SUPPORTING INFOMATION

Near-infrared chromogenic sensing of organotin species by a cyclopalladated azo dye

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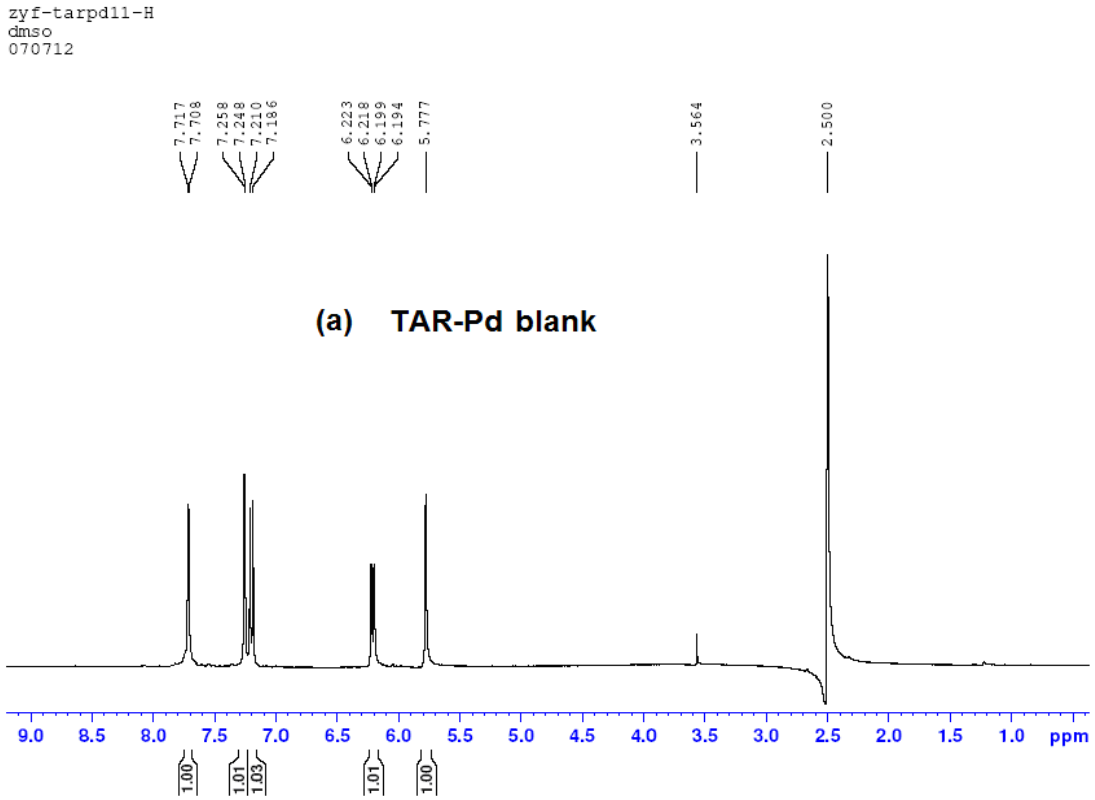
Contents

1. Reagents

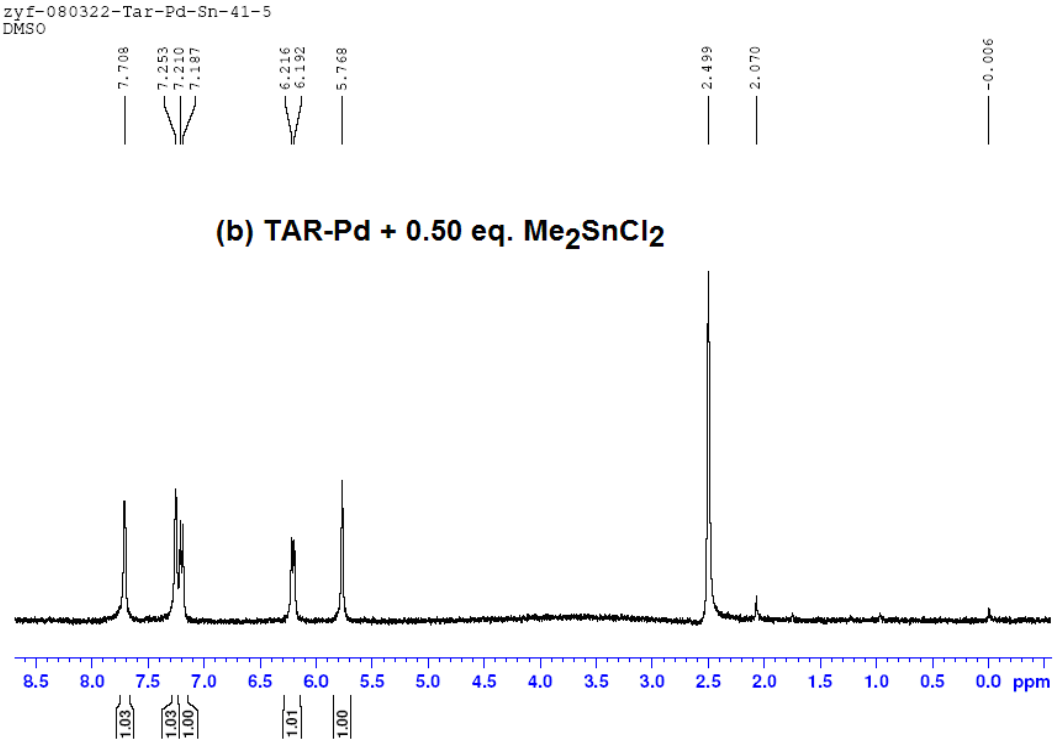
All the organotin compounds (OTC) and potassium tetrachloropalladate(II) were purchased from Sigma-Aldrich Co., Ltd. 4-(2-Thiazolylazo)resorcinol (TAR) was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and used without further purification.

In a typical preparation, TAR (45 mg, 0.2 mmol) and potassium tetrachloropalladate(II) (66 mg, 0.2 mmol) were dissolved in 30 mL dioxane-water (1:1) mixture. The mixture was stirred at room temperature for a week to give a dark green solution. The solvent was evaporated to ca. 1.5 mL under vacuum. The precipitate was collected and washed with ethanol and diethyl ether, respectively. The obtained solid was dried under vacuum to give 61 mg of TAR-Pd (76% yield). The high-quality single crystal of TAR-Pd was unavailable despite of many attempts. The selected spectroscopic data of TAR-Pd are as follows. XPS: Pd (4d, 2p, 3p, MNV, $3d_{5/2}$ = 337.5 eV, $3d_{3/2}$ = 342.9 eV); Cl (2p, $2d_{3/2}$ = 197.35 eV, $2d_{1/2}$ = 198.88 eV); S (2p); C (1s); N (1s); O(1s). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 5.78 (s, 1 H, Ph-H), 6.21 (d, 1 H, J(HH) = 8 Hz，=C(H)S=), 7.20 (d, 1 H, J(HH) = 8Hz，=C(H)N=), 7.25 (s, 1 H, Ph-H), 7.71 (s, 1 H, OH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 104.27, 116.35, 121.35, 122.01, 138.55, 139.46, 174.58, 181.12, 188.73. MOLDI-TOF-MS: m/z 800.11 (M), 842.19 (M + CH_3CN), 401.63 (M/2 + H).

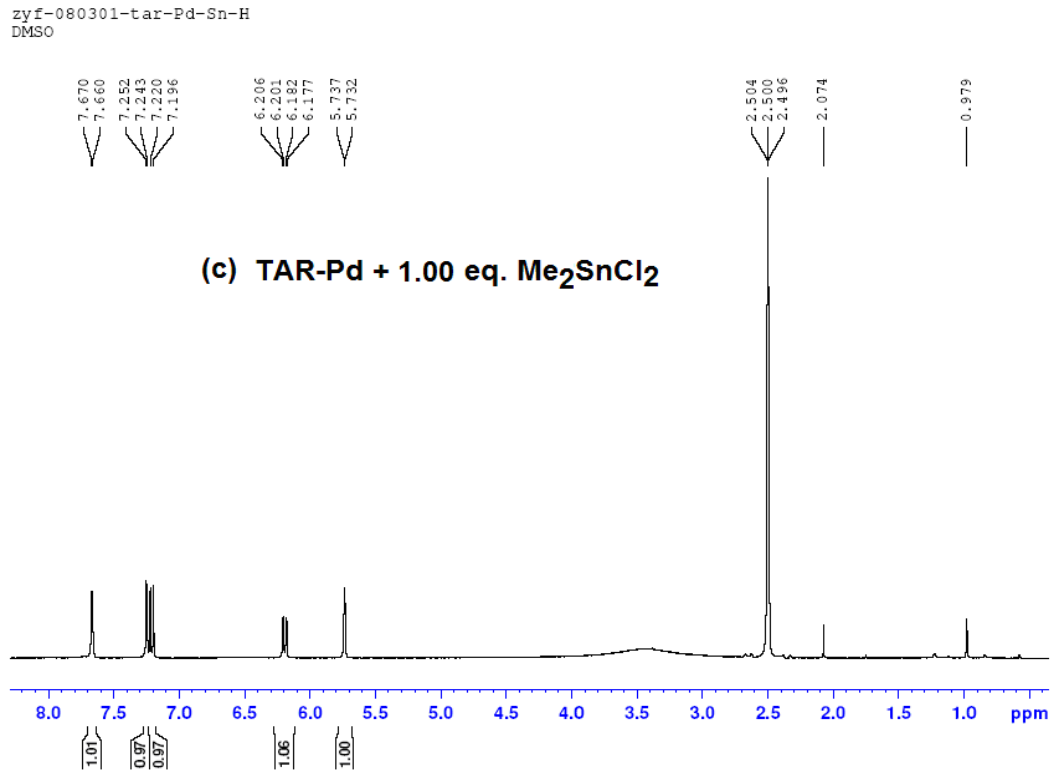
2. ^{1}H NMR spectra of TAR-Pd and its tin-sensing products (Fig. S1)



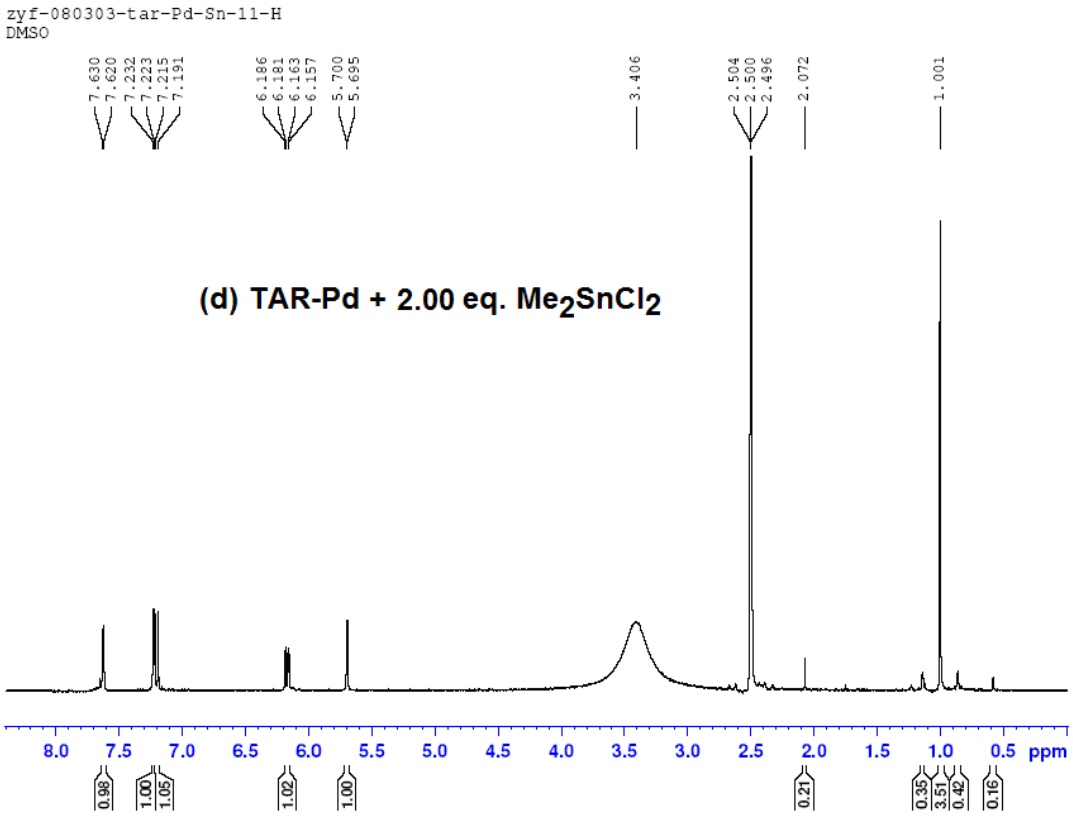
^{1}H NMR (400 MHz, DMSO-d_6, ppm) for (a): δ = 5.78 (s, 1 H, Ph-H), 6.21 (d, 1 H, J(HH) = 8Hz，=C(H)S=), 7.20 (d, 1 H, J(HH) = 8Hz，=C(H)N=), 7.25 (s, 1 H, Ph-H), 7.71 (s, 1 H, OH), 2.50 (DMSO), 3.56 (H_2O).



^{1}H NMR (400 MHz, DMSO-d_6, ppm) for (b): δ = 5.77 (s, 1 H, Ph-H), 6.21 (d, 1 H, J(HH) = 8Hz，=C(H)S=), 7.20 (d, 1 H, J(HH) = 8Hz，=C(H)N=), 7.25 (s, 1 H, Ph-H), 7.71 (s, 1 H, OH), 2.499 (DMSO).



^{1}H NMR (400 MHz, DMSO-d_6, ppm) for (c): δ = 5.73 (s, 1 H, Ph-H), 6.19 (d, 1 H, J(HH) = 8Hz，=C(H)S=), 7.21 (d, 1 H, J(HH) = 8Hz，=C(H)N=), 7.25 (s, 1 H, Ph-H), 7.67 (s, 1 H, OH), 2.50 (DMSO).



^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) for (d): δ = 5.70 (s, 1 H, Ph-H), 6.17 (d, 1 H, J(HH) = 8Hz，=C(H)S=), 7.20 (d, 1 H, J(HH) = 8Hz，=C(H)N=), 7.23 (s, 1 H, Ph-H), 7.63 (s, 1 H, OH), 2.50 (DMSO), 3.40 (H_2O).

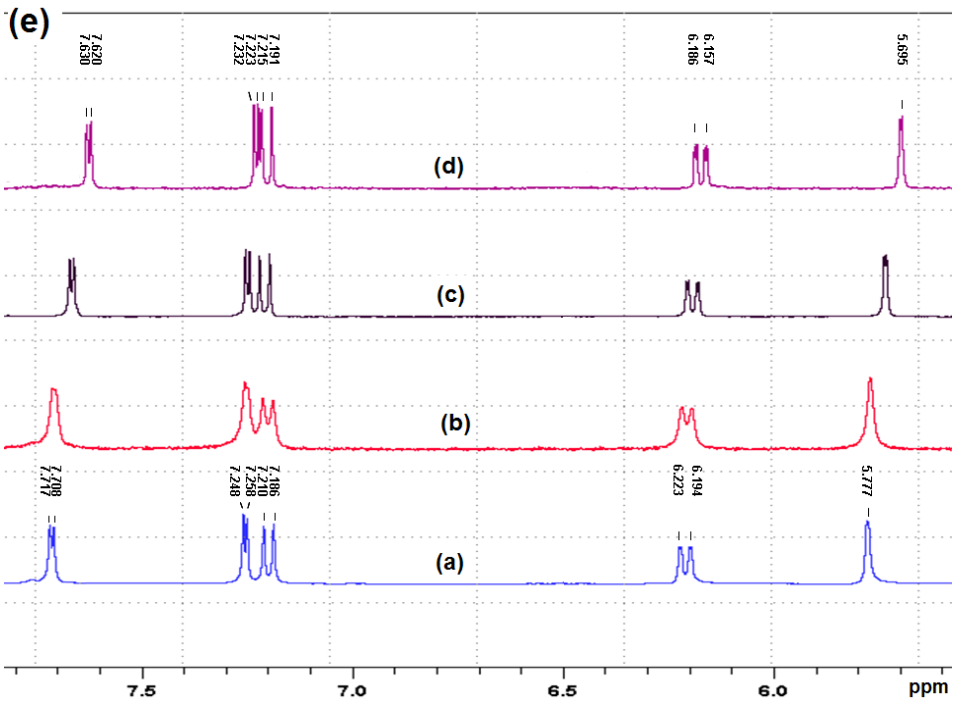


Fig. S1 ^{1}H NMR spetra (400 MHz, DMSO-d$_6$, rt) of TAR-Pd and its tin-sensing products.

3. ^{13}C NMR spectra of TAR-Pd (Fig. S2)

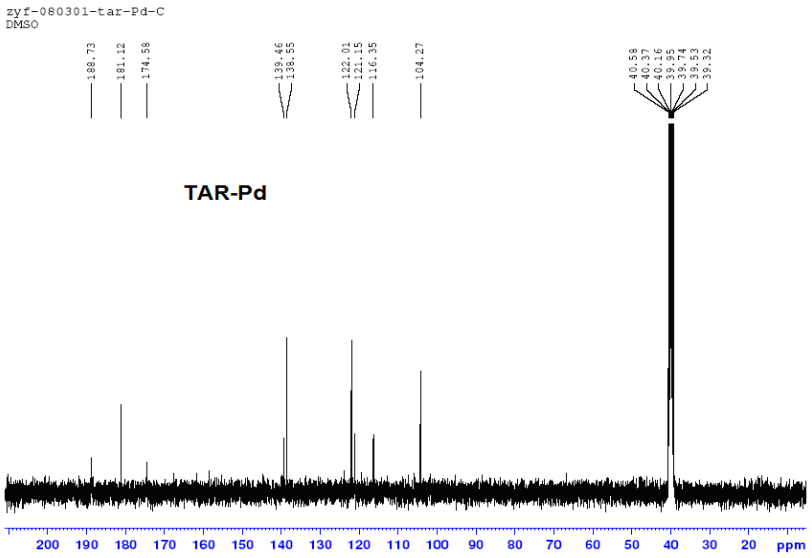


Fig. S2 ^{13}C NMR spectra (100 MHz, DMSO-d_6, rt) of TAR-Pd.

^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 104.27, 116.35, 121.35, 122.01, 138.55, 139.46, 174.58, 181.12, 188.73.

4. TOF-MS spectrum of TAR-Pd (Fig. S3)

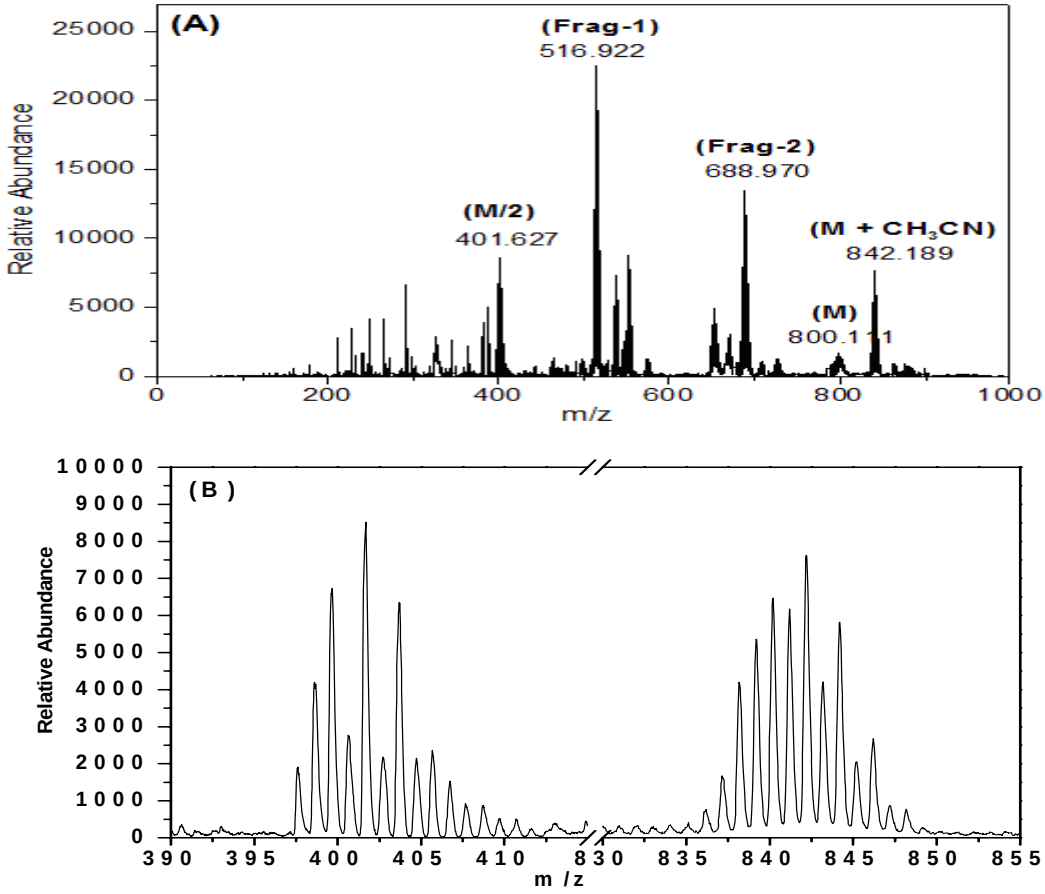
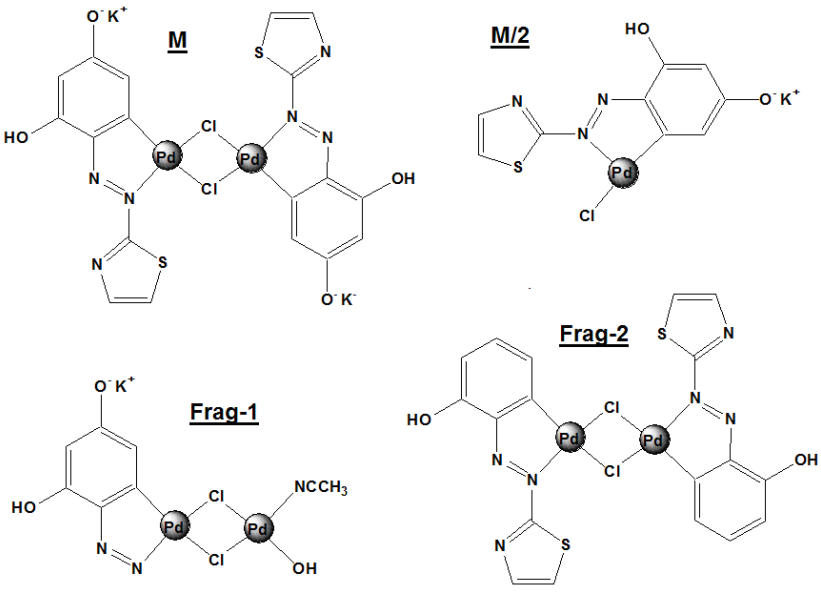


Fig. S3 (A) MALDI-TOF-MS spectrum of TAR-Pd and (B) a local amplification. See ***Scheme S1*** for a detailed assignment of the MS signals. Solvent: acetonitrile-water (1:1, v/v).

Scheme S1



5. XPS spectra of TAR-Pd (Fig. S4)

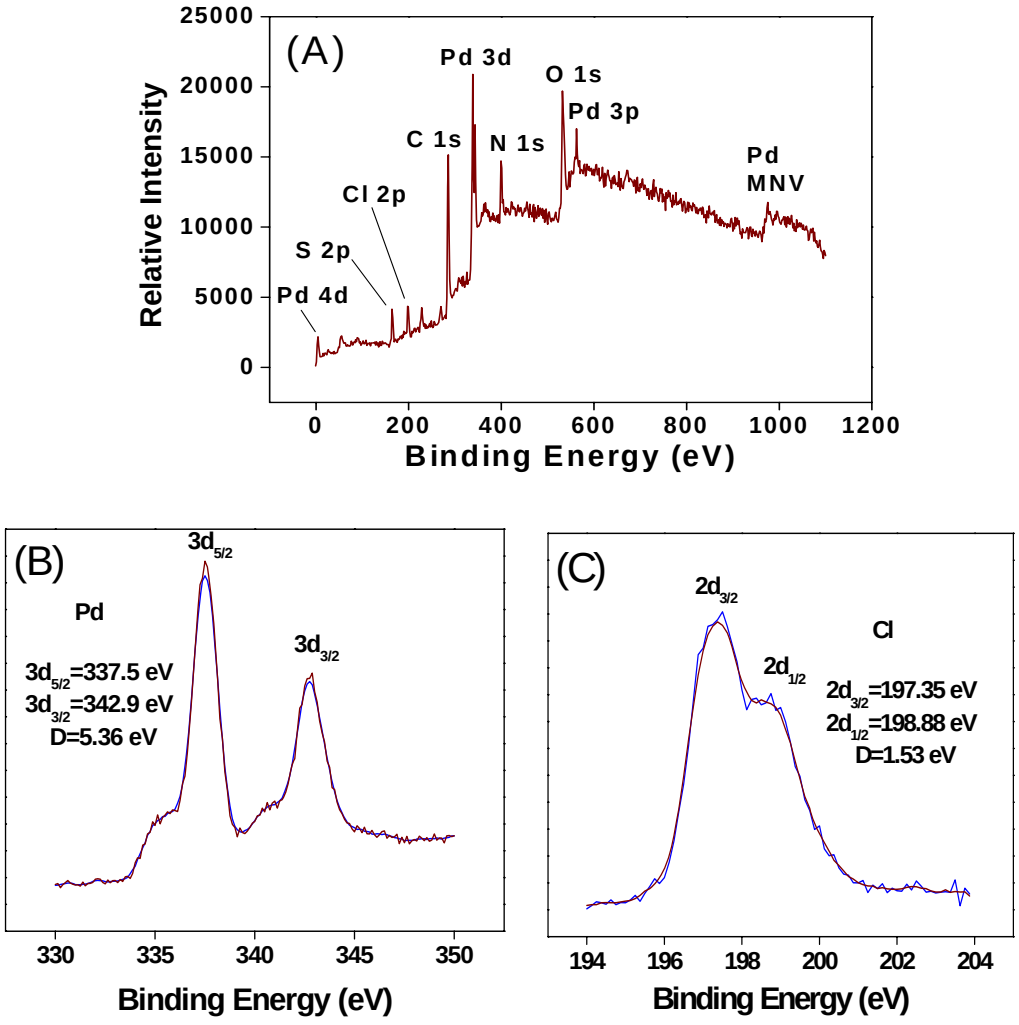


Fig. S4 Total (A), Pd 3d (B) and Cl 2d (C) XPS spectra of dried TAR-Pd solid.

6. FT-IR spectra of the relative compounds (Fig. S5)

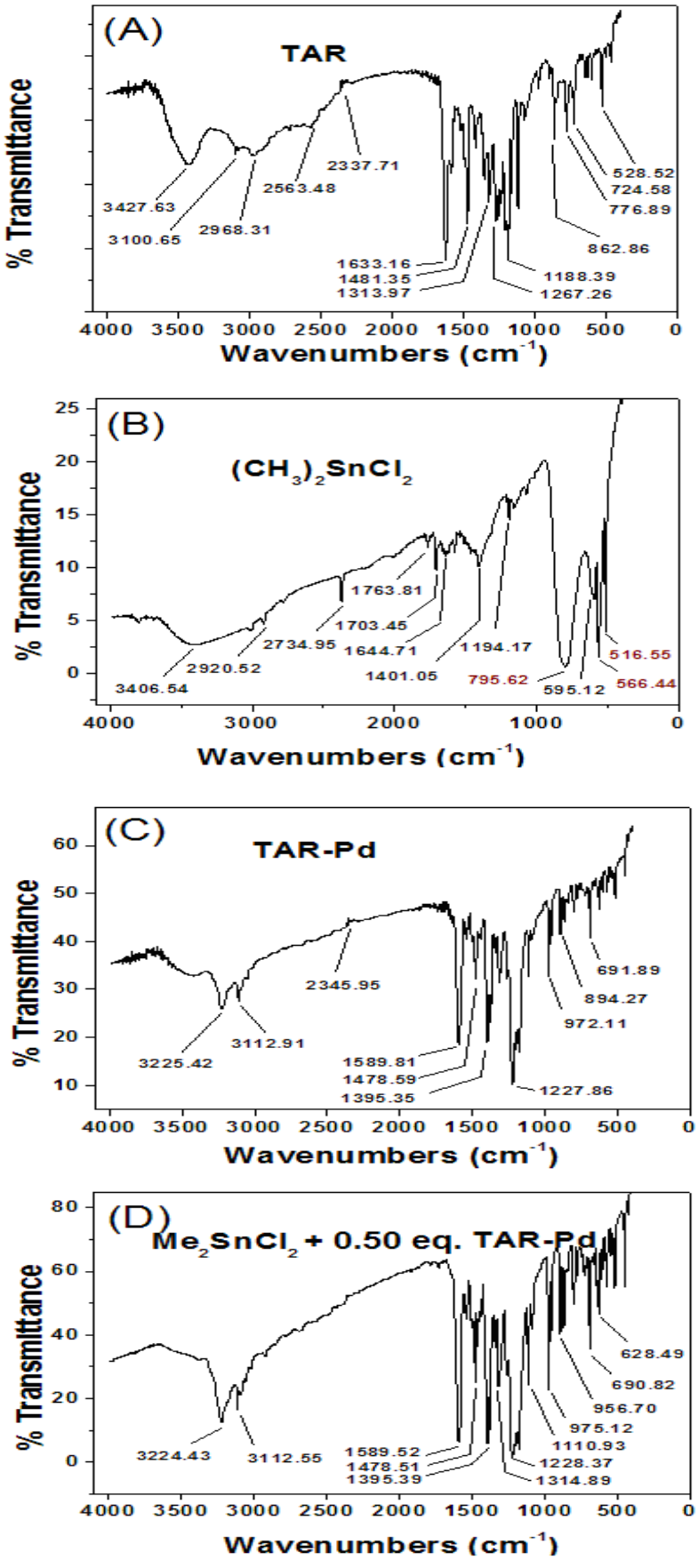


Fig. S5 IR absorption spectra of related complexes in KBr.

7. Solid absorption spectra of the related compounds (Fig. S6)

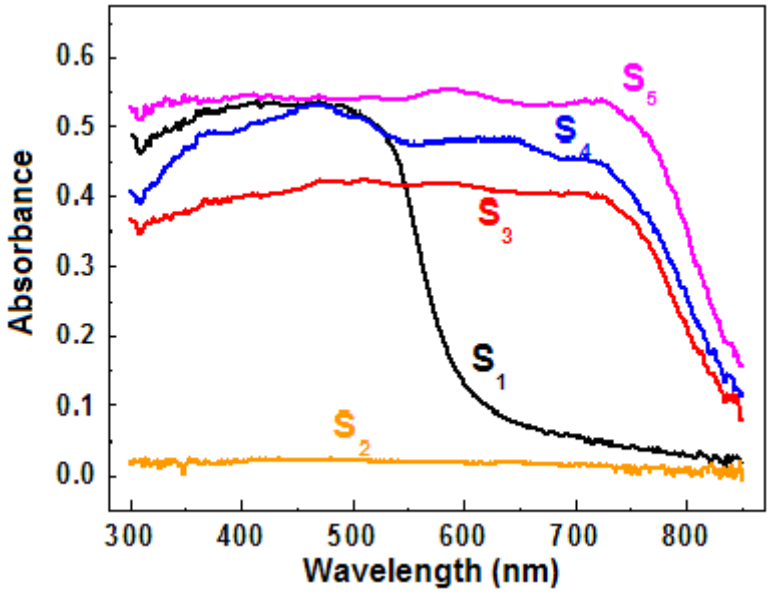


Fig. S6 Absorption spectra of the related complexes in solid state. (S_1) TAR, (S_2) Me_2SnCl_2, (S_3) TAR-Pd, (S_4) TAR-Pd + 1.0 equiv. Me_2SnCl_2 and (S_5) TAR-Pd + 2.0 equiv. Me_2SnCl_2.

8. Photographs (Fig. S7 & S8)

Fig. S7 Colours of TAR-Pd. (A) 1.0×10^{-5} mol·L^{-1} in different solvents: a, water; b, acetonitrile; c, DMSO; d, ethanol; e, ethyl acetate; f, 1,4-dioxane. (B) in 9:1 (v/v) acetonitrile-water mixture at varied concentrations (a → j: 0.5×10^{-5} mol L^{-1} → 4.5×10^{-5} mol L^{-1}).

Fig. S8 Colour changes of TAR-Pd sensing solutions (1.0×10^{-5} mol L^{-1} in 80% (v/v) acetonitrile-water) titrated with increased amounts of Me_2SnCl_2 (a → h: 0, 0.50 equiv., 1.00 equiv., 1.50 equiv., 2.00 equiv., 2.50 equiv., 3.00 equiv. and 4.00 equiv.).