Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

A Novel Ratiometric AIEE/ESIPT Probe for Palladium Species Detection with ultra-sensitivity

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Contents

1. Materials and Methods

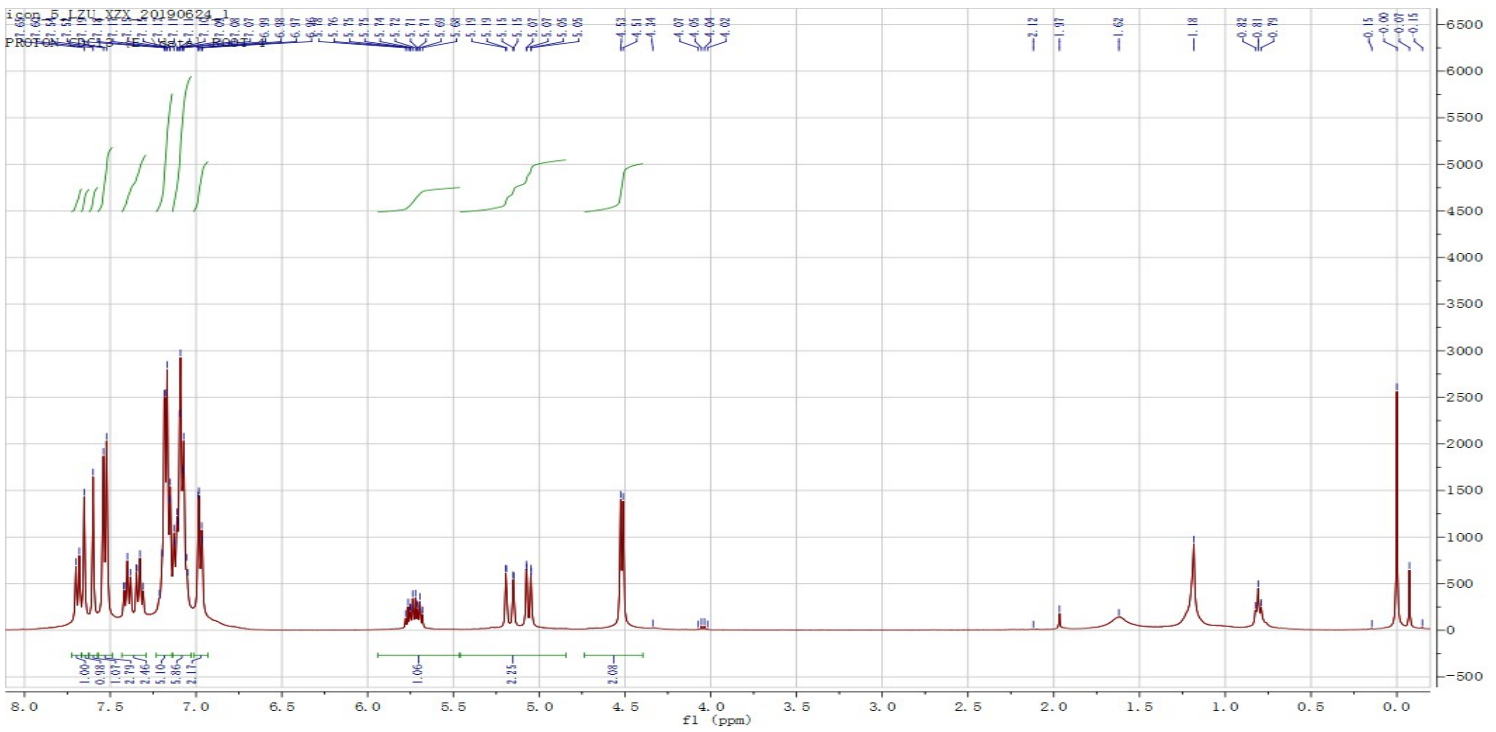
Entry	Reagent	Quantity	Solvent (50mL)	Conc.
A	HPNI	21.9 mg	THF	1 mM
B	HPNI-1	26.1 mg	THF	1 mM
C	$Pd(PPh_3)_4$	5.8 mg	DMSO	0.1 mM

D	$Pd(PPh_3)_2Cl_2$	5.3 mg	DMSO	0.1 mM
E	$Pd_2(dba)_3$	4.6 mg	DMSO	0.1 mM
F	$(C_3H_5)_2PdCl_2$	1.8 mg	DMSO	0.1 mM
G	K_2PdCl_6	2.0 mg	H2O	0.1 mM

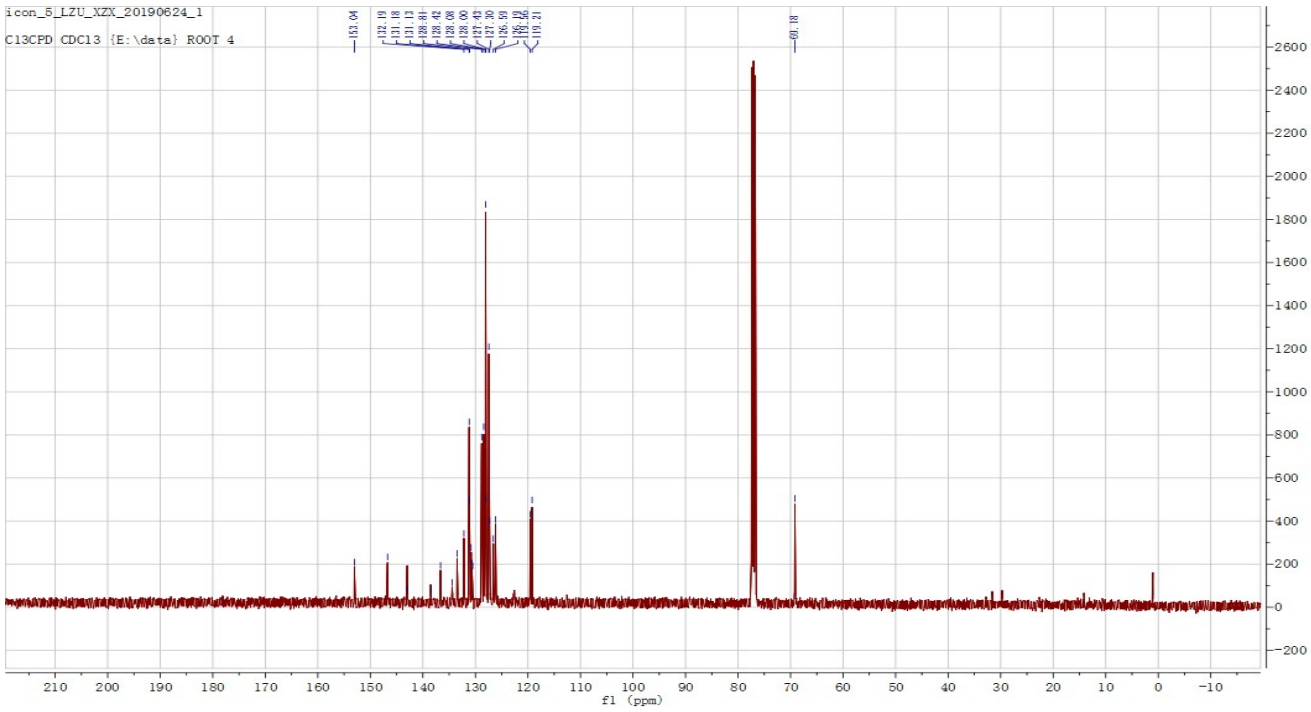
Notes: All reagents and solvents were obtained commercially and used without further purification unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOLBCS 400M spectrometer. Mass spectra (ESI) were recorded on a LQC system (Finngan MAT, USA). All UV－visible spectra was recorded by a Varian Cary 100 spectrophotometer. Fluorescence spectra were recorded using an Edinburgh FLSP920. Fluorescence spectra were measured after addition of palladium for 1min.

3. The characterization data of HPNI-1

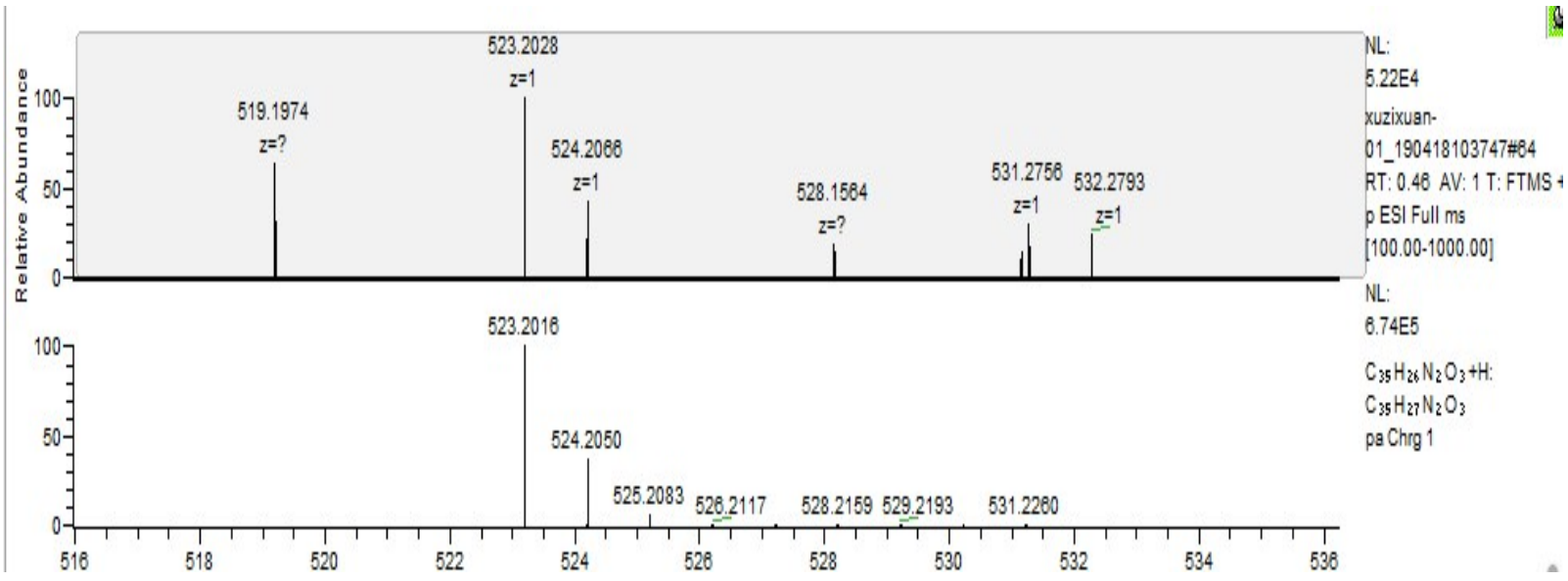
^{1}H NMR spectra of HPNI-1



^{13}C NMR spectra of HPNI-1



ESI spectra of HPNI-1



3. Additional Spectra

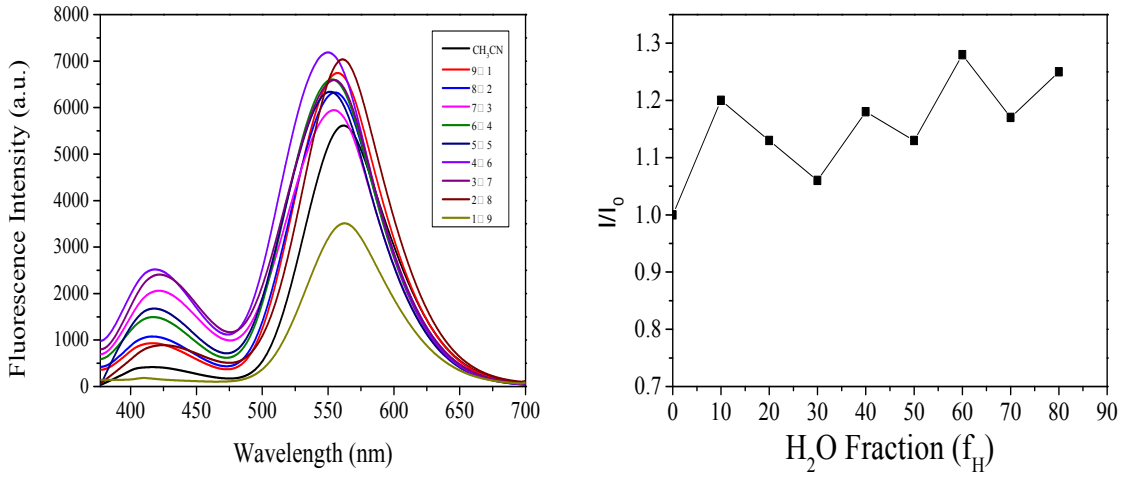


Figure S1. (a) Emission spectra of HPNI in CH_3CN/H_2O mixture with different H_2O fractions (F_H) (b) the plot of relative emission intensity (I/I_0) at 560 nm

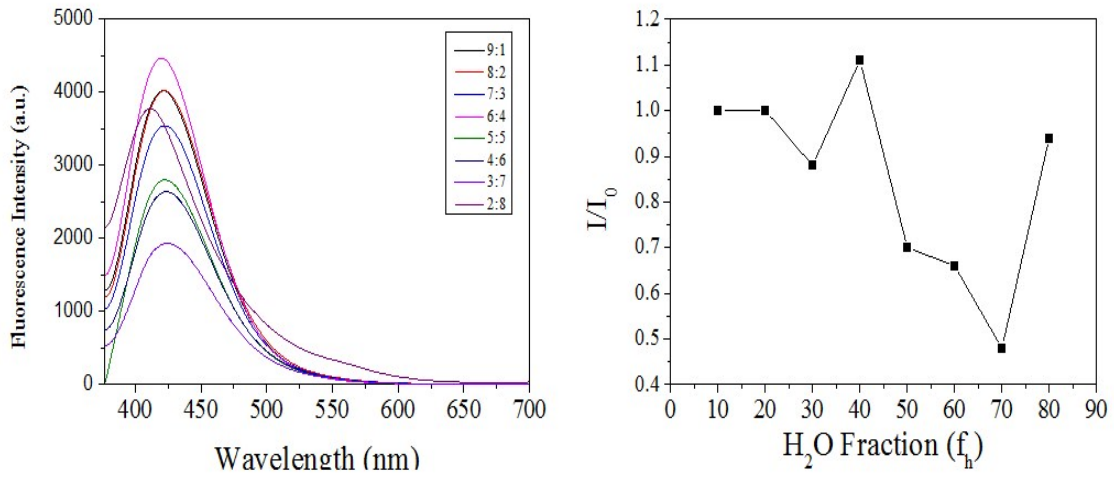
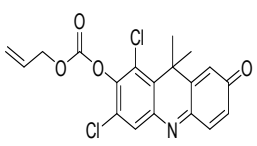
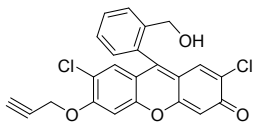
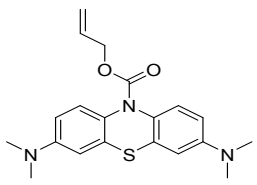
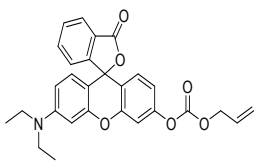
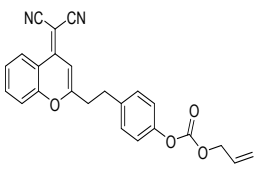
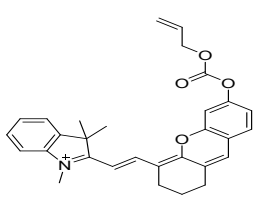
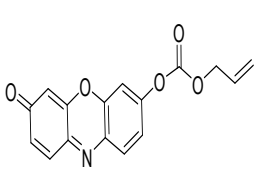
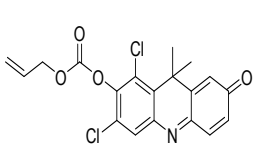
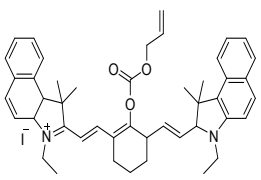
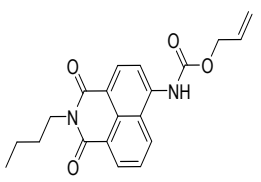
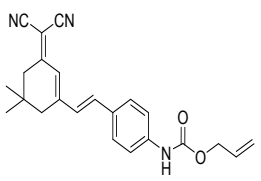
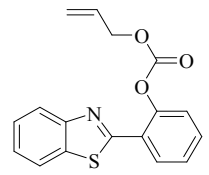
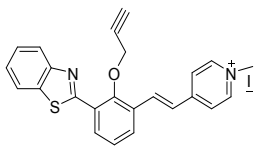
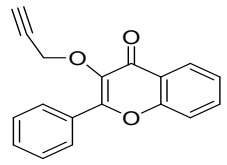
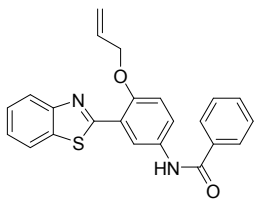
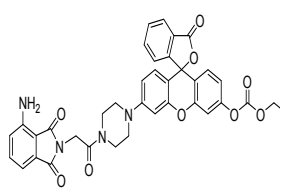
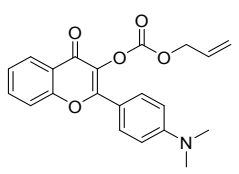
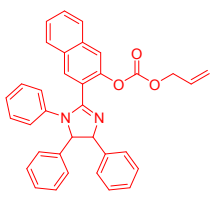


Figure S2. (a) Emission spectra of HPNI-1 in CH_3CN/H_2O mixture with different H_2O fractions (F_H) (b) the plot of relative emission intensity (I/I_0) at 420 nm

Table S1. Comparison of fluorescent probes for palladium detection

References	Probe	Detection medium	$\lambda_{ex}/\lambda_{em}$ (nm)	Stokes shift	Detection time	Detection limit		
RSC Adv. 2017, 7, 20369-20372		CH_3CN–PBS (v/v = 1/1, pH 7.4, 10 mM)	588/621	33 nm	80 min	0.78 nM	Turn on	ICT
Chem. Commun. 2010, 46, 3964–3966		CH_3CN–PBS (v/v = 1/9, pH 7.4, 10 mM)	480/520	40 nm	180 min	30 nM	Turn on	ICT
RSC Adv. 2017, 7, 6583–6586		EtOH : PBS (9 : 1, v/v, 10 mM)	650/681	31 nm	30 min	5.7 nM.	Turn on	ICT
J. Photochem. Photobiol. A: Chem. 2017, 337, 25–32		THF/PBS (1:1 v/v, pH = 7.4, 20 mM)	500/547	47 nm	75 min	1.14 nM	Turn on	ICT
Tetrahedron Lett. 2015, 56, 6491–6494		PBS buffer (90% DMSO, v/v, pH 7.4, 20 mM)	560/700	140 nm	30 min	52 nM	Turn on	ICT
Dyes Pigm. 2017, 137, 293-298		PBS/DMSO (19:1, v/v, pH 7.4 10 mM)	670/721	51 nm	30 min	22.4 nM	Turn on	ICT
Analyst, 2016, 141, 2376-2379		10 mM PBS, pH 7.4	570/590	20 nm	30 min	2.1 nM	Turn on	ICT
Sensors and Actuators B 2018, 98-104		PBS buffer (10 mM, pH 7.4, 20% DMSO, v/v)	602/665	63 nm	2 min	2.2 nM	Turn on	ICT

Chem. Commun. 2014, 50, 13525–13528		CH_3CN–PBS (v/v = 1/3, pH 7.4, 10 mM)	λ_{ex} = 545 nm, λ_{em} = 810/655 nm	110 nm	20 min	2.8 nM	ratiometric	ICT
Org. Lett. 2011, 13, 4922–4925		$CH_3CN:H_2O$ = 4:1 $NaBH_4$ -PPh_3 (10 mM) and morpholine (10 mM))	λ_{ex} = 403 nm λ_{em} = 462/524 nm	121 nm	5 min	6.1 nM	ratiometric	ICT
RSC Adv. 2015, 5, 52516-52521		DMSO/PBS (1/1, v/v, Ph7.4, 20 mM).	λ_{ex} = 420 nm, λ_{em} = 570/643 nm	171 nm	30 min	24.2 nM	ratiometric	ICT
J. Mater. Chem. B., 2016, 4, 3911-3915.		PBS buffer (10 mM, pH 7.4, with 10% CH_3CN, v/v).	λ_{ex} = 320 nm λ_{em} = 388/476 nm/	156 nm	20 min	15.6 nM	ratiometric	ESIPT
Chem. Asian J., 2015, 10, 1142-1145.		PBS buffer (10 mM, pH 7.4)	λ_{ex} = 320 nm λ_{em}= 495/635 nm/	315 nm	30 min	57 nM	ratiometric	ESIPT
Chem. Commun., 2012, 48, 2867-2869		CH_3CN–H_2O (1: 4, v/v)	λ_{ex} = 360 nm λ_{em}= 412/517 nm/	157 nm	180 min	87 nM	ratiometric	ESIPT
Anal. Chim. Acta., 2013, 786, 139-145.		PBS buffer, pH = 7.0, 10 mL, 20 mM	λ_{em}= 415/555 nm	--	5 min	1 μM	ratiometric	ESIPT
Sensors and Actuators B 2018, 554-562		HEPES buffer (10 mM, pH 7.4, with 20% CH_3CN, v/v).	λ_{ex} = 511 nm λ_{em} = 490/547 nm/	36 nm	10 min	31 nM	ratiometric	ESIPT-FRET.
Org. Biomol. Chem., 2017,15, 5846-5850		PBS buffer (pH = 7.4, with 10% THF) $NaBH_4$	λ_{em} = 470/552 nm	--	1.5 min	9.0 nM	ratiometric	ESIPT
This work		$CH_3CN:H_2O$ = 3:2 KBH_4 (1 mM)	λ_{ex} = 340 nm λ_{em} = 410/570 nm	230 nm	2 min	1.34 nM	ratiometric	ESIPT-AIEE