

New Journal of Chemistry-Supporting information

Ratiometric fluorescent determination of palladium based on the C-N bond cleavage
of allyl quaternary ammonium

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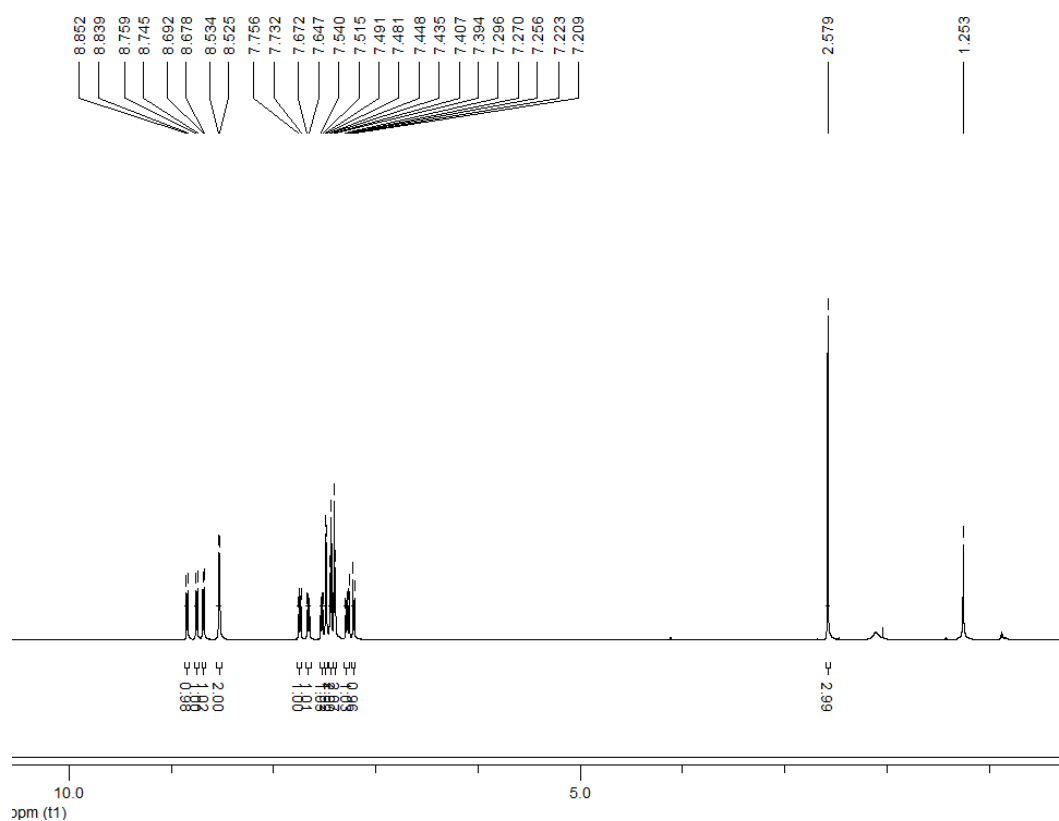


Fig. S1 ^1H NMR spectrum of PPI in CDCl_3 .

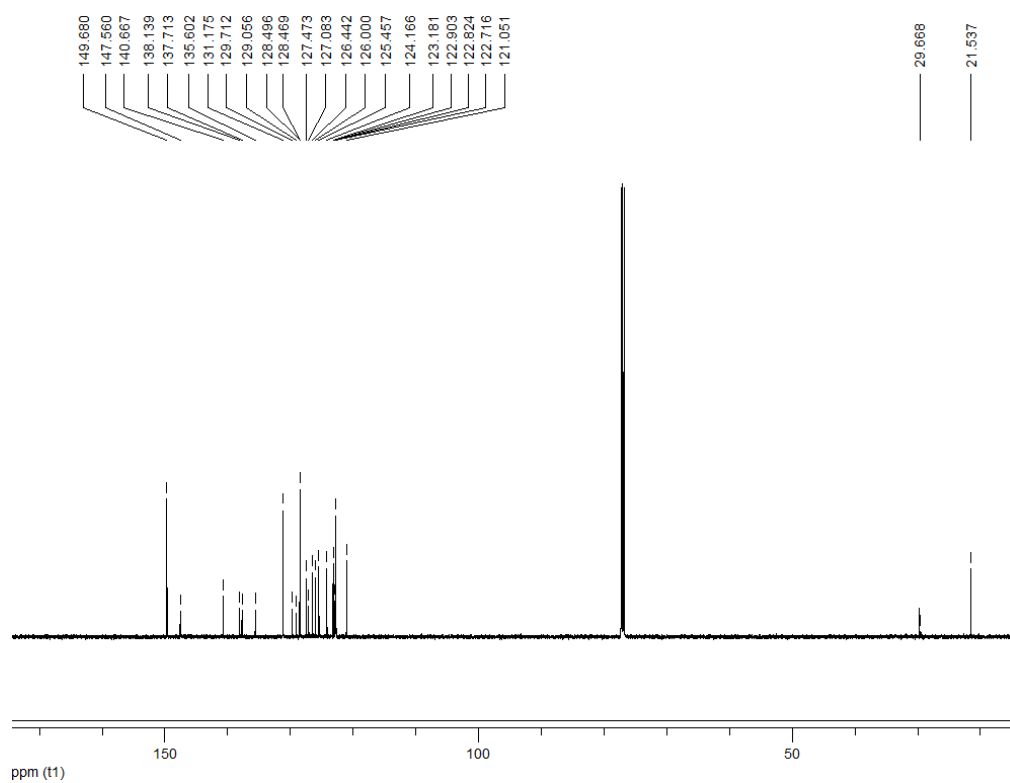


Fig. S2 ^{13}C NMR spectrum of **PPI** in CDCl_3 .

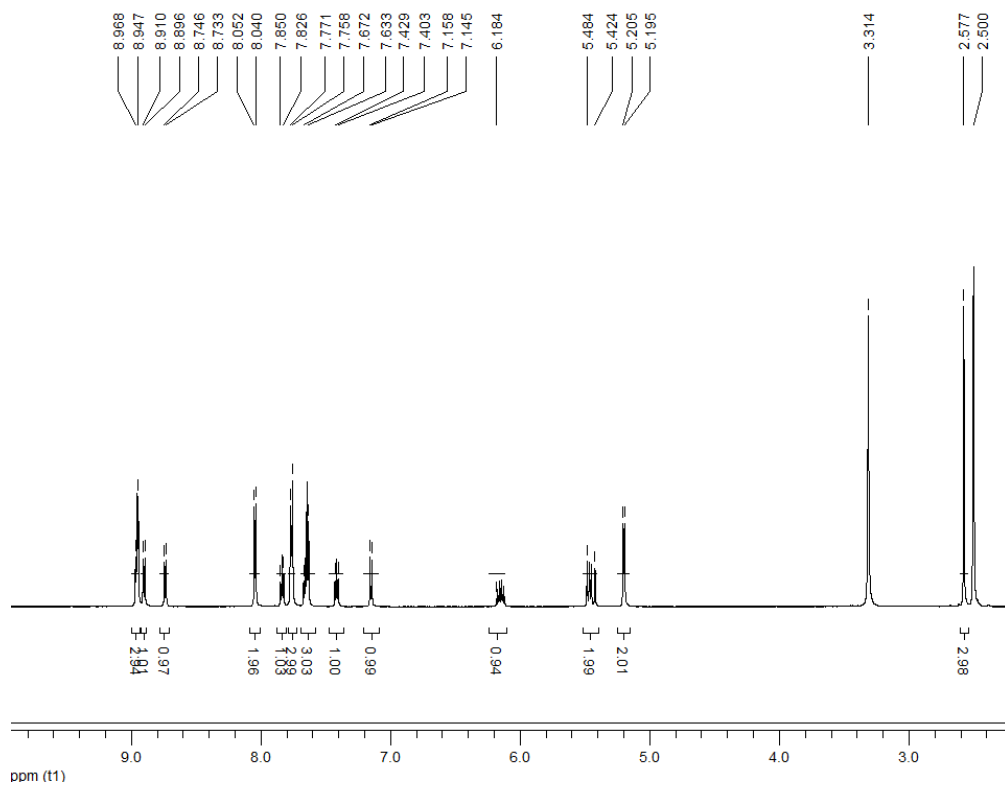


Fig. S3 ^1H NMR spectrum of AL-PPI in $\text{DMSO-}d_6$.

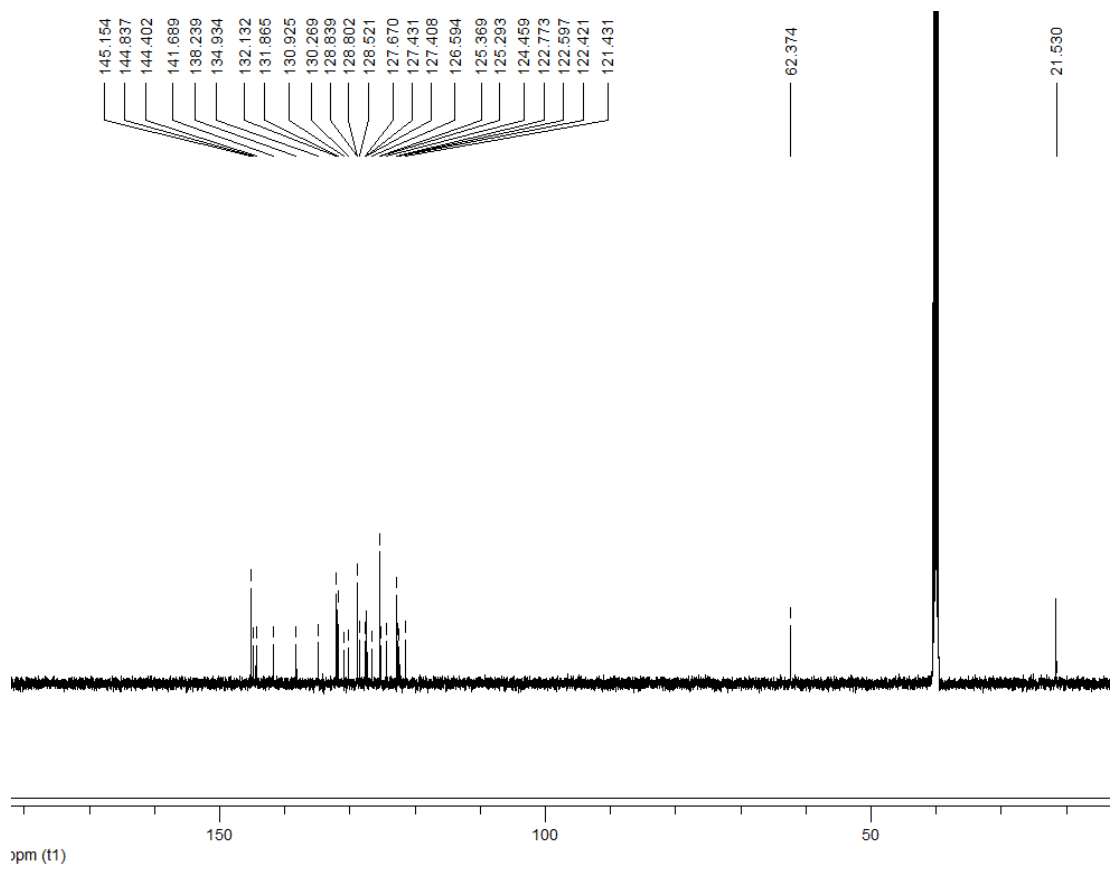


Fig. S4 ^{13}C NMR spectrum of AL-PPI in $\text{DMSO-}d_6$.

Analysis Info

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Acquisition Date 10/22/2019 2:17:56 PM

Sample Name C-1

Instrument solariX

Acquisition Parameter

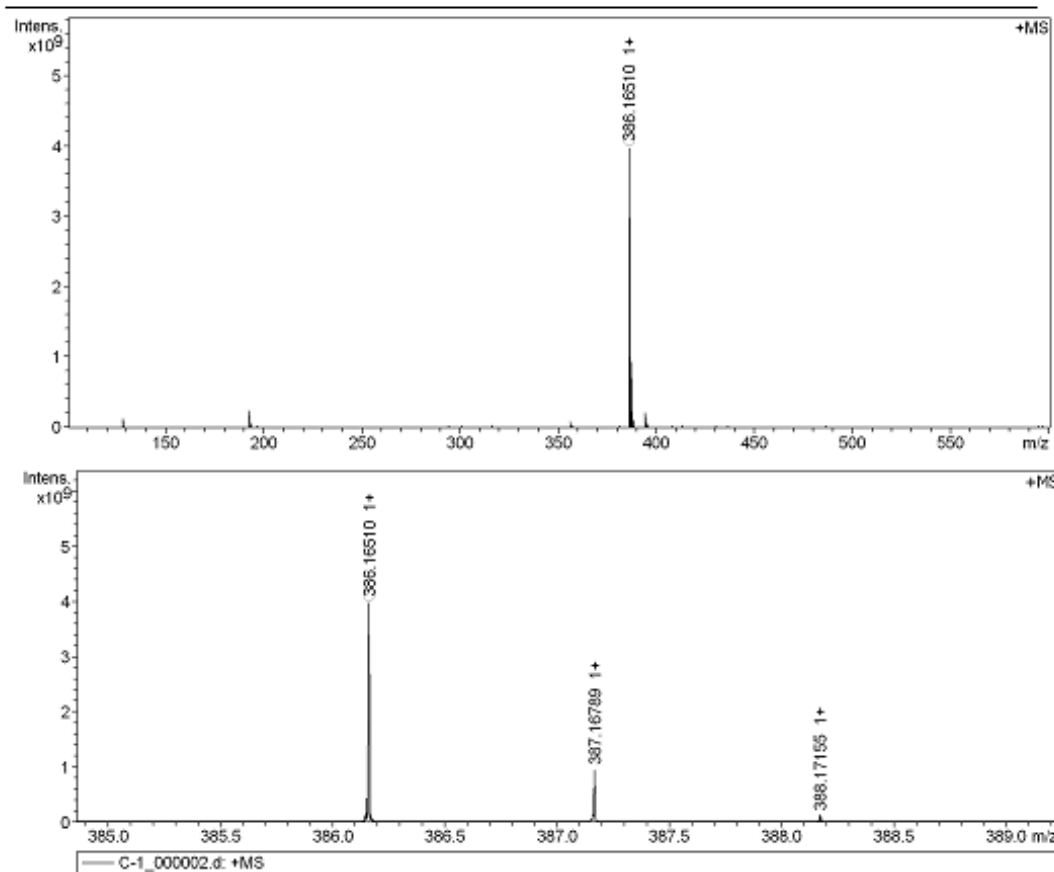
Acquisition Mode Single MS

Acquired Scans 2

Polarity Positive

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Broadband High Mass 600.0 m/z

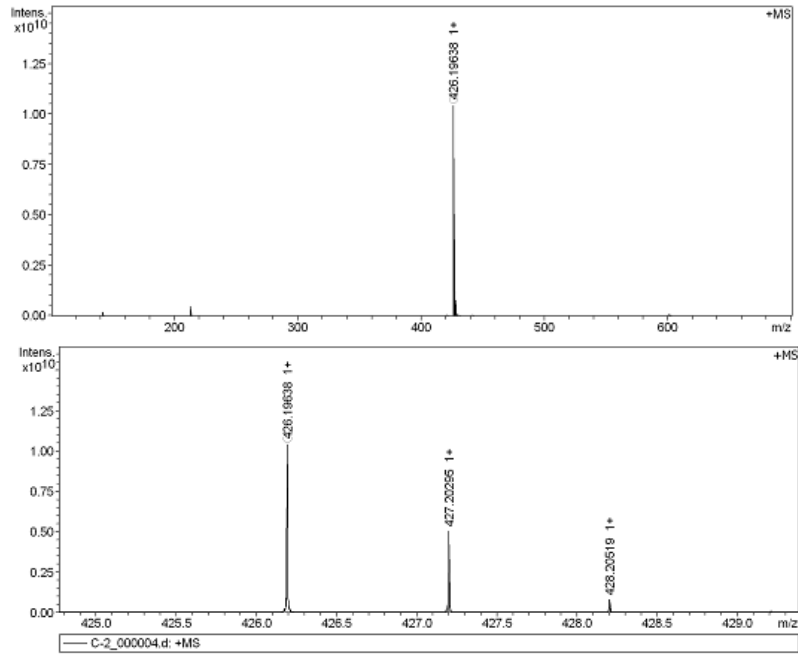


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdB	e ⁻ Conf	N-Rule
386.165095	1	C ₂₇ H ₂₀ N ₃	100.00	386.165174	-0.2	0.4	35.5	19.5	even	ok

Fig. S5 ESI-HRMS spectra of **PPI**.

Analysis Info
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Sample Name C-2 Instrument solarX

Acquisition Parameter
Acquisition Mode Single MS Acquired Scans 2
Polarity Positive
Broadband Low Mass 101.1 m/z Broadband High Mass 700.0 m/z



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
426.196378	1	C ₃₀ H ₂₄ N ₃	100.00	426.196474	-0.2	-0.2	169.5	20.5	even	ok

Fig. S6 ESI-HRMS spectra of AL-PPI.

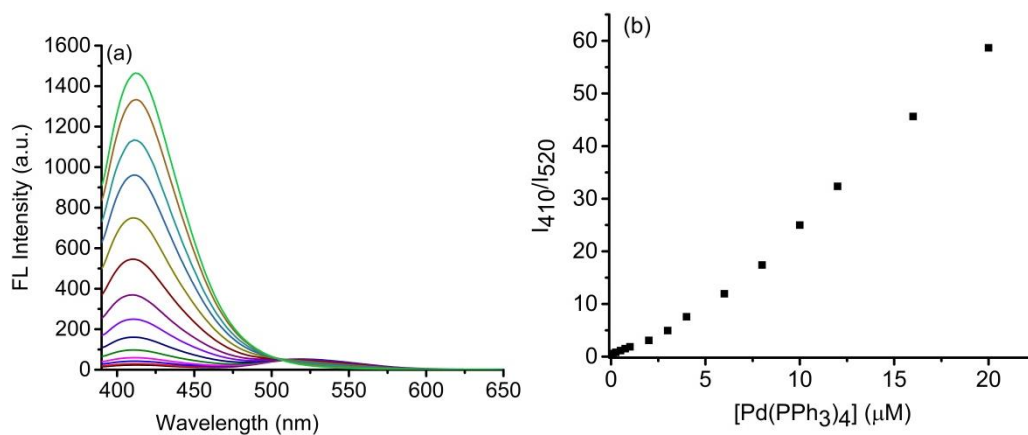


Fig. S7 (a) Fluorescence spectra of **AL-PPI** (10 μM) in the presence of different concentrations of $\text{Pd}(\text{PPh}_3)_4$ in ethanol. (b) Fluorescence intensity ratio (I_{410}/I_{520}) as a function of Pd^0 concentration.

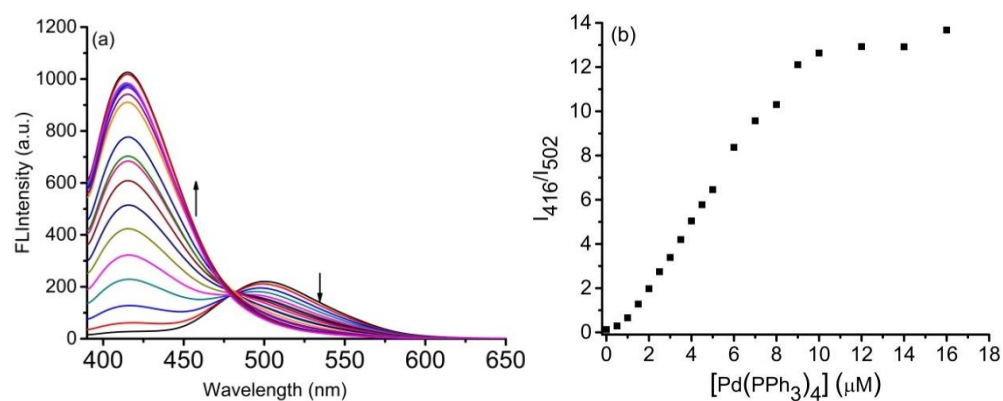


Fig. S8 (a) Fluorescence spectra of **AL-PPI** (10 μM) upon addition of $\text{Pd}(\text{PPh}_3)_4$ in CTAC (2 mM) aqueous solution ($\lambda_{\text{ex}} = 375 \text{ nm}$). (b) The fluorescence intensity ratio (I_{416}/I_{502}) versus concentration of $\text{Pd}(\text{PPh}_3)_4$.

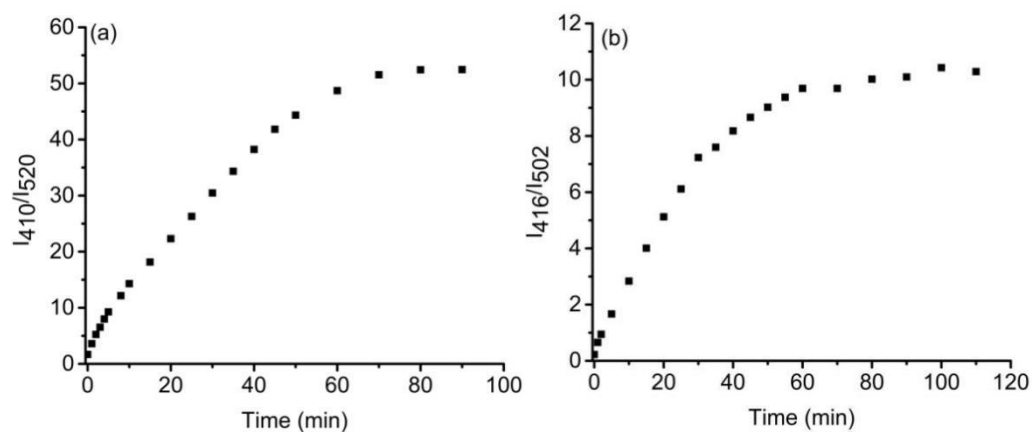


Fig. S9 Time course of emission intensity ratio of **AL-PPI** (10 μM) after addition of $\text{Pd}(\text{PPh}_3)_4$ (10 μM) in (a) ethanol and (b) in PBS (10 mM, pH 7.4) containing CTAC (2 mM).

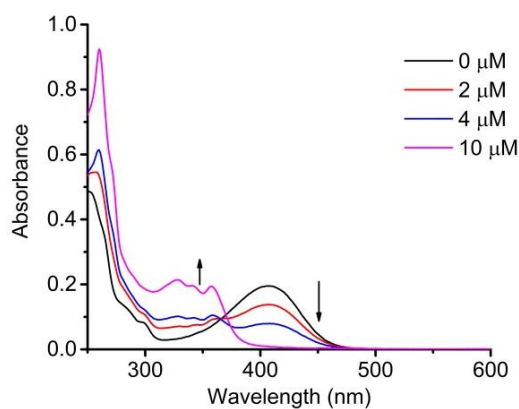


Fig. S10 The changes of absorption spectra of **AL-PPI** (10 μM) upon addition of $\text{Pd}(\text{PPh}_3)_4$ in CTAC aqueous solution.

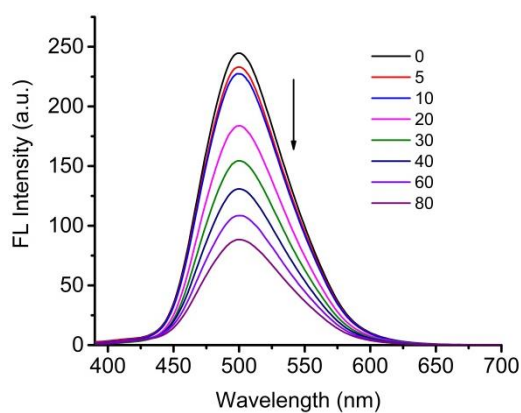


Fig. S11 Fluorescence spectral changes of **AL-PPI** (10 μM) upon addition of Pd^{2+} (0-80 μM) in CTAC aqueous solution ($\lambda_{\text{ex}} = 375 \text{ nm}$).

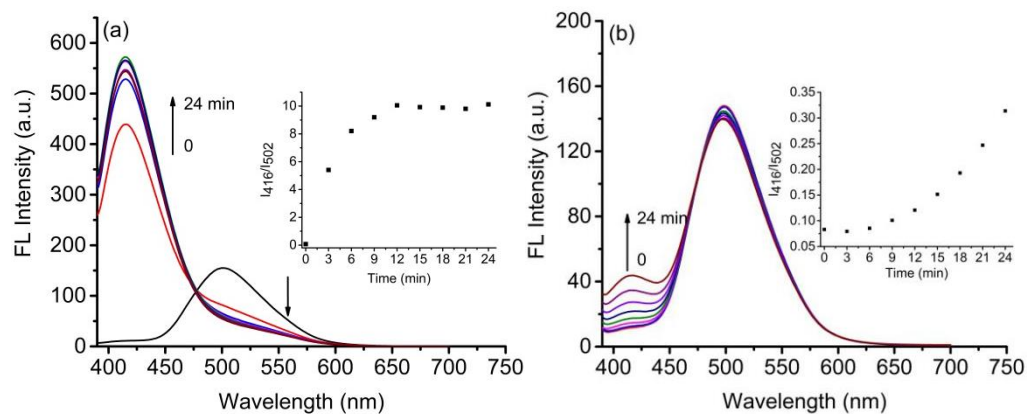


Fig. S12 (a) Fluorescence spectra of **AL-PPI** (10 μM) in the presence of (a) TFP (75 μM) and (b) PPh_3 (75 μM) in PBS buffer (10 mM, pH 7.4) containing Pd^{2+} (10 μM) and CTAC (2 mM). Inset: time-dependent fluorescence response of **AL-PPI** toward Pd^{2+} in the presence of phosphine ligand.

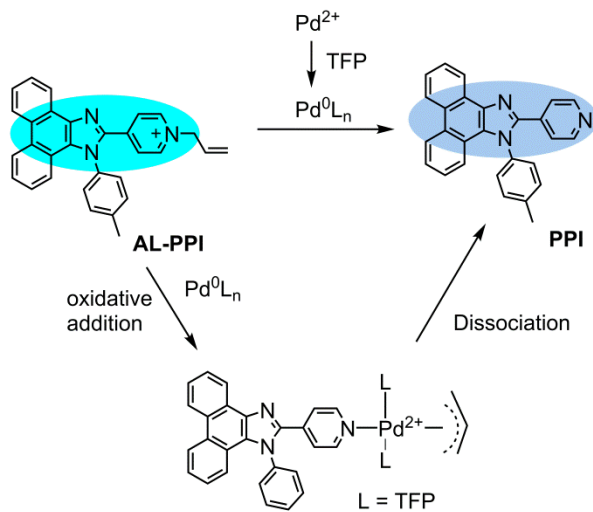


Fig. S13 Mechanism for selective recognition of Pd^{2+} by **AL-PPI** with the aid of TFP.

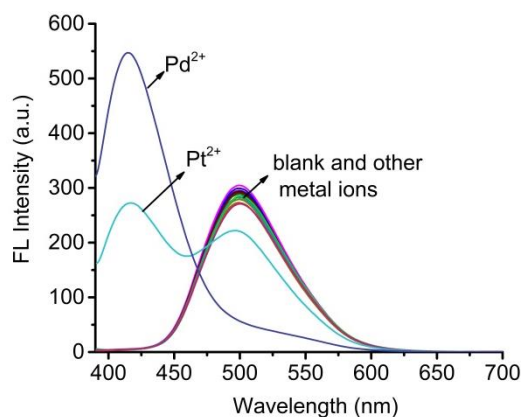


Fig. S14 Fluorescence spectra of a mixed solution of **AL-PPI** (10 μM), TFP (75 μM) upon addition of Pd^{2+} (10 μM) and other metal ions, including Mg^{2+} , Ca^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Sn^{2+} , Al^{3+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Pb^{2+} and Pt^{2+} (20 μM , respectively) ($\lambda_{\text{ex}} = 375 \text{ nm}$). All spectra were recorded at 15 min after mixing of **AL-PPI** and analyte in PBS (10 mM, pH 7.4) containing CTAC (2 mM) ($\lambda_{\text{ex}} = 375 \text{ nm}$).

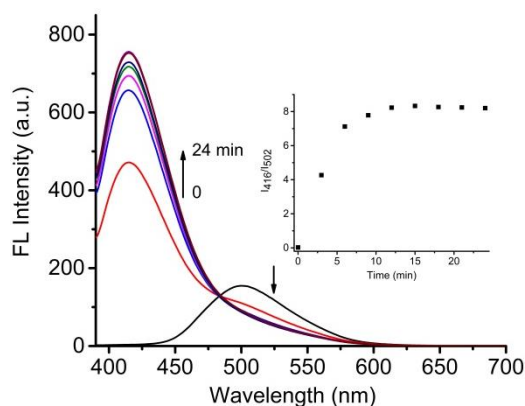


Fig. S15 Fluorescence emission spectra of **AL-PPI** (10 μM) upon addition of in NaOAc-HOAc buffer solution (10 mM, pH = 5.0) containing CTAC (2 mM). Inset: time-dependent fluorescence change of **AL-PPI** (10 μM) in the presence of TFP (75 μM) and Pd^{2+} (10 μM).

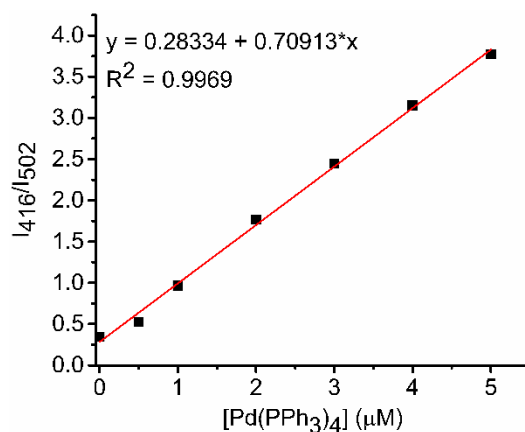


Fig. S16 The linear relationship of the I_{416}/I_{502} as a function of the concentration of $\text{Pd}(\text{PPh}_3)_4$ (0-5 μM) in the Qizhen Lake water containing **AL-PPI** (10 μM) and CTAC (2 mM).

Table S1 Analysis results of Pd^0 in real water samples ($n = 4$)^{a,b}

AL-PPI	Added (μM)	Found (μM)	RSD (%)	Recovery (%)
1	0.5	0.453	0.25	90.6
2	1.0	1.257	2.67	125.7
3	3.0	3.041	5.37	101.3
4	5.0	5.399	1.37	108.4

^alake water from Qizhen Lake, Northwestern Polytechnical University. ^b $\text{Pd}(\text{PPh}_3)_4$ is used as source of Pd^0 .