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Molecular Sensors

Luminescence Detection of Open-Shell Transition-Metal Ions by Photoinduced Electron Transfer Controlled by Internal Charge Transfer of a Receptor**

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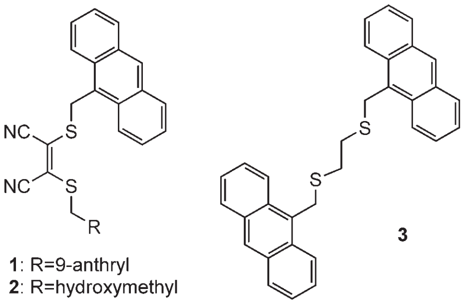
Dedicated to Professor Erich Kleinpeter on the occasion of his 60th birthday

The development of fluorescent chemosensors for many heavy- and (inner-) transition-metal (HTM) ions is still a challenge, because many of these ions are typical fluorescence quenchers.[1,2] So far, only a few examples of ligands that form fluorescent complexes with inner transition-metal ions have been reported (Cu^{2+},[3a–d,f] Ni^{2+},[3a] Fe^{3+},[3e] Co^{3+}[3f]). In a trianthryl cryptand system, Cu^{2+} and Ni^{2+} cause enhancement of fluorescence.[3a] As a result of the special topology of the cryptand host, the peripherally located anthryl groups cannot interact sterically or electronically with the complexed open-shell ions. Fluorescent sensor molecules, with electronically decoupled, rigidly fixed, and sterically preoriented architectures (a 1,3,5-triaryl-Δ^2-pyrazoline and a *meso*-substituted borondipyrromethene) containing a 1-oxa-4,10-dithia-7-azacyclododecane receptor unit, show selective Fe^{III}-amplified emission in various media.[3e]

A set of simple fluorescent sensors that contain dialkylamine receptors spaced from several fluorophores (e.g. 1,8-naphthalimide[4a] and 4-amino-1,8-dicyanonaphthalene[4b]) gave high fluorescence enhancement values with many open-shell ions (Fe^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}), but caution should be exercised in the interpretation of the fluorescence enhancement.[1] Herein, we employ a new concept for the photoinduced electron transfer (PET) fluorophore in the fluorophore–spacer–receptor system. The fluorescent probes **1** and **2** (Scheme 1) consist of one or two anthryl groups, methylene spacers, and a dithiomaleonitrile receptor. In these probes, the oxidative PET from anthryl to maleonitrile is accelerated by internal charge transfer (ICT) of the "push–pull" π-electron system of the dithiomaleonitrile unit. Selective complexation of the receptor by $PdCl_2$ switches off the ICT and stops the PET, and the fluorescence is enhanced. While some of the factors that influence PET have been uncovered,[1,2,5] the control of an oxidative PET by ICT of the receptor was unknown.



Scheme 1. Structures of the fluorescent probes studied.

The strong fluorescence quencher Pd^{II} could, up to now, only be detected by fluorescent ligands through fluorescence quenching.[6] Moreover, the ligands used, for example, bathophenanthroline,[6a] *meso*-tetrakis[4-(carboxymethyleneoxy)-phenyl]porphyrin,[6b] *N*-9-anthrylmethyl-*N*-methyl-*N'*-benzoylthiourea,[6c] and bis(naphthalenemethyleneoxy)tetrathia-16-crown-4,[6d] are not selective for Pd^{II}. Palladium-selective fluorescence sensors could be useful for online monitoring of the Pd^{II} concentration in palladium refining using molecular recognition technology.[7] We found that selective chelate ligands for $PdCl_2$ are acyclic and macrocyclic bis(alkylthio)-maleonitrile.[8a] These ligands coordinate to $PdCl_2$ through the two sulfur atoms of the 1,2-dithioethene unit, thus forming planar five-membered palladacycles.[8b]

To obtain Pd^{II}-selective fluoroionophores of the fluorophore–spacer–receptor format, 1,2-bis(9-anthrylmethylthio)-maleonitrile (**1**) and 9-anthrylmethylthio(2-hydroxyethylthio)maleonitrile (**2**) were synthesized.[9] The known bis-(anthryl)dithioether 1,6-bis(9'-anthryl)-2,5-dithiahexane[10] (**3**) and the anthryl-free 1,2-bis(benzylthio)maleonitrile[11] (**4**) were used as reference compounds. The UV/Vis spectrum of **3** (Figure 1) displays the typical absorptions of the anthracene chromophore in the range of 320–400 nm, and that of **4** at 345 nm displays the ICT band of the push–pull dithiomaleonitrile electron system with the sulfur atoms as donors and the maleonitrile unit as acceptor. The UV/Vis

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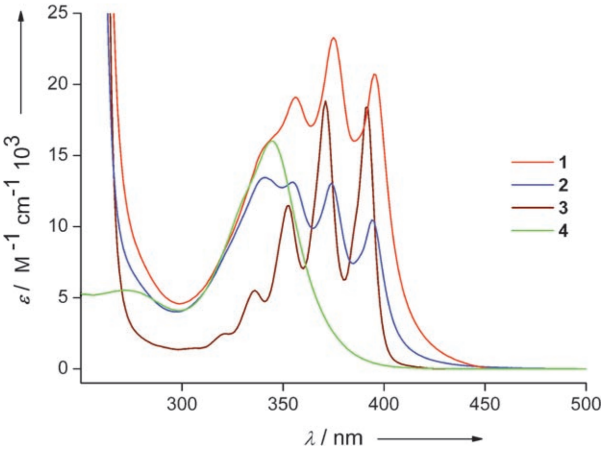

Figure 1. UV/Vis absorption spectra of ligands **1**–**4** in THF; c(ligand) $= 5\times10^{-5}$ M.

absorption bands of new ligands **1** and **2** at 300 nm can be seen as a superimposition of an ICT band and the anthryl bands. The ICT character of the absorption near 340 nm in the spectrum of **2** was confirmed by time-dependent DFT calculations. These show as the most intense transition a signal at $\lambda = 339$ nm, which is dominated by an excitation from HOMO$-$1 to the LUMO. The two orbitals are π orbitals localized at the dithiomaleonitrile, and the excitation corresponds to a charge transfer from the sulfur atoms to the maleonitrile unit.[9] Moreover, the fairly broad and intense ICT band in the spectrum of **2** is shifted bathochromically with increasing polarity (hexane: 335 nm; CH_3CN: 344 nm),[12] which is characteristic for an ICT band.[13]

The fluorescence quantum yield (Φ_f) of the reference compound bis(anthryl)dithioether **3** (Φ_f (THF) $= 0.040$; see Table 1) is clearly lower than that of 9-methylanthracene **5** (Φ_f (THF) $= 0.29$), because in **3** the fluorescence is decreased by quenching interactions of the lone pairs of the sulfur atoms with the anthracene rings and heavy sulfur atom quenching.[14] The fluorescence of bis(anthryl)maleonitrile dithiother **1** (Φ_f (THF) $= 0.012$) amounts to less than a third of that of **3**. This effect is caused by an additional quenching process in **1**. An oxidative PET probably occurs from anthryl to the dithiomaleonitrile unit.[15]

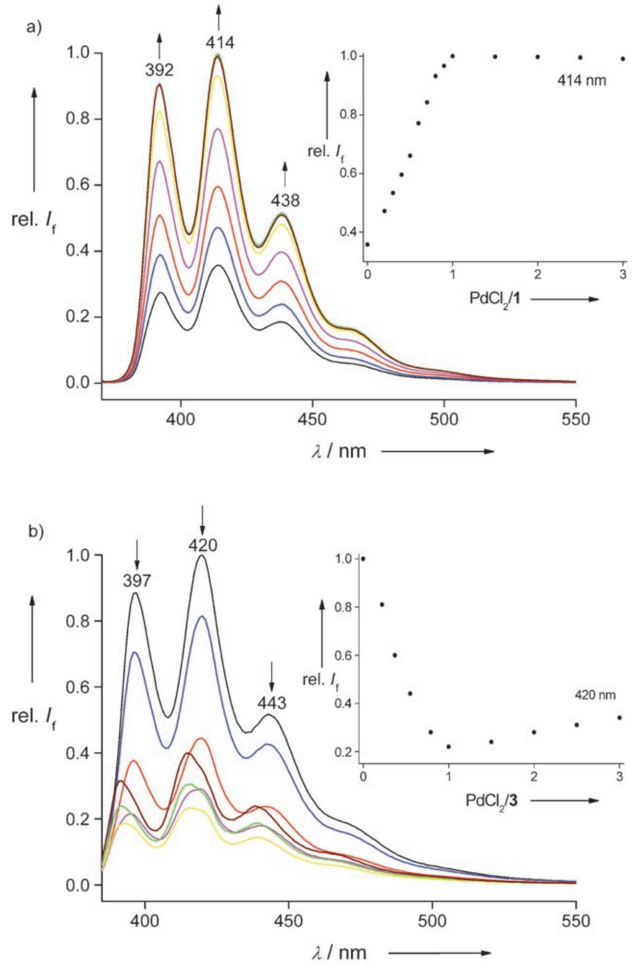

Figure 2. Uncorrected fluorescence emission spectra in THF: a) **1** (c(**1**) $= 5\times10^{-6}$ M, $\lambda_{ex.} = 366$ nm) in the presence of 0.0 (——), 0.2 (——), 0.4 (——), 0.6 (——), 0.8 (——), 1 equiv (——), and 3 equiv (——) [$PdCl_2(C_6H_5CN)$]; b) reference compound **3** (c(**3**) $= 5\times10^{-6}$ M, $\lambda_{ex.} = 374$ nm) in the presence of 0.00 (——), 0.25 (——), 0.5 (——), 0.75 (——), 1 (——), 2 (——), and 3 equiv (——) [$PdCl_2(C_6H_5CN)$]. Insets: titration curves.

The fluorescence of chelate ligand **1** is enhanced upon complexation with $PdCl_2$, as required of a fluorescent PET HTM-ion sensor. Figure 2a shows the fluorescence enhancement of **1** in THF as a function of added equivalents of [$PdCl_2(C_6H_5CN)_2$] and the titration curve at 414 nm. In the presence of one equivalent of $PdCl_2$, a fluorescence enhancement factor (I/I_0) of 3.2 is achieved. The fluorescence of monoanthryl-maleonitrile dithioether **2** is also enhanced by complex formation with $PdCl_2$ ($I/I_0 = 2$). In addition to the increase in Φ_f, **1** and **2** also show an increase in fluorescence lifetime (τ_f) upon complexation with $PdCl_2$ in CH_3CN (Table 1). However, the fluorescence rate constants, k_f, which can be calculated from Φ_f and τ_f, remain constant within experimental error. Thus, the decrease in the calculated decay constants, k_i ($k_i = 1/\tau_f$), has to be attributed to reduced nonradiative decay rates.

Table 1: Fluorescence quantum yields (Φ_f) for ligands **1**–**3**, the corresponding $PdCl_2$ complexes, and 9-methylanthracene (**5**) in THF and CH_3CN, and fluorescence lifetimes (τ_f), fluorescence rate constants (k_f), and decay constants ($k_i = 1/\tau_f$) in CH_3CN.

Compound	Φ_f (THF)	Φ_f (CH_3CN)	k_f [10^6 s^{-1}]	τ_f(CH_3CN) [ns]	k_i [10^9 s^{-1}]
1	0.012 ± 0.002	0.008 ± 0.002	1.45	5.5 ± 0.8	0.18
2	0.008 ± 0.002	0.003 ± 0.001	0.68	4.4 ± 0.7	0.23
3	0.040 ± 0.008	0.038 ± 0.008	3.6	10.7 ± 1.6	0.09
[$PdCl_2$(**1**)]	0.030 ± 0.006	0.020 ± 0.004	1.48	13.5 ± 2.0	0.074
[$PdCl_2$(**2**)]	0.010 ± 0.002	0.012 ± 0.002	0.89	13.4 ± 2.0	0.075
[$PdCl_2$(**3**)]	0.005 ± 0.001	0.004 ± 0.001	10	0.4 ± 0.1	2.5
5[17]	0.29	0.33		5.8	

The fluorescence enhancements of **1** and **2** in the presence of $PdCl_2$ are not subject to interference by Hg^{2+}, Ag^{+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, or other platinum-group metal ions, such as Rh^{3+}[18] and Pt^{4+}.[18] Both **1** and **2** are the first Pd^{II}-selective molecular sensors for the fluorescence spectrophotometric detection of Pd^{II} by increasing fluorescence.

As opposed to the fluorescence enhancement of maleonitrile dithioether **1** by complexation with $PdCl_2$, the fluorescence of the reference dithioether **3** is decreased (Figure 2b). In contrast to **1** and **2**, the k_f value for **3** changes, which indicates a direct interaction of the palladium ion with the anthracene fluorophore. Relative to dithioether **1, 3** is not a preorganized chelate ligand for $PdCl_2$. Ligand **3** can also coordinate $PdCl_2$ in a monodentate fashion. In complexes such as $[PdCl_2(\mathbf{3})(thf)]$, palladium could interact with the anthryl moieties and quench the fluorescence. The crystal structure of **3** (Figure 3a) shows a ligand conformation that is useful for acting as a monodentate ligand. The crystal structure of free **1** (Figure 3b) shows the preorganized chelate ligand. In the chelate complexes $[PdCl_2(L)]$ (L = **1**; **2**), the fluorescence is not quenched by the planar coordinated palladium because Pd^{II} could not directly interact sterically or electronically with the anthryl moieties. These findings are further substantiated by the results of theoretical calculations. The molecular orbital dominated by the Pd d_{z^2} atomic orbital is shown in Figure 4. This occupied molecular orbital has only very small amplitudes on the anthryl unit and is dominated by the interaction with the Cl atoms. Therefore, a significant electronic interaction of Pd^{II} with the anthryl unit can be ruled out.

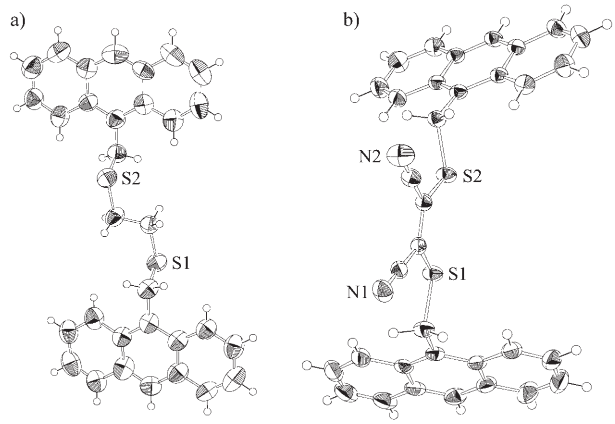

Figure 3. Crystal structures of a) reference dithioether **3** and b) preorganized S_2-chelate ligand **1**.

The fluorescence enhancement of ligands **1** and **2** in $PdCl_2$ complexes can be rationalized according to Figure 5. The push–pull π-electron system of the dithiomaleonitrile unit leads to an ICT in the lowest excited singlet state and a dipole moment (positive poles at the sulfur atoms). The dipole moment gives rise to a photogenerated electric field, which accelerates the electron transfer from the anthryl moiety to the maleonitrile group across the sulfur atom (Figure 5a). The acceleration of PET by a photogenerated electric field was observed by de Silva et al.[5] and Wang and Qian[19] for molecular sensors with the push–pull fluorophore 4-aminophthalimide. The ICTs of the ligands are suppressed by the complexation of **1** and **2** with $PdCl_2$. Figure 6 shows the absorption spectra of **2** taken in the course of titration with $[PdCl_2(C_6H_5CN)_2]$ in THF. After the addition of one equivalent, the ICT band of **2** at 341 nm disappeared.[20] The off-switching of the ICT by complexation stops the oxidative PET, and the fluorescence is enhanced (Figure 5b). Again,

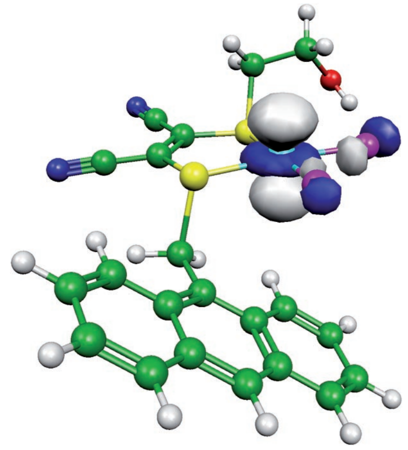

Figure 4. Calculated occupied molecular orbital, which is dominated by the Pd d_{z^2} atomic orbital, for the $[PdCl_2(\mathbf{2})]$ complex. The calculations were carried out at the B3LYP/CEP-31G level of theory.[9] (C green, H white, N blue, S yellow, O red, Cl pink).

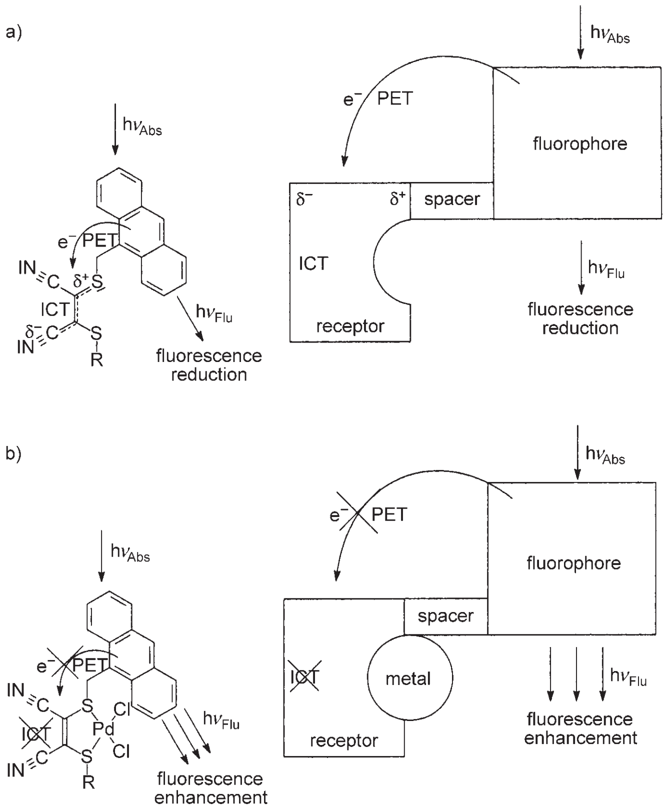

Figure 5. Schematic representation of the regulation of oxidative PET in anthrylmethylthiomaleonitrile by ICT in the receptor. a) Free ligand: ICT in the receptor accelerates the oxidative PET, and the fluorescence is reduced. b) $PdCl_2$ complex: ICT is switched off, PET stops, and the fluorescence is enhanced.

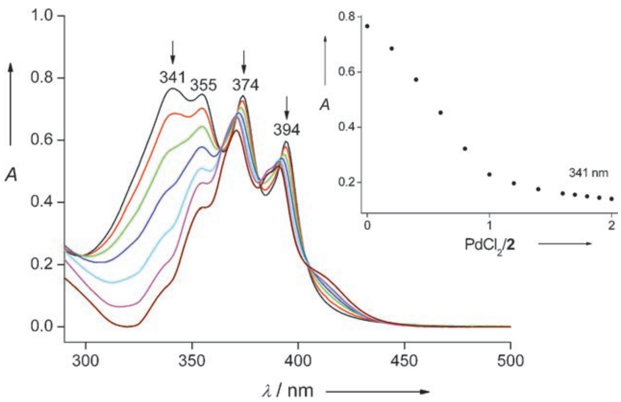

Figure 6. UV/Vis absorption spectra of **2** (c(**2**) = 5×10^{-5} M) in the presence of 0.0 (——), 0.2 (——), 0.4 (——), 0.6 (——), 0.8 (——), 1 (——), and 2 equiv (——) [PdCl$_2$(C$_6$H$_5$CN)] in THF. Inset: titration curve.

this picture is supported by theoretical and excited-state calculations for the [PdCl$_2$(**2**)] complex. We find a reduced charge transfer from the substituents to the maleonitrile unit in the electronic ground state of the complex compared to the free ligand, from −0.267 to −0.055 e (electrostatic potential charges[9]). At the same time, in the excited-state calculations for the complex the ICT transition at $\lambda = 339$ nm found in the free ligand is now nearly completely missing.[9]

Solvent effects on the Φ_f value are found for **1** and **2** (Table 1) because their PET processes are accelerated in polar solvents. The corresponding effects are very small for the complexes [PdCl$_2$(L)] (L = **1**, **2**), as PET processes are suppressed as discussed above. The reference compound, which lacks a maleonitrile unit as electron acceptor, does not undergo PET processes, and solvent effects are minor.

In summary, we have shown for the first time that oxidative PET in a molecular sensor of the fluorophore–spacer–receptor system can be regulated by the ICT of a push–pull receptor. Metal complexation switches off the ICT, stops the oxidative PET, and thus enhances the fluorescence. At present, we are determining Fe^{2+} and Mn^{2+} ions selectively by using the new concept with push–pull diaminomaleonitrile receptors.

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[15] For **1** and **2**, an oxidative PET process from the anthryl fluorophore to the dithiomaleonitrile unit across the methylene spacer has $\Delta G_{\mathrm{PET}} = -0.79$ eV according to the Rehm–Weller equation $\Delta G_{\mathrm{PET}} = E_{\mathrm{ox}}(\text{fluorophore}) - E_{\mathrm{red}}(\text{receptor}) - \Delta E_{00}(\text{fluorophore}) - \Delta(G_{\text{ion pair}})$.[16] The oxidation potential (E_{ox}) of the fluorophore 9-methylanthracene is 0.84 V and the reduction potential (E_{red}) of the receptor bis(methylthio)maleonitrile is −1.47 V (Fc/Fc$^+$ = 0.09 V in MeCN).[9] In MeCN, the $E_{00}^{h\nu}$ value of 9-methylanthracene is observed at 388 nm (≈3.2 eV). The attractive energy, $\Delta G_{\text{ion pair}}$, (which is the product of the PET process) is assumed to be −0.1 V.[5]

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[20] The stability constants of complexes [PdCl$_2$(L)] (L = **1**, **2**) were determined by spectrophotometric titration: $\log K$ PdCl$_2$(**1**) = 5.4 ± 0.2, $\log K$ PdCl$_2$(**2**) = 5.8 ± 0.3.