gave the detection limit.

Equation used for calculating detection limit (DL):

DL = CL×CT

CL = Conc. of Ligand; CT = Conc. of Titrant at which change observed.

Detection limit (DL) of Au^{3+} ions with 3:

Thus; DL = $0.036 \times 10^{-6} = 36 \times \mathbf{10^{-9}} = \mathbf{36\ nM}$.

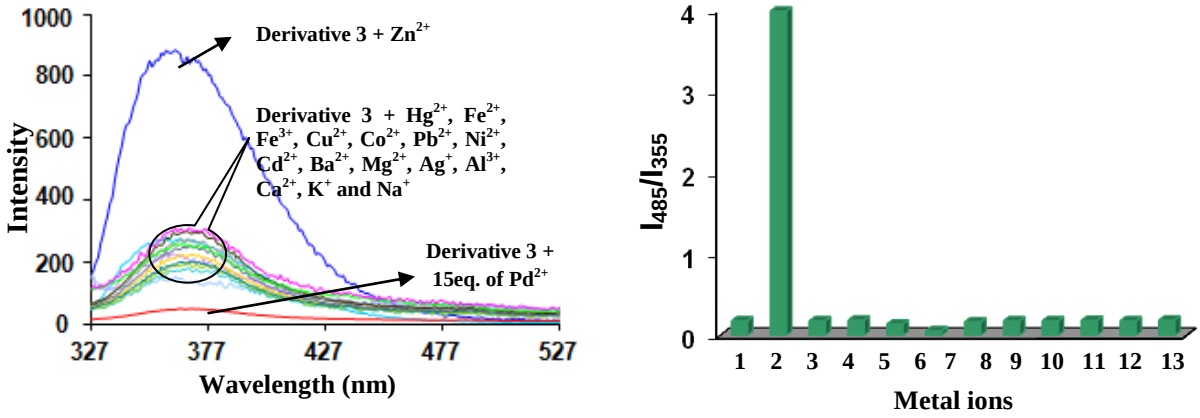

Fig. S11 Fluorescence emission spectra of derivative **3** (5 µM) with the addition of different metal ions (25 equiv.) in H_2O/CH_3CN (6:4), buffered with HEPES pH = 7.2 (B) Fluorescence selectivity (I_{490}/I_{363}) of **3** (5 µM) in the presence of various metal ions (25 equiv each);,1 = Hg^{2+}, 2 = Co^{2+}, 3 = Pb^{2+}, 4 = Ni^{2+}, 5 = Cd^{2+}, 6 = Pd^{2+}, 7 = Zn^{2+}, 8 = Cu^{2+}, 9 = Ba^{2+}, 10 = Mg^{2+}, 11 = K^{+}, 12 = Na^{+}, and 13 = Li^{+}

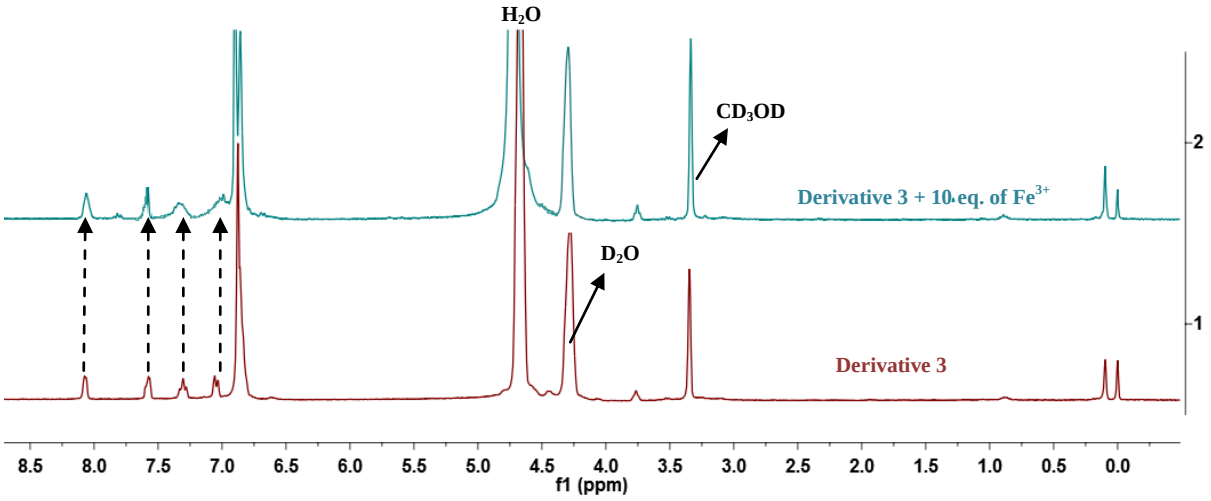

Fig. S12 ^1H NMR titration of compound **3** with Fe^{3+} ions in $CDCl_3/CD_3OD/D_2O$ (1:6:3).

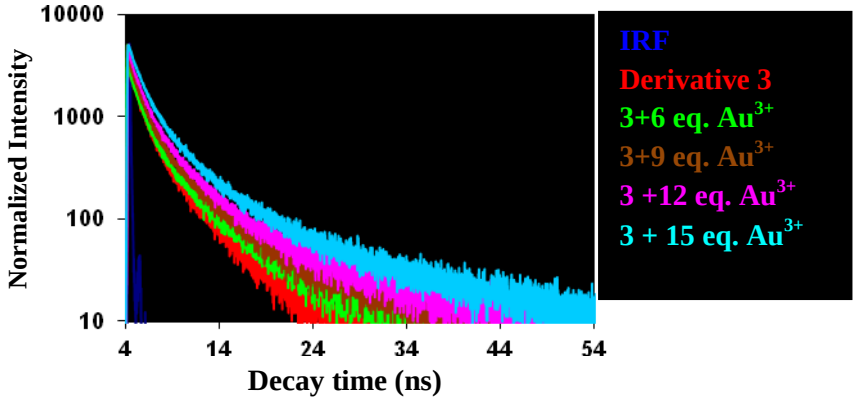

Fig. S13 Exponential fluorescence decays of **3** on addition of different amount of Au^{3+} ions measured at 485 nm. Spectra were acquired in H_2O/CH_3CN (6:4,v/v) mixture, λ_{ex}= 375 nm.

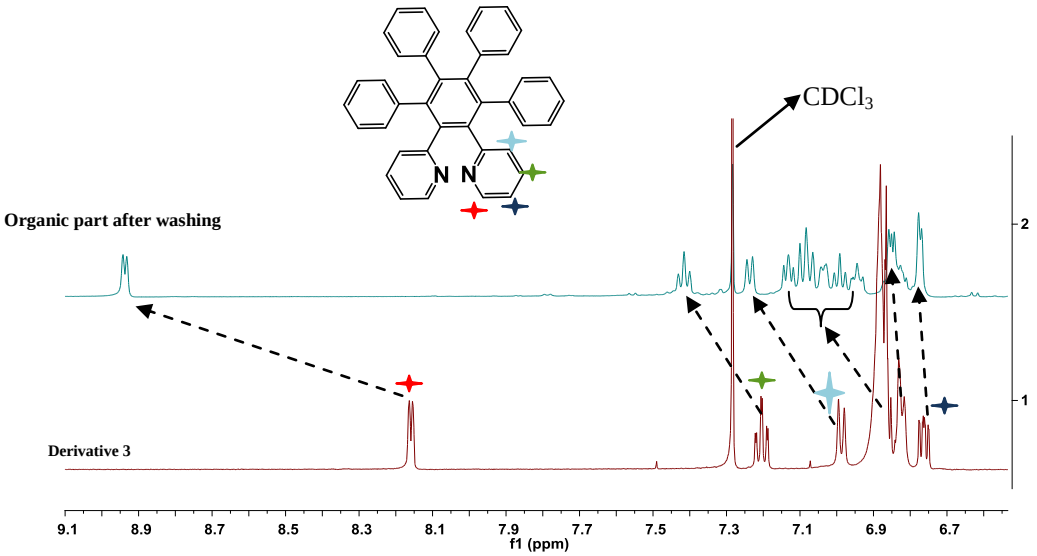

Fig. S14a Overlay ^{1}H NMR spectra of derivative **3** in $CDCl_3$ and organic part obtained after washing in-situ generated gold nanoparticles.

Derivative 3 (δ_1 ppm)	Organic part after treatment with gold (δ_2 ppm)	$\Delta\delta = \delta1 - \delta2$
8.16 (d, 2H, ArH)	8.95 (d)	0.79
7.20-7.28 (m, 2H, ArH)	7.39-7.42 (m)	0.14
6.99 (d, 2H, ArH)	7.21 (d)	0.22
6.88-6.82 (m, 20H, ArH)	Downfield spliting	------
6.75-6.77 (m, 2H, ArH)	6.77-6.79	0.02

Fig. S14b Change in chemical shift (δ) value of compound **3** before and after formation of gold nanoparticles in $CDCl_3$.

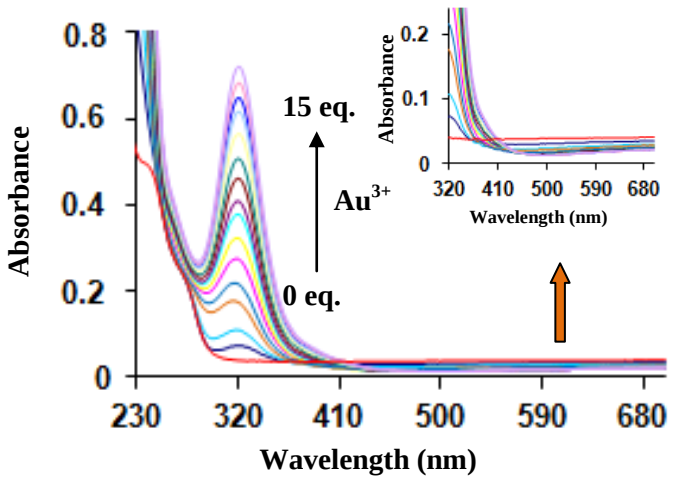

Fig. S15 UV-vis spectra of compound **3** (5 μM) upon additions of 15 eq. of Au^{3+} ions in CH_3CN. Inset showing no Surface Plasmon Resonance band was appeared around 550 nm.

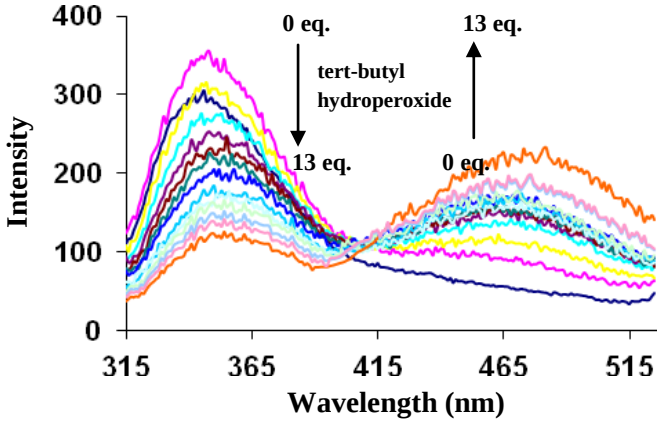

Fig S16 Fluorescence emission spectra of derivative **3** (5μM) upon additions of 13 equiv. of 70 wt% tert-butyl hydroperoxide solution in H_2O:CH_3CN (6/4) mixture.

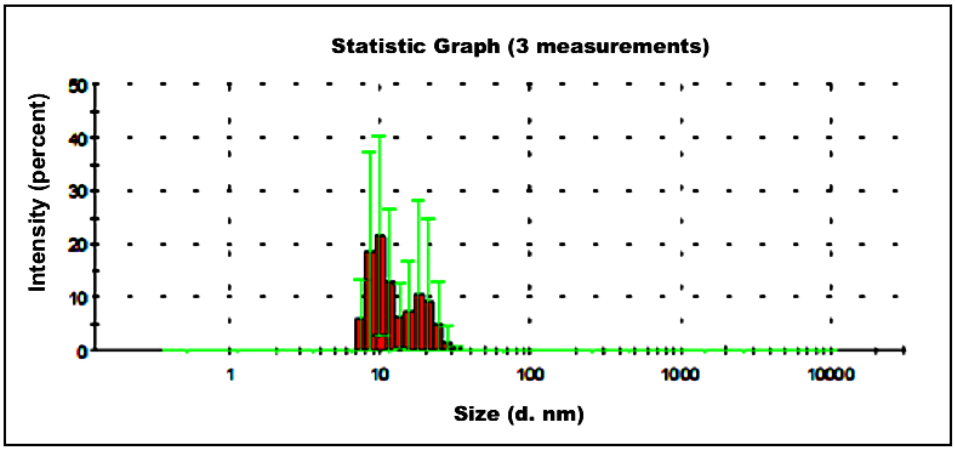

Fig. S17 The dynamic light scattering (DLS) studies of *in-situ* generated gold nanoparticles.

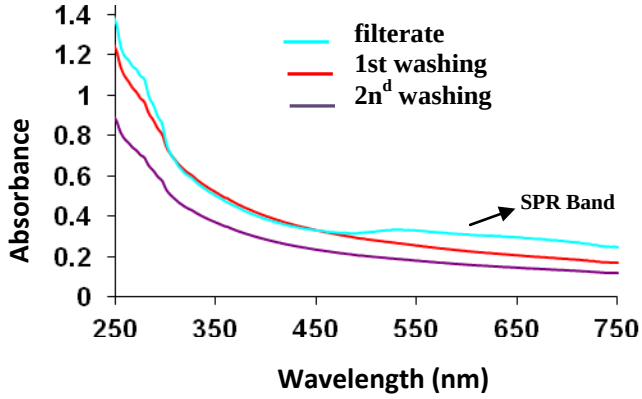

Fig. S18 Absorption spectra of the supernatants obtained subsequent washing steps in the preparation of AuNPs@MWCNTs nanohybrids.

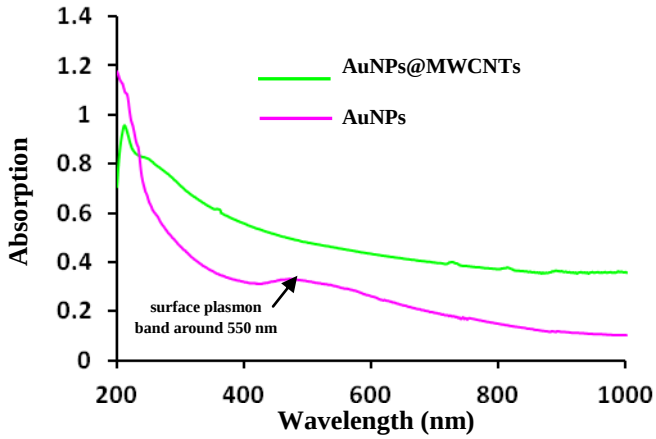

Fig. S19 UV−vis spectra of gold nanoparticles before and after they are adsorbed onto the surface of multi walled carbon nanotubes.

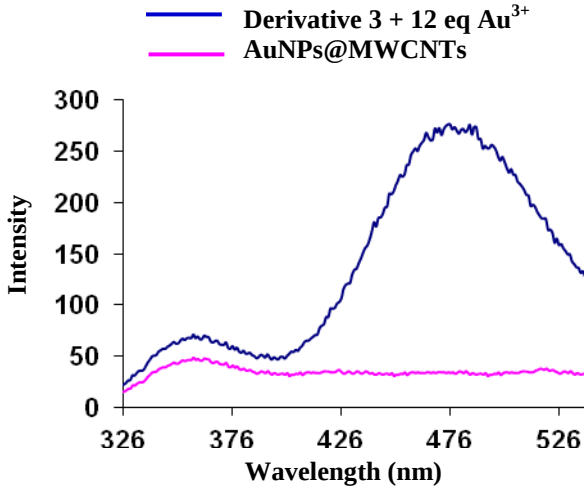

Fig S20 Fluorescence emission spectra of derivative **3** in presence of Au^{3+} and so prepared AuNPs@MWCNTs nanohybrid.

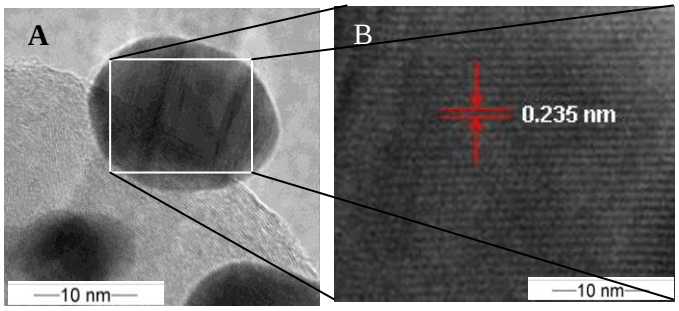

Fig. S21 (A) Magnified TEM images of AuNP@MWCNTs composites aligned Au NPs on the MWCNTs; (B) HRTEM of AuNPs decorated on MWCNTs.

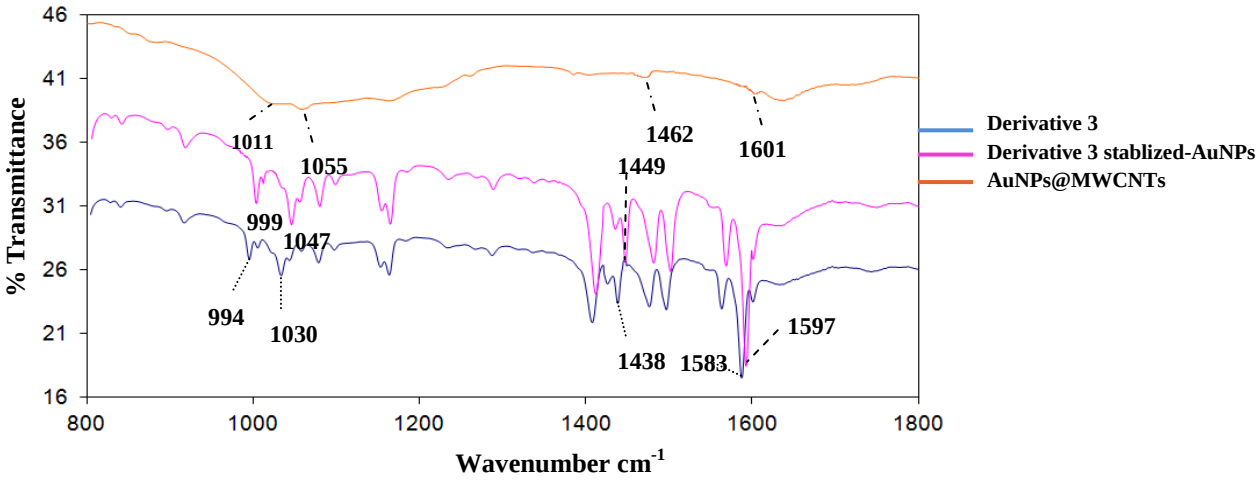

Fig. S22 The overlay FT-IR spectrum of derivative **3**, derivative **3** stabilized-AuNPs and AuNPs@MWCNTs hybrid material.

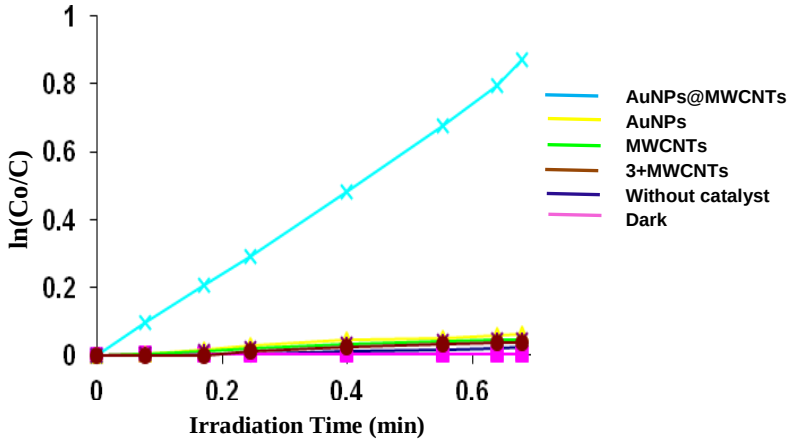

Fig. S23 The pseudo-first-order kinetic for the photodegradation of RhD B over AuNPs@MWCNTs, AuNPS, without catalyst and in dark.

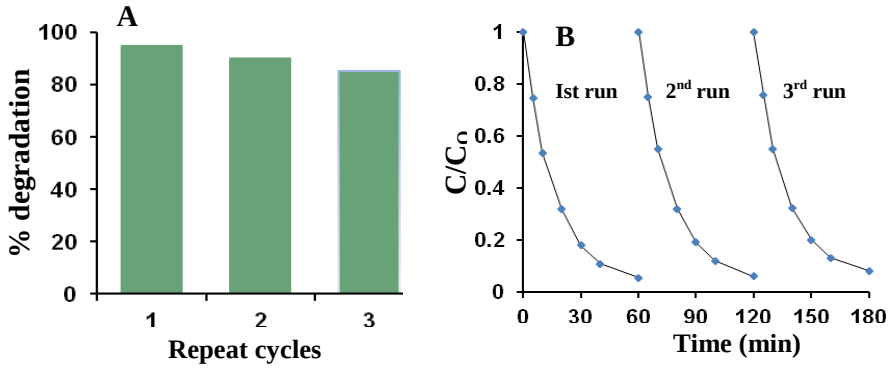

Fig. S24 (A) Dye adsorption efficiency and photocatalytic efficiency of the recycled AuNPs@MWCNTs nanocatalyst to RhB of separate 3 cycles of the continuous dark-adsorption and photocatalytic processes. (B) Repeated photocatalytic degradation of RhB on AuNPs@MWCNTs nanocatalyst under Visible light illumination.

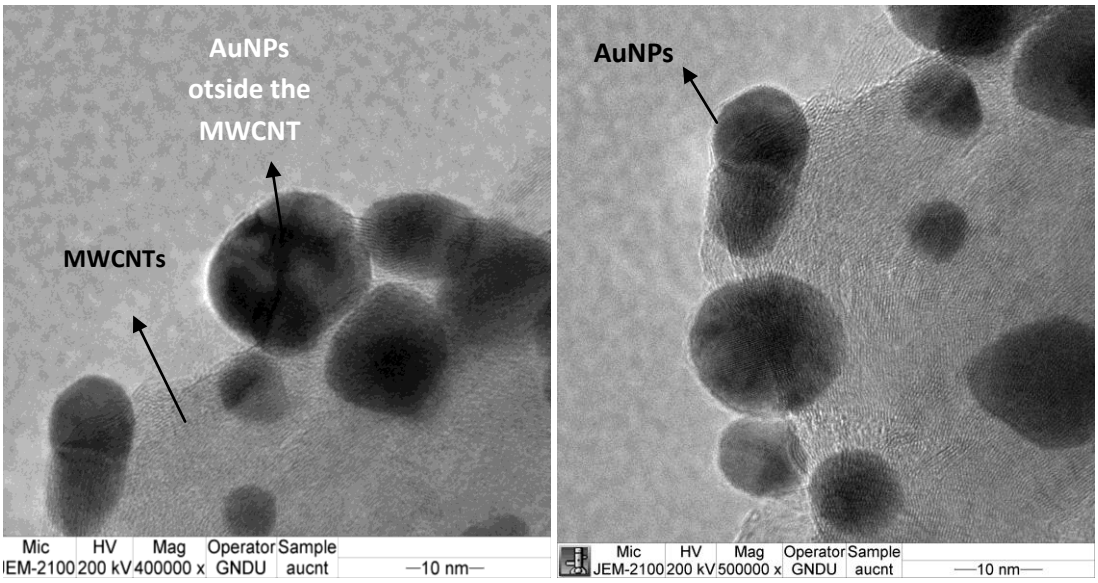

Fig. S25 TEM images of the AuNPs@MWCNTs nanohybrid catalyst after three runs of photocatalytic degradation of RhB.

Table S1: Fluorescence lifetime of derivative **3** in absence and presence of Au^{3+}ions (15 equiv) in H_2O/CH_3CN (6:4, v/v) mixture at 485 nm. A_1, A_2, A_3: fractional amount of molecules in each environment. τ_1, τ_2 and τ_3: biexponential life time of aggregates in 60 vol% of water in CH_3CN; k_f: radiative rate constant ($k_f = \Phi/\tau_{avg}$); k_{nr}: nonradiative rate constant ($k_{nr} = (1- \Phi)/\tau_{avg}$); λ_{ex} = 375 nm

Sample	Quantum Yield	$A_1/A_2/A_3$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_{avg} (Average lifetime, ns)	$k_f(10^9S^{-1})$	$k_{nr}(10^9S^{-1})$
Derivative 3	**0.21**	**49.85/50.15**	**0.272**	**2.568**	**----**	**1.42**	**0.126**	**0.55**
3+15 eq. Au^{3+}	**0.32**	**51.16/26.74/22.10**	**3.531**	**0.919**	**17.470**	**5.91**	**0.05**	**0.116**

Table S2: Comparison of present method for the preparation of AuNPs@CNTs nanohybrid materials over other reported procedure in literature.

S.No	Publication	Method of formation of AuNPs@CNTs nanohybrid	Reagent used	Reducing agent	Temp.	Total Time taken to prepare AuNPs@CNTs nanohybrid	Reusability
1.	Present Manuscript	Wet-chemical method	Derivative 3 in H_2o/CH_3CN, H_2SO_4, MWCNT and gold chloride	No	RT	Overnight	Yes
2.	Analyst,2015,140,134–139	Frens' method	ammonium hydroxide, H_2SO_4,HNO_3,tetraethoxysilane), 3-aminopropyl-trimethoxysilane, 4-nitro thiophenol, Hydrogen tetrachloroaurate and MWCNT	trisodium citrate dihydrate	Room temp.	23 hrs	No
3.	Beilstein J. Nanotechnol. 2014, 5,910–918	plasma enhanced chemical vapour deposition (PECVD	VA-CNT, Ag paste, Pt resistor and Au wires	------	170 °C	30 min	No
4.	ACS Sustainable Chem. Eng.2013, 1, 746−752	layer-by-layer (LBL) assembly method	Polyethyleneimine, $HAuCl_4$, trisodium citrate and vertically aligned CNTs	trisodium citrate	100°C	24 hr	No
5.	Nanoscale Research Letters 2014,9:207	chemical vapor deposition	O_2/Ar atmosphere, $HAuCl_4$/2-propanol and CNT-AAO composite	------	450°C	26 hr	No
6.	J. Phys. Chem. C 2014, 118, 27028−27038	--------	Dioctylamine, tetraoctylammonium chloride, $NABH_4$, pyr-SH derivative, $HAuCl_4$ and SWCNTs	$NABH_4$	RT	overnight	No

Table S3: Comparison of catalytic activity of AuNPs@MWCNTs nanohybrid generated by utilizing derivative **3** for photocatalytic dye degradation of Rhodamine B under visible light source over other nanohybrid materials reported in literature.

S.No	Publication	Catalyst used	Time taken for dye degradation	Source of light used	Rate constant	reusability
1	Present manuscript	AuNP@MWCNTs	45 min	300 W tungsten lamp	0.066 min^{-1}	Yes
2	J. Am. Chem. Soc. 2015, 137, 2975 −2983	Ti-Defected TiO_2 material	3 hr	300 W Xenon lamp	----	-------
2	ACS Appl. Mater. Interfaces 2015, 7, 4368 −4380	TiO_2 materials	60 min	1000W Xe arc lamp	0.0183 x 10^{-3} min^{-1}	No
3	ACS Appl. Mater. Interfaces 2015, 7, 1616 −1623	Au decorated $ZnSe \cdot 0.5N_2H_4$ Hybrid	240 min	500W Xe arc lamp	0.007 min^{-1}	No
4	DOI: 10.1021/jp5108679 J. Phys. Chem. C, 2015	BiF_3−Bi_2NbO_5F	90 min	300 W Xenon lamp	0.023 min^{-1}	Yes
5	J. Phys. Chem. C 2014, 118, 21447−21456	CdS nano structures	75 min	850 W xenon lamp	0.012 min^{-1}	No
6	ACS Appl. Mater. Interfaces2014, 6, 613−621	graphene−SnO_2 aerosol nanocomposites	40 min	300 W xenon lamp ($\lambda > 420$ nm)	0.091 min^{-1}	No
7	DOI: 10.1021/am507085u ACS Appl. Mater. Interfaces	Au-Decorated $ZnSe{\cdot}0.5N_2H_4$ Nanowires	90 min	xenon lamp (500 W)	0.013 min^{-1}	No
8	DOI: 10.1021/sc5006473 ACS Sustainable Chem. Eng	A BiOBr/reduced graphene oxide (RGO) composite	5 hr	A 300 W Xe lamp	------	Yes
9	Ind. Eng. Chem. Res. 2015, 54, 153−16	Graphene/MIL-53(Fe) composites	60 min	500W Xe arc lamp	0.07 min^{-1}	Yes
10	ACS Appl. Mater. Interfaces2012, 4, 3084−3090	Graphene Oxide/ZnO nano Composite	60 min	sunlight	--------	Yes
11.	DOI: 10.1021/acsami.5b00980ACS Appl. Mater. Interfaces	ZnO:I/TiO_2 NRs	6 hr	500 W Xe lamp	-------	Yes