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s-tetrazines functionalized with phenols: synthesis and physico-chemical properties

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s-tetrazines functionalized with phenols substituted by electron withdrawing or electron donating groups have been synthesized. The electrochemical and photophysical properties of these series of compounds have been investigated. All the new tetrazines prepared can be reversibly reduced into their anion-radical, and the reduction potential of the tetrazine is sensitive (ΔE of 0.1-0.2V) to the *meta*- and the *para*-substitution of the phenoxy group on its 6-position. Whereas tetrazines substituted by phenoxy possessing an electron donating moiety are virtually non emissive, the ones substituted by a phenoxy possessing an electron withdrawing group are fluorescent compounds (quantum yield up to 0.36). Fluorescence quenching experiments have been performed on all the fluorescent compounds. A moderate fluorescence quenching is observed in the presence of toluene, *m*-xylene and styrene, whereas an efficient quenching occurs in the presence of bisphenol A, in agreement with a quenching through a photoinduced electron transfer, which depends on the electron-rich character of the quencher.

Introduction

The search of new compounds that display both emission and electrochemical properties arises a high interest for the design of new chemosensors.[1,2] *s*-Tetrazines are long ago discovered molecules, the first synthesis dating back to the end of the 19th century.[3] All *s*-tetrazines[4,5] derivatives are highly colored (because of a weakly allowed n-π* transition in the visible) and electroactive aromatic heterocycles, that display a very high electron affinity. Their straightforward electrochemical properties allow these compounds to be reduced in their stable anions-radical at high potentials. *s*-Tetrazines have been used in coordination chemistry,[6] polymers[7] and in sensors applications.[8] We,[8,9] and others,[10] have noticed and studied the fluorescence properties of some tetrazines substituted with heteroatoms. Plus, they are fluorescent even in the crystalline state.

Various fluorescent probes have been evaluated for the detection of anions, cations, biological molecules and biologically relevant analytes,[11,12,13,14,15,16] amongst which some experimental evidences of anion binding ability of *s*-tetrazines have been first time published.[17] Concerning the development of sensors for neutral organic molecules, a lot of research have been focused on the development of sensors for nitroaromatics,[18] as they are well known to be a class of explosives materials. Nitroaromatics are quite electrodeficient because of the attractor mesomeric effect of the nitro moiety. So the strategy adopted was the development of electron rich fluorophores to occur a Photoinduced Electron Transfer (PET). Much less research has been dedicated to the other strategy, the development of electron poor fluorophores for the detection of electron rich materials.

In this respect, the emission properties of tetrazines (some of them substituted by an heteroatom display a high fluorescence quantum yield and also a relatively good photochemical stability) and their small size make them very attractive candidates. Indeed, they combine a high oxidizing power in the excited state, with an unusually long fluorescence lifetime. So, we have studied the fluorescence quenching of some tetrazines by electron-rich aromatics.[8,19] We are interested in developing a family of tetrazines that display a fluorescence response to a wider range of aromatics, from electron enriched to electron

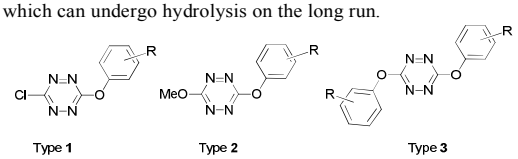
neutral hydrocarbons aromatics. To achieve this goal, the tetrazine core needs to be functionalized with different substituents that allow a modulation of the reduction potential while preserving or increasing the fluorescent character.

We have prepared a series of tetrazines functionalized by phenol moieties and we have studied their photophysical and electrochemical properties. The fluorimetric sensing of aromatics by some of these new tetrazines has also been investigated.

Results and discussion

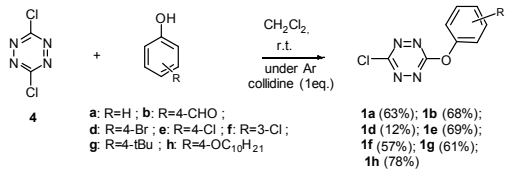
Synthesis

Two types of *para*- or *meta*- substituted phenol derivatives have been used to target phenoxytetrazines bearing either electron withdrawing substituents (phenols **b**, **c**, **d**, **e**, **f** – scheme 1), or electron donating ones (**g**, **h** - scheme 1). The unsubstituted phenol (**a**) should be lead to reference phenoxy-tetrazine compounds. As electrophilic chlorotetrazines are known to undergo easy aromatic nucleophilic substitution with various nucleophiles, we aimed at synthesizing three families of phenoxytetrazine compounds: monosubstituted chlorophenoxytetrazines of type **1**, methoxytetrazines of type **2** and symmetrical disubstituted phenoxytetrazines of type **3** (scheme 1). The advantage of compounds of series **2** and **3** is that they are usually more stable than their more electrodeficient counterparts, the chlorotetrazines of type **1**, which can undergo hydrolysis on the long run.



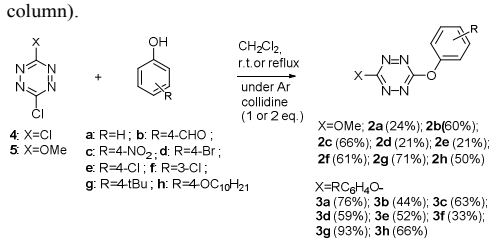
Scheme 1. Families of tetrazines of type **1**, **2** and **3**

These three families of compounds were synthesized from dichlorotetrazine **4** using classical conditions of S_NAr for tetrazines derivatives: use of 2,4,6-trimethylpyridine as base in dry dichloromethane under argon atmosphere.[9] A major synthetic difference between the families is that 3,6-dichlorotetrazine **4** comes up with a very electrodeficient core, leading to easy monosubstitutions when conducted in mild conditions (room temperature, fast reaction). By comparison, alkoxychlorotetrazines are weaker electrophiles which need harder conditions (temperature, pression) to undergo SNAr. Therefore when 3,6-dichlorotetrazine **4** is used, monosubstitution reactions were realized at room temperature using reaction times between 45 mn and 4 hours (scheme 2), leading to compounds **1a-1h**. Yields are quite good (57 to 78%) except for compound **1d**: this is due to a difficult purification as product decomposes upon chromatography. For this compound, we used less than one equivalent of phenol derivative because of its high reactivity (a test with one equivalent of phenol derivative conducted to the disubstituted product).



Scheme 2. Synthesis of chlorotetrazines **1a-h**

Most of the symmetrical disubstituted compounds of type **3** were synthesized at room temperature (except for **3e** and 3**h** which required reflux) with two equivalents of the corresponding phenol **a-h** and of 2,4,6-trimethylpyridine (scheme 3). These conditions are very mild comparing to the usual disubstitution of chlorotetrazines **4** or **5** with aliphatic alcohol nucleophiles which required a long reflux and even occasionally the use of a pressure tube[9]. This difference can be explained in terms of the better nucleophilicity of phenols as compared to alcohols. Besides it must be noted that compounds **3c** and **3g** precipitate in dichloromethane. When the less electrophilic 3-chloro-6-methoxy-*s*-tetrazine **5** was used, synthesis of compound of type **2** required reflux for a few days. Compounds of type **2** are obtained with reasonable yields in the 50-70% range, except for compounds **2a**, **2d** and **2e,** a fact that can again be explained by the difficulties encountered for the purification steps (degradation on silica chromatography column).



Scheme 3. Synthesis of phenoxytetrazines **2a-h** and **3a-h**

Electrochemistry

The electrochemical behavior of tetrazines **1-3 a-h** was investigated in dichloromethane. All the compounds exhibit a reversible cyclic voltamogramm, corresponding to the reduction of the tetrazine into its anion-radical (Figure 1). The corresponding redox potentials are gathered in Table 1. Comparison of the redox potentials of tetrazines **1**, **2** and **3** shows a diminution of about 0.22 to 0.33 V when the chlorine atom is substituted by an alkoxy or a phenoxy group because of the stabilization of the anion radical by the inductive attractor effect of the chlorine atom (-0.77V for **1b**, -1.04V for **2b** and -0.88V for **3b** for example).

On the other hand, the presence of an electron withdrawing group on the phenyl ring shifts upwards the reduction potential of the tetrazine core by 0.04 to 0.18 V. For example, we measured a reduction potential of ca. –0.96 V for tetrazine **3a** and ca. -0.88 V for tetrazine **3b**. On the contrary, an electron donating substituent on the phenoxy group did not have a similarly significative effect on the reduction potential (ca. -0.99 V for tetrazine **3h**). The same behavior is observed again when comparing phenoxytetrazine **1a** with the corresponding ones **1b, 1g** and **1h.** These results show that the reduction potential of the tetrazine core can be tailored through the substitution of the phenyl, and that the variation of the reduction potential stays in a lower range than the one obtained by substituting the chlorine atom by a methoxy group or a phenoxy group on the 3-position.

Table 1: Reduction Potential of the tetrazine derivatives **1-3 a-h**

	$E^0_{fundamental}$		$E^0_{fundamental}$		$E^0_{fundamental}$
1a	-0.87	**2a**	-1.09	**3a**	-0.96
1b	-0.77	**2b**	-1.04	**3b**	-0.88
		2c	-0.98	**3c**	-0.82
1d	-0.69	**2d**	-1.02	**3d**	-0.90
1e	-0.76	**2e**	-1.07	**3e**	-0.92
1f	-0.78	**2f**	-1.08	**3f**	-0.92
1g	-0.82	**2g**	-1.11	**3g**	-0.99
1h	-0.83	**2h**	-1.09	**3h**	-0.99

$E^0_{fundamental}$ in volts/ferrocene

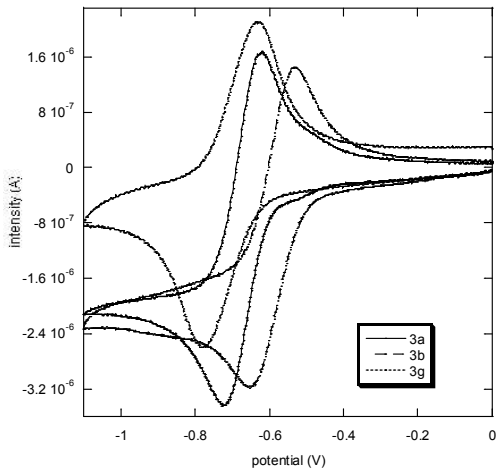


Figure 1. Cyclic Voltammetry of **3a** (—), **3b** (––), **3g** (....) (V *vs* Ag^+/Ag), in dichloromethane (with 0.1M Bu_4NPF_6 as electrolyte) on glassy carbon electrode at 0.1 $V.s^{-1}$. Concentrations are about 10 mM. Scan rate: 50 $mV.s^{-1}$

For the compounds of the families **e** and **f**, the *para* or *meta* position of the chlorine atom does not seems to have an influence on the reduction potential of the tetrazine core.

For the compounds **2c** and **3c**, we observed a second reduction (Figure 2) due to the nitro moiety on the phenoxy group (-1.61V/ferrocene and -1.28V/ferrocene). The reduction potential of **3c** is higher (less negative) than the one of **2c** as expected.[20]

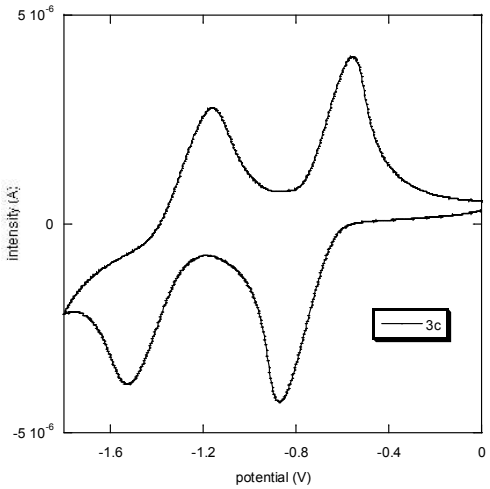


Figure 2. Cyclic Voltammetry of **3c** (V *vs* Ag^+/Ag), in dichloromethane (with 0.1M Bu_4N PF_6 as electrolyte) on glassy carbon electrode at 0.1 $V.s^{-1}$. Concentrations are about 10 mM. Scan rate: 50 $mV.s^{-1}$

Photophysical properties

The absorption and fluorescence emission were studied in dichloromethane, and the relevant data are gathered in Table 2; an example of absorption spectra is displayed in Figure 3.

Table 2. Photophysical properties for compounds **1-3 a-h** in dichloromethane: absorption wavelength ($\lambda_{max,}$ nm), molar absorption coefficient (ε, L.mol^{-1}.cm^{-1}), emission wavelength ($\lambda_{em,}$ nm), fluorescence quantum yield (ϕ_F), fluorescence lifetime (τ, ns).

	λ_{max1}	ε	λ_{max2}	ε	λ_{max3}	$\varepsilon\times10^{-3}$	λ_{em}	ϕ_F	τ (ns)
1a	522	630	323	2200	234	6.6	565	0.04	-
2a	529	800	344	3700	232	8.4	575	0.19	80
3a	531	620	343	2300	237	11.5	577	0.16	95
1b	521	500	323	1700	253	15.2	566	0.33	155
2b	528	620	342	2800	256	20	574	0.21	100
3b	530	700	341	2900	256	35	577	0.24	140
2c	528	600	340	3200	276	10	575	0.28	110
3c	528	500	338(sh)	3500	272	20	575	0.36	155
1d	522	600	310	2100	231	12	565	0.013	-
2d	528	550	343	2400	233	14	573	0.21	85
3d	531	600	341	1200	232	25	577	0.12	55
1e	522	600	314	2000	231	10	565	0.018	-
2e	529	600	343	2500	233	11	576	0.21	85
3e	531	600	340	2000	232	21	577	0.14	60
1f	522	600	321	2000	232	7.9	571	0.28	130
2f	528	600	343	3000	231	8.3	575	0.24	95
3f	530	600	339	2500	235	13	578	0.27	130
1g	523	600	311	2100	235	6.5	564	-	-
2g	530	600	345	2700	231	6.6	575	-	-
3g	533	500	343	1700	234	17	575	-	-
1h	524	600	312	2700	232	7.8	566	-	-
2h	530	550	331	2600	232	9.1	575	-	-
3h	535	600	350 (sh)	1500	232	24	576	-	-

Fluorescence quantum yield measured with rhodamine 6G in ethanol as a standard (ϕ_F =0.95)[21]; sh=shoulder

All these compounds display three bands in absorption. For all compounds, a band is located at ca. 520-530 nm in dichloromethane and displays a weak molar absorption coefficient (ca. 600 L.mol^{-1}.cm^{-1}). This band is attributed to the weakly allowed n-π* transition centered on the tetrazine core and it is weakly sensitive to the substitution on the tetrazine moiety as expected.[22] A second band in the near UV region (located at 310-345 nm) corresponding to a π-π* transition centered on the tetrazine core is observed and the molar absorption coefficient is ca. 2500 L.mol^{-1}.cm^{-1}, higher than for the tetrazine compounds substituted by a sulfur heteroatom (ca. 1000 L.mol^{-1}.cm^{-1}).[23] This value is similar to the one obtained for chloroalkoxy- or dialkoxytetrazine. The absorption maxima of the π-π* transition increases of about 20 to 30 nm between compounds **1** and **2** (323 nm for **1a** to 344 for **2a** for example). This is due to the replacement of the chlorine atom by an oxygen atom as expected.[4] A third band located at ca. 230 nm is attributed to a π-π* transition on the phenoxy ring and displays a high molar absorption coefficient (15000 to 20000 L.mol^{-1}.cm^{-1}). For the compounds **1b, 2b, 2c, 3b** and **3c**, a bathochromic shift from 10 to 30 nm is attributed to the strong attractive mesomeric effect of the formyl or the nitro group that increases the electron delocalisation from the phenoxy core to the electron withdrawing group.[24]

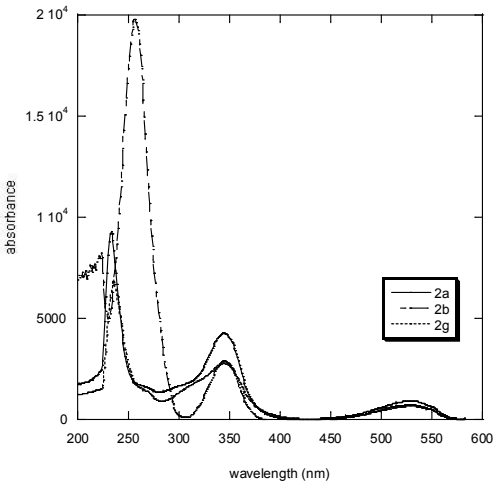


Figure 3. UV-Vis absorption spectra of compounds **2a**, **2b** and **2g** in dichloromethane.

We studied the influence of the polarity of the solvent on the absorption wavelengths. For all the compounds, the n-π* transition is quite sensitive to the polarity of the solvent (Figure 4). In fact, we observed an hypsochromic effect with the increasing solvent polarity (up to 20 nm from toluene to DMSO). The extent of this solvatochromic shift does not depend significantly on the substitution on the tetrazine core or on the phenolic moiety. Results are gathered in Table 3.

In the ground state, the C-N covalent bound is polarized and may be more stabilized in a polar solvent, due to the electrostatic attraction between the compound and the solvent. This will have the effect of requiring more energy to trigger the n-π* transition and so we observed a shift of the maximum absorption to shorter wavelengths (hypsochromic effect) compared to the position of the absorption band in a non-polar solvent.

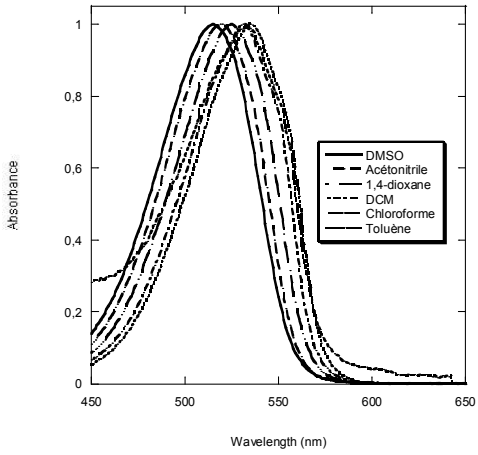


Figure 4. Solvatochromic effect: Normalized absorption spectra of compound **3d** in DMSO, acetonitrile, 1,4-dioxane, dichloromethane, chloroform and toluene.

Table 3. Absorption wavelength ($\lambda_{n-\pi^*}$, nm) in six solvents (DMSO, CH_3CN, 1,4-dioxane, CH_2Cl_2, $CHCl_3$ and toluene) for compounds **1-3 a-e**

	$\lambda_{n-\pi^*}$ DMSO	$\lambda_{n-\pi^*}$ Acetonitrile	$\lambda_{n-\pi^*}$ 1,4-dioxane	$\lambda_{n-\pi^*}$ DCM	$\lambda_{n-\pi^*}$ $CHCl_3$	$\lambda_{n-\pi^*}$ Toluene
1a	507	511	514	522	525	524
3a	517	521	525	532	533	536
1b	504	509	513	521	523	522
2b	514	518	522	528	529	531
2c	513	518	522	527	529	530
1d	506	510	514	522	524	525
2d	516	519	523	529	530	532
3d	515	519	525	531	533	535
1e	506	511	515	522	525	524
2e	516	519	523	529	530	532
3e	515	520	525	531	533	535

On the contrary, we did not observe this phenomenon with the π–π* transition that does not seem to be affected by the polarity of the solvent.

Concerning the emission properties, fluorescence maxima in DCM are around 575 nm for all the compounds of type **1**, **2** or **3** (Table 2) and correspond to the tetrazine fluorescence. It is very weakly sensitive to the substitution on the tetrazine core, contrary to the quantum yields which are very dependent on the substitution on the tetrazine core and more specifically, on the phenyl group. The quantum yields can plunge to extremely low or not measurable for the families **g** and **h**. For these compounds, there is an electron donor moiety on the phenyl (^{t}Bu or $OC_{10}H_{21}$). A photoinduced electron transfer from the phenyl part to the tetrazine part occurs, and the tetrazine fluorescence is quenched. For the compounds of the family **a**, bearing no group on the phenyl, the quantum yield is ca. 0.04 for compound **1a** but we observed higher quantum yields for the compounds **2a** and **3a** (respectively 0.19 and 0.16). We can notice that for compounds **1e** and **1f**, the position of the chlorine atom on the phenyl moiety greatly modifies the fluorescence quantum yield. That could be explained by an electronic effect. Indeed, on a *meta* position, the chlorine atom did not display a donor mesomeric effect but just an inductive attractor effect which can lead to a fluorescent material. On the contrary, on a *para* position, the donor mesomeric effect prevails to the inductive one. For all the other compounds bearing an electron withdrawing group, we can observe a large panel of quantum yields, between 0.12 to 0.36. The fluorescence decays can all be fitted with single exponential decays and lifetimes are long (up to 155 ns for compounds **1b** and **3c**) for fluorescence phenomena because of the n-π* almost forbidden transition as mentioned previously.

Fluorescence quenching experiments

Amongst these new tetrazine derivatives, those which display the highest reduction potentials and the longest fluorescence lifetimes were selected for fluorescence quenching experiments. Their sensing properties were evaluated towards 4 different pollutants: on one hand, benzene derivatives as styrene, xylene and toluene, which are Volatile Organic Compounds (VOCs) and displays some effect on health[25] and on the other hand a strong electron rich pollutant, bisphenol A which is employed for the production of epoxy resins and polycarbonate plastics.[26] Though its use is more and more limited, it has been widely used for nursing bottles and beverage containers,[27] but it is also a potential endocrine-disrupting chemical with potential hazardous effects on health.[28] Each time, the addition of the pollutant to a tetrazine solution in DCM leads to a decrease of the fluorescence intensity (Figure 5).

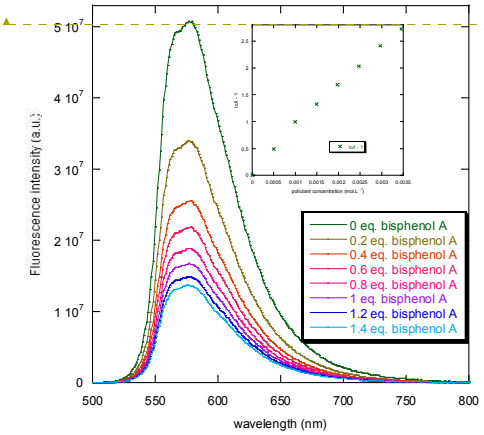


Figure 5. Fluorescence quenching of **3f** with bisphenol A in dichloromethane (λ_{exc}=490 nm).

The decrease of the fluorescence follows the Stern-Volmer equation (equation 1).

$$\frac{I_0}{I} - 1 = K_{SV}[Q] \qquad \text{(equation 1)}$$

For each Stern-Volmer plot, linear correlations are obtained, which allow the determination of Stern-Volmer constants K_{SV}.

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Results are gathered in Table 4. The values of Stern-Volmer constants increase from toluene to bisphenol A. Indeed, it is correlated to the electron density of each quencher, which is in good agreement with a quenching by photoinduced electron transfer.

		K_{SV} (L.mol^{-1})			
	E_0*	toluene	*m*-xylene	styrene	Bisphenol A
1a	1.41	-	1.4	5.8	455
2a	1.15	-	0.2	0.9	435
3a	1.28	-	0.5	3.3	900
1b	1.51	12	135	195	895
2b	1.21	-	0.8	3	655
3b	1.36	0.8	11	20	645
2c	1.27	-	1.5	5	700
3c	1.51	3	38	60	820
2d	1.23	-	0.6	2	510
3d	1.34	-	0.9	3	310
1e	1.52	-	1.0	4	410
3e	1.32	-	1.0	4.2	785
1f	1.48	5	85	100	885
3f	1.32	0.5	4	11	775

Table 4. Stern-Volmer constants for the new tetrazine derivatives in the presence of toluene, *m*-xylene, styrene or bisphenol A

Time-resolved experiments allow us to check if it is a static or a dynamic quenching. These experiments were performed on some of these new compounds (see ESI): with styrene, dynamic quenching is observed but for toluene a static contribution appears, probably because in this case the photoinduced electron transfer reaction is too slow to be the dominant quenching mechanism anymore. This is due to the difference between the reduction potential of the excited tetrazine and the oxidation potentials of toluene (1.86V *vs.* Fc^+/Fc[29]), *m*-xylene (1.70V *vs.* Fc^+/Fc[29]) and styrene (1.48V *vs.* Fc^+/Fc[30]). The standard free enthalpy ΔG^0 for the quenching reaction can be calculated by using the redox potential for the reactants, as it is shown in equation 2, where D is the electron rich pollutant, A the tetrazine derivative and C a constant term to take into account the solvation effects and the Coulombic energy.

$$\Delta G^0 = E^0(D^+/D) - E^0(A^*/A^-) - C \qquad \text{(equation 2).}$$

Redox potentials in the excited state can be deduced from the reduction potential in the ground state and ΔE_{00}, the excitation energy, calculated as the half-sum of the absorption and emission maxima (equation 3):

$$E^0(A^*/A^-) = E^0(A/A^-) + \Delta E_{00} \qquad \text{(equation 3).}$$

By combination of these two equations, we obtain the Rehm-Weller equation.[31] Reduction potentials in the excited state are gathered in Table 4: in each case, the reaction between the excited tetrazine and the benzene derivative conducts to a positive value of ΔG^0, which corresponds to a slow electron transfer reaction (the rate constant decreases when ΔG^0 increases: it is the normal region of Marcus theory).

Fluorescence quenching is much more efficient with bisphenol A, according to the electron-rich character of this pollutant, with Stern-Volmer constants in the 300-900 L.mol^{-1} range, much higher than for tetrazines with a C-S link on the tetrazine core.[23] This again can be explained by comparing the reduction potential of the excited tetrazine with the oxidation potentials of bisphenol A (+0.47V *vs.* Fc^+/Fc[32]). According to the gap between the two potentials, the quenching reaction conducts to a negative value of ΔG^0, and if we calculate the bimolecular quenching constant k_q (that can be calculated using $k_q = K_{SV}/\tau_0$), the values lie between 5 and 13. 10^9 L.mol^{-1}.s^{-1}, showing that for some compounds, the bimolecular quenching process is diffusion-limited (by comparing k_q with the diffusional rate constant k_{dif}, given by Smoluchowski[33]). The combination of a long fluorescence lifetime and a high reduction potential is the key to the efficiency of sensing. This explains that **1b** is the best candidate between all these new tetrazine derivatives for the detection of bisphenol A.

Conclusions

In summary, some new tetrazines substituted by phenol derivatives have been synthetized and their electrochemical and photophysical properties have been studied. The ones with an electron withdrawing group show a higher reduction potential and display fluorescence emission, whereas the ones with an electron donating moiety on the phenyl group are virtually non emissive.

Extinction of the fluorescence by a photoinduced electron transfer between an electron rich pollutant and an excited tetrazine core is observed, can be very efficient in some cases, and is linked to the concentration of the pollutant. To be useful for pollutant detection by fluorescence quenching, the fluorophore must display not only a high reduction potential but also a long fluorescence lifetime.

Experimental section

General synthetic procedures:

- Procedure A: General monosubstitution procedure, type **1**

In a one-neck-round-bottom-flask was placed 3,6-dichlorotetrazine **4** (1 eq.) and a phenol derivative **a-h** (1 eq.) in anhydrous CH_2Cl_2 (concentrations are about 6.10^{-2} M). 2,4,6-trimethylpyridine (1 eq.) was added slowly. The mixture was then stirred at room temperature, under argon atmosphere, during 45min to 4 hours (followed by TLC). Then the mixture was concentrated under reduced pressure.

- Procedure B: General disubstitution procedure, type **3**

In a one-neck-round-bottom flask was placed 3,6-dichlorotetrazine **4** (1 eq.) and a phenol derivative **a-h** (2 or 3 eq.) in anhydrous CH_2Cl_2 (concentrations are about 8.10^{-2} M). 2,4,6-trimethylpyridine (2 or 3 eq.) was added slowly. The mixture was stirred under argon atmosphere at room temperature or heated under reflux. In the few cases where was no progression of the reaction, the mixture

was placed in a sealed tube under pressure up to 4 days (followed by TLC). Then the mixture was concentrated under reduced pressure or a precipitate was filtered and washed with cold dichloromethane.

- Procedure C: General monosubstitution procedure, type **2**

In a one-neck-round-bottom-flask was placed 3-chloro-6-methoxy-*s*-tetrazine **5** (1 eq.) and a phenol derivative **a-h** (1 eq.) in anhydrous CH_2Cl_2 (concentrations are about 6.10^{-2} M). 2,4,6-trimethylpyridine (1 eq.) was added slowly. The mixture was then stirred and heated under reflux, under argon atmosphere up to 6 days (followed by TLC). Then the mixture was concentrated under reduced pressure.

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