Highly selective and sensitive Hg^{2+} fluorescent sensors based on a phosphane sulfide derivative

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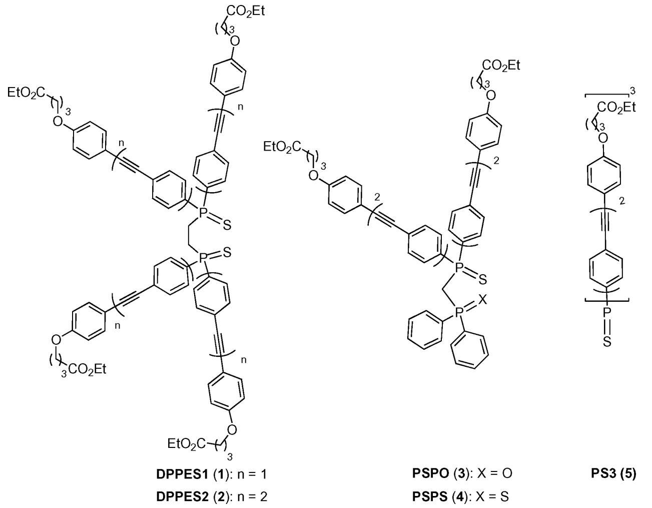
A series of fluorescent sensor molecules based on a phosphane sulfide derivative were designed and synthesized. The effect of the distance between the complex entities as well as the number and the length of fluorophores was investigated using both steady-state and time-resolved fluorescence methods. The complexation behavior of these sensor molecules, which have a distinct affinity for Hg^{2+}, is reported. The coordination of Hg^{2+} induces a photoinduced electron transfer from fluorophore to the complexed mercury and results in a significant decrease of the fluorescence. Theses sensors exhibit very low detection limits in CH_3CN/H_2O (80/20 v:v) and excellent sensitivity to Hg^{2+} over other potentially interfering cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+} and Pb^{2+}.

Introduction

Mercury is certainly the most toxic of the heavy metals, and causes environmental and health problems;[1] a wide variety of symptoms including digestive, kidney and especially neurological diseases are observed upon exposure. Thus, the level of this detrimental ion is the object of several official norms, the World Health Organisation having established in 2004 a guideline for drinking-water quality which included a mercury maximal value of 1 μg L^{-1}.[2] Currently the level of this detrimental ion is measured by analytical techniques (atomic absorption, atomic emission and inductively coupled plasma spectroscopy), which require complicated and sophisticated instrumentation. The use of fluorescent molecular sensors offers numerous advantages in terms of sensitivity, selectivity, response time and low cost.[3–5] A large number of fluorescent molecular sensors for Hg^{2+} have therefore been proposed so far, but many have limitations, including irreversibility, incompatibility with aqueous solutions and lack of selectivity.[6,7] Recently, some examples that can overcome these problems have been described in the literature, but the design of new efficient systems remains of current interest.[8–11]

We have previously reported the synthesis and the photophysical characterization of new fluorescent molecular sensors based on phosphane oxide[12,13] and phosphane sulfide derivatives.[14,15] In particular, the compound **DDPES1** was found to be very selective and sensitive for the Hg^{2+} ion, the detection limit being 3.8 nM. Since there has been no previous study on such fluorescent probes, we wished to evaluate the properties of a wider family, varying the length and the number of the phenylethynyl arms (Scheme 1, compounds **2** and **4**). Anticipating that the nature of the complexing unit might be of major importance, we also wanted to prepare a P=O/P=S mixed ligand **3**. In order to study the influence of steric hindrance, the preparation of fluorescent sensors containing only two polyphenyl ethynyl fluorophores (PSPO and PSPS) was targeted. In this paper, we report a detailed study based on our preliminary research with the emphasis on new derivatives (Scheme 1), their spectroscopic properties, and a thorough investigation of cation-induced photophysical changes and complexing properties, with the aim of studying the relationship between the structures of the fluorescent molecular sensors and their mercury-complexing ability.



DPPES1 (**1**): n = 1
DPPES2 (**2**): n = 2
PSPO (**3**): X = O
PSPS (**4**): X = S
PS3 (**5**)

Scheme 1 Fluorescent phosphane sulfide probes.

Results and discussion

Synthesis

Starting from the commercially available 4-bromotrimethylsilylphenyl acetylene **6**, phosphorylation using the Grignard derivative in the presence of 1,2-bis(dichlorophosphano)ethane afforded the formation of tetraarylated phosphanes (Scheme 2). Treatment with elemental sulfur gave the thiophosphano product, which

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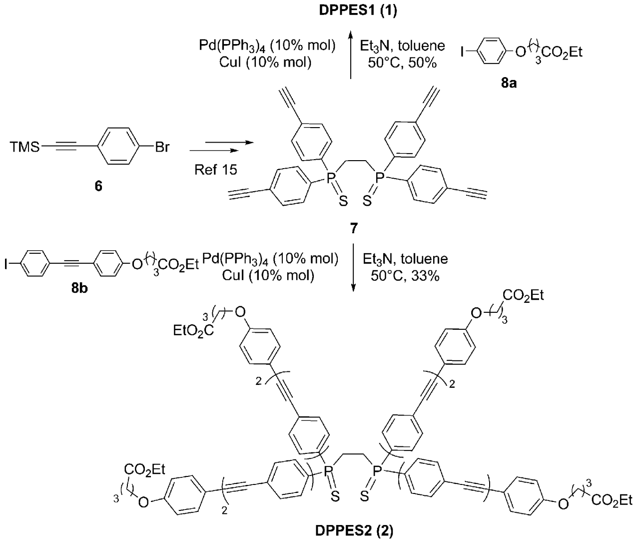


Scheme 2 Syntheses of DPPES1 (**1**) and DPPES2 (**2**) ligands.

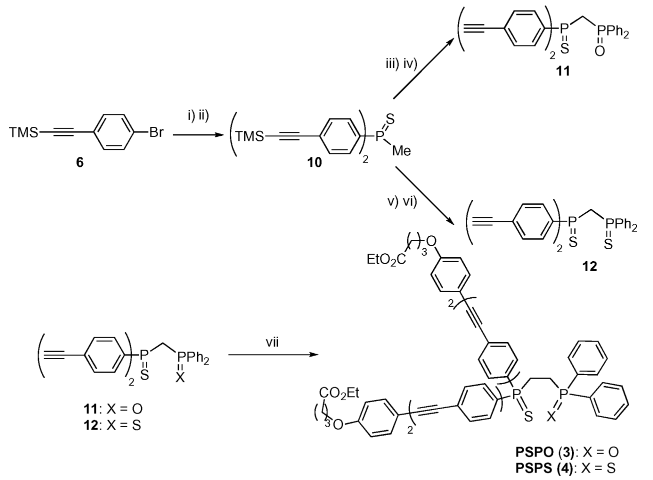
was then desilylated. The resulting phosphane sulfide **7**[15] was a key intermediate for the preparation of **1** and **2**. The Sonogashira cross-coupling[16] between the phosphano product **7** and the iodides **8a**[17] or **8b** was then performed in the presence of 10 mol% of Pd catalyst and 10 mol% of copper iodide and led to the desired ligands **1** and **2** in 50% and 33% yield, respectively.

In order to study the influence of the number of fluorescent arms for the complexation properties, we also synthesized the non-symmetrical derivatives **3** and **4** (Scheme 1). The structures of these ligands were also designed for a comparison of the affinity toward the mercury ion between the phosphane oxide and sulfide groups. As the desymmetrization step was not possible starting from **7**, we decided to take advantage of the functionalization of methyldichlorophosphane (**9**). Scheme 3 shows the complete synthetic pathway for the two non-symmetrical derivatives **PSPO** and **PSPS**. The classic Grignard derived from (4-bromophenyl)trimethylsilylacetylene **6** was phosphorylated with methyldichlorophosphine (**9**).[13] The phosphorus atom was sulfurized in the presence of elemental sulfur in toluene to give the thiophosphano product **10** in 86% yield. Then, a treatment with a hindered base, lithium 2,2,6,6-tetramethylpiperidine (LTMP),[18] followed by the addition of chlorodiphenylphosphane oxide gave the mixed P=O/P=S ligand in 53% yield. The addition of chlorodiphenylphosphane followed by a phosphorus sulfurization step led to the disulfide phosphane ligand in 22% yield. Desilylation using K_2CO_3 in CH_2Cl_2/MeOH afforded the desired phosphane sulfides **11** and **12** in 92% and 97% yields, respectively. Sonogashira cross-coupling reactions between the thiophosphano products **11**/**12** and the iodide **8b** were then performed in the presence of 6 mol% palladium catalyst and 12 mol% copper iodide, affording the final thiophosphanes **PSPO** (**3**) and **PSPS** (**4**) in 64% and 36% isolated yields, respectively. Phosphane sulfide **PS3** (**5**) was prepared according to a previously described procedure.[14]

Table 1 Photophysical properties of thiophosphano derivatives in CH_3CN/H_2O (9:1 with **DPPES2** and 8:2 with the others)

Product	λ_{abs}/nm	ε/10^4 M^{-1} cm^{-1}	λ_{em}/nm	Φ_F[a]
PS3 (**5**)	336	15	444	0.54
DPPES1 (**1**)	313	15	405	0.1
DPPES2 (**2**)	334	20	440	0.32
PSPO (**3**)	334	12	440	0.55
PSPS (**4**)	335	11	437	0.32

[a] Maxima of the absorption λ_{abs} (nm) and of steady-state emission λ_{em} (nm), molar absorption coefficient ε (10^4 M^{-1} cm^{-1}), and fluorescence quantum yield Φ_F (with 10% error).



Scheme 3 Syntheses of the ligands PSPO (**3**) and PSPS (**4**). Reagents and conditions: i) Mg, THF, 50 °C, 1.5 h then Cl_2PCH_3 (**9**), THF, RT, 18 h, 46%; ii) S_8, toluene, 95 °C, 4 h, 86%; iii) LTMP (2.3 equiv), THF, RT, –40 °C, 1 h 30 min then $Ph_2P(O)Cl$ (1.1 equiv), –40 °C, THF, 4 h (53%). iv) K_2CO_3 (2 equiv), CH_2Cl_2, MeOH, RT, 4 h, 92%; v) a) LTMP (2.3 equiv), THF, RT, –40 °C, 1 h 30 min then Ph_2PCl (1.1 equiv), –40 °C, THF, 4 h, b) S_8, toluene, 95 °C, 4 h, 22%; vi) K_2CO_3 (2 equiv), CH_2Cl_2, MeOH, RT, 4 h, 97%; vii) 6 mol% $Pd(PPh_3)_4$, 12 mol% CuI, $I–C_6H_4–C{\equiv}C–C_6H_4–O(CH_2)_3CO_2Et$ (**8b**), Et_3N, toluene, 50 °C, 64% (X = O), 36% (X = S).

Photophysical properties of the ligands

The absorption and fluorescence spectra of the thiophosphano ligands are shown in Fig. 1 and their photophysical characteristics are summarized in Table 1. All the fluorophores show an intense absorption band in the near-UV region. The absorption spectra of the long-arm fluorophores (**DPPES2** (**2**), **PSPO** (**3**) and **PSPS** (**4**)) are similar to the reference fluorophore **PS3** (**5**). The molar absorption coefficient at the maximal absorption wavelength is almost proportional to the number of fluorescent arms, indicating a weak interaction between the chromophores in the ground state. Only in the case of short fluorescent arm compound **DPPES1** (**1**) is a blue shift observed, as a result of the decrease in the π-conjugated chain. The fluorescence of the compounds are intense in the visible region, with quantum yields ranging from 0.1 to 0.54. A large Stokes shift and the unresolved vibronic structure of the fluorescence spectra of the compounds indicate the formation of an intramolecular charge transition. A blue shift and a decrease in the fluorescence quantum yield are observed for the fluorophore **DPPES1** (**1**) due to the decrease of the chromophoric length. However, this compound could be interesting thanks to its better solubility in organoaqueous solvents (CH_3CN/H_2O).

In order to have further information on the photophysical properties of the fluorophores, we performed time-resolved

Table 2 Analysis of the fluorescence decays of thiophosphano derivatives in CH_3CN/H_2O (8:2 and 9:1 for **DPPES2 (2)**) (λ_{exc} = 330 nm)

Product	λ_{em}/nm	τ_1/ns	α_1	τ_2/ns	α_2	τ_3/ns	α_3	χ^2_R
DPPES1 (1)	370	0.32	0.52	4.05	0.00	0.02	0.48	1.41
	400	0.32	0.59	4.05	0.01	0.02	0.40	1.37
	450	0.32	0.70	4.05	0.03	0.02	0.27	1.33
DPPES2 (2)	400	1.03	0.70	6.14	0.05	0.25	0.17	1.04
	444	1.03	0.80	6.14	0.03	0.25	0.19	1.10
	500	1.03	0.71	6.14	0.04	0.25	0.19	1.14
PS3 (5)	444	1.24	1.00	—	—	—	—	1.21
PSPO (3)	440	1.16	1.00	—	—	—	—	1.19
PSPS (4)	500	0.86	0.92	0.23	0.08	—	—	1.3

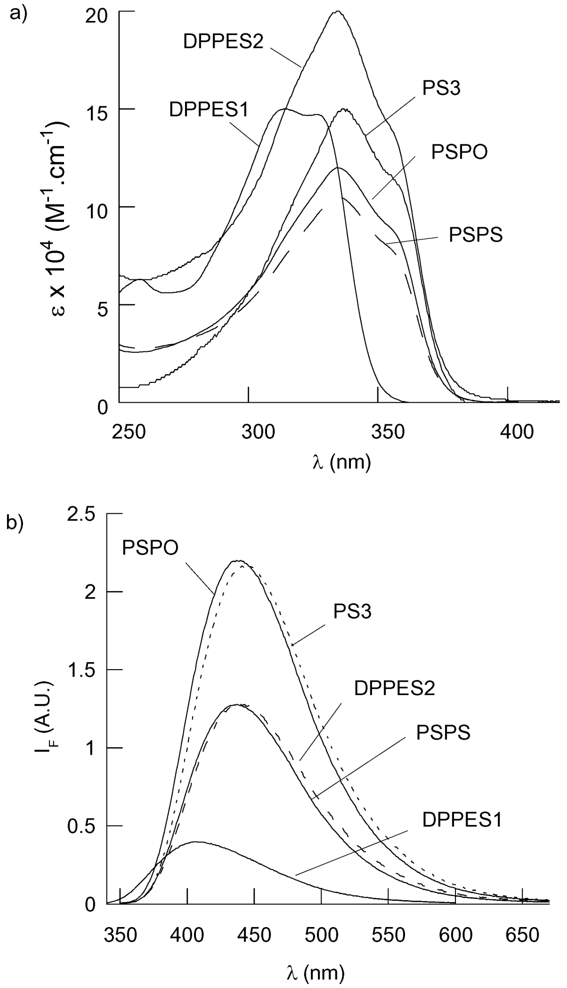


Fig. 1 Absorption spectra (a) and corrected normalized emission spectra (b) of thiophosphano derivatives in CH_3CN/H_2O (8:2 and 9:1 with **DPPES2 (2)**). λ_{exc} = 340 nm for PS3, PSPO, PSPS, λ_{exc} = 324 nm for DPPES1 and λ_{exc} = 343 nm for DPPES2.

fluorescence measurements by the single-photon counting method with picosecond laser excitation. The fluorescence decays of the compounds are displayed in Fig. 2. Satisfactory fits can be obtained by considering a single exponential (χ^2_R < 1.25) for the reference compound **PS3 (5)** and the non-symmetrical derivative **PSPO (3)**. Those results suggest the presence of only one emitting species, as in the case of phosphane oxide derivatives.[13] The fluorescence decay of **PSPS (4)** is almost mono-exponential in form, with only a small secondary component. In contrast, the fluorescence decays of **DPPES1 (1)** and **DPPES2 (2)** are more complicated and tri-exponential model is needed to obtain satisfactory fits. Time-resolved fluorescence measurements were done at different observation wavelengths and global analysis was used to fit the decays. The obtained decay times and preexponential factors fitted are displayed in Table 2. As we demonstrated in the case of phosphane oxide fluorophores,[13] the three components observed for the symmetric thiophosphano derivatives could be explained in the following way. Considering at first the long fluorescent arm derivative **DPPES2 (2)**, the medium component of around 1 ns, which is very close to the lifetime of **PS3 (5)** or **PSPO (3)**, may be attributed to the emission of the monomer. The longer component (6.1 ns), dominating at the long-wavelength part of the spectra, is assumed to correspond to an excimer formation. The shortest component (0.25 ns) could be attributed to the decay of the monomer able to form an excimer.[19,20] The same behaviour can be found in the case of short fluorescent arm derivative **DPPES1 (1)**. The only difference is that the time constants are shorter due to the decrease of the fluorophore length. All these data suggest, as previously observed for phosphane oxide derivatives,[13] the presence of different conformers: one may envisage the presence of an expanded structure (leading to monomer emission) and a sandwich-like geometry (responsible for preformed excimer emission).

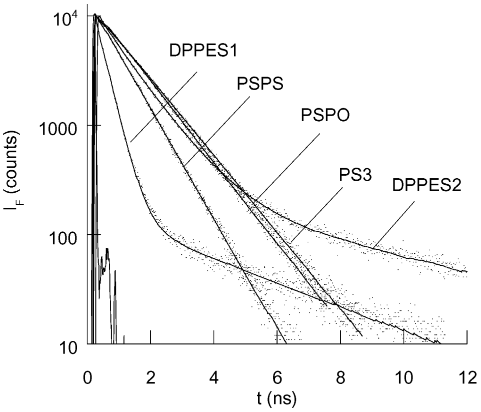


Fig. 2 Fluorescence decays of the thiophosphano derivatives in CH_3CN/H_2O 8:2 and 9:1 (**DPPES2 (2)**), λexc= 330 nm.

Cation-induced photophysical changes

Complexation studies of mercury with **PSPO (3)**, **PSPS (4)** and **DPPES1 (1)** were performed in a mixture CH_3CN/H_2O 8:2 at pH 4.0 with practical applications in mind.[6] The choice of pH 4 was made in order to prevent precipitation of the mercury cation (especially for the stock solution for the complexation studies). Furthermore, since these compounds do not contain any pH-sensitive function, no effect was observed upon changing the pH of the solution. For the symmetric long-arm derivative **DPPES2** (**2**), CH_3CN/H_2O 9:1 at pH 4.0 was used because of inadequate solubility of the compound with four long phenylethynyl arms.

The evolution of the absorption spectra (a) and the emission spectra (b) of **PSPO** (**3**) and **PSPS** (**4**), upon complexation with Hg^{2+} are displayed in Fig. 3 and Fig. 4, respectively. The insets in Fig. 3b and Fig. 4b show a decrease of the fluorescence intensity at 438 nm upon progressive addition of Hg^{2+}. Mercury complexation induces a bathochromic shift of the absorption spectra, because of an enhancement of the electron-withdrawing character of the phosphane sulfide and oxide groups due to interaction of their oxygen and sulfur atoms with the Hg^{2+}. A strong decrease of the fluorescence is observed upon mercury complexation for these two compounds, which can be attributed to an electron transfer between the excited fluorophore to the complexed mercury cation, as previously shown for the **DPPES1** (**1**).[15]

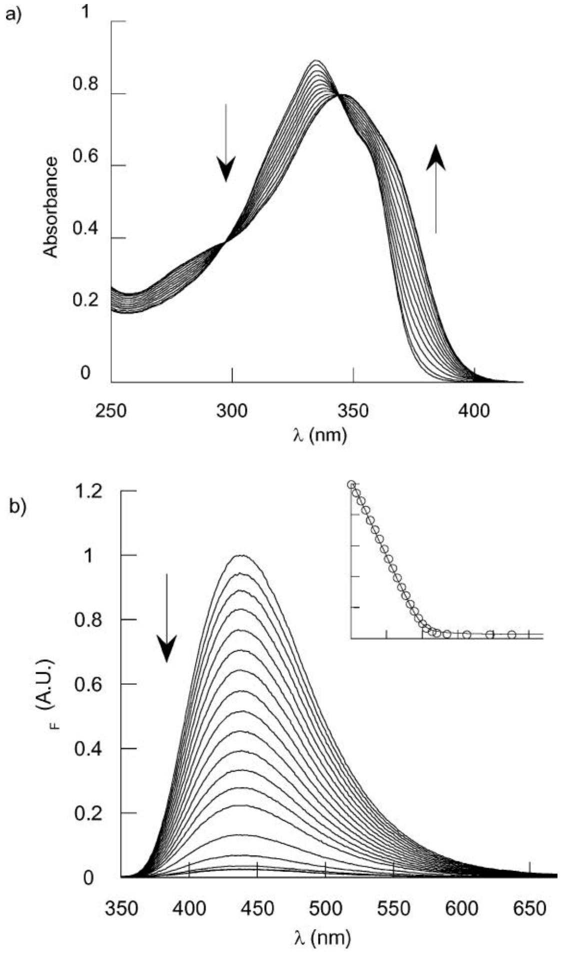


Fig. 3 Absorption (7.1×10^{-6} M) (a) and corrected emission (9.6×10^{-7} M) (b) spectra of **PSPO** (**3**) in the presence of an increasing concentration of Hg^{2+} in CH_3CN/H_2O 8:2 at pH 4.0. $\lambda_{exc} = 344$ nm. Inset: Calibration curve as a function of mercury concentration.

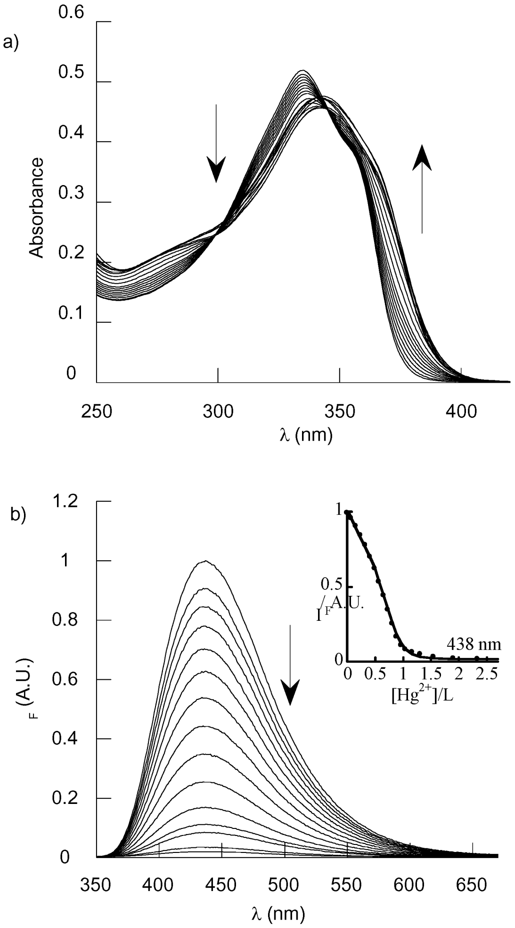


Fig. 4 Absorption (7.1×10^{-6} M) (a) and corrected emission (3.0×10^{-7} M) (b) spectra of **PSPS** (**4**) in the presence of an increasing concentration of Hg^{2+} in CH_3CN/H_2O 8:2 at pH 4.0. $\lambda_{exc} = 344$ nm. Inset: Calibration curve as a function of mercury concentration.

Global analysis of the evolution of the absorption and the emission spectra upon mercury binding (by means of the SPECFIT program) reveals that the formation of complexes of different stoichiometries (1:2, 1:1 and 2:1); the apparent stability constants are provided in Table 3.

For the **PS3** (**5**) ligand, two complexes are successively formed with stoichiometries of 1:2 (ML_2) and 1:1 (ML). These stoichiometries have been previously reported for mercury complexes with

Table 3 Stability constants[a] of thiophosphano derivatives with mercury

Product	$\log\beta_{11}$ (HgL)[a]	$\log\beta_{12}$ (HgL_2)	$\log\beta_{21}$ (Hg_2L)
PS3 (**5**)	5.0 ± 0.2	11.7 ± 0.1	—
PSPO (**3**)	8.2 ± 0.1	—	—
DPPES1 (**1**)	8.4 ± 0.4	15.5 ± 0.5	13.8 ± 0.4
PSPS (**4**)	10.7 ± 0.4	19.2 ± 0.6	16.5 ± 0.4
DPPES2 (**2**)	6.9 ± 0.2	—	13.8 ± 0.2

[a]

$$\beta_{ij} = \frac{[M_iL_j]}{[M]^i[L]^j}$$

the thiophosphano derivatives $R_3P{=}S$ (R = Me and Ph).[21–23] As previously shown for **DPPES1** (**1**), the three complexes were formed successively, with very high stability constants in the case of **PSPS** (**4**). The observed stoichiometries are in agreement with the results previously reported on the compound $Ph_2P(S)CH_2P(S)Ph_2$.[23] The stability constants of **PSPS** (**4**) with mercury are slightly higher than those found for **DPPES1** (**1**), probably because of the higher flexibility with the compound containing only two phenylethynyl groups. In contrast, the complexation with mercury is less effective with **DPPES2** (**2**) compared to **DPPES1** (**1**) because of higher steric hindrance. Thus the formation of a ML_2 complex has not been observed for this compound.

In contrast, the formation of only one complex with a 1:1 stoichiometry is observed with **PSPO** (**3**). As can be seen from Fig. 3a, there is a clear isobestic point at 344 nm, which indicates the presence of a single evolution from 0 to 1 equivalents corresponding to the formation of a single 1:1 complex. Its stability constant is also lower than in the case of **DPPES1** (**1**) or **PSPS** (**4**), which can be explained by the preference of mercury for the softer sulfur atom rather than the harder oxygen atom.[24] This is also the reason why a complex ML_2 is not observed for **PSPO** (**3**), since the affinity of the phosphine oxide group for mercury is not sufficient to form a complex.

The calibration curves shown in the inset of Fig. 3b and Fig. 4b represent the fluorescence intensities at 438 nm as a function of Hg^{2+} concentration for **PSPO** (**3**) and **PSPS** (**4**). The detection limits, calculated as three times the standard deviation of the background noise, were found to be 4.8 μg L^{-1} (23.9 nM) and 1.8 μg L^{-1} (8.9 nM) for **PSPO** (**3**) and **PSPS** (**4**), respectively. These values are slightly higher than that obtained for **DPPSE1** (**1**), but they remain close to the level defined by the World Health Organization.[2] A linear response as a function of mercury concentration was obtained from 0 to 162 and 200 μg.L^{-1} for **PSPO** (**3**) and **PSPS** (**4**), respectively.

The binding abilities of **PSPO** (**3**) and **PSPS** (**4**) over a range of other cations including alkali (Na^+, K^+), alkaline-earth (Ca^{2+}, Mg^{2+}) and transition metal ions (Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ag^+) were evaluated. Fig. 5 and Fig. 6 show the fluorescence spectra of these fluorophores and their complexes, determined by titration experiments. No significant change of the fluorescence was observed upon addition of a large excess of these interfering cations. Except for Ag^+ with **PSPS** (**4**), the stability constants of the complexes of these ions were too low to be determined. The stability constants obtained in the case of Ag^+ complexes with **PSPS** (**4**) were $\log K_{11} = 6.1$ and $\log K_{12} = 11.1$. The selectivity toward Hg^{2+}, expressed as the ratio of the apparent stability constants, was found to be higher than 10^4. In contrast to **PSPS** (**4**), this ion induced no significant effect on the absorption and fluorescence of **PSPO** (**3**) ligand, because of the weak interaction of the phosphine oxide group with this cation. The compound **PSPO** (**3**) consequently shows an outstanding performance in terms of selectivity towards Hg^{2+} over all the interfering cations.

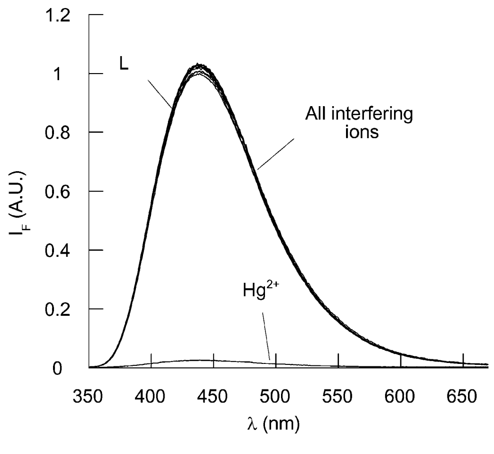


Fig. 5 Absorption (a) and emission (b) spectra (λ_{exc} = 344 nm) of **PSPO** (**3**) and its complexes in CH_3CN/H_2O 8:2 at pH 4.0.

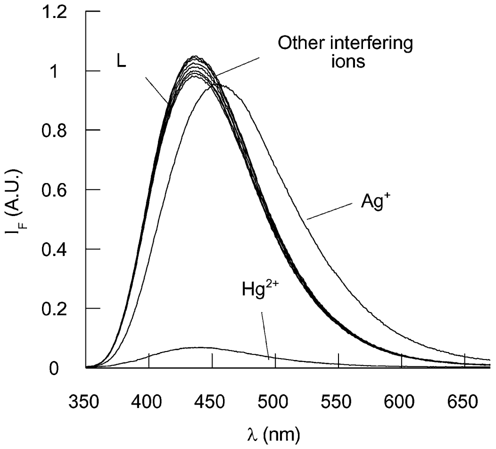


Fig. 6 Absorption (a) and emission (b) spectra (λ_{exc} = 340 nm) of **PSPS** (**4**) and its complexes in CH_3CN/H_2O 8:2 at pH 4.0.

The competition-based fluorescence profiles for these cations are shown in Fig. 7 and Fig. 8 for **PSPO** (**3**) and **PSPS** (**4**), respectively. No significant change of the sensor response is observed despite a large excess of interfering cations being added. Only Cd^{2+} slightly modifies the fluorescence response with **PSPO** (**3**). This behavior was not observed in the case of **PSPS** (**4**) derivative, which can be explained by the better affinity of cadmium for the phosphane oxide groups than the phosphane sulfide groups. In contrast with **PSPS** (**4**), the addition of Ag^+ in large excess (10^{-3} M) does not modify the complexation of **PSPO** (**3**) with Hg^{2+}.

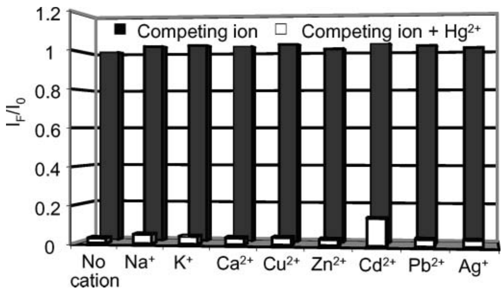


Fig. 7 I_F/I_0 response of **PSPO** (**3**) (λ_{exc} = 340 nm, λ_{em} = 438 nm) in CH_3CN/H_2O (8:2 v/v) at pH = 4 in the presence of Hg^{2+} (1.5 μM) and interfering ions Na^+, K^+, Ca^{2+} at 1 mM; Zn^{2+}, Ag^+ at 0.1 mM; Cu^{2+}, Cd^{2+}, Pb^{2+} at 0.05 mM.

In the case of **PSPS** (**4**) derivative, we have observed that Ag^+ was the main interfering ion. However, the addition of mercury

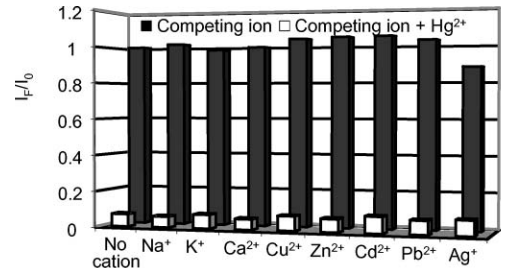


Fig. 8 I_F/I_0 response of **PSPS** (**4**) (λ_{exc} = 340 nm, λ_{em} = 438 nm) in CH_3CN/H_2O (8:2 v/v) at pH = 4 in the presence of Hg^{2+} (0.6 μM) and interfering ions Na^+, K^+, Ca^{2+} at 1 mM; Zn^{2+}, Cd^{2+} at 0.05 mM and Ag^+, Pb^{2+}, Cu^{2+} à 10^{-5} M.

always leads to fluorescence quenching thanks to its higher affinity constant of Hg^{2+} than Ag^+. The Fig. 8 shows a remarkably high selectivity of the **PSPS** for Hg^{2+}.

Conclusion

We have described the synthesis, the photophysical and complexing properties of a new family of fluorescent molecular sensors based on phosphorus ligands. The photophysical studies revealed interesting properties of this new family: an intense absorption band in near-UV region and an intense fluorescence band in the visible region. Time-resolved fluorescence experiments clearly demonstrated that the non-symmetrical ligands (**PSPO** (**3**) or **PSPS** (**4**)) behave like the mono-thiophosphane compound **PS3** (**5**): there is therefore no interaction between the chromophores in these multichromophoric fluorophores. However, as previously observed for the phosphane oxide ligand, interactions between the fluorescent arms have been revealed for the symmetrical ligands (**DPPES1** (**1**), **DPPES2** (**2**)), through the presence of several time constants in the fluorescence decays.

The fluorescent molecular sensors **PSPS** (**4**), **PSPO** (**3**) and **DPPES1** (**1**) showed remarkable sensitivity to and selectivity for Hg^{2+} in acetonitrile/water media. The addition of mercury ions to solutions of these compounds induces an significant bathochromic shift of the absorption spectra and a complete quenching of the fluorescence spectra. The selectivity of these systems for Hg^{2+} over other metal ions is remarkably high, and their estimated detection limit is compatible with the level defined by the World Health Organization for drinking water.

Experimental section

General

Reagents were commercially available from Acros, Aldrich, or Avocado and were used without further purification unless otherwise stated. Chloroform and acetonitrile (spectrometric grade from Aldrich or SDS) were employed as solvents for absorption and fluorescence measurements. Sodium thiocyanate, potassium thiocyanate, calcium perchlorate, zinc perchlorate, cadmium perchlorate, lead(II) perchlorate, silver(I) perchlorate and mercury(II) perchlorate, from Aldrich or Alfa Aesar, were of the highest quality available and were vacuum-dried over P_2O_5 prior to use. The solution at pH 4.0 was prepared with perchloric acid (99.99%) in water. Column chromatography was performed with E.Merck 0.04–0.063 mm Art. 11567 silica gel. ^1H NMR, ^{13}C NMR, and ^{31}P NMR were recorded on Bruker AV 300 or AV 400 instruments. All signals were expressed as ppm downfield from Me_4Si for ^1H and ^{13}C NMR and from H_3PO_4 for ^{31}P NMR used as an internal standard (d). Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. Melting points were measured in open capillary tubes. Mass spectrometry analyses were performed at the Ecole Nationale Supérieure de Chimie de Paris by using a Hewlett-Packard HP 5989 A instrument. Direct introduction experiments were performed by chemical ionization with ammonia. Elemental analyses and high-resolution mass spectra were performed at the Institut de Chimie des Substances Naturelles.

Synthesis

Methylene-bis(4-trimethylsilylethynylphenyl)phosphane. To 569 mg (43 mmol) of activated Mg under argon, a solution of (4-bromophenylethynyl)trimethylsilane (5.41 g, 21.3 mmol) in anhydrous THF (12.5 ml) was added in one portion. The mixture was then heated at 55 °C for 2h and then canulated to a solution of CH_3PCl_2 (942 μl, 10.65 mmol) in anhydrous THF (12.5 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and then for 18h at room temperature. The reaction was then quenched with a solution of saturated aqueous NH_4Cl (20 ml) and water (5 ml). After extraction, drying (Na_2SO_4), and filtration, the volatiles were evaporated and the crude oil was purified by flash chromatography (eluant: CH_2Cl_2–dichloromethane 9:1) to afford the corresponding product as a white solid (1.92 g, 46%).

M.p. 114 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.39 (m, 4H), 7.31 (m, 4H), 1.58 (d, 3H, J = 3.52 Hz), 0.24 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.8, 140.6, 132.1, 131.9, 131.8, 126.8, 123.3, 104.8, 95.4, 12.59, 12.3, 0.0. ^{31}P NMR ($CDCl_3$, 121 MHz): δ –25.6. MS (ESI): $C_{23}H_{29}PSi_2$: m/z: 392 $[M + H]^+$.

Methylene-bis(4-trimethylsilylethynylphenyl)phosphane sulfide 10. To a solution of methylene-bis(4-trimethylsilylethynylphenyl)phosphane (1.923 g, 4.9 mmol) in toluene (80 ml), 156 g (4.9 mmol) of S_8 were added and the reaction was heated at 95 °C for 4h under argon. The solvent was evaporated under reduced pressure and the crude yellow solid was purified by filtration on a short pad of silica gel (eluant: AcOEt) to afford a white solid (1.78 g, 86%).

M.p. 124 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52 (m, 4H), 7.25 (m, 4H), 2.24 (d, 3H, J = 13.23 Hz), 0.25 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.3, 133.2, 132.3, 132.1, 130.8, 130.6, 126.8, 103.8, 97.8, 22.1, 21.3, 0.0. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.7. MS (ESI): $C_{23}H_{29}PSi_2S$: *m/z*: 424 $[M + H]^+$. HRMS (TOF MALDI) calcd for $C_{23}H_{29}PSi_2SNa$ 447.1164, found 447.1191 $[M + Na]^+$.

Bis(4-trimethylsilylethynylphenyl)phosphanthioyl-diphenylphosphanoylmethane. A solution of LTMP was prepared for 5 minutes at 0 °C from *n*-BuLi (2.5 M) (460 μl, 1.15 mmol) and TMPH (195 μl, 1.15 mmol) in 1 mL of THF under argon. This solution was then cannulated at –40 °C to a solution of methylene-bis(4-trimethylsilylethynylphenyl)phosphane sulfide (212 mg, 0.5 mmol) in THF (2 mL) under argon. The mixture was stirred for 1h30 at 40 °C and 114 μl (0.6 mmol) of diphenylphosphinic chloride were added dropwise to this solution at –40 °C under argon. The solution was stirred for 4h at –40 °C then quenched with saturated aqueous NH_4Cl solution (5 ml) and extracted with dichloromethane (5 ml). The organic layer was dried (Na_2SO_4), filtered and evaporated under reduced pressure. The crude yellow solid was purified by flash chromatography (eluant: CH_2Cl_2 to CH_2Cl_2/AcOEt 9:1, Rf(CH_2Cl_2) = 0.2) to afford the corresponding product as a white solid (166 mg, 53%). M.p. 202 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (m, 4H), 7.62 (m, 4H), 7.48 (m, 2H), 7.39 (m, 8H), 3.71 (m, 2H), 0.28 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.2, 132.2, 132.0, 131.9, 131.9, 131.7, 131.1, 131.0, 130.8, 128.8, 128.6, 126.9, 126.9, 104.0, 97.7, 39.2, 38.6, 38.5, 37.9, 0.0. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 36.0 (d, J = 16 Hz), 23.4 (d, J = 16 Hz). MS (IC): $C_{35}H_{38}OP_2SSi_2$: *m/z*: 624 [M + H]$^+$. HRMS (MALDI) calcd for $C_{35}H_{39}OP_2SSi_2$ 625.1730, found 625.1752 [M + H]$^+$.

Bis(4-trimethylsilylethynylphenyl)phosphanthioyl-diphenyl phosphanthioylmethane. According to the experimental procedure to prepare bis(4-trimethylsilyl ethynylphenyl)phosphanthioyl-diphenyl phosphanoyl methane, and starting from the solution of LTMP (1.15 mmol in 1 ml of THF), the methylene-bis(4-trimethylsilylethynylphenyl)phosphane sulfide (212 mg, 0.5 mmol), the diphenylphosphane chloride Ph_2PCl (104 µL, 0.6 mmol), the phosphane product was obtained. This product was not isolated and directly engaged in the sulfuration with S_8 (1 equiv.) added dropwise after solubilisation in toluene. The mixture was then stirred at 95 °C for 4h. Then volatiles were evaporated and the corresponding mixture of phosphane sulfide (2/3) and phosphane oxide (1/3) was purified by flash chromatography (eluant: cyclohexane/CH_2Cl_2 1:1) and trituration with a small amount of AcOEt to afford 70 mg (22%) of the desired product as a white solid. M.p. 91 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (m, 8H), 7.36 (m, 10H), 3.93 (t, 2H, J = 13.4 Hz), 0.25 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.8, 132.7, 132.5, 132.4, 132.3, 132.2, 131.8, 131.8, 131.7, 131.7, 131.6, 131.6, 131.3, 131.2, 131.1, 131.1, 131.0, 130.9, 128.8, 128.6, 128.5, 126.9, 126.8, 103.9, 97.8, 39.4, 0.0. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.2 (d, J = 14 Hz), 34.8 (d, J = 14 Hz). MS (IC): $C_{35}H_{38}P_2S_2Si_2$: m/z: 640 [M + H]$^+$. HRMS (MALDI) calcd for $C_{35}H_{39}P_2S_2Si_2$: 641.1502, found 641.1478 [M + H]$^+$.

Bis(4-ethynylphenyl)phosphanthioyl-diphenylphosphanoyl methane 11. To a solution of bis(4-trimethylsilylethynylphenyl)-phosphanthioyl-diphenylphosphanoylmethane (160 mg, 0.26 mmol) in a mixture of dichloromethane (2 ml) and MeOH (4 ml), 77 mg (0.1 mmol) of K_2CO_3 were added and the reaction was stirred at room temperature for 4h. After complete conversion 4 mL of water were added and the mixture was extracted with dichloromethane (5 mL). The organic layer was then dried (Na_2SO_4), filtrated and evaporated in vacuo. The crude oil was then triturated in Et_2O/cyclohexane (1:1) to afford a white solid (116 mg, 92%).

M.p. 193 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83–7.91 (m, 4H), 7.54–7.61 (m, 4H), 7.32–7.43 (m, 8H), 3.71 (dd, J = 15 Hz and 15 Hz, 2H), 3.19 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.9, 131.8, 131.7, 130.7, 130.6, 128.6, 128.5, 82.6, 79.9, 39.0, 38.4, 38.3, 37.7. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 36.1 (d, J = 16 Hz), 23.4 (d, J = 15 Hz). MS (IC): $C_{29}H_{22}OP_2S$: m/z: 480 [M + H]$^+$. HRMS (ES) calcd for $C_{29}H_{22}OP_2SNa$: 503.0764, found 503.0796 [M + Na]$^+$.

Bis(4-ethynylphenyl)phosphanthioyl-diphenylphosphane thioyl methane 12. According to the experimental procedure to prepare bis(4-ethynylphenyl)phosphanthioyl-diphenyl phosphanoyl methane and starting from a solution of bis(4-trimethylsilyl-ethynylphenyl)phosphinthioyl-diphenyl phosphanthioylmethane (160 mg, 0.25 mmol) in mmol in a mixture of dichloromethane (2 ml) and MeOH (4 ml) with 68 mg (0.1 mmol) of K_2CO_3, 121 mg of desired product was obtained as a white solid (97%). M.p. 86 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59–7.66 (m, 8H), 7.19-7.29 (m, 10H), 3.81 (t, 2H, J = 13.4 Hz), 3.05 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.3, 131.2, 131.1, 130.5, 130.3, 130.2, 130.1, 130.0, 129.8, 127.3, 127.1, 127.0, 124.3, 81.1, 78.7, 37.6 (t, J = 44.3 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.1 (d, J = 14 Hz), 35.0 (d, J = 14 Hz). MS (IC): $C_{29}H_{22}P_2S_2$: m/z: 496 [M + H]$^+$.HRMS (ES) calcd for $C_{29}H_{22}P_2S_2Na$: 519.0536, found 519.0541 [M + Na]$^+$.

Bis-4-[ethyl4-(4-di(phenyleneethynylene)-phenoxy)butyrate] phosphinthioyl-diphenylphosphynoyl methane PSPO (3). To a solution of bis(4-ethynylphenyl)phosphanthioyl-diphenyl phosphanoylmethane (40 mg, 0.083 mmol) and in toluene (4 ml) and triethylamine (2 ml), 130 mg of **8b** (0.30 mmol, 3.6equiv.) are added. The mixture is degassed under argon and CuI (2 mg, 12 mol%) and $Pd(PPh_3)_4$ (5 mg, 6 mol%) are added quickly. The reaction mixture is then stirred for 20h at 50 °C under argon. The volatiles are evaporated in vacuo and the residue is dissolved in dichloromethane (10mL). The organic layer is washed with HCl (10%), dried (Na_2SO_4), filtrated and the solvents are evaporated under reduced pressure. The crude product is then purified by flash chromatography (silica gel: CH_2Cl_2 100% to CH_2Cl_2/acetone 1:1) to afford the desired product PSPO (58 mg, 64%) as an yellow solid. M.p. 147 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81–7.88 (m, 4H), 7.51–7.58 (m, 4H), 7.28–7.45 (m, 22H), 6.78 (d, J = 8.81 Hz, 4H), 4.07 (q, 4H, J = 7.2 Hz), 3.95 (t, 4H, J = 6.1 Hz), 3.69 (dd, J = 13 Hz and 15 Hz), 2.43 (t, 4H, J = 7.34 Hz), 2.03 (m, 4H), 1.17 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.1, 159.1, 133.1, 132.0, 131.9, 131.8, 131.7, 131.5, 131.4, 131.2, 130.8, 130.7, 128.7, 128.5, 126.8, 126.7, 124.1, 122.0, 115.1, 114.6, 91.9, 91.8, 90.1, 87.8, 66.8, 60.5, 38.3, 30.7, 24.6, 14.2. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 36.2 (d, J = 15 Hz), 23.4 (d, J = 13 Hz). HRMS (TOF MALDI) calcd for $C_{69}H_{59}O_7P_2S$ [M]$^+$ 1093.3471, found. 1093.3451.

Bis-4-[ethyl 4-(4-di(phenylene ethynylene)-phenoxy)butyrate] phosphanthioyl-diphenylphosphanthioylmethane PSPS (4). To a solution of bis(4-ethynylphenyl)phosphinthioyl-diphenyl phosphinthioylmethane (47 mg, 0.09 mmol) and in toluene (4 ml) and triethylamine (2 ml), 123 mg of **8b** (0.28 mmol, 3.2equiv.) are added. The mixture is degassed under argon and CuI (2 mg, 12%mol) and $Pd(PPh_3)_4$ (5 mg, 6%mol) are added quickly. The reaction mixture is then stirred for 20h at 50 °C under argon. The volatiles are evaporated in vacuo and the residue is dissolved in dichloromethane (10mL). The organic layer is washed with HCl (10%), dried (Na_2SO_4), filtrated and the solvents are evaporated under reduced pressure. The crude product is then purified by flash chromatography (silica gel: CH_2Cl_2 100% to CH_2Cl_2/acetone 1:1) to afford the desired product (36 mg, 36%) as an yellow solid.

M.p. 111 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76–7.69 (m, 8H), 7.42–7.28 (m, 20H), 6.78 (dd, 4H, J = 1.8 Hz and 8.8 Hz,), 4.07

(q, 4H, J = 7.2 Hz), 3.97–3.87 (m, 6H), 2.44 (t, 4H, J = 7.3 Hz,), 2.04 (m, 4H), 1.18 (t, 6H, J = 7.2 Hz,). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.1, 159.1, 133.1, 132.7, 132.6, 132.5, 132.2, 132.1, 132.0, 131.8, 131.7, 131.6, 131.4, 131.3, 131.2, 131.0, 130.9, 128.5, 128.3, 126.7, 126.7, 124.1, 122.0, 115.0, 115.0, 114.6, 92.0, 91.8, 90.0, 87.8, 66.8, 60.5, 39.9, 39.3, 38.7, 30.7, 24.5, 14.2. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.3 (d, J = 14 Hz), 35.1 (d, J = 14 Hz). MS (FIA) $C_{69}H_{59}O_7P_2S$: m/z: $[M-H]^+$ 1109.

Ethylene 1,2-bis-4-[ethyl 4-(4-di(phenylene ethynylene)-phenoxy)butyrate]diphosphane sulfide DPPS2 (2). To a solution of ethylene 1,2-bis(4-trimethylsilylethynylphenyl)diphosphane sulfide **6**[25,15] (50 mg, 0.085 mmol) in toluene (5 ml) and triethylamine (2 ml) and 240 mg of **8b** (0.55 mmol, 6.5equiv.) are added. The mixture is degassed under argon and CuI (1.6 mg, 12%mol) and $Pd(PPh_3)_4$ (9.8 mg, 10%mol) are added quickly. The reaction mixture is then stirred for 20h at 50 °C under argon. The volatiles are evaporated in vacuo and the residue is dissolved in dichloromethane (10mL). The organic layer is washed with HCl (10%), dried (Na_2SO_4), filtrated and the solvents are evaporated under reduced pressure. The crude product is then purified by flash chromatography (silica gel: CH_2Cl_2 100% to CH_2Cl_2/acetone 1:1) to afford the desired product **DPPES2** (**2**) (51 mg, 33%) as a brownish solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77 (m, 8H), 7.43–7.60 (m, 32H), 6.85 (m, 8H), 4.14 (q, 8H, J = 7.05 Hz), 4.02 (t, 8H, J = 6.08 Hz), 2.72 (m, 4H), 2.51 (t, 8H, J = 7.23 Hz), 2.12 (m, 8H), 1.26 (t, 8H, J = 7.14 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.4, 159.4, 133.4, 133.0, 132.1, 132.0, 131.7, 131.3, 127.4, 124.4, 122.1, 115.3, 114.8, 92.6, 92.1, 90.0, 88.1, 67.1, 60.7, 31.0, 25.8, 24.8, 14.5. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 44.1. HRMS (TOF MALDI) calcd for $C_{114}H_{97}O_{12}P_2S_2$ $[M + H]^+$ 1783.5891, found. 1783.5864.

Spectroscopic measurements

UV/Vis absorption spectra were recorded on a Varian Cary5E spectrophotometer and corrected emission spectra were obtained on a Jobin–Yvon Spex Fluorolog 1681 spectrofluorimeter. The fluorescence quantum yields were determined by using quinine sulfate dihydrate in sulfuric acid (0.5 N; $\Phi_F = 0.546$[26]) as references. For the emission measurements, the absorbance at the excitation wavelengths were below 0.1 and so the concentrations were below 10^{5} $molL^{-1}$. The fluorescence intensity decays were obtained by the single-photon timing method with picosecond laser excitation by use of a Spectra-Physics setup composed of a titanium sapphire Tsunami laser pumped by an argon ion laser, a pulse detector, and doubling (LBO) and tripling (BBO) crystals. Light pulses were selected by optoaccoustic crystals at the repetition rate of 4 MHz. Fluorescence photons were detected through a long-pass filter (375 nm) by means of a Hamamatsu MCP R3809U photomultiplier, connected to a constant-fraction discriminator. The time-to-amplitude converter was purchased from Tennelec. Data were analyzed by a nonlinear least-squares method with the aid of Globals software (Globals Unlimited, University of Illinois at Urbana-Champaign, Laboratory of Fluorescence Dynamics). The complexation constants were determined by global analysis of the evolution of all absorption and/or emission spectra by using the Specfit Global Analysis System V3.0 for 32-bit Windows system. This software uses singular value decomposition and non-linear regression modeling by the Levenberg–Marquardt method.[26]

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References

1 (*a*) T. C. Hutchinson and K. M. Meema, in *Lead, Mercury, Cadmium and Arsenic in the Environment*, John Wiley, New York 1987; (*b*) G. H. Scoullos, M. J. Vonkeman, L. Thorton, Z. Makuch, in *Mercury, Cadmium, Lead: Handbook for Sustainable Heavy Metals Policy and Regulation (Environment & Policy, V. 31)*, Kluwer Academic, 2001; (*c*) C. J. Coester, *Anal. Chem.*, 2005, **77**, 3737–3754; (*d*) S. D. Richardson and T. A. Temes, *Anal. Chem.*, 2005, **77**, 3807–3838.

2 *World Health Organization, Guidelines for drinking-water quality, 3rd edn*, Vol. 1, Geneva, 2004, p. 188.

3 A. P. deSilva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515–1566.

4 B. Valeur and I. Leray, *Inorg. Chim. Acta*, 2007, **360**, 765–774.

5 B. Valeur and I. Leray, *Coord. Chem. Rev.*, 2000, **205**, 3–40.

6 E. M. Nolan and S. J. Lippard, *Chem. Rev.*, 2008, **108**, 3443–3480 and references cited therein.

7 (*a*) I. B. Kim, B. Ergodan, J. N. Wilson and U. H. F. Bunz, *Chem. Eur. J.*, 2004, **10**, 6247–6254; (*b*) A. Caballero, R. Martinez, V. Lloveras, Ratera, I. Vidal-Gancedo, J. K. Wurst, A. Tarraga, P. Molina and J. Veiana, *J. Am. Chem. Soc.*, 2005, **127**, 15666–15667; (*c*) J. Wang and X. Qian, *Chem. Commun.*, 2006, 109–111; (*d*) J. D. Winkler, C. M. Bowen and V. Michelet, *J. Am. Chem. Soc.*, 1998, **120**, 3237–3242; (*e*) R. Metivier, I. Leray and B. Valeur, *Chem. Eur. J.*, 2004, **10**, 4480–4490; (*f*) R. Metivier, I. Leray, B. Lebeau and B. Valeur, *J. Mater. Chem.*, 2005, **15**, 2965–2973; (*g*) H. Zheng, Z.-H. Qian, L. Xu, F.-F. Yuan, L.-D. Lan and J.-G. Xu, *Org. Lett.*, 2006, **8**, 859–861; (*h*) Y. Zhao and Z. Zhong, *J. Am. Chem. Soc.*, 2006, **128**, 9988–9989.

8 (*a*) A. Ono and H. Togashi, *Angew. Chem. Int. Ed.*, 2004, **43**, 4300–4302; (*b*) S. Yoon, A. E. Albers, A. P. Wong and C. Chang, *J. Am. Chem. Soc.*, 2005, **127**, 16030–16031; (*c*) Y. K. Yang, K. J. Yook and J. Tae, *J. Am. Chem. Soc.*, 2005, **127**, 16760–16761; (*d*) E. M. Nolan, M. E. Racine and S. J. Lippard, *Inorg. Chem.*, 2006, **45**, 2742–2749; (*e*) E. M. Nolan and S. J. Lippard, *J. Am. Chem. Soc.*, 2003, **125**, 14270–14271.

9 M. Zhu, M. J. Yuan, X. F. Liu, J. L. Xu, J. Lv, C. S. Huang, H. B. Liu, Y. L. Li, S. Wang and D. B. Zhu, *Org. Lett.*, 2008, **10**, 1481–1484.

10 O. del Campo, A. Carbayo, J. V. Cuevas, A. Munoz, G. Garcia-Herbosa, D. Moreno, E. Ballesteros, S. Basurto, T. Gomez and T. Torroba, *Chem. Commun.*, 2008, 4576–4578.

11 Y. Shiraishi, S. Sumiya, Y. Kohno and T. Hirai, *J. Org. Chem.*, 2008, **73**, 8571–8574.

12 M. H. Ha-Thi, V. Souchon, A. Hamdi, R. Metivier, V. Alain, K. Nakatani, P. G. Lacroix, J. P. Genet, V. Michelet and I. Leray, *Chem. Eur. J.*, 2006, **12**, 9056–9065.

13 M. H. Ha-Thi, M. Penhoat, D. Drouin, M. Blanchard-Desce, V. Michelet and I. Leray, *Chem. Eur. J.*, 2008, **14**, 5941–5950.

14 M. H. Ha-Thi, V. Souchon, M. Penhoat, F. Miomandre, J. P. Genet, I. Leray and V. Michelet, *Lett. Org. Chem.*, 2007, **4**, 185–188.

15 M. H. Ha-Thi, M. Penhoat, V. Michelet and I. Leray, *Org. Lett.*, 2007, **9**, 1133–1136.

16 R. Chinchilla and C. Najera, *Chem. Rev.*, 2007, **107**, 874–922.

17 P. J. Hajduk, G. Sheppard, D. G. Nettesheim, E. T. Olejniczak, S. B. Shuker, R. P. Meadows, D. H. Steinman, G. M. Carrera, P. A. Marcotte, J. Severin, K. Walter, H. Smith, E. Gubbins, R. Simmer, T. F. Holzman, D. W. Morgan, S. K. Davidsen, J. B. Summers and S. W. Fesik, *J. Am. Chem. Soc.*, 1997, **119**, 5818–5827.

18 G. Bartoli, M. Bosco and L. Sambri, *Tetrahedron Lett.*, 1996, **37**, 7421–7424.

19 S. Akimoto, H. Nishizawa, T. Yamazaki, I. Yamazaki, Y. Hayashi, M. Fujimaki and K. Ichimura, *Chem. Phys. Lett.*, 1997, **276**, 405–410.

20 M. N. Berberan-Santos, J. Canceill, J. C. Brochon, L. Jullien, J. M. Lehn, J. Pouget, P. Tauc and B. Valeur, *J. Am. Chem. Soc.*, 1992, **114**, 6427–6436.

21 M. G. King and G. P. McQuillan, *J. Chem. Soc.*, 1967, 898–901.

22 N. M. Karayannis, C. M. Mikulski and L. L. Pytleweski, *Inorg. Chim. Acta Rev.*, 1971, **5**, 69–105.

23 E. W. Ainscough, H. A. Bergen, A. M. Brodie and K. A. Brown, *J. Chem. Soc. Dalton Trans.*, 1976, 1649–1656.

24 S. E. Livingstone, ‘Other sulfur-containing ligands’, *Comprehensive Coordination Chemistry (vol. 2)*, Pergamon Press, 1987, pp. 633–659.

25 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991–1024.

26 H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, **32**, 95–101.