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

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A simple cyclopalladated complex of 4-(2-thiazolylazo)resorcinol showed a specific red-to-green colour change upon addition of organotin species in the acetonitrile–water medium.

Organotin compounds (OTC) are known for their wide distribution and strongly toxic effect on marine organisms.[1] For example, toxicity of n-tributyltin is exhibited at low μg L^{-1} to ng L^{-1} levels.[1e] Determination of OTC in environmental samples is a complex process involving a number of analytical steps.[2] The use of colorimetric chemosensors offers a big advantage for allowing "naked-eye" detection of these compounds in a straightforward and inexpensive manner. Ever-increasing examples of optical chemosensors for metal ions have been reported.[3] However, design of specific and sensitive optical chemosensors for OTC remains a challenging task.[4] Chemically OTC are represented by the type formula $R_nSnX_{(4-n)}$, where Sn is the tin atom, R is an alkyl or aryl group, X is an anion, and n ranges from 1 to 4. Although the Sn atom is covalently bound to one or more organic substituents, there is still a fascinating range of coordination diversity for OTC. Five-, six- and even seven-coordinated Sn(IV) centers can be found in many reported organotin species.[5] On the other hand, the degradation products of OTC usually exist as diorganotin or monoorganotin complexes,[2a] both with high coordination substitution activities. Therefore, it is reasonable that metal–ligand interaction, which is widely used as the driving force for capturing metal cations, can be also employed in sensing of OTC. As an experimental validation, herein reported is a near-infrared chromogenic chemosensor for OTC based on the simple cyclopalladated complex of a common azo dye, 4-(2-thiazolylazo)resorcinol (TAR). Near-infrared absorbing/fluorescent sensors are highly desirable in studying biological or environmental samples, because spectral interference caused by unspecific absorption of the complex matrix is generally lower in the near-infrared range than in the visible.[6]

Many azo dyes have been used as metal ion indicators in traditional coordination titration analysis. These azo chelands show a sensitive colour change upon metal binding but usually suffer from low selectivities. We expected that increasing the rigidity of the coordination sites by cyclopalladation of the azo moiety would result in an enhanced selectivity of the metal receptor. A series of commercially available azo chelands have been tested for this purpose and the cyclopalladation product of TAR, TAR-Pd (Scheme 1), was selected as a candidate for chromogenic OTC sensor.

TAR-Pd was synthesized by simple treatment of TAR with stoichiometric amount of potassium tetrachloropalladate(II) in a dioxane-water mixture.[7] The colour of TAR-Pd in solution was observed to be heavily dependent on concentration level and solvent polarity. Decreasing solvent polarity or increasing the concentration of TAR-Pd in a given solvent led to the onset of a near-infrared absorption band and a colour change from magenta to green (Fig. 1). This phenomenon was explained by occurrence of the aggregation of TAR-Pd most possibly through π–π stacking of the planar palladacycles. In cyclopalladated complexes of azobenzenes or aromatic nitrogen heterocyclics, the presence of an sp^2-hybridized N atom and the square-planar palladium(II) centre within the five-membered cyclopalladated ring assure planarity and metalloaromaticity of the molecular fragment.[8] As evidences of metalloaromaticity, π–π stacking interactions generated by the planar palladacycles have been found in some ensembles of these compounds.[9] The distinctively red-shifted absorption indicated that the aggregation of TAR-Pd mainly led to a "J"-type aggregate.[10] This was consistent with what had been observed in all of the π–π stacking aggregates of cyclopalladated complexes referred above.[9] In theory, such an aggregation of TAR-Pd would be efficiently enhanced by increasing the planarity of the

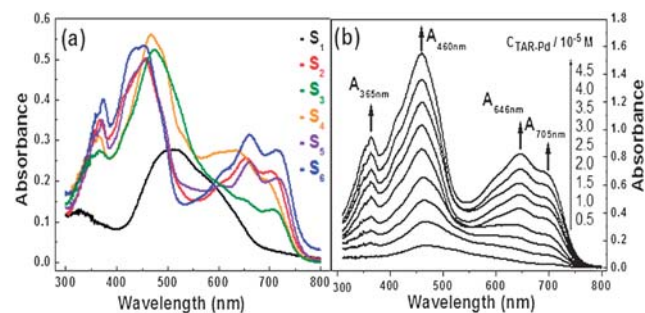**Scheme 1** Structure and sensing mechanism of the developed sensor.

Fig. 1 Absorption spectra of TAR-Pd. (a) TAR-Pd (1.0×10^{-5} mol L^{-1}) in (S_1) water, (S_2) acetonitrile, (S_3) DMSO, (S_4) ethanol, (S_5) ethyl acetate and (S_6) 1,4-dioxane. (b) TAR-Pd in an acetonitrile–water (9 : 1, v/v) mixture at various concentration levels.

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whole π-conjugated molecule.[11] Following this presumption, binding of a metal guest on TAR-Pd was expected to be responded by a sensitive colour change in solution due to the chelation-induced coplanarity of the palladacycle and thiazolyl moieties.

A series of transition metal cations were tested in the sensing solution of TAR-Pd. For sensitivity consideration, sensing solutions were prepared in an acetonitrile–water mixture in which TAR-Pd existed in free monomers before binding the guest species. Addition of tin(II) or tin(IV) cations induces rapid colour and spectral changes (Fig. 2), whereas no such phenomenons occurred upon addition of other cations including Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+} and Ag^{+}, and alkaline-earth metal ions. Compared with TAR, TAR-Pd displayed a distinct improvement in binding selectivity. This was attributed to the efficient increase in rigidity of the azo moiety induced by the cyclopalladation reaction. The facile structure of the azo moiety supports a great coordination variability of free TAR ligand. However, the azo-centred chelating groups of TAR-Pd become sterically restricted in capturing metal targets due to the formation of the rigid and planar palladacycles. We think this is the main reason for the improvement in the metal-binding selectivity of TAR after cyclopalladation. The tin-sensing products in the polar solvent of acetonitrile–water mixture exhibited a spectral behavior similar to that of TAR-Pd in nonpolar solvents or at high concentration levels. This suggested that the possible π–π stacking aggregate of TAR-Pd was formed at a concentration level below normal in the presence of Sn^{4+} or Sn^{2+} cations.

Spectral and colour behaviors of a variety of OTC in the sensing solutions were also examined (Fig. 2). The response sensitivity of TAR-Pd increased in a general sequence of trialkyltin, dialkyltin, monoalkyltin to inorganic tin cations in accord with the variation of their coordination capabilities,[5] whereas no response was observed in the case of tetraalkyltin. This was explained by a binding mechanism based on the ligand substitution of TCS, which was further supported by IR study of the tin-binding products (Fig. S5, ESI†). The strong triple absorption bands observed at 795, 565 and 515 cm^{-1}, characteristic of Sn–Cl bond stretching, disappeared in the IR spectrum of dimethyltin dichloride after reaction with 0.5 equiv. of TAR-Pd. Results of ^{1}H NMR titration confirmed the coordination reaction (Fig. 3). Upon addition of Me_2SnCl_2, signals of all aromatic C–H protons were shifted up-field in the complex as compared to their positions in blank TAR-Pd, except that the signal of 5-H was almost
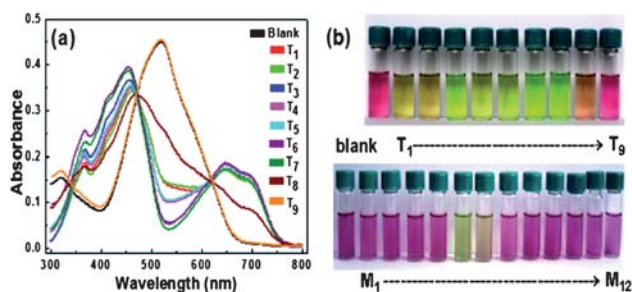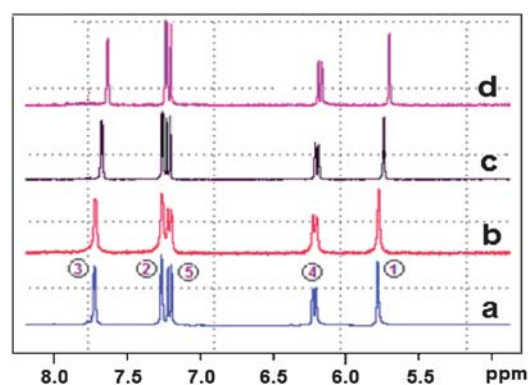
Fig. 3 Characteristic ^{1}H NMR signal regions of TAR-Pd in the presence of (a) 0, (b) 0.50, (c) 1.0 and (d) 2.0 equiv. of Me_2SnCl_2 in DMSO-d_6. The signal peaks were numbered according to the structure described in Scheme 1.

unchanged. The degree of this up-field shift reached its maximum in the presence of 2.0 equiv. of Me_2SnCl_2. A further increase in the addition amount of Me_2SnCl_2 caused no obvious changes of the characteristic signals of TAR-Pd. This confirmed the 1 : 2 binding stoichiometry between TAR-Pd and the investigated OTC. Furthermore, the signal of the hydroxyl proton (3-H) in TAR-Pd did not fall off with increased amounts of Me_2SnCl_2. These facts indicated that the hydroxyl group was not involved in the tin-binding reactions and a five-membered N,N- or N,S-chelating ring was responsible for coordination of OTC. Such a coordination mode assures an increased degree of planarity in TAR-Pd and results in an efficient enhancement of the aggregation of TAR-Pd after binding to OTC. Therefore, the near-infrared absorption response to tin-containing species (TCS) can be explained. No spectral response was observed when other toxic organometallic species such as methyl-mercury chloride were tested in the sensing solution.

To confirm the proposed aggregation-based signaling mechanism, solid absorption behaviors of blank TAR-Pd and the Me_2SnCl_2-titrated products were studied (Fig. S6, ESI†). Powder of blank TAR-Pd showed an intense absorption band up to ca. 750 nm, which was strictly consistent with its absorption behavior in nonpolar solvents (Fig. 1a) and the OTC-titrated responses (Fig. 2a). Solid state enabled the spontaneous formation of the TAR-Pd aggregate. It is therefore reasonable to assign the intense near-infrared absorption of the sensing solutions to an aggregation of the sensor molecules. As expected, absorption spectra of the Me_2SnCl_2-titrated products showed a resemblance to that of blank TAR-Pd in solid state, indicating that the same chromogenic aggregate was involved in these cases.

Absorption spectra of the sensing solutions of TAR-Pd titrated with varied concentrations of TCS were recorded. As shown in Fig. 4, a linear increase of absorbance at 700 nm at the expense of the absorbance at 520 nm was observed with increasing tin concentration. The high molar absorption coefficient ($\varepsilon_{520\ nm} > 4.0 \times 10^4$ cm^{-1} mol^{-1} L) allowed for sensitive determination of TCS. Inorganic tin cations and OTC could be easily detected with naked eyes at concentration levels of 10^{-6} mol L^{-1} and 10^{-5} mol L^{-1} (Fig. S8, ESI†), respectively. The efficiency of the chromogenic sensing of OTC was further evaluated in the coexistence of other metals. The presence of 50 equiv. of Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+},
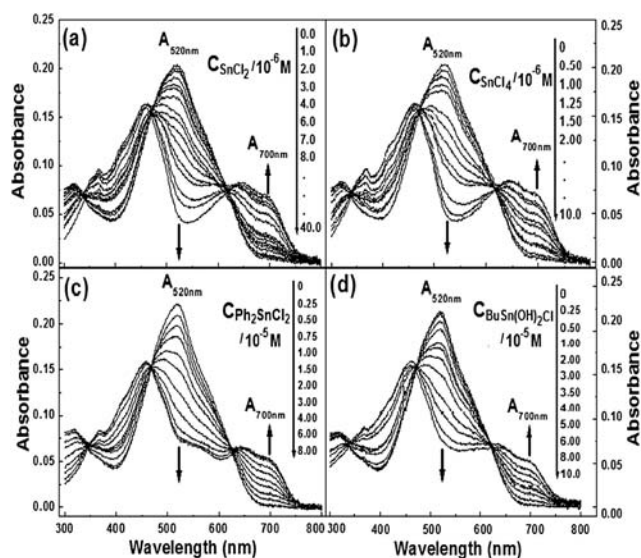
Fig. 2 (a) Spectral and (b) colour responses of TAR-Pd (1.0×10^{-5} mol L^{-1}) toward different metal species (10 equiv.) in 85% (v/v) acetonitrile–water solvent. Tin-containing species (T_1 to T_9): Me_2SnCl_2, Bu_2SnCl_2, $BuSn(OH)_2Cl$, Ph_2SnCl_2, $BuSnCl_3$, $SnCl_2$, $SnCl_4$, Me_3SnCl and Bu_4Sn. Metal species (M_1 to M_{12}): $CuCl_2$, $CoCl_2$, $ZnCl_2$, $NiCl_2$, $SnCl_4$, Me_2SnCl_2, $MnCl_2$, $CdCl_2$, $CrCl_3$, $HgCl_2$, $PbCl_2$ and $AgNO_3$.

Fig. 4 Spectral traces of TAR-Pd (5.0×10^{-6} mol L^{-1}) upon addition of tin-containing species (a, SnCl$_2$; b, SnCl$_4$; c, Ph$_2$SnCl$_2$; d, BuSn(OH)$_2$Cl) in acetonitrile–water (a & b: 80%, v/v; c & d: 85%, v/v).
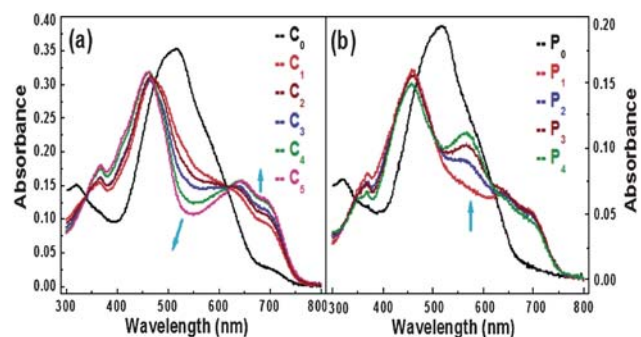

Fig. 5 Variations of the tin-sensing spectral response of TAR-Pd in 85% (v/v) acetonitrile–water in the presence of Cr(III) or Cu(II) cations. (a) TAR-Pd (8.0×10^{-6} mol L^{-1}) with 2.0 equiv. of Me$_2$SnCl$_2$ and (C$_1$) 0, (C$_2$) 1.0, (C$_3$) 2.0 and (C$_4$) 4.0 equiv. of CrCl$_3$. (b) TAR-Pd (4.0×10^{-6} mol L^{-1}) with 2.0 equiv. of Me$_2$SnCl$_2$ and (P$_1$) 0, (P$_2$) 0.5, (P$_3$) 1.0 and (P$_4$) 2.0 equiv. of CuCl$_2$.

Mn^{2+}, Cd^{2+}, Al^{3+}, Hg^{2+}, Pb^{2+} and Ag$^+$ did not cause obvious interferences in sensing Me$_2$SnCl$_2$. However, the coexistence of Cr^{3+} or Cu^{2+} induced a slight variation of the spectral response (Fig. 5). Since addition of Cr^{3+} or Cu^{2+} had not caused any spectral change of the sensing solution in the absence of TCS, these spectral disturbances were attributed to the influence of metal ions on the palladacycle aggregate, most probably through the hydroxyl groups on the two TAR ligands. Importantly, the near-infrared absorption response to TCS only suffered slightly from these coexisting effects. It may be a little pity that TAR-Pd can not function as a sensor for TCS in aqueous solution. However, it is still regarded as a simple but useful tool for OTC detection. In analytical practices, the determination process of OTC usually involves the extraction of OTC by organic solvents. This analytical step supports the applicability of the developed sensor.

In summary, we have designed a specific chromogenic sensor for TCS based on a simple cyclopalladated complex. This sensor can be easily synthesized by treatment of a common azo dye with potassium tetrachloropalladate(II). Addition of TCS induces a sensitive near-infrared absorption and a remarkable red-to-green colour change due to aggregation of the sensor molecules in solution. This design provides a straightforward and inexpensive strategy for detection of OTC in biological or environmental samples. Development of the concerning analytical platforms is currently under way.

Notes and references

1 (a) C. Pellerito, L. Nagy, L. Pellerito and A. Szorcsik, *J. Organomet. Chem.*, 2006, **691**, 1733; (b) K. E. Appel, *Drug Metab. Rev.*, 2004, **36**, 763; (c) M. Hoch, *Appl. Geochem.*, 2000, **16**, 719; (d) V. C. Karpiak and C. L. Eyer, *Cell Biol. Toxicol.*, 1999, **15**, 261; (e) R. J. Huggett, M. A. Unger, P. F. Seligman and A. O. Valkirs, *Environ. Sci. Technol.*, 1992, **26**, 232.

2 (a) M. Staniszewska, B. Radke, J. Namieśnik and J. Bolalek, *Int. J. Environ. Anal. Chem.*, 2008, **88**, 747; (b) M. Takeuchi, K. Mizuishi and T. Hobo, *Anal. Sci.*, 2000, **16**, 349; (c) M. Abalos, J.-M. Bayona, R. Compañó, M. Granados, C. Leal and M.-D. Prat, *J. Chromatogr., A*, 1997, **788**, 1.

3 Selected reviews concerning molecular sensors for metal ions: (a) I. Leray and B. Valeur, *Eur. J. Inorg. Chem.*, 2009, 3525; (b) E. M. Nolan and S. J. Lippard, *Acc. Chem. Res.*, 2009, **42**, 193; (c) H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim and J. Yoon, *Chem. Soc. Rev.*, 2008, **37**, 1465; (d) E. L. Que, D. W. Domaille and C. J. Chang, *Chem. Rev.*, 2008, **108**, 1517; (e) D. W. Domaille, E. L. Que and C. J. Chang, *Nat. Chem. Biol.*, 2008, **4**, 168; (f) J. S. Kim and D. T. Quang, *Chem. Rev.*, 2007, **107**, 3780; (g) W.-P. Zhu, Y.-F. Xu and X.-H. Qian, *Prog. Chem.*, 2007, **19**, 1229; (h) A. Ajayaghosh, *Acc. Chem. Res.*, 2005, **38**, 449; (i) G. W. Gokel, W. M. Leevy and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723; (j) P.-J. Jiang and Z.-J. Guo, *Coord. Chem. Rev.*, 2004, **248**, 205; (k) K. Kikuchi, K. Komatsu and T. Nagano, *Curr. Opin. Chem. Biol.*, 2004, **8**, 182; (l) D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537; (m) K. Rurack, *Spectrochim. Acta, Part A*, 2001, **57**, 2161; (n) B. Valeur and I. Leray, *Coord. Chem. Rev.*, 2000, **205**, 3; (o) I. Oehme and O. S. Wolfbeis, *Mikrochim. Acta.*, 1997, **126**, 3.

4 S.-H. Li, F.-R. Chen, Y.-F. Zhou, J.-N. Wang, H. Zhang and J.-G. Xu, *Chem. Commun.*, 2009, 4179.

5 S. Shahzadi and S. Ali, *J. Iran. Chem. Soc.*, 2008, **5**, 16.

6 G. Patonay and M. D. Antoine, *Anal. Chem.*, 1991, **63**, 321A.

7 (a) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, 1965, **87**, 3272; (b) M. Ghedini, M. Longeri and R. Bartolino, *Mol. Cryst. Liq. Cryst.*, 1982, **84**, 206.

8 (a) M. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. La Deda and D. Pucci, *Coord. Chem. Rev.*, 2006, **250**, 1373; (b) J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527.

9 (a) J. J. Fernández, M. Fernández, M. López-Torres, D. Vázquez-García, A. Rodríguez, A. Varela and J. M. Vila, *J. Organomet. Chem.*, 2009, **694**, 2234; (b) K. Molčanov, M. Ćurić, D. Babić and B. Kojić-Prodić, *J. Organomet. Chem.*, 2007, **692**, 3874; (c) M. Ghedini, I. Aiello, A. Crispini and M. La Deda, *Dalton Trans.*, 2004, 1386.

10 (a) M. Kasha, H. R. Rawis and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371; (b) K. Ya. Burshtein, A. A. Bagatur'yants and M. V. Alfimov, *Chem. Phys. Lett.*, 1995, **239**, 195.

11 (a) W. Chen, S. A. Elfeky, Y. Nonne, L. Male, K. Ahmed, C. Amiable, P. Axe, S. Yamada, T. D. James, S. D. Bull and J. S. Fossey, *Chem. Commun.*, 2010, DOI: 10.1039/C0CC01420F; (b) N. Inukai, J. Yuasa and T. Kawai, *Chem. Commun.*, 2010, **46**, 3929; (c) L. Zeng, W. Liu, X. Zhuang, J. Wu, P. Wang and W. Zhang, *Chem. Commun.*, 2010, **46**, 2435; (d) K. Mondragón-Vásquez and H. Morales-Rojas, *Chem. Commun.*, 2009, 6726; (e) H.-J. Schneider, *Angew. Chem., Int. Ed.*, 2009, **48**, 3924; (f) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303.