Supplementary Information

A colorimetric and ratiometric fluorescence probe for detection of palladium in the red light region

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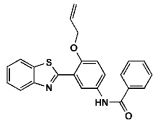
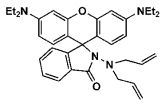
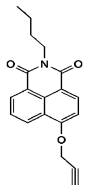
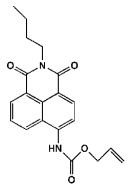
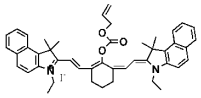
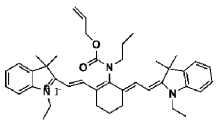
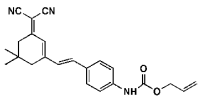
Table S1. Photophysical date of probe 1 and compound 2

Compound	λ_{abs}/nm	λ_{em}/nm	ε/ $M^{-1}cm^{-1}$	Φ[a]
Probe 1	420	570	31000	0.003
Compound 2	472	643	36000	0.016

[a]The fluorescent quantum yields were determined using rhodamine 6G as a reference dye (Φ = 0.94 in EtOH).

Table S2. Comparison of determined detection limit with those of some literatures.

Probe	$\lambda_{ex}/\lambda_{em}$ (nm)	Linear range (μM)	Detection limit	Reference
	350/550	1−8	5.2 nM	Anal. Chim. Acta. 2013, 786, 139-145.
	530/580	0−33.3	185 nM	Chem. Commun. 2010, 46, 1079–1081.
	410/480 410/553	0−7	70 nM	Chem. Commun. 2011, 47 , 8656–8658
	403/498 403/524	0−1	6.1 nM	Org. Lett. 2011, 13 (18), 4922-4925.
	740/805 545/655	0−50	2.47 nM	Chem. Commun. 2014,50, 13525-13528.
	640/750	0−1	3.8 nM	Analyst, 2013, 138, 3667-3672.
	472/570 472/643	0−1	24.2 nM	This Work

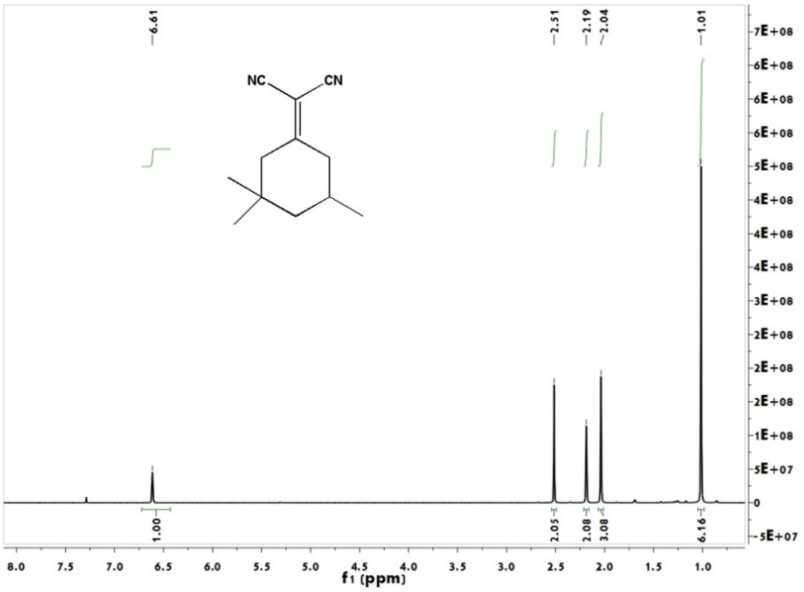


Fig. S1. ^{1}H NMR spectrum of compound 3 in $CDCl_3$

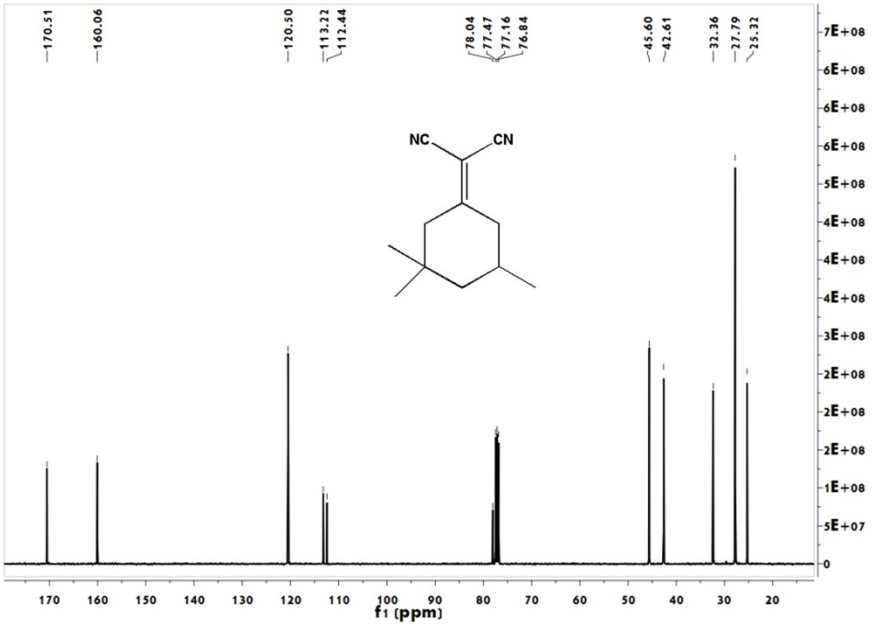


Fig. S2. ^{13}C NMR spectrum of compound 3 in $CDCl_3$

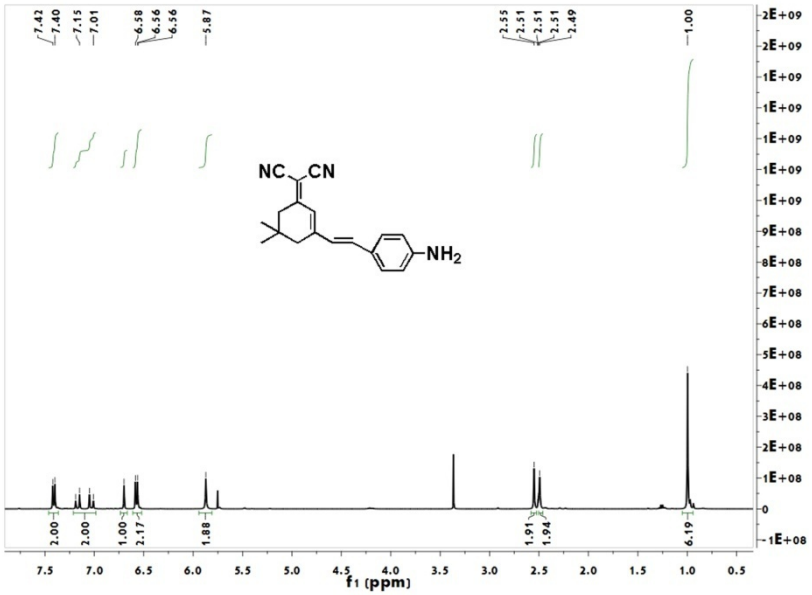


Fig. S3. ^{1}H NMR spectrum of compound 2 in $CDCl_3$.

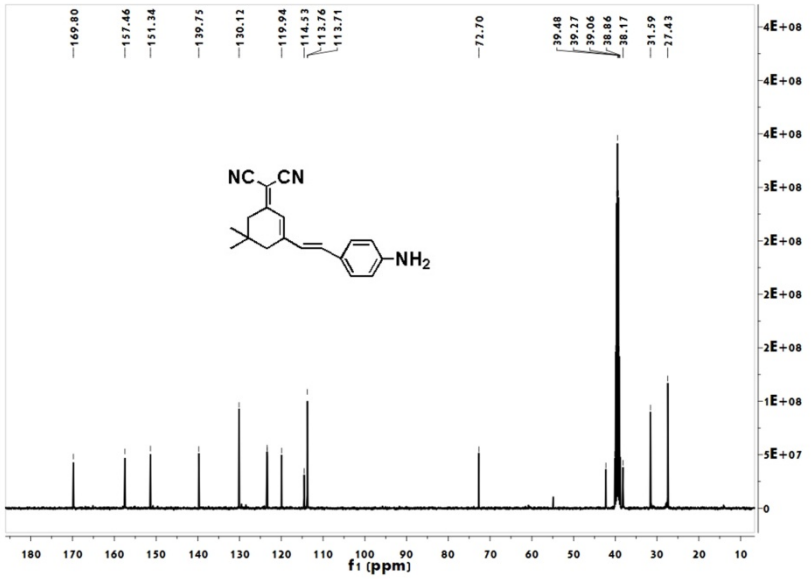


Fig. S4. ^{13}C NMR spectrum of compound 2 in DMSO.

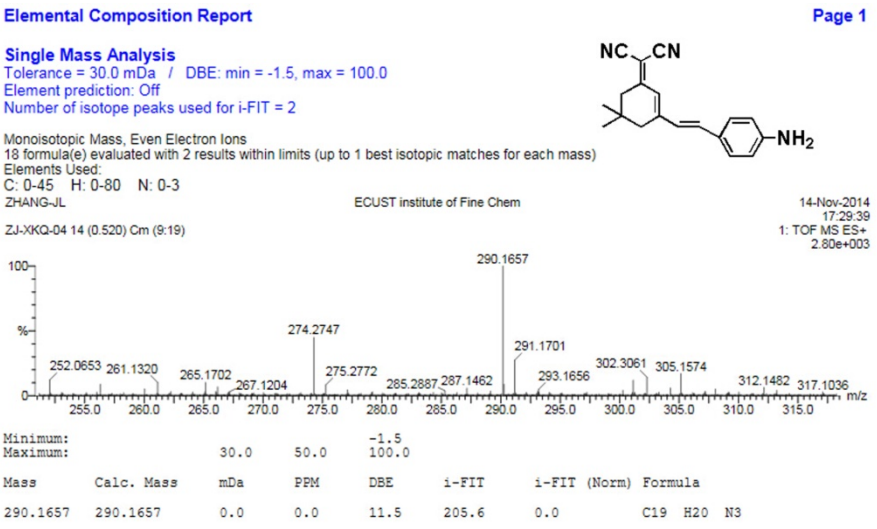


Fig. S5. HRMS spectrum of compound 2.

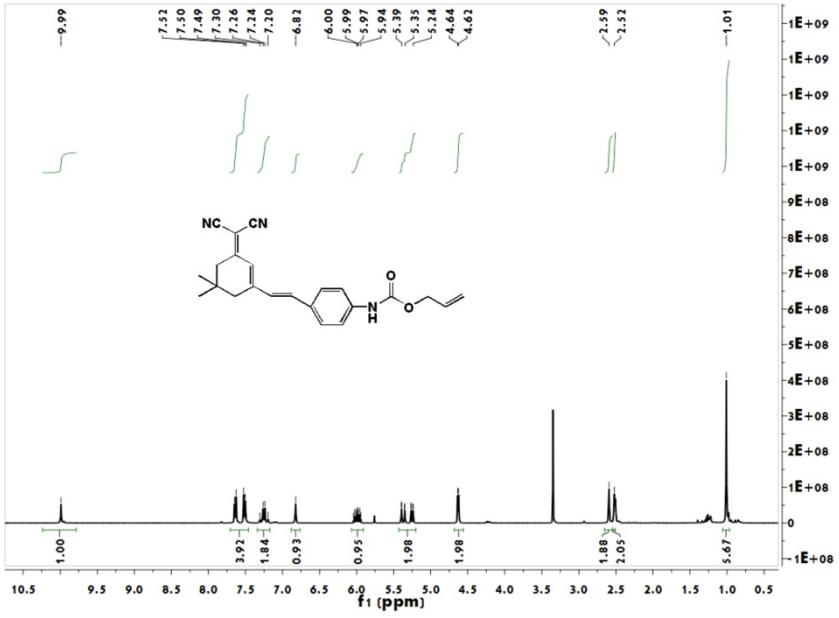


Fig. S6. ^{1}H NMR spectrum of Probe 1 in DMSO.

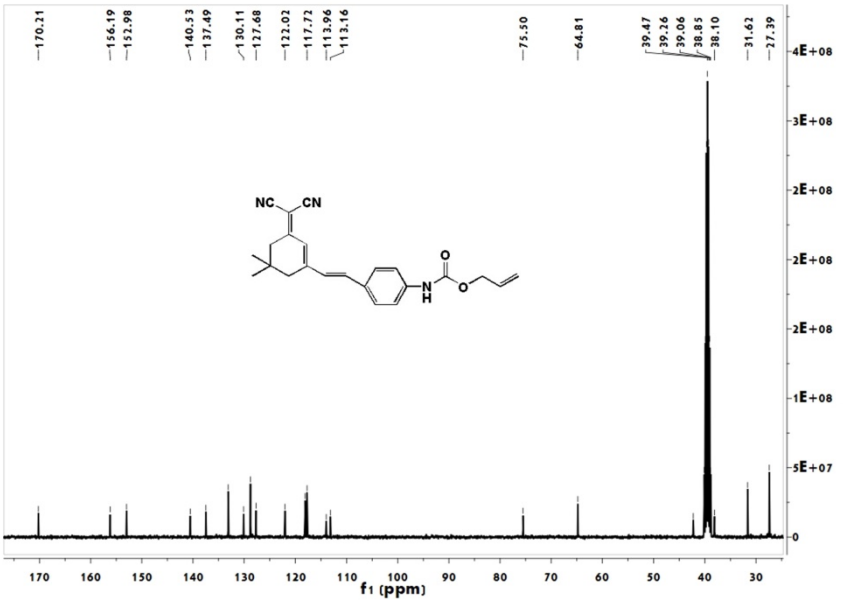


Fig. S7. ^{13}C NMR spectrum of Probe 1 in DMSO.

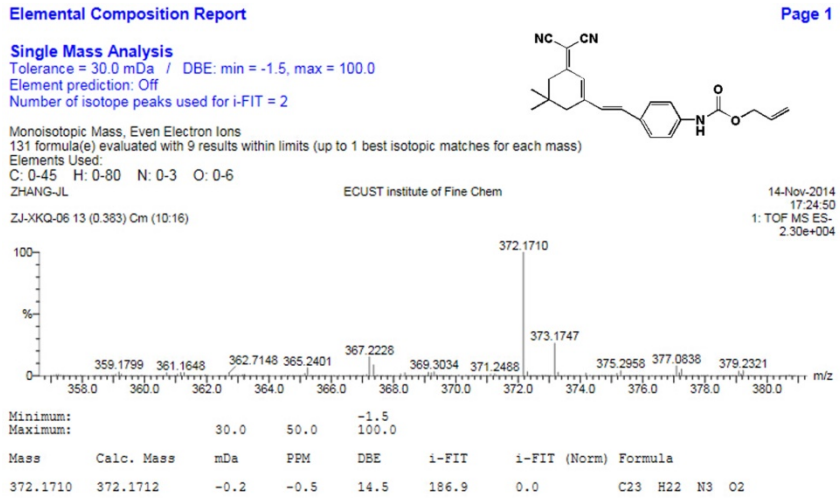


Fig. S8. HR-MS spectrum of Probe 1

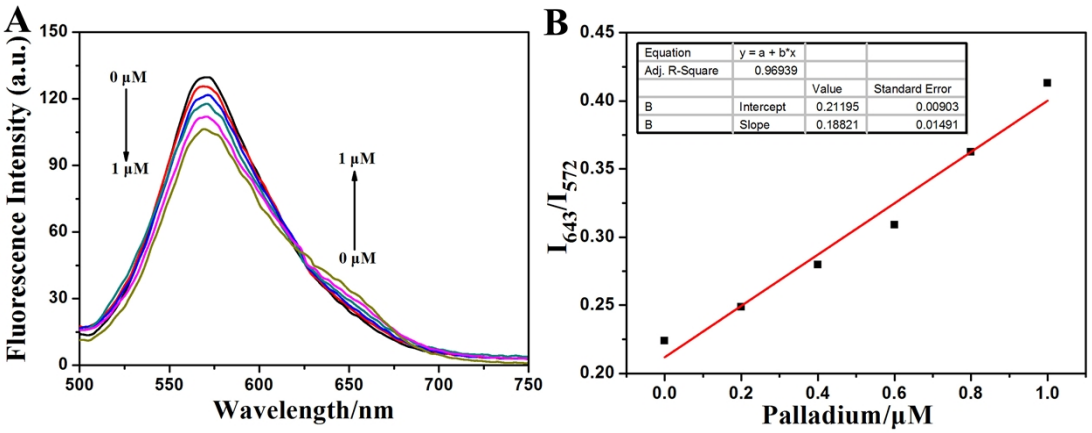


Fig. S9. Fluorescence (A) spectra of Probe 1 (10μM) towards palladium (0) at different concentrations (0-1 μM) in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20mM). B) Ratiometric calibration curve (I_{643}/I_{570}) as a function of Pd (0) concentration. λ_{ex} = 472 nm. Slit: 5 nm/5 nm. Note: Pd represents palladium (0).

The detection limit was calculated with the following equation [1-3]:

$$\text{Detection limit} = 3\sigma/S$$

Where, σ represents the standard deviation and S is the slope of the fitted straight line (Origin software). Here, the standard deviation σ was estimated by according to five times of blank measurement. The I_{643}/I_{570} values of five blank measurements for Probe 1 were 0.204, 0.204, 0.205, 0.207, and 0.203, respectively. σ = 0.001517μM; S = 0.18821. The detection limit was calculated to be 24.2 nM (3σ/S).

[1] M. Cigáň, K. Jakusová, J. Donovalová, et a. RSC Adv., 2014, **4**, 54072-54079

[2] B. C. Zhu, C. C. Gao, Y. Z. Zhao, et al. *Chem. Commun.*, 2011, **47**, 8656-8658.

[3] C. Hu, W. Sun, J. Cao, et al. Org. Lett. 2013, ***15***, 4022-4025.

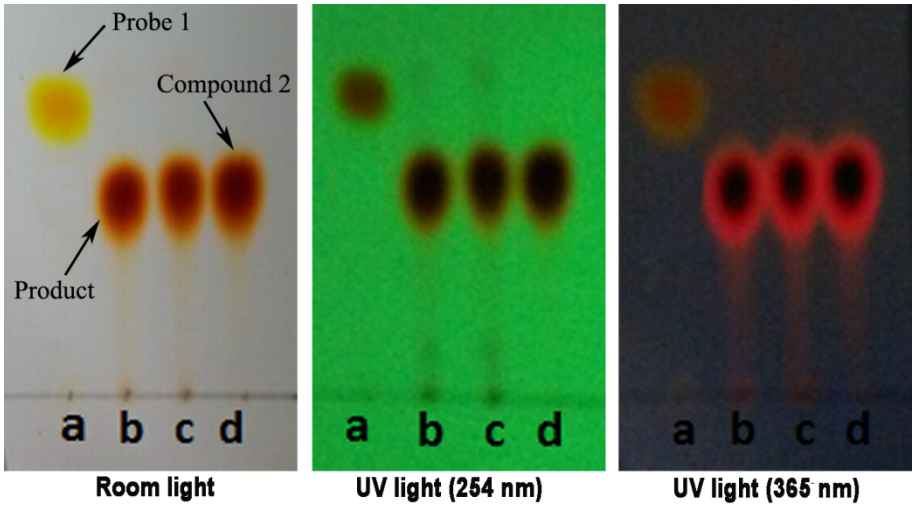


Fig. S10. Pictures of the thin layer chromatography (TLC) plates under different light used to compare Probe 1, the reference sample compound 2, reaction mixture Probe 1 with $Pd(PPh_3)_4$. Spots on the TLC plate: (a) Probe 1; (b) Reaction product of Probe 1 and $Pd(PPh_3)_4$; (c) mixture of b and compound 2; (d) Compound 2. The eluent for TLC: Petroleum ether/ethyl acetate = 5:2 (v/v).

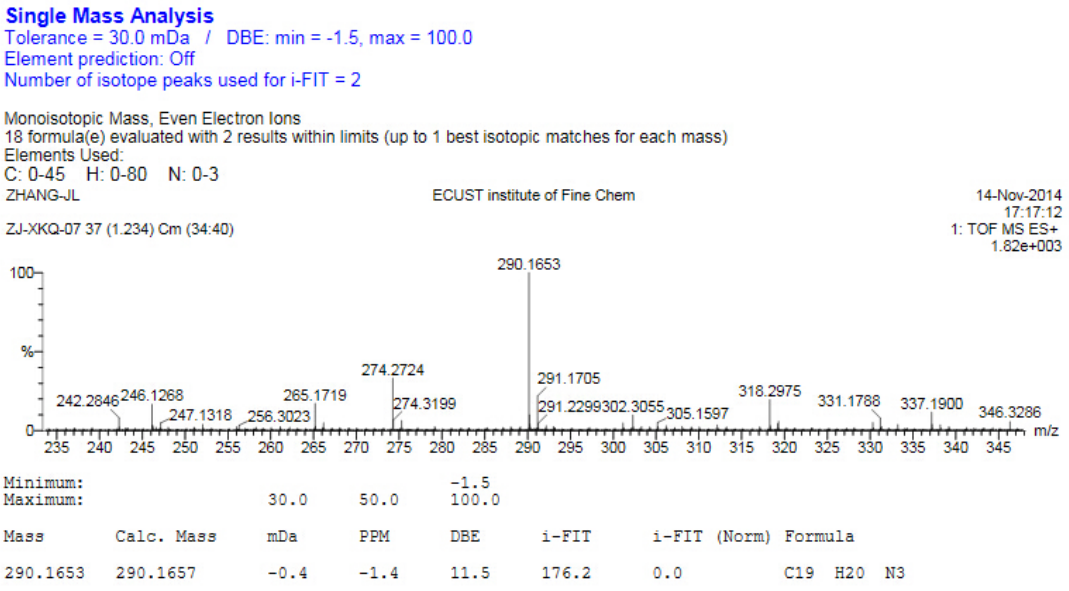


Fig. S11. HRMS spectra of Probe 1 after upon addition of palladium (0).

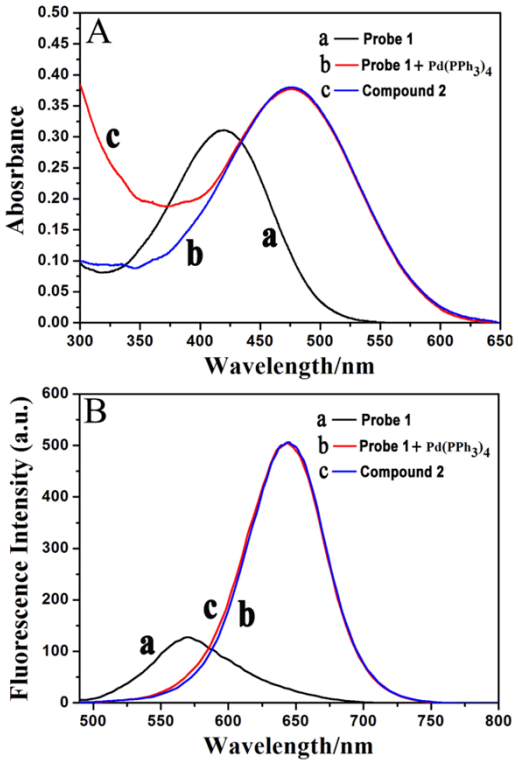


Fig. S12. UV–vis absorption and fluorescence spectra of Probe 1, compound 2, and the reaction product of Probe 1 and palladium (0). All spectra were recorded in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm.

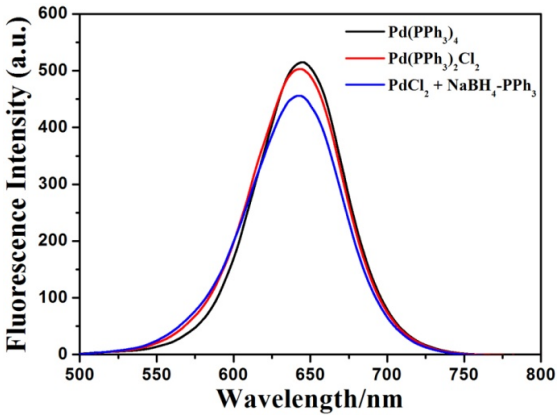


Fig. S13. Fluorescence spectra of Probe 1(10 μM) in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM) after addition of different kinds of palladium species (50 μM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm. All measures were carried out after palladium species and Probe reacted for 30 min.

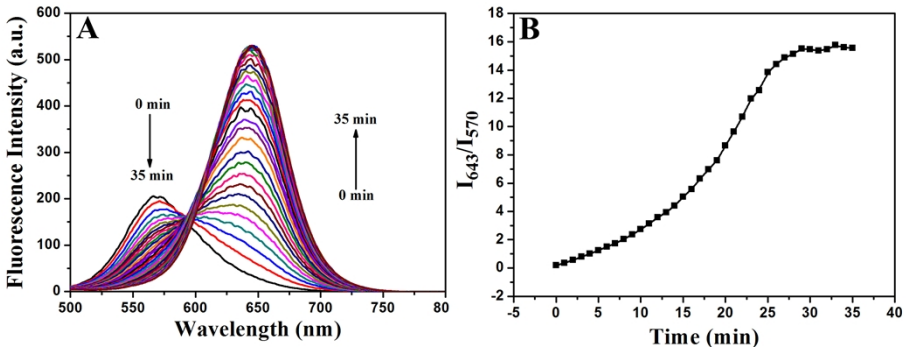


Fig. S14. (A) Time dependent fluorescence spectra and (B) I_{643}/I_{570} evolution of Probe 1 upon addition of $PdCl_2$ (II) (50 μM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm.