Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Palladium Encapsulated Mesoporous Silica Nanoparticles for the Rapid Detection of Analytes.

Tianwei Jia[1], Ying Luo[1], Xiaolin Sheng[1], Jieqiong Fang[1], Didier Merlin[2] and Suri S. Iyer[1,*]

[1]788 Petit Science Center, Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, GA 30302, USA. E-mail: siyer@gsu.edu

[2] 790 Petit Science Center, Institute of Biomedical Science, Georgia State University, Atlanta, GA 30302, USA and Atlanta Veterans Affairs Medical Center, Atlanta, GA 30033, USA.

1. Experimental section

1.1 Materials and general techniques

Cetyltrimethylammonium bromide (CTAB), potassium tetrachloropalladate (K_2PdCl_4), ascorbic acid (AA), sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxysilane (APTES), Rhodamine 110 and silica mesostructured MCM-41 type (hexagonal) were purchased from Sigma-Aldrich. Human Serum Albumin (HSA) protein and Human Serum Albumin antibody were purchased from Fitzgerald. All the sequences were synthesized and purified with HPLC by Thermo Fisher. Column chromatography was performed using silica gel (230-400 mesh). Analytical thin-layer chromatography (TLC) was performed on silica gel 230-400 mesh (Sicicycle). Plates were visualized under UV light, and/or by staining with acidic $CeH_8Mo_3N_2O_{12}$ followed by heating. ^1H and ^{13}C NMR spectra were recorded on Bruker 400MHz spectrometer. Chemical shifts are reported in δ (ppm) units using residual ^{13}C and ^1H signals from deuterated solvents as references. Spectra were analyzed with MestReNova® (Mestrelab Research). Reported yields refer to spectroscopically and chromatographically pure compounds that were dried under high vacuum (10–2 mbar) before analytical characterization unless otherwise specified.

2. Characterization

2.1 Scanning transmission electron microscopy (STEM)

All the samples were dispersed in ethanol and the Pd@$mSiO_2$-OH, Pd@$mSiO_2$-NH_2-CTAB, and Pd@$mSiO_2$-NH_2 were respectively dropped onto a carbon-coated copper grid followed by naturally evaporating the solvent. The STEM was Hitachi SU9000EA.

2.2 Zeta potential measurement

All the samples were dispersed in PBS buffer before measurement. Zeta potential measured by Zetasizer Nano-zs90 from Malvern Instruments.

3. Sequence

Table S1. Sequence for the assays

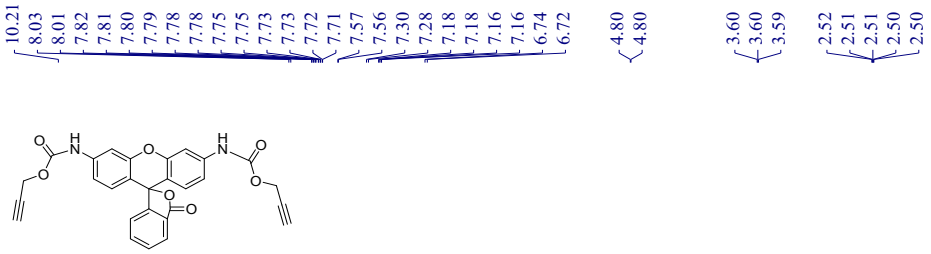
Name	Sequence
DNA gate	**5' TCCCATTCTGCA*GCTTC*CTCATTGATGGT 3'**
HIV-gag	**5' ACCAUCAAUGAG*GAAGC*UGCAGAAUGGGA 3'**
Mismatch-3	**5' ACCAUCAAUGAGG*TUC*CUGCAGAAUGGGA 3'**
Mismatch-5	**5' ACCAUCAAUGAG*CTUCG*UGCAGAAUGGGA 3'**

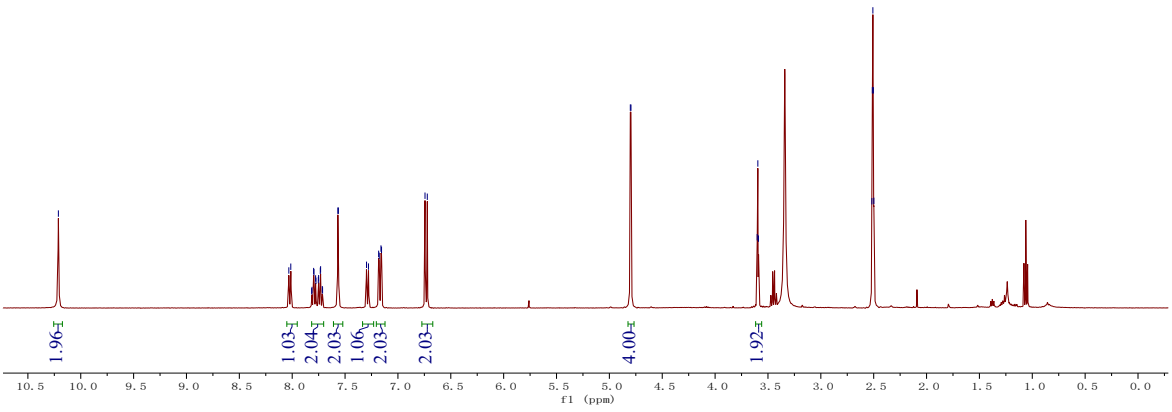
Sequences of the synthetic DNA gate, HIV-gag target, and two mismatch targets for the assay.

4. NMR spectra

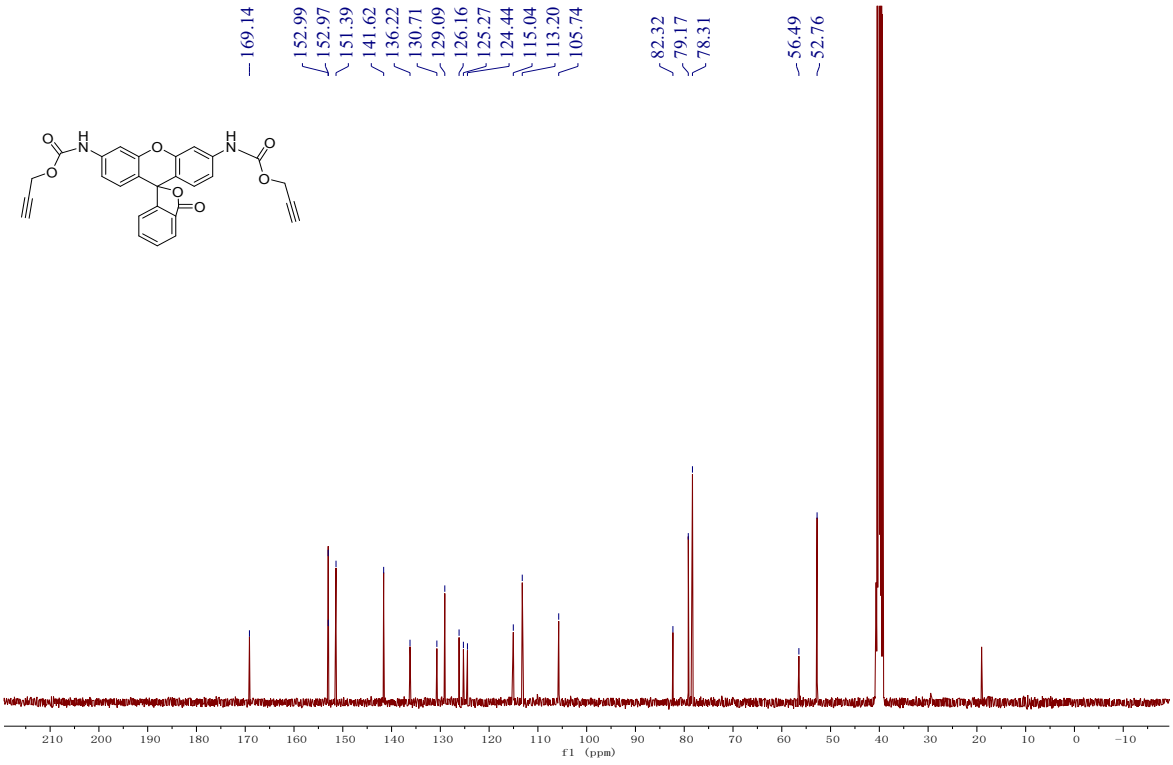
Bio-propargyloxycarbonyl-protected rhodamine (Turn-off fluorescent probe) was characterized by NMR spectra.

^{1}H NMR DMSO-d_6, 400 MHz (H_2O δ=3.3, DMSO-d_6 δ=2.5)





^{13}C NMR DMSO-d_6, 100 MHz



5. Proposed mechanism for Pd-catalyzed de-propargylation reaction

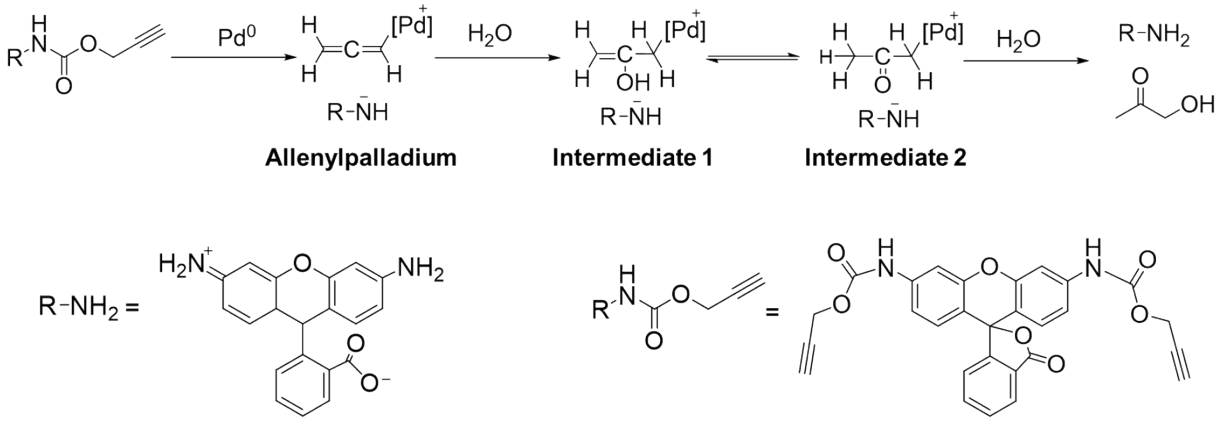


Figure S1. Proposed mechanism for Pd-catalyzed de-propargylation reaction. Pd (0) in situ reacts with the turn-off fluorescent probe leading to the formation of allenylpalladium. Once generated, the allenylpalladium species then undergoes nucleophilic attack on the central sp carbon by water molecules followed by tautomerization to afford the Pd carbonyl intermediate 2. Subsequently, hydrolysis of intermediate 2 released the turn-on fluorescent probe and hydroxyacetone as the final products.

5. Calculation of %RFU

1. The %RFU calculated in Figure 6 is shown below:

Figure 6a: $$\%RFU = 100\% * \frac{FI\ Pd@mSiO2 - NH2 - HSA}{FI\ Pd@mSiO2 - NH2}$$

Figure 6b: $$\%RFU = 100\% * \frac{FI\ Pd@mSiO2 - NH2 - ssDNA}{FI\ Pd@mSiO2 - NH2}$$

% RFU represents the FI (fluorescent intensity) of the Pd@mSiO$_2$-NH$_2$-HSA divided by the FI of Pd@mSiO$_2$-NH$_2$, and FI of the Pd@mSiO$_2$-NH$_2$-ssDNA divided by the FI of Pd@mSiO$_2$-NH$_2$.

2. The %RFU calculated in Figures 7 and 8 was shown below:

Figures 7 and 8 control group: $$\%RFU = 100\% * \frac{FI\ absence\ of\ target - FI\ reference}{50\ nM\ Rhodamine\ 110}$$

% RFU represents the FI (fluorescent intensity) of the absence of the target and subtracts the FI of reference divided by 50 nM Rhodamine 110.

Figures 7 and 8 experimental groups:

$$\%RFU = 100\% * \frac{FI\ presence\ of\ target - FI\ reference}{50\ nM\ Rhodamine\ 110}$$

% RFU represents the FI (fluorescent intensity) of the presence of the target and subtracts the FI of reference divided by 50 nM Rhodamine 110.

The reference is the 10 μM turn-off fluorescence probe mixed with 40 μg HSA or 8 μM ssDNA capped Pd@mSiO$_2$-NH$_2$ in the equation and the reference is the different group with the absence of the target.

6. Absorption and fluorescence spectra

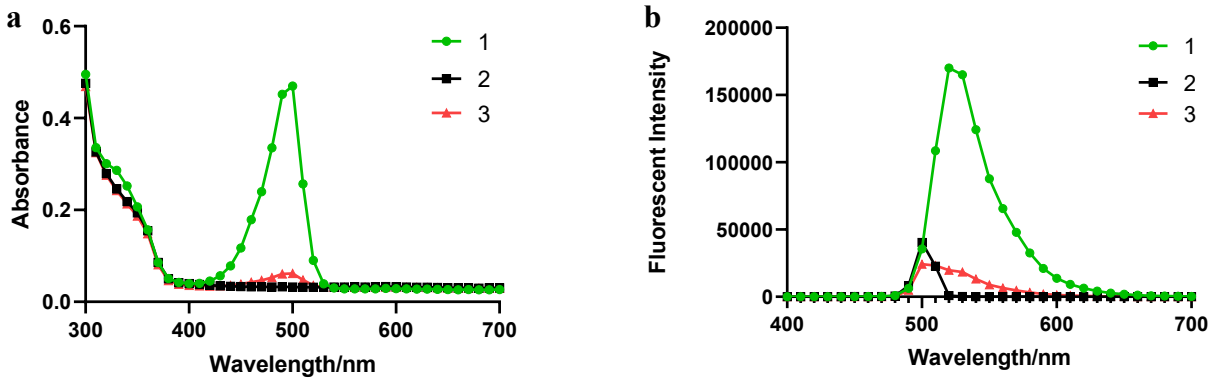


Figure S2. Absorption spectra (a) and fluorescence spectra (b). 10 μM Rhodamine 110 (1, green line), 10 μM Turn-off fluorescent probe (2, black line), 10 μM Turn-off fluorescent probe incubated with Pd@mSiO$_2$NH$_2$ for 3 h. (3, red line).

7. T-test of capping efficiency

Table S1 P value of different concentrations of HSA at 3h time point.

	0	0.1	0.5	1	5	10	20	40	60	80
0		0.6177	0.1001	0.0096	0.0016	0.0002	<0.0001	<0.0001	0.0001	0.0004
0.1			0.2724	0.1558	0.0106	0.0126	0.0067	0.0061	0.0075	0.0089
0.5				0.9854	0.0509	0.0951	0.0466	0.0398	0.0514	0.0548
1					0.0172	0.0172	0.0056	0.0052	0.0073	0.0111
5						0.2445	0.5860	0.7622	0.5521	0.6359
10							0.2286	0.1540	0.2947	0.3251
20								0.6618	0.9018	0.9752
40									0.6058	0.7628
60										0.9022
80										

Table S2 P value of different concentrations of ssDNA at 3h time point.

	0	2	4	6	8	10	12
0		0.0002	0.0074	0.0018	<0.0001	0.0020	0.0054
2			0.4802	0.1809	0.0154	0.1460	0.7473
4				0.7162	0.4200	0.5956	0.7128
6					0.6030	0.8285	0.4181
8						0.8285	0.1727
10							0.3377
12							