

Fluorescence Switches

Redox- and Protonation-Induced Fluorescence Switch in a New Triphenylamine with Six Stable Active or Non-Active Forms

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Abstract: The synthesis, photophysical and electrochemical properties as well as theoretical calculation studies of a newly designed triphenylamine derivative are described. This original compound displays one neutral form, three oxidized forms, and two protonated forms with distinct photo-

Introduction

Electrochromism deals with compounds or materials whose absorption properties can be modified in relation with their oxidation or reduction state.^[1] Similarly, electrofluorochromism describes the fluorescence response of a given molecule, or device, to an electrochemical stimulation or by extension, to a change in its redox state, and is receiving more and more attention nowadays.^[2] Molecules bearing different fluorescence properties related to their redox state (i.e., neutral, oxidized, or reduced state) have already been reported.^[3] Amatore et al. reported the fluorescence change with the redox state for bioanalytical applications.^[4] We have recently described the electrofluorochromism of tetrazines,^[5] metal complexes,^[6] and multichromophoric compounds based on tetrazines and boron-dipyrromethene (Bodipy) dyes.^[7]

However, to the best of our knowledge, there is no report on fluorescence changes resulting from different oxidation states of a triphenylamine derivative. Some electron-rich triphenylamines are known to be easily oxidized into stable cation radicals and the oxidation process is always associated with a noticeable change of coloration. For example a recent article by Tanaka et al. describes the electrochemistry and electrochromism of an extended triphenylamine derivative.^[8] Polymers containing triphenylamine moleties are also well known for their electrochromic properties.^[9] Some of them can present up to four different colors^[10] depending on their redox

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physical characteristics. The interplay of the emission with the protonation or the redox state (electrofluorochromism) has been explored and an on-off-on-off fluorescence switching was observed in the case of oxidation and an onon-off fluorescence switching in the case of protonation.

states, whereas others can present absorption bands in the NIR area. $^{\left[9d,e\right] }$

The new triphenylamine derivative 3 (Scheme 1) was prepared and its original photophysical and electrochemical properties were studied. In order to obtain several protonation and redox states, three amine groups are present on the molecule as well as two biphenyl links, which allow extended electron delocalization on the molecule and therefore a better stabilization of the redox states. In addition an electron-donating methoxy group has been added to increase the electron-rich character and the stability of the different forms of the molecule. Thanks to these features, this new compound has been found to display four stable redox states (see Scheme 2), and three protonated states (see Figure 10). The absorption and fluorescence variations, not only with the oxidation state, but also with the protonation state, were investigated, and are described therein. Theoretical quantum calculations were also performed providing a correlation with the experimental results.

Results and Discussion

Synthesis

The design of the triphenylamine **3** (Scheme 1) was rationalized in order to obtain a molecule sensitive to both potential and proton quantity variations. Dimethylamino substituents were chosen as both proton sensors and electron-donating groups, and a methoxy moiety was added in order to contribute to the delocalization. We also chose to place methoxy and dimethylamino substituents on the *para* positions of the phenyl groups, in order to stabilize the cation radical of the triphenylamine and avoid its polymerization. The synthesis of this new triphenylamine derivative **3** has been successfully realized in few steps through cross-coupling reactions. First, the diphenylamine derivative **1** was synthesized by using a Hartwig–Buchwald coupling reaction^[11] between anisidine and 1,4-

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 $\label{eq:scheme1.} Scheme1. Synthetic route to the triphenylamine derivative3. Dba = dibenzylideneacetone, DPPF = 1,1'-bis(diphenylphosphino) ferrocene.$

dibromobenzene. It should be noted that the triphenylamine **2** was also isolated during this one-pot reaction (12%). A second coupling step allowed us to transform quantitatively compound **1** into the triphenylamine precursor **2**. Finally, the use of standard Miyaura–Suzuki conditions^[12] led us to the expected final compound **3** in a very good yield (89%).

Electrochemical properties and electrofluorochromism

The redox properties of compound **3** were investigated by cyclic voltammetry (CV). As can be seen in Figure 1, compound



Figure 1. Cyclic voltammetry of compound **3** ($5 \times 10^{-4} \text{ M}$) in dichloromethane and 0.1 M Bu₄NPF₆ on C. Potentials are referenced to the ferrocene/ferrocenium (Fc⁺/Fc) couple. Scan rate: 40 mVs⁻¹.

3 exhibits three well-defined peaks corresponding to the successive oxidation steps involving each amine moiety through a one-electron process. The peaks are fully reversible and the standard potentials referenced to ferrocene are 0.02, 0.23, and 0.54 V, respectively. The structures of the different oxidized forms of compound 3 are proposed in Scheme 2. The first value corresponds to the oxidation of the central nitrogen atom on the triphenylamine in order to obtain compound 3(I). This oxidation is the easiest because of the electronic delocalization with the phenyl rings. Its low value in comparison with other triphenylamine derivatives^[11d, 13] can be explained by the presence of the dimethylamino and the methoxy electron-donating groups, which stabilize by mesomeric effect the first cation radical 3(I). The two higher values correspond to the oxidations of the two dimethylamino moieties, which are not independent leading successively to compounds 3(II) and 3(III).



Scheme 2. Representation of the oxidized forms of compound 3.



Figure 2. Absorption (black solid line, left *y* axis) and fluorescence emission spectra (gray dash line, right *y* axis) of compound **3** in acetonitrile. Excitation wavelength: $\lambda_{\text{exc}} = 264$ nm.

The absorption and emission spectra of compound **3** are displayed in Figure 2 and the photophysical data for both compounds **2** and **3** are gathered in Table 1. These triphenylamine derivatives display one intense absorption band in the UV region at $\lambda = 304$ and 346 nm, respectively for compounds **2** and **3**.

In order to ascribe the origin of the absorption band, timedependent (TD) DFT calculations were done on both compounds after geometry optimization and the results are gathered in Table 1 as well as Tables S1 and S2 in the Supporting Information. For compounds **2** and **3**, this band is in fact due to two π - π * transitions: the first one (λ_{th} =319 and 359 nm, re-

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Table 1. Experimental and calculated absorption wavelength (λ) , molar absorption coefficient (ε) , emission wavelength (λ_{em}) , fluorescence quantum yield $(\varPhi_{\rm F})$ and fluorescence lifetime (r) for compounds 2 and 3 in acetonitrile.

	λ _{exptl} [nm]	$arepsilon_{ ext{exptl}}$ [L mol ⁻¹ cm ⁻¹]	λ _{calcd} [nm]	ε_{calcd} [Lmol ⁻¹ cm ⁻¹]	λ _{em} [nm]	$\Phi_{ extsf{F}}^{[a]}$	τ [ns]
2	304	26000	316	41 500	392	0.0004	n.d. ^[b]
3	346	43 400	357	93 300	424	0.39	2.2
[a] Fluorescence quantum yields measured with quinine sulfate in H_2SO_4							

(0.5 N) as a standard ($\Phi_{\rm F}$ = 0.546).^[15] [b] Not determined.



Figure 3. Representation of the main molecular orbitals involved in the electronic transitions of compounds 2 and 3 and their corresponding energy levels.

spectively) from the HOMO localized on the whole molecule to a π^* orbital localized on the two identical branches (L+1 and LUMO, respectively) and the second one ($\lambda_{th} = 303$ and 332 nm, respectively) from the HOMO to the L+2 localized on the whole molecule (Figure 3). Absorption spectra constructed from these theoretical data (Figures S5 and S6 in the Supporting Information) gave calculated absorption maxima at $\lambda = 316$ and 357 nm for compounds 2 and 3, respectively (Table 1). This band is very sensitive to the substituents on the triphenylamine core. Indeed compound 2 is substituted with two electron-withdrawing bromine atoms, which lower the π and π^* levels compared to compound 3, which is substituted with two electron-donating dimethylaminophenyl groups (Figure S10 in the Supporting Information). As the π^* orbital is less influenced, the energy gap for compound **2** is therefore higher and thus the absorption wavelength is red shifted from compound 2 to compound 3. Molecules 2 and 3 display high molar absorption coefficients because of the transition nature and an important overlap of the orbitals. It can be noticed that the molar absorption coefficient of compound 3 is closely equal to the ratio 5:3 of the corresponding one of compound **2**, as it could be expected given the presence of five absorbing phenyl units in compound **3** against three in compound **2**.

Both triphenylamine derivatives display a fluorescence band around $\lambda = 400$ nm. The shift between the emission bands can be explained similarly to the absorption band shift. The fluorescence quantum yields of compounds **2** and **3** are 0.0004 and 0.39, respectively. In fact the fluorescence of compound **2** is quenched by a heavy-atom effect due to the bromine atoms. Conversely, compound **3** has a pretty high quantum yield (0.39) and a lifetime around 2.2 ns comparable to other triphenylamine compounds.^[14]

The spectroscopic properties of compound **3** upon oxidation have been studied. The photophysical data of all the species are gathered in the Table 2. The generation of the different oxi-

Table 2. Experimental and calculated absorption wavelength (λ), emission wavelength (λ_{em}) and fluorescence quantum yield (Φ_{F}) for the different species of compound 3 in acetonitrile.							
	λ ₁ [nm]	λ ₂ [nm]	λ ₃ [nm]	λ₄ [nm]	λ₅ [nm]	λ _{em} [nm]	$\Phi_{ extsf{F}}^{[a]}$
3	346	_				424	0.39
3(I) ^[b]	326	472	1361	-	-	409-519	0.06 ^[b]
3(II) ^[b]	326	472	1136	-	-	513	0.12
3(III)	313	540	591	664	728	-	< 0.0001
3(H ⁺) ₂	355	-	-	-	-	492	0.20
3 (H ⁺)₃	266	499	591	658	728	-	< 0.0001
[a] Fluorescence quantum yields measured with quinine sulfate in H_2SO_4							

(0.5 N) as a standard ($\Phi_{\rm F}$ =0.546).^[15] [b] Approximate estimation due to a mixture with species with lower and higher oxidation degrees.

dized forms (two cation radicals and one dication) of compound 3 (Scheme 2) can be achieved either by electrochemical or by chemical oxidation. First of all, a one-electron chemical oxidation was chosen and Cu(ClO₄)₂ was used as a mild and clean oxidant, which has been recently reported to effectively generate arylaminium cation radicals by our group and others.^[11d, 13a, 16] Another advantage of using Cu(ClO₄)₂ is that it gives no absorption nor emission in the UV/Vis domain at low concentrations and its reduction potential in acetonitrile is 0.7 V versus Fc/Fc⁺, which matches well with the different redox potentials of compound 3. In order to prove that only an oxidation occurred with $Cu(ClO_4)_2$ (no complexation reaction for example between Cu^{II} and the triphenylamine derivatives), other oxidants could be used. Fe(ClO₄)₃ was also chosen because as for Cu(ClO₄)₂, Fe(ClO₄)₃ gives no absorption nor emission in the UV/Vis domain at low concentrations and its reduction potential in acetonitrile is 1.07 V versus Fc/Fc $^{+\, [17]}$ which matches well too with the different redox potentials of compound 3. The cation radicals of compound 3 were thus generated by either using $Cu(ClO_4)_2$ or $Fe(ClO_4)_3$ in acetonitrile and characterized by absorption and emission spectroscopy. Indeed compound 3 has three oxidizable sites and, as shown in the electrochemistry section, these oxidations occur step by step.

Here, only the evolution of the absorption spectra of compound **3** upon oxidation with $Cu(ClO_4)_2$ is displayed in

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Figure 4. Absorption spectra recorded upon oxidation of compound **3** by $Cu(ClO_4)_2$ in CH₃CN as a function of $R = [Cu^{H}]/[3]$, $[3] = 6.4 \times 10^{-5}$ mol L⁻¹. a) From R = 0 (black solid line) to R = 1 (black dashed line), b) from R = 1 (black solid line) to R = 2 (black dashed line), and c) from R = 2 (black solid line) to R = 3 (black dashed line).

Figure 4. The evolution of the absorption spectra of compound 3 upon oxidation with Fe(ClO₄)₃ shows a similar behavior (compare Figure S5 in the Supporting Information). Figure 4a displays the evolution of the absorption spectra of compound 3 upon oxidation with $Cu(ClO_4)_2$ from zero to one equivalent. Two bands gradually appear, one in the visible region at $\lambda =$ 472 nm, the other in the IR region at $\lambda = 1361$ nm, whereas the absorption band centered at $\lambda = 346$ nm decreases and shifts to $\lambda = 326$ nm. The new bands are attributed to the formation of the monocation radical centered on the triphenylamine core, that is, compound 3(I). TD-DFT calculations allow attributing these bands to various $\pi - \pi^*$ transitions. At $\lambda = 326$ nm, it comes from two transitions: one ($\lambda_{th}\!=\!370$ nm) from the S–2 orbital (delocalized on the entire molecule) to the S+1 orbital (localized on the two branches to which the dimethylamino groups belong) and one (λ_{th} = 337 nm) from the S-1 orbital (localized on the two branches where the dimethylamino



Figure 5. Representation of the main molecular orbitals involved in the electronic transitions of compound 3(I).

groups are) to the S+1 orbital (Figure 5). At $\lambda = 472$ and 1361 nm only one transition is involved: one from the SOMO to the S+1 orbital and one from the S-1 to the SOMO, respectively (Table S3 in the Supporting Information). Furthermore the SOMO is delocalized on the entire molecule.

One can observe in the UV/Vis region the appearance of isosbestic points: one around $\lambda = 264$ nm and another one at $\lambda = 386$ nm, which is in agreement with an equilibrium between only two different forms, that is, compounds **3** and **3(I)**.

By increasing the amount of $Cu(ClO_4)_2$, from R = 1 to 2, one dimethylamino moiety is then oxidized and compound 3(I) is transformed in compound 3(II). The evolution of the absorption spectra is shown in Figure 4b. The bands located at $\lambda =$ 326 and 472 nm decrease slightly and the band in the IR region is blue shifted from $\lambda = 1361$ to 1136 nm. Similarly, the band at $\lambda = 326$ nm corresponds to two $\pi - \pi^*$ transitions ($\lambda_{th} =$ 330 nm, HOMO \rightarrow L+2 and λ_{th} =320 nm, H-1 \rightarrow L+1), at λ = 472 nm to one π - π * transition (λ_{th} = 360 nm, HOMO \rightarrow L+1), and at $\lambda = 1136 \text{ nm}$ to one $\pi - \pi^*$ transition ($\lambda_{th} = 947 \text{ nm}$, HOMO \rightarrow LUMO), Table S4 in the Supporting Information). Isosbestic points are located at $\lambda = 271$, 375, and 410 nm, which is in agreement with an equilibrium between compounds 3(I) and **3(II)**. Similarly, from R=2 to R=3, the bands located at $\lambda =$ 313 and 1136 nm decrease, whereas new bands between $\lambda =$ 540 (S-2 \rightarrow SOMO), and 728 nm (SOMO \rightarrow S+1 and S-1 \rightarrow S+1) appear (Figure 4c) (see Table S5 in the Supporting Information). Isosbestic points are located at $\lambda = 284$, 380, 437, 472, and 848 nm corresponding to the equilibrium between compounds 3(II) and 3(III). These isosbestic points show that the oxidation is indeed achieved step by step and these different compounds can be observed one by one.

The fluorescence spectra upon oxidation were recorded in the same ranges of [oxidant]/[3] ratios as those used for the spectrophotometric oxidations and are shown in Figure 6. One can observe a similar behavior in the fluorescence spectra evolution upon oxidation with Cu(ClO₄)₂ or Fe(ClO₄)₃. This evolu-

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Figure 6. Emission spectra recorded upon oxidation of compound **3** by using $Cu(ClO_4)_2$ or $Fe(ClO_4)_3$ in CH₃CN as a function of $R = [\text{oxidant}]/[\mathbf{3}]$, $[\mathbf{3}] = 10^{-5} \text{ mol L}^{-1}$. a) From R = 0 (black solid line) to R = 1 (black dashed line), b) from R = 1 (black solid line) to R = 2 (black dashed line), and c) from R = 2 (black solid line) to R = 3.3 (black dashed line).

tion is not dependent of the oxidant that is used. As shown in the electrochemistry section, these oxidations occur step by step and because no particular reaction could occur in the excited state, one can suppose that the emission evolution is following the absorption one. So in this case, for one equivalent of oxidant, compound **3(I)** is the major form, and it is compound **3(II)** and compound **3(III)** with two and three equivalents, respectively.

One can observe a decrease of fluorescence intensity at $\lambda =$ 424 nm upon oxidation by either Cu(ClO₄)₂ or Fe(ClO₄)₃ from R = 0 to R = 1 (Figure 6a) and, respectively, with a factor of 4.4 and 5.0. The decrease of the overall fluorescence intensity is linear with the transformation of **3(0)** into **3(I)** (see Figure 57 in the Supporting Information) and the fluorescence quantum yield is calculated to be 0.39 for compound **3** and estimated to be 0.06 for compound **3(I)**. Then with oxidation of **3(I)** into **3(I)**, the fluorescence intensity at $\lambda = 424$ nm further decreases and concomitantly a new red-shifted band grows at $\lambda =$ 513 nm (Figure 6b). Compound **3(II)** is slightly fluorescent ($\Phi_F = 0.12$). Fluorescence is interestingly observed at $\lambda =$

513 nm, whereas an absorption band is observed at lower energies in the IR domain; this relatively rare situation probably indicates that, in this very delocalized species, fluorescence can be observed stemming from a S_n - S_0 transition, with n > 1. As shown in Figure 6 c, the fluorescence intensity decreases simultaneously to the appearance of compound **3(III)**, the fluorescence of which is negligible (quantum yield estimated below 0.0001).

One important characteristic of electrofluorochromic materials is the contrast ratio /fmax//fmin involving the fluorescence intensity at the same wavelength for compound 3 at different oxidation degrees. These results are gathered in Table 3. We can note that the contrast ratio between compounds 3 and 3(I) is ten because the solution contains compound 3 and compound 3(II) in a small amount. This is also the reason why the contrast ratio between compounds 3(I) and 3(II) is only three. The contrast ratio of ten (between compounds **3** and **3(I)** at $\lambda = 424$ nm) or 29 (between compounds 3 and **3(II)** at $\lambda = 424$ nm) is moderate. What is the most impres-

Table 3. Contrast ratio between the different oxidized species of compound 3.							
	3 ^[a]	3(I) ^[a]	3(II) ^[a]	3(III) ^[a]			
3 ^[b]	-	10	29	8344			
3(I) ^[b]	3	-	3	870			
3(II) ^[b]	1	2	-	290			
3(III) ^[b]	3232	1182	2915	-			
[a] At $\lambda =$ 513 nm [b] At $\lambda =$ 424 nm.							

sive observation is the contrast ratio of compound **3(III)** with all other species at $\lambda = 424$ or 513 nm, which is at least 290 and can be as high as 8344.

Finally, compound **3** is stable in four redox states with different spectroscopic properties. This behavior is not dependent of the used oxidant because one can observe the same evolution in the case of two different oxidants, that is, $Cu(ClO_4)_2$ or $Fe(ClO_4)_3$. Indeed it shows four different color states. In the neutral state, compound **3** is colorless whereas upon oxidation

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Figure 7. a) Absorption and b) fluorescence properties of the four redox states of compound 3.

it becomes yellow (compound **3(I)**) and then turns into green (compound **3(II)**) and blue (compound **3(III)**) when completely oxidized. Besides one of the redox states, namely compound **3(III)**, is not fluorescent and the three others emit light, compounds **3(0)** and **3(II)** at $\lambda = 424$ and 513 nm, respectively. In

the presence of one equivalent of oxidant, one can observe a low fluorescence band, which is more diffuse from $\lambda = 400$ to 600 nm. These properties are summarized in Figure 7.

In order to test the reversibility of the system, spectroelectrochemistry was performed in a tailored thin layer electrochemical cell.^[18]

Electronic absorption spectroelectrochemistry was recorded for a 5×10^{-4} m solution of compound **3** in acetonitrile. The results are shown in Figure 8. Upon gradual oxidation (Figure 8a), a broad band in the NIR region starts to appear simultaneously to another one centered at $\lambda = 470$ nm, whereas the band centered at $\lambda = 345$ nm gradually disappears. This NIR band is related to an intervalence chargetransfer (IVCT) process as was already observed in conjugated triphenylamine derivatives,^[19] but this time the IVCT process is observed with only one triphenylamine core. At intermediate potential (0.8 V) the NIR band starts to decrease in intensity and becomes blue shifted, whereas a new band first centered at $\lambda = 700$ nm and then progressively shifting to $\lambda =$ 740 nm starts to grow. All those data fit perfectly well with the behavior observed for chemical oxidation, evidencing that the same oxidized species are formed whatever the oxidation process is. Upon reduction from the fully oxidized state (Figure 8b), the recorded spectra show the same trend in the band evolution in the opposite direction: namely the NIR band increases at first and then decreases again, the $\lambda =$ 700 nm band quickly vanishes, whereas the $\lambda =$ 345 and 470 nm bands increases and decreases, respectively, in a symmetrical way. Even if the overall reduction process takes some time to convert the oxidized forms into the fully reduced one, one can estimate that the process is actually reversible with the same intermediate species formed at the forward and backward steps.

Then, the fluorescence intensity at $\lambda = 530$ nm was recorded in the same cell as a function of time, along with a CV curve at low scan rate (Figure 9). Comparison between the current and the fluorescence intensity when varying the potential clearly shows that the first oxidation leads to a dramatic quenching, whereas the second oxidation step leads to a slowdown in the fluorescence quenching with a small plateau. The third oxidation step induces quenching again. The process is reversible, as shown by the shape of the curves after the potential reversal, although the amplitude of the variation is smaller for the backward step. Compared to the fluorescence variation recorded upon chemical oxidation, it can be noticed that a non-monotonic behavior is observed in both cases, evidencing the fact



Figure 8. Electronic absorption (UV/Vis/NIR) spectroelectrochemistry of compound **3** in acetonitrile $(5 \times 10^{-4} \text{ M})$. a) Variation of the absorbance versus the wavelength upon increasing the potential from 0.2 V to the indicated value. The inset highlights the NIR region. b) Variation of the absorbance versus the wavelength upon decreasing the potential from 1.4 V to the indicated value. The inset highlights the NIR region. A background spectrum is recorded under open circuit potential and substracted from all other spectra.

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Figure 9. Current intensity (black dashed line, right scale) and fluorescence intensity (gray line, left scale) versus time for a cyclic voltammetry between 0.2 and 1.4 V at 10 mV s⁻¹ of compound **3** in acetonitrile and 0.1 m Bu₄NPF₆ on Pt. Potential measured versus a pseudo-reference Ag wire. Excitation wavelength: $\lambda = 375$ nm. Fluorescence intensity recorded at 530 nm.

that the successive oxidation steps have various influences on the fluorescence: the mono- and tricationic states are clearly non-fluorescent, whereas the dicationic one is probably weakly fluorescent. The contrast ratio lf_{max}/lf_{min} of five is the same order as the one obtained for thienoviologens (i.e,. lf_{max}/lf_{min} = 10). These values are enough to be seen at naked eye, even if they are lower than for other compounds.^[20]

We investigated the origin of the fluorescence at $\lambda = 530$ nm by recording excitation spectra when cycling the potential (see Figure S6 in the Supporting Information). Upon oxidation, a gradual decrease of the band centered near $\lambda = 355$ nm in the excitation spectra is clearly observed in the 0.5-1.0 V range, whereas in the 0-0.5 V potential range, that is, when compounds 3(0) and 3(I) are the main redox species, this band is unaffected. No new band in the excitation spectra below the emission wavelength ($\lambda = 530$ nm) can be seen upon oxidation. This behavior is reversible, cycling back the potential in the negative direction making the excitation band at $\lambda = 355$ nm growing again with the same shape. Thus, it can be concluded that the fluorescence observed at $\lambda = 530$ nm upon oxidation is correlated with the disappearance of the band at $\lambda = 355$ nm in the excitation spectra, which is also observed in the absorption spectra (see Figure 8). Thus, although compound 3(II) is actually luminescent, it is not surprising not to observe an increase in the fluorescence intensity in Figure 9, because the absorption at the excitation wavelength gradually decreases as compound 3(II) is formed. The exact origin of this fluorescence remains however still unclear because: 1) no new band appears in the excitation spectra when transforming compound 3(I) into compound 3(II) and 2) the fluorescence switch is not fully reversible when the potential is pushed toward the second and third oxidation states (see below). When the potential is slowly scanned upon the whole range allowing to reach the four redox states of compound 3, a modulation in the fluorescence intensity is observed, with a loss at the end of the first backward scan and a kind of steady-state behavior for the following scans (Figure S18 in the Supporting Information).

The cyclability of the fluorescence switch was also assessed upon successive potential steps by using the same system as above (described in the Experimental Section). Figure 10 (top) displays the corresponding variations of the fluorescence intensity measured at $\lambda = 430$ nm (excitation wavelength $\lambda =$ 265 nm) and the coulombic charges when potential steps are applied between -0.2 and +0.55 V, that is, when switching between compounds 3(0) and 3(1). One can observe that the fluorescence behavior totally follows the electrochemical signal, especially the fluorescence is fully recovered at the end of each cycle. This is not the case when the upper potential is pushed further to reach the second oxidation state 3(II). (Figure 10, bottom): as expected the amplitude of the first fluorescence decrease is higher, but the reversibility is clearly lower. It may seem not consistent with the result in Figure 9, in which the fluorescence intensity is almost reversible after the third oxidation, but Figure 10 shows a chronocoulometry during only 40 s. A longer time would give back a higher signal. The time required for a good cyclicibility is higher than the one observed for thienoviologens which is only five seconds. $\ensuremath{^{[21]}}$ The amount of recovered fluorescence at the end of each cycle depends on the potential values (not only the upper limit but also the lower one) and on the duration of each cycle. Leaving more time or bringing back the potential to a lower value has a positive impact on the reversibility.

Behavior upon protonation

Because of the presence of dimethylamino groups, compound **3** is not only sensitive to oxidation as previously demonstrated but also to acido–basic conditions. To the best of our knowledge, only few proton sensors based on triphenylamine derivatives have already been published, either based on chromic^[22] or fluorescent^[23] switch.

The acidic constants for the nitrogen atoms of the dimethylphenylamine and of the triphenylamine are around 11.5 and 1 in acetonitrile, respectively.^[24] Hence, the dimethylamino groups are more basic than the triphenylamine moiety and are protonated first. The lone electron pair of the nitrogen atom on the triphenylamine might be quaternized at higher proton concentrations. The structures of the different protonated forms of compound **3** are proposed in Scheme 3.

Therefore, a preliminary study of compound **3** was realized in order to check if the central nitrogen atom of the triphenylamine core could be protonated. A strong acid, the perchloric acid (pKa around -1 in acetonitrile)^[25] was used and the evolution of the absorption spectra upon protonation is shown in Figure 11. At low amount of protons, it is likely that only the nitrogen atoms on the dimethylamino groups could be protonated, then the third protonation occurred with about 10⁵ equivalents of protons and the solution became slightly blue.

Then the spectroscopic properties of compound **3** upon protonation by perchloric acid were investigated in more depth. The amounts effectively employed rose up to five equivalents of perchloric acid but in Figure 12 the evolution over the addition of only three equivalents is displayed, because no significant change in absorption or in fluorescence could then be detected before very high acid concentrations were reached (Scheme 3). During all the acidification process (from zero to more than three equivalents of $HClO_4$), the ab-



Figure 10. Comparison of the fluorescence intensity (black solid line) and the coulombic charge (gray dashed line) variations upon five successive potential steps from -0.2 to +0.55 (top) or -0.2 to +0.75 V (bottom) of compound **3** in acetonitrile and 0.1 M Bu₄NPF₆ on Pt. Potential measured versus a pseudo-reference Ag wire. Excitation wavelength: $\lambda = 265$ nm. Fluorescence intensity recorded at $\lambda = 430$ nm.



Figure 11. Absorption spectra recorded upon acidification of compound 3 by HClO₄ in CH₃CN, [3] = 1.0×10^{-5} mol L⁻¹.

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sorption band located around $\lambda = 340$ nm decreases and two isosbestic points appear at $\lambda = 265$ and 380 nm. Only one set of isosbestic points is observed even if there are normally two acid/base equilibriums because of the two nitrogen atoms.

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In order to know exactly which forms are in the solution upon protonation, an analysis of the spectrophotometric protonation data by the SPECFIT program was performed. Three hypotheses were investigated: only one protonation, two successive protonation steps, and two simultaneous protonation steps. Only the third hypothesis was confirmed. The reconstruction, from the calculated equilibrium constant, of the absorption spectra of compounds 3 and 3(H⁺)₂ (Figure 13a) is consistent with the experimental results, which provides a criterion for acceptability of the fit. Accordingly, Figure 13b presents the calculated distribution curves of compounds 3 and 3(H⁺)₂ and one can see that with three equivalents of protons, around 80% of compound 3 is transformed into compound 3(H⁺)₂, which is in agreement with the fact that no significant evolution in the absorption is observed after three equivalents of protons have been added. So the last spectrum (for three equivalents of HCIO₄) corresponds to the absorption of compound 3(H⁺)₂ and we cannot observe the formation of the monoprotonated form 3(H⁺).

Concerning the fluorescence behavior, the fluorescence intensity centered at $\lambda = 424$ nm decreases upon protonation, which is in agreement with the decreasing quantity of compound **3** and a band centered at $\lambda = 492$ nm appears at the same time. This latter band is characteristic of the **3(H**⁺)₂ form.

When three equivalents of H⁺ were added, no evolution in absorption nor in emission is observed and the absorption and emission spectra still correspond to the one of compound $3(H^+)_2$ (see Figure 12). The fluorescence intensity is thus modulated from the neutral form to the diprotonated form with two emission wavelengths, one centered at $\lambda = 424$ nm and the other one at $\lambda = 492$ nm. The quantum yield decreases from 0.39 for compound **3** to 0.20 for compound **3**(H⁺)₂. The **3**(H⁺)₃ form, formed at very low pH values, is non-emissive.

In summary, the spectroscopic properties of compound **3** can be influenced by addition of perchloric acid. By increasing the amount of protons in the solution, the strongly fluorescent compound **3** at $\lambda = 424$ nm turns into the slightly less fluorescent derivative **3**(**H**⁺)₂, which emits at $\lambda = 492$ nm and subsequently to the non-emissive compound **3**(**H**⁺)₃. The results clearly indicate that the triphenylamine derivative **3** is a highly efficient "on–on–off" switch for protons, displaying two specific emission wavelengths for the on-state system. In conclusion, the fluorescence modification of compound **3** in solution with the amount of protons shows that compound **3** can be used to monitor local acidity variations.

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Scheme 3. Representation of the successive protonated forms of compound 3



Figure 12. Spectra recorded upon acidification of compound 3 by HClO₄ in CH₃CN as a function of $R = [HCIO_4]/[3]$, $[3] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$. a) Absorbance and b) fluorescence behavior. $\lambda_{\rm exc} =$ 265 nm.

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Conclusion

In summary, N,N-di-[4"-(N',N'-dimethyl)-1',1"-biphenyl]-4-anisidine was synthesized by cross-coupling reactions and then studied by cyclic voltammetry, UV/Vis spectroscopy, and fluorescence spectroscopy. Spectroelectrochemistry reveals that this triphenylamine derivative has distinct electrochromic properties with four different color states (colorless, yellow, green, and blue) and three different emission properties (not emissive, purple, and green fluorescent), according to its redox state. These redox states can be reached either by chemical or electrochemical oxidation. Furthermore, upon successive protonation steps, this compound displays also three different behaviors in absorption (colorless, yellow, and blue) and in emission (purple, cyan, and non-emissive at increasing proton concentration). An on-on-off fluorescence switch by using only one molecule could therefore be observed with both redox and acid-base inputs.

Experimental Section

Spectroscopic measurements: UV/Vis absorption spectra were recorded on a Cary 5000 spectrophotometer in 1 cm optical length quartz cuvettes. The data were globally analyzed by the program SPECFIT Global Analysis System V3.0 for 32-bit Window System to determine the species obtained upon protonation and the thermodynamic constants. This program uses singular value decomposition and non-linear regression modeling by the Levenberg-Marquardt method.^[26] Corrected emission spectra were obtained on a Jobin-Yvon Horiba Spex FluoroMax-3 spectrofluorometer. Acetonitrile (SDS, spectrometric grade) was used as the solvent for absorption and fluorescence measurements. The fluorescence quantum yields were determined by using quinine sulfate in H_2SO_4 (0.5 N) as a standard ($\Phi_F = 0.546$).^[13b] The estimated experimental error is less than 10%. For the emission measurements, a right-angle configuration was used. Fluorescence decay curves in solution were obtained by using a time-correlated single-photon counting method by using a titanium-sapphire laser pumped by an argon ion laser (Tsunami, by Spectra-Physics, 82 MHz, 1 ps pulse width, repetition rate lowered to 4 MHz with a pulse peaker, a doubling crystal was used to reach $\lambda =$ 495 nm excitation). The Levenberg–Marquardt algorithm was used for the non-linear least-squares fit. Copper(II) perchlorate hexahydrate was commercially available from Aldrich.

Electrochemistry: Dichloromethane or acetonitrile (SDS, HPLC grade) and electrolyte salts (tetrabutylammonium hexafluorophosphate from Fluka, puriss.) were used without further purification. Cyclic voltammetry was performed in a three-electrode cell with a potentiostat (VersaSTAT4, Princeton Applied Research) driven by a PC. A carbon electrode disk (1 mm diameter) was used as the working electrode, whereas a platinum wire and Ag⁺ (0.01 M in acetonitrile)/Ag were used, respectively, as the counter and reference electrodes. All the investigated solutions were desaerated by argon-bubbling for at least 2 min before performing the electrochemical measure-



Figure 13. Reconstruction, from the calculated equilibrium constant of a) the absorption spectra of compounds **3** and of $3(H^+)_2$ and b) the calculated distribution curves of compounds **3** and $3(H^+)_2$ versus $[H^+]$. $[\mathbf{3}] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$.

ments. The reference electrode was checked versus ferrocene as recommended by IUPAC.

Electrofluorochromism: A thin-layer electrochemical cell (Pt minigrid working electrode, Ag pseudo-reference electrode, Pt counter electrode) was filled with the solution of the compound of interest. For fluorescence spectroelectrochemistry, excitation and emission were focused on the working electrode through optical fibers connected to a Jobin–Yvon Fluorolog 3 spectrophotometer. The fluorescence near the maximum emission wavelength was recorded versus the time simultaneously to the current corresponding to low scan rate cyclic voltammetry (10 mV s^{-1}). The electrochemical cell was connected to a CHInstruments (CHI 600) potentiostat driven by a PC. For UV/Vis spectroelectrochemistry, the thin-layer cell was directly inserted in the spectrophotometer (Cary 5000, Varian). The spectrum for open circuit potential was recorded and used as background for all other subsequent spectra.

Quantum chemical calculations: Calculations were performed at the MESO calculation centre of the ENS Cachan (Nec TX7 with 32 processors of type Itanium 2). Molecules were drawn with the Gaussview 03 software by using included templates and their geometry optimized at the B3LYP/3-21g(d) level of theory.^[27] Infrared spectra were calculated on the final geometry to ascertain that a minimum was obtained (no negative frequencies). Time-dependant density functional theory (TDDFT) calculations at the PBE0 level of theory with the 6-31g(d) basis set were subsequently performed. Reconstructed absorption spectra have been obtained by convolution of Gaussian functions for each calculated transition with a full width at half maximum (FWHM) of 2500 cm⁻¹ and a surface equals

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to the oscillator strength as implemented in GaussSum^{^{[28]}} The $\varepsilon_{\rm calcd}$ value was thus obtained at the maximum of the band.

Synthesis: Reagents were commercially available from Aldrich and used without further purification. Column chromatography was performed with SDS 0.040–0.063 mm silica gel. All compounds were characterized by the usual analytical methods:¹H and ¹³C NMR spectra were recorded with a JEOL ECS (400 MHz) spectrometer. All chemical shifts are referenced to the solvent peak (*J* values are given in Hz). Melting points were measured with a Kofler melting-point apparatus. IR spectra were recorded with a Nicolet Avatar 330 FTIR spectrometer.

N-4-Bromophenyl-4-anisidine (1): To a solution of palladium chloride (35 mg, 0.197 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (148 mg, 0.271 mmol) in dried toluene (5 mL) under an argon atmosphere was added 1,4-dibromobenzene (5.81 g, 24.63 mmol) at room temperature. The resulting mixture was stirred for 10 min. Then sodium tert-butoxide (1.92 g, 19.98 mmol) and 4-anisidine (1.06 g, 8.61 mmol) were added to this mixture and stirred at 110 °C for 44 h. The reaction mixture was cooled to room temperature and water (10 mL) was added. The aqueous layer was extracted with CH₂Cl₂ (3×10 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by a silica gel flash chromatography (dichloromethane/PE (2:8) to dichloromethane) to give compound 1 (1.33 g, 81%) as a gray solid. M.p. 84°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.29$ (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 8.7 Hz, 2H), 6.89 (d, J=8.7 Hz, 2H), 6.76 (d, J=8.7 Hz, 2H), 5.52 (s, 1H), 3.82 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.7, 144.5, 135.1, 132.1, 122.8, 117.0, 114.8, 111.0, 55.6 ppm; IR: $\tilde{\nu}$ = 3419, 3050-2850, 1594, 1508, 1491, 1243, 1030, 813cm⁻¹.

N,N-Di(4-bromophenyl)-4-anisidine (2): To a solution of tris(dibenzylideneacetone)dipalladium(0) (282 mg, 0.308 mmol) and 1,1'-bis-(diphenylphosphino)ferrocene (230 mg, 0.421 mmol) in dried toluene (10 mL) under an argon atmosphere was added 1,4-dibromobenzene (5.17 mg, 21.92 mmol) at room temperature. The resulting mixture was stirred for 10 min. Then sodium tert-butoxide (1.53 g, 15.92 mmol) and N-4-bromophenyl-4-anisidine (1) (1.12 g, 5.25 mmol) were added to this mixture and stirred at 110 $^{\circ}$ C for 15 h. At this time, the starting materials had disappeared as judged by TLC. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was purified by a silica gel flash chromatography [dichloromethane/PE (2:8) to dichloromethane/PE (3:1)] to give compound 2 (1.74 g, quantitative yield) as a white solid. M.p. 75 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.32$ (d, J = 9.2 Hz, 4H), 7.07 (d, J = 9.2 Hz, 2H), 6.93 (d, J=8.7 Hz, 4H), 6.88 (d, J=8.7 Hz, 2H), 3.82 ppm (s, 3 H); $^{13}{\rm C}$ NMR (100 MHz, CDCl_3): $\delta\!=\!156.7,\;146.8,\;139.7,\;132.2,$ 127.4, 124.3, 115.1, 114.6, 55.5 ppm; UV/Vis (CH₂Cl₂): λ_{max} (ε) = 304 nm (26000 L cm⁻¹ mol⁻¹); IR: $\tilde{\nu} = 3050 - 2830$, 1578, 1504, 1482, 1237, 813cm⁻¹; $\Phi_{\rm F}$ = 0.0004 in CH₃CN.

N,N-Di-[4"-(*N',N'*-dimethyl)-1',1"-biphenyl]-4-anisidine (3): In a Schlenk flask under an argon tetrakistriphenylphosphine (130 mg, 0.112 mmol, 0.05 equiv) was added to a solution of *N,N*bis-(4'-bromophenyl)-4-anisidine (999 mg, 2.31 mmol, 1.0 equiv) in toluene (15 mL). The mixture was stirred at room temperature for 15 min and then solutions of 4-(*N,N*-dimethylamino)phenylboronic acid (846 mg, 5.13 mmol, 2.2 equiv) in methanol (7 mL) and of sodium carbonate (985 mg, 9.29 mmol, 4.0 equiv) in distilled water (4.6 mL) were added. The mixture was heated at 80 °C for 7 h. After the mixture was cooled down, dichloromethane (50 mL) and saturated ammonium chloride solution (50 mL) were added. Organic compounds were extracted with dichloromethane (3×50 mL). The combined organic phases were dried over anhydrous sodium sul-

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fate, filtrated, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (dichloromethane/PE (2:8) to dichloromethane) to give compound **3** (1.06 g, 89%) as a white solid. M.p. 243 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (d, *J* = 8.7 Hz, 4 H), 7.44 (d, *J* = 8.2 Hz, 4 H), 7.15 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 4 H), 6.87 (d, *J* = 9.2 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 4 H), 3.82 (s, 3 H), 2.99 ppm (s, 12 H); ¹³C NMR (100 MHz, CDCl₃): δ = 156.2, 149.7, 146.5, 141.0, 134.8, 129.2, 127.4, 127.3, 126.9, 123.3, 114.9, 113.0, 55.6, 40.8 ppm; UV/Vis (CH₃CN): λ_{max} (ε) = 346 nm (43400 L cm⁻¹mol⁻¹); IR: $\tilde{\nu}$ = 3029, 2890, 1608, 1494, 1444, 1317, 1285, 1233, 1164, 1028, 945, 840, 807 cm⁻¹; MS: calcd for C₃₅H₃₅N₃O: 514.2853 [*M*+H]⁺; found: 514.2845; $\Phi_{\rm F}$ = 0.39 in CH₃CN; τ = 2.2 ns; E° (C, CH₂Cl₂) versus ferrocene: 0.02, 0.23, 0.54 V.

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FULL PAPER



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Redox- and Protonation-Induced Fluorescence Switch in a New Triphenylamine with Six Stable Active or Non-Active Forms



On-off-on-off: A triphenylamine (TPA) derivative (see figure) sensible to oxidation and protonation was designed and synthesized. Its photophysical and electrochemical properties were investigated. This compound leads to six redox or acidic stable states with various colors (yellow, green, blue, colorless). The emission properties can also be modulated with oxidation or protonation (purple, cyan, green, no fluorescence).

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