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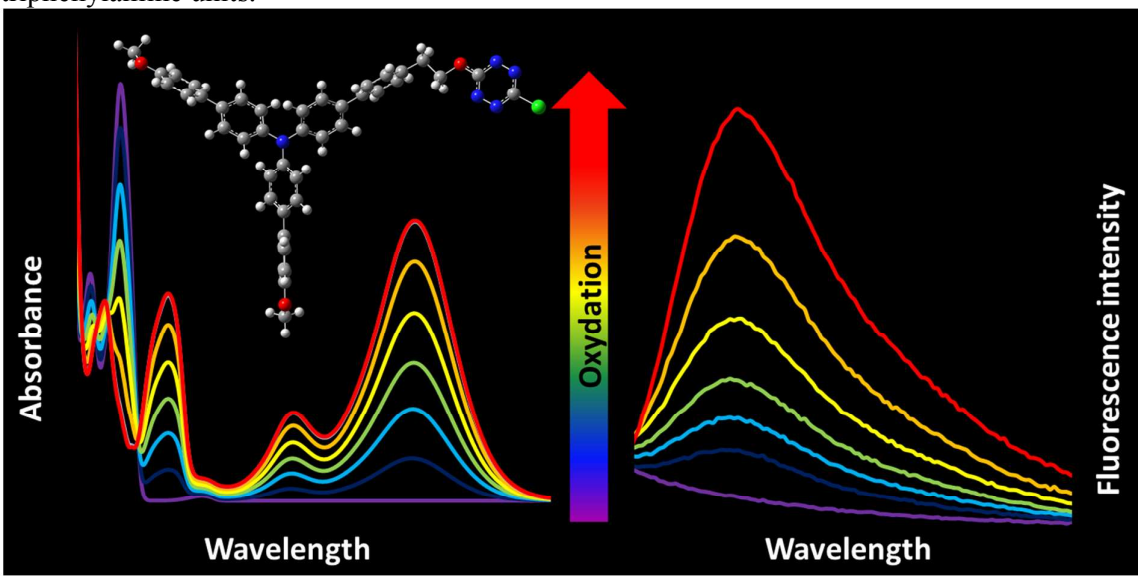
This study allowed us to design efficient electrofluorochromic dyads based on tetrazine and triphenylamine units.



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ARTICLE

Original electroactive and fluorescent bichromophores based on non-conjugated tetrazine and triphenylamine derivatives: Towards more efficient fluorescent switches.

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The synthesis, photophysical and electrochemical properties and their interplay as well as theoretical calculations studies of newly designed fluorescent and electroactive derivatives are described. These molecules are composed of two fluorophores: one triphenylamine, electron-rich unit, and one tetrazine, electron-poor unit, connected by two different links. While in the neutral state the bichromophores are not fluorescent, due to a photoinduced electron transfer from the triphenylamine unit to the tetrazine unit, the fluorescence is restored in the oxidative state (oxidation of the triphenylamine moiety).

Introduction

For some years now, we showed interest in the study of fluorescent electroactive chromophores based on tetrazine[1-5] or triphenylamine.[6, 7] These molecules present a different behaviour in their photophysical properties according to the redox state of the molecule (neutral, oxidized or reduced state). For example, interplay between fluorescence and redox characteristics has been studied in the case of *N*,*N*,*N*-tri-(4-methoxy-1,10-biphenyl)amine and led to a reversible switching of the fluorescence.[7] However, while there is interest and possible applications to study the reversible fluorescence electrochemical switch of a molecule composed of a single both fluorescent and electroactive unit,[8-10] multiple fluorophore systems[11-15] present their own advantages (e.g., on-off two states system, multiwavelength switch, more recyclable system since the chromophore is not destroyed). Recently, we studied dyads composed of a triphenylamine as electroactive donating group and a tetrazine as fluorophore accepting group.[13, 14] The goal was to get tetrazine-triphenylamine dyads which behave as a redox mediated off-on fluorescence switch (Figure 1). The major issue of these bichromophores is that emission of tetrazine was weakly restored upon oxidation with low fluorescence quantum yields because of a possible energy transfer.[13] In order to avoid this latter transfer and so to enhance the fluorescence quantum yield, design of new bichromophores with a bathochromic shift of the cation radical absorption has been explored. Thus we have synthesised several dyads featuring one triphenylamine moiety bearing different donating groups on their *para* position (to insure the bathochromic shift)[7] and a chlorotetrazine that stands for the electron poor fluorescent moiety (Figure 1). Chloroalkoxytetrazine are known to be more fluorescent than dialkoxytetrazine[5, 16] which explains why bichromophoric compounds based on chlorotetrazine are more efficient.[13] In addition we have chosen a link composed of 3 or 4 atoms (C and O atoms) instead of a unique oxygen atom because the phenoxytetrazine derivatives are not highly fluorescent.[17, 18]

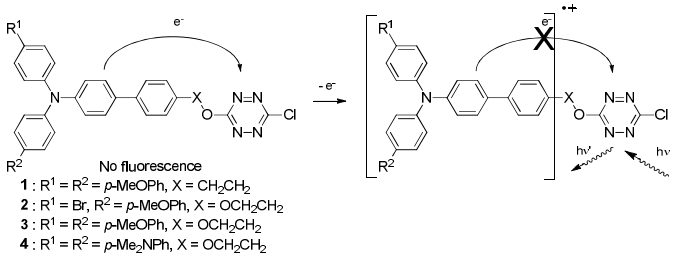


Figure 1. Design of two redox states system with different fluorescence properties.

Results and discussion

Synthesis

Designs of triphenylamine precursors were rationalized in order to make possible nucleophilic aromatic monosubstitution of 3,6-dichloro-*s*-tetrazine, $TzCl_2$ (Figure 2). Knowing that $TzCl_2$ can undergo easily monosubstitution with alcohol compounds,[1, 5] we therefore decided to synthesize triphenylamine derivatives functionalized with a short chain ended with a primary alcohol function. Triphenylamines are well known to form stable cation-radicals[7, 19, 20] but also to polymerize by their *para* positions when this latter remains unsubstituted.[21, 22] For our future applications, it was thus necessary to also prepare triphenylamine compounds bearing groups in the *para* positions of phenyl groups such as bromo, methoxy phenyl or dimethylaminophenyl groups to avoid the possible polymerization. Precursor compounds **5**, **6**, **7** and **8** were then targeted.

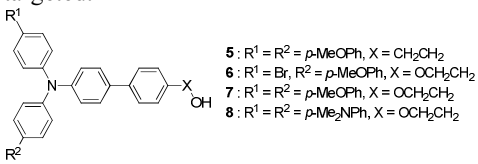


Figure 2. Design of nucleophilic triphenylamine derivatives.

On the one hand, 2-(4-bromophenyl)-ethanol was protected through an acetal function[23] in a quantitative way to give **9**. On the other hand, 2-bromoethanol was protected in its THP adduct[23] to give compound **10** in 84% yield (Figure 3). A Williamson reaction between **10** and *p*-iodophenol with usual heating[24] led to product **11** in quasi-quantitative way.

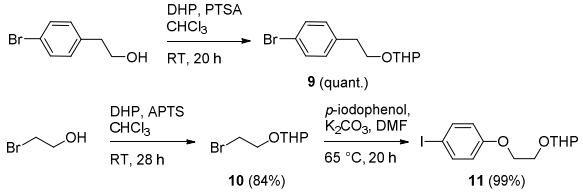


Figure 3. Synthetic route to protected precursors **9** and **11**.

The synthetic route to the nucleophilic triphenylamine derivatives **5**, **6**, **7** and **8** is shown in Figure 4. The brominated intermediaries **9** or **11** were placed in the Suzuki-Miyaura[25-28] reaction conditions with the corresponding triphenylamine boronic acid to give the triphenylamine derivatives **12** and **13** in good yields (respectively 84% and 91%).

The compounds **14** and **15** were then obtained by dibromination of **12** and **13** using *N*-bromosuccinimide.[29] The presence of bromine atoms in *para* positions on the triphenylamine derivatives **14** and **15** opens the possibilities to several further functionalizations. In particular, having on these *para* positions more electron donating group could induce an absorption shift of the cation-radical and we could thus avoid the fluorescence extinction due to an energy transfer which has already been observed in the case of bromine or methyl substituents.[13] Suzuki-Miyaura reactions were therefore realized between, on one hand the dibrominated compound **14** or **15**, and on the other hand *p*-methoxyphenylboronic acid or *p*-dimethylaminophenylboronic acid to give the precursors **16**, **17**, **18** and **19**. They were then deprotected[30, 31] to give the nucleophilic triphenylamine derivatives **5**, **6**, **7** and **8**.

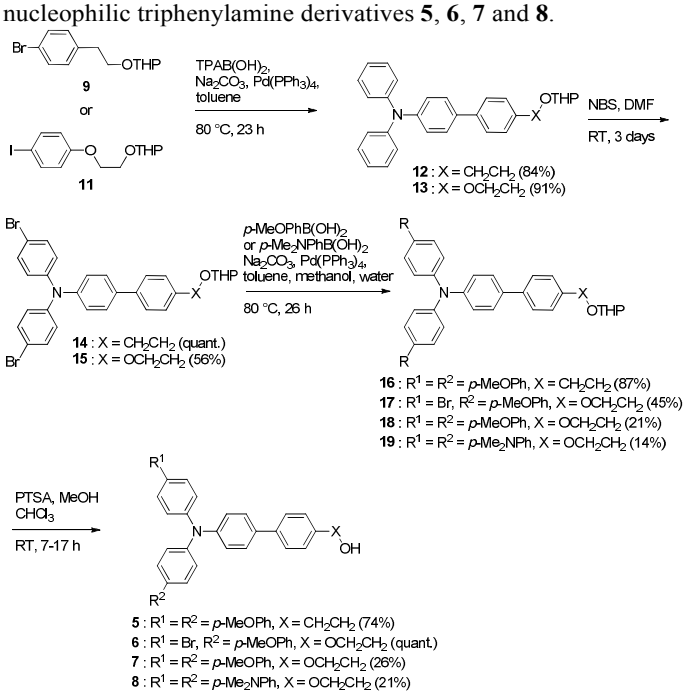
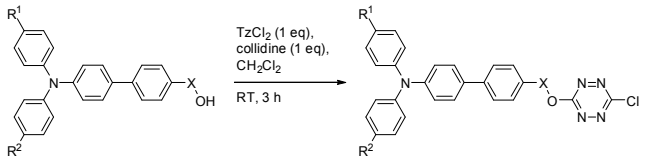


Figure 4. Synthetic route to nucleophilic triphenylamine derivatives **5**, **6**, **7** and **8**.

The bichromophoric derivatives **1**, **2**, **3** and **4** were synthesized employing SN_{Ar} on $TzCl_2$. Benefiting from the pioneering work of Hiskey and Chavez,[32-34] multi-grams synthesis of $TzCl_2$ has been previously optimized in our group.[5] The nucleophilic aromatic monosubstitution of $TzCl_2$ has been achieved in the presence of one equivalent of collidine, with a large variety of nucleophiles, particularly with alcohols.[4, 35-40] The introduction of one equivalent of nucleophiles **5**, **6**, **7** and **8** were realized on $TzCl_2$ at room temperature with the usual procedure,[5] affording compounds **1**, **2**, **3** and **4** in reasonable yields, from 43 to 83% (Figure 5).



5 : $R^1 = R^2 =$ *p*-MeOPh, X = CH_2CH_2
6 : R^1 = Br, R^2 = *p*-MeOPh, X = OCH_2CH_2
7 : $R^1 = R^2$ = *p*-MeOPh, X = OCH_2CH_2
8 : $R^1 = R^2$ = *p*-Me_2NPh, X = OCH_2CH_2

1 : $R^1 = R^2$ = *p*-MeOPh, X = CH_2CH_2 (83%)
2 : R^1 = Br, R^2 = *p*-MeOPh, X = OCH_2CH_2 (69%)
3 : $R^1 = R^2$ = *p*-MeOPh, X = OCH_2CH_2 (81%)
4 : $R^1 = R^2$ = *p*-Me_2NPh, X = OCH_2CH_2 (43%)

Figure 5. Synthetic routes to bichromophoric compounds **1**, **2**, **3** and **4** *via* SN_{Ar} on $TzCl_2$.

Hence, the syntheses of four new bichromophoric compounds based on tetrazine and triphenylamine moieties have been successfully realized in few steps using the key SN_{Ar} on 3,6-dichloro-*s*-tetrazine, $TzCl_2$.

Electrochemical investigations

The redox properties of the bichromophores **1**, **2**, **3** and **4** were investigated by cyclic voltammetry (CV). Electrochemical data are summarized in Table 1. Concerning **1**, **2** and **3**, three well defined redox systems can be identified corresponding to the reduction of tetrazine moiety into its anion radical and to the two successive oxidation of triphenylamine moiety (see Figure 6 for **1** and SI for **2** and **3**). The four potentials measured in the case of **4** (see SI) correspond to the reduction of the tetrazine moiety and to successive oxidation steps involving each amine moiety through a one electron process, as we already observed on another triphenylamine derivative.[6] The value of 0.13 V corresponds to the oxidation of the central nitrogen on triphenylamine. This oxidation is the easiest one due to the electronic delocalization with the phenyl rings. The two higher values correspond to the oxidations of the two dimethylamino moieties, which are not independent. These peaks are fully reversible although the peak-to-peak separation is greater than 60 mV, due to electron transfer kinetics as already mentioned for tetrazine.[13, 35, 36] The CVs also confirm that substitution on the *para* positions of the triphenylamine inhibits its polymerization. **4** shows a first oxidation potential lower than **3** because the dimethylamino group is more electron donor than the methoxy group and, thus, make the oxidation easier. Similarly, **2** has a higher oxidation peak than **3** because **2** has an electron withdrawing bromine atom, instead of a methoxyphenyl group, which destabilizes the cation radical. Interestingly, the nature of the substituents of the triphenylamine and the nature of the link also influence the reduction potential of the tetrazine. Especially compound **4** which bears a highly donating triphenylamine displays a lower potential (more negative) than the one of **3** which is itself lower than the one of **2**, in agreement with successive replacement of a strong electron donor group (dimethylamino) by a lower one (methoxy) and an electron withdrawing bromine atom. In comparison, generic 3-(adamantan-1-yl)methoxy)-6-chloro-*s*-tetrazine is reduced at -0.85V.[1] There is also an influence of the linker. **1** presents a lower (more negative) reduction potential than **2.** This is not clear if this is due to the shorter link (CH_2-CH_2-O compared to O-CH_2-CH_2-O), or to the different electronegativity of the atoms (C versus O). These conclusions, especially the ones concerning the influence of the triphénylamine through a non-conjugated link, appear unusual for a two carbons non-conjugated link.

Table 1. Electrochemical data for compounds **1**, **2**, **3** and **4**. Potentials are referenced to Fc^+/Fc. All measurements in dichloromethane + 0.1 M Bu_4NPF_6 on glassy carbon C.

Compounds	1	2	3	4
$E^{0/-1}$ (V)	-0.97	-0.82	-0.96	-1.27
$E^{1/0}$ (V)	0.39	0.54	0.31	0.13
$E^{2/1}$ (V)	0.97	1.4	1.15	0.48
$E^{3/2}$ (V)	-	-	-	0.66

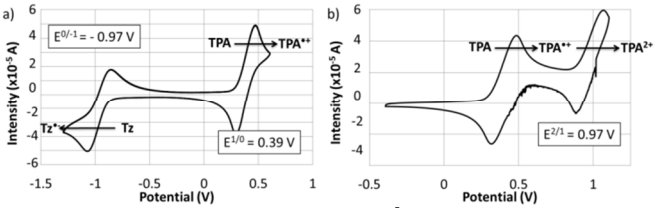


Figure 6. Cyclic voltammetry of **1** (10^{-5} M) in dichloromethane + 0.1 M Bu_4NPF_6 on glassy carbon C. Potentials are referenced to Fc^+/Fc. Scan rate: 80 mV/s.

In conclusion, the two redox moieties are indeed electroactive and behave independently in the various dyads.

Photophysical studies

The absorption spectra of these new synthesized compounds were registered and the one of **1** is displayed in Figure 7 as a typical example; the absorption data have been otherwise collected in Supporting Information. The transitions types were determined from quantum chemical calculations (TDDFT, data in table S1 and S3). These bichromophores display three bands and their absorption properties are similar to the sum of the disconnected parts. For all compounds, there are two intense bands in the UV region which are attributed to π–π* transitions located both on tetrazine and triphenylamine units (see Figure 8 for **1** and SI for **2**). We can note that the band localized at around 260 nm is not dependent of the substituents on the triphenylamine (or the link) whereas the band localized between 326 and 345 nm is influenced. The third band is located around 510 nm and displays a weak molar absorption coefficient (around 700 $L.mol^{-1}.cm^{-1}$) because of a forbidden n-π* transition centered on the tetrazine unit. This transition is very weakly sensitive to substituents effects on the triphenylamine moiety.[1, 4, 13, 14]

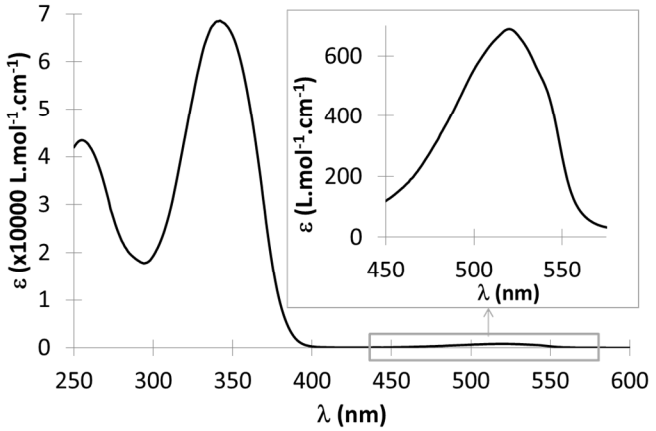


Figure 7. Molar absorption coefficient of compound **1** in dichloromethane. Inset shows the molar absorption coefficient of **1** in 450-600 nm region.

Table 2. Absorption wavelength (λ, nm), molar absorption coefficient (ε, $L.mol^{-1}.cm^{-1}$), emission wavelength (λ_{em}, nm), fluorescence quantum yield (Φ) and fluorescence lifetime (τ, ns) for **1**, **2**, **3** and **4** in acetonitrile.

Compounds	λ_{abs}	ε	λ_{em}	Φ	τ
1	255 342 520	43400 68600 690	418	0.004[a]	n.d.[b]
2	257 326 511	30200 55000 690	415	0.001[a]	1.18 and 0.018
3	258 337 511	36200 57800 670	417	0.008[a]	1.61 and 0.015
4	n.d.[b] 345 507]	n.d.[b] 43500 690	426	0.06[a]	n.d.[b]

[a] Fluorescence quantum yields measured with quinine sulfate in H_2SO_4 (0.5 N) as a standard (Φ_F =0.546), λ_{exc}=326 nm.[41] [b] not determined

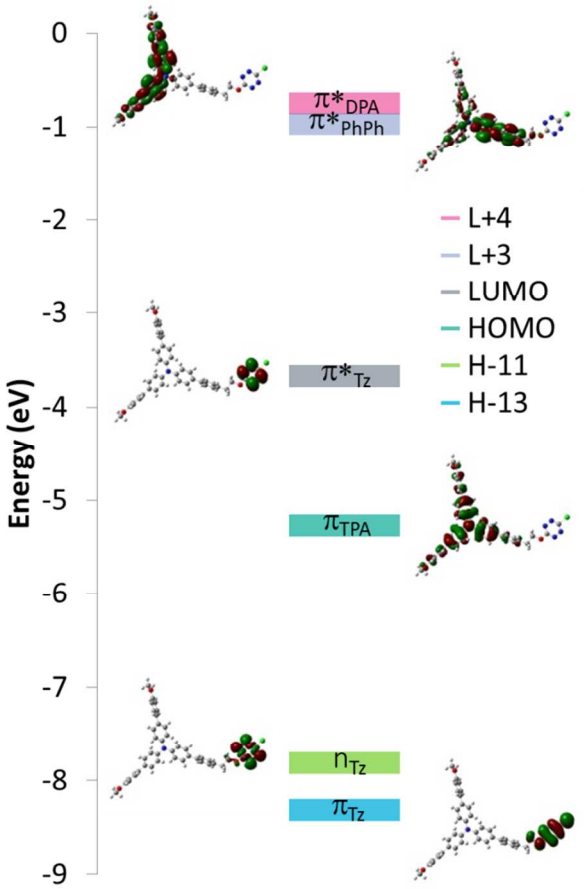


Figure 8. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **1**.

Even if the triphenylamine and tetrazine units can be highly fluorescent when they are disconnected, the bichromophoric compounds **1-4** are very weakly fluorescent in their neutral state as expected. This is due to a quenching by a photoinduced electron transfer from the triphenylamine to the tetrazine moiety because of the proximity of the two parts. Indeed this behaviour was previously observed in a bimolecular process in solution[4] and in some other bichromophoric compounds.[13, 14] For all bichromophoric compounds, the fluorescence quantum yields are much lower than 0.1. Estimation for **1**, **2**, **3** and **4** is collected in Table 2. For example, the fluorescence quantum yield of **3** is 0.008 even when it is 0.37 and 0.38 for *N*,*N*,*N*-tri-(4'-methoxy-1,1'-biphenyl)amine[7] and 3-chloro-6-methoxytetrazine[1] respectively. The excitation wavelength is 326 nm where both triphenylamine and tetrazine units absorb. The emission maxima localized at around 420 nm and the lifetimes correspond to the triphenylamine core. The lifetimes of the precursor **6** are namely 1.23 and 0.023 ns. Despite the quenching, the triphenylamine part still slightly emits, while the tetrazine fluorescence is completely quenched.

Redox-dependent spectroscopy

At neutral state, there is no fluorescence of the bichromophoric compounds in the tetrazine emission region but there is still

some remaining fluorescence from the triphenylamine unit. Fluorescence of both triphenylamine (electron donor moiety) or tetrazine (electron acceptor moiety) parts are nearly or completely cancelled out by an electron transfer from triphenylamine to tetrazine. When triphenylamine will be oxidized, the electron transfer should not occur and thus the fluorescence of tetrazine should be restored (Figure 1). To check this assumption, the triphenylamine was oxidized into its cation radical. We chose a one-electron chemical oxidant: $Cu(ClO_4)_2$ was used as a mild and clean oxidant and has been recently reported to effectively generate arylaminium cation-radicals.[6, 13, 14, 42-44] Another advantage of using $Cu(ClO_4)_2$ is that it gives no absorption or emission in the UV-visible domain at low concentrations and its reduction potential in acetonitrile is 0.7 V *vs.* Fc/Fc^+, which matches well with the first oxidation potentials of **1**, **2**, **3** and **4**. The cation-radicals of the triphenylamine derivatives are thus generated using $Cu(ClO_4)_2$ in acetonitrile, this being the most suitable solvent to dissolve both the oxidant and the bichromophoric compounds, and are characterized by absorption and emission spectroscopies.

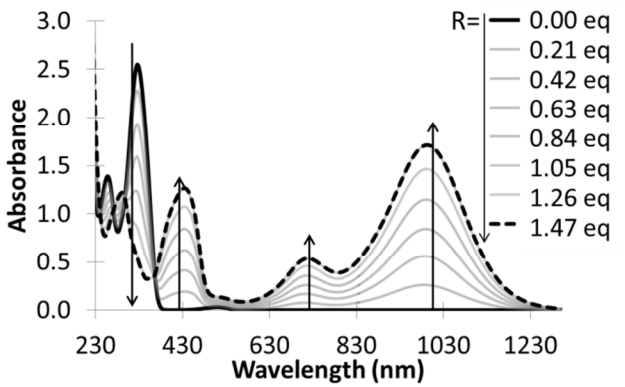


Figure 9. Absorption spectra recorded upon oxidation of **2** by $Cu(ClO_4)_2$ in CH_3CN as a function of $R=[Cu^{II}]/[\mathbf{2}]$, $[\mathbf{2}]=1.1\ 10^{-5}$ $mol.L^{-1}$.

Upon titration with $Cu(ClO_4)_2$, two absorption bands in the UV region (λ=257 and 326 nm) decrease whereas four bands gradually appear at 291, 434, 718 and 991 nm for **2** (Figure 9**Error! Reference source not found.**; Supporting Information for **1**, **3** and **4**). The new absorption bands are attributed to the formation of the cation-radical centered on the triphenylamine core by comparison with the absorption spectrum of the radical cation of triphenylamine derivatives.[7] One can also observe the appearance of four isosbestic points at 240, 271, 297 and 367 nm for **2** in agreement with the existence of an equilibrium between the triphenylamine derivative and its cation-radical. Since the absorption spectra with 1.26 and 1.47 equivalent of oxidant overlap, oxidation is complete when 1.26 equivalents of $Cu(ClO_4)_2$ is added for **2**. $Cu(ClO_4)_2$ is clearly not strong enough to perform further oxidations. Similar behaviours upon oxidation have been noticed in the cases of **1**, **3** and **4**. Note that in the case of **4** at least three equivalents of oxidant are necessary to complete the compound conversion, in agreement with the three oxidation potentials which all lie below 0.7 V.

It is important to note that these four oxidized bichomophoric compounds **1**, **2**, **3** and **4** have a really weak absorption between 500 and 625 nm, which corresponds to the fluorescence domain of the tetrazine unit. In the case of previously reported compounds having weaker donor substituents on the triphenylamine,[13, 14] an energy transfer towards the cation-radical (made possible by an overlap of its absorbance and its emission) partially quenches the fluorescence of the tetrazine at the oxidized state (through FRET). From this perspective, these four compounds demonstrate a significant improvement compared to the previous studied bichromophoric compounds thanks to the donor substituents on the triphenylamine part.

The fluorescence spectra were recorded upon oxidation in the same $[Cu^{II}]/[dyad]$ ratios as those used for the spectrophotometric titrations. In order to determine the ideal excitation wavelength, excitation spectra of the oxidized bichromophoric compounds were measured (as exemplified for 3 on Figure 10).

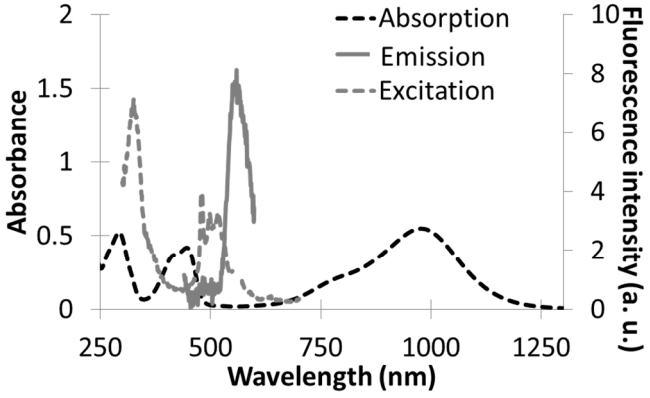


Figure 10. Absorption emission (λ_{exc}=330 nm) and excitation (λ_{em}=560 nm) of oxidized **3** in acetonitrile.

In general, isosbestic points are often chosen for excitation. But in our case, the tetrazine part does not absorb at all the isosbestic points. Therefore they are not suitable for excitation. The maximal absorption wavelength is around 326 nm in the excitation spectra for all these compounds. This is the reason why this wavelength has been chosen as the excitation wavelength for the study of the changes of the emission upon oxidation. The diminution of absorption at 326 nm during the process comes from the oxidation of the triphenylamine in its cation-radical, but the quantity of tetrazine remains the same and the number of photons absorbed by tetrazine core remains constant.

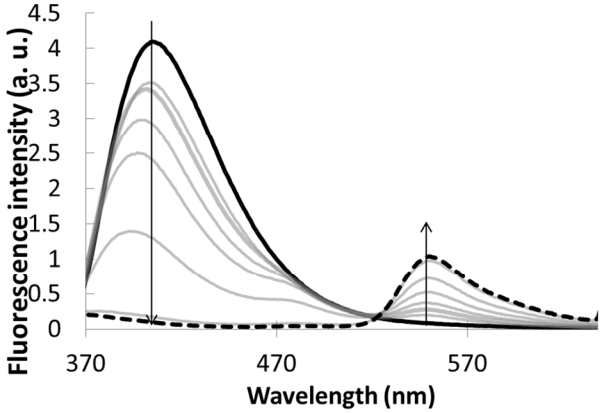


Figure 11. Emission spectra recorded upon oxidation of **2** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**2**], [**2**]=1.1 10^{-5} mol.L^{-1}, λ_{exc}=326 nm.

Emission spectra upon gradual addition of $Cu(ClO_4)_2$ are displayed in Figure 11 for compound **2** (see Supporting Information for **1**, **3** and **4**). A decrease of the band localized at 415 nm (respectively 429 and 417 for **1** and **3**) typical of the remaining triphenylamine emission is observed. Indeed the quantity of triphenylamine diminished upon oxidation and its cation-radical does not emit. In the case of **4** a more complex evolution of the fluorescence is observed that is attributed to the formation of various oxidized forms of the triphenyl amine. Similar behavior has been studied by us on the related triphenylamine compound *N,N*-di-[4''-(*N',N'*-dimethyl)-1',1''-biphenyl]-4-anisidine.[6]

A fluorescence band localized at 550 nm for **2** (558 nm for **3**) appears concomitantly to the disappearance of the emission of the triphenylamine. The emission wavelength and the lifetime of 153 ns for **2** (155 ns for **3**) are typical of the tetrazine emission. It has thus been possible to regenerate the tetrazine fluorescence with compounds **2** and **3** upon oxidation of the triphenylamine moiety with Cu(II). Unfortunately the recovery is only partial. In the case of **1** and **4**, the tetrazine fluorescence could not be restored. For compound **4**, the tetrazine fluorescence is probably not strong enough and could be hidden by the triphenylamine fluorescence. We did not try to oxidize electrochemically the compounds in a suitable cell, because it was likely that the electrochemical switch of fluorescence (electrofluorochromism) would be observable with difficulties in these conditions, because of the partial recovery.

In order to explain the evolution of the fluorescence of these bichromophoric compounds upon oxidation, we identified the relative redox properties of the various neutral, ionic and excited states of both chromophores thanks to the electrochemical and spectroscopic data. The results are summarized on a redox scale in Figure 12. The value of the potential Tz^*/Tz^- has been determined according to the formula:

$$E^0_{Tz*/Tz^{\bullet-}} = E^0_{Tz/Tz^{\bullet-}} + \Delta E_{0-0}(Tz)$$

Where $E^0_{Tz*/Tz^{\bullet-}}$ is the reduction potential of the bichromophoric compound in its excited state and $\Delta E_{0-0}(Tz)$ is the difference between the lower vibrational energy levels of the excited and fundamental states of the tetrazine part and estimated from the n-π^* band.

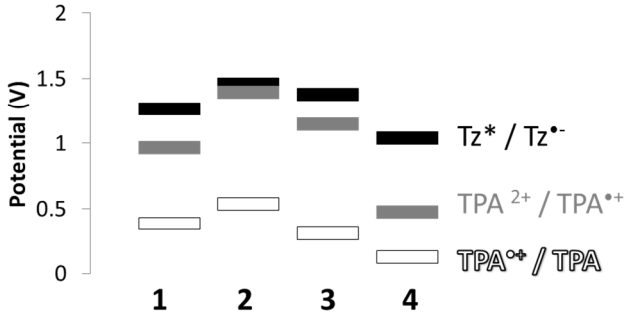


Figure 12. Redox scale for the neutral, ionic and excited-state tetrazine (Tz) and triphenylamine (TPA) couples vs. ferrocene.

The lack of fluorescence corresponding to the tetrazine in the bichromophoric species can be explained when one looks at all redox potentials. Indeed, in any case, the absorption of one photon leads to an excited state in which a photinduced electron-transfer (PET) is thermodynamically favored from the triphenylamine or its radical-cation to the tetrazine. This is due to the donating substituents on the triphenylamine part which lowers the first two oxidation potentials combine with the exceptionally high reduction potential of the tetrazine in its excited state. The magnitude of the difference

$$E^0_{Tz*/Tz^{\bullet-}} - E^0_{TPA^{2+}/TPA^{\bullet+}}$$

can be related to the retrieval or not of the fluorescence in the dyads. For **2** this difference is quite small, indicating that in this case the PET when the triphenylamine is oxidized is less favorable and allows a partial recovery of the tetrazine fluorescence. This difference is larger for **3** but not enough for a complete PET leading to a marginal fluorescence recovery. Finally in the case of **1** and **4** the difference is too large and no fluorescence from the tetrazine could be restored because of a favorable PET process.

Conclusions

New bichromophoric compounds for improved electrofluorochromic properties based on triphenylamine and tetrazine cores were designed and synthesized and their photophysical and electrochemical properties have been investigated. The generation of triphenylaminium cations could be achieved by chemical oxidation and their photophysical properties have been investigated too. It appears that the absorption properties are similar to the disconnected parts (this fact is supported by theoretical calculations). As expected, the bichromophores exhibit very low fluorescence quantum yields in their neutral state in the blue region, because of a photoinduced electron transfer from the triphenylamine to the tetrazine. But upon one-electron oxidation of the triphenyl amine moiety, emission of tetrazine was restored in two cases though fluorescence quantum yields remain moderate because of a second possible unexpected PET. Our previous studies

showed that triphenylamine should be substituted by electron rich groups in order to shift the absorption band of the cation-radical at higher wavelengths than the emission wavelength of the tetrazine. Thus, the energy transfer that impeded the recovery of the tetrazine fluorescence could be avoided. Conversely, the present study demonstrates that the substituents of the triphenylamine should not be too strong donors in order to prevent a photoinduced electron transfer between the tetrazine and the cation-radical of the triphenylamine, which is the reason why the fluorescence of the tetrazine is only partially restored in the present dyads upon oxidation. Both studies highlight the necessity for a fine tuning of the electronic properties of both moieties to achieve efficient electrofluorochromism in dyads.

However, a true fluorescence switch by oxidation was demonstrated featuring a neutral state with blue fluorescence and a stable cation-radical state with yellow fluorescence for molecular dyads **2** and **3**. We are currently trying to achieve a third state with these dyads with enhanced fluorescence of the triphenylamine moiety by reducing the tetrazine ring. Fluorescence modulation by electrochemistry[10, 45] is also currently under study in our laboratory. Further theoretical calculations are also being investigated in order to precisely design new triphenylamine derivatives which could give more efficient electrofluorochromic dyads.

Experimental Section

Spectroscopic measurements

UV-visible absorption spectra were recorded on a Cary 5000 spectrophotometer in 1 cm optical length quartz cuvettes. Corrected emission spectra were obtained on a Jobin-Yvon Horiba Spex FluoroMax-3 spectrofluorometer. Acetonitrile (Aldrich, spectrometric grade or SDS, spectrometric grade) was employed as solvents for absorption and fluorescence measurements. The fluorescence quantum yields were determined by using coumarine 153 in ethanol as a standard (Φ_F=0.53) or quinine sulfate in H_2SO_4 (0.5 N) as a standard (Φ_F=0.546). The estimated experimental error is less than 10%. For the emission measurements, a right-angle configuration was used and the absorbance at the excitation wavelength are kept below 0.1 in order to avoid reabsorption artefacts.

Electrochemistry

S Solvents (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 (CH Instruments 600) driven by a PC. Carbon electrode (1 mm diameter) was used as working electrode, whereas platinum wire and Ag^+ (0.01 M in acetonitrile)/Ag were used, respectively, as the counter and reference electrodes. All the investigated solutions were deaerated by argon-bubbling for at least 2 min before performing the electrochemical measurements. The reference electrode was checked versus ferrocene as recommended by IUPAC.

Quantum Chemical Calculations

Calculations were performed with the Gaussian 03 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 using included templates and their geometry optimized at the PBE0 level of theory. Infrared spectra were calculated on the final geometry to ascertain that a minimum was obtained (no negative frequencies). Time-dependant density functional theory (TD-DFT) calculations at the PBE0 level of theory with the 6-31+g(d) basis set were subsequently performed.

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, ^{13}C 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 FT-IR spectrometer. This work has benefited from the facilities and expertise of the Small Molecule Mass Spectrometry platform of IMAGIF (Centre de Recherche de Gif - www.imagif.cnrs.fr).

3,6-Dichloro-*s*-tetrazine was synthesized as previously described by our group.[5]

Procedure A for protection of alcohol with THP: In a round-bottom-flask were placed *p*-toluenesulfonic acid (1 mol%), and dihydropyrane (1.5 eq) in chloroform. The alcohol compound (1.0 eq, 1.0 M) was added dropwise. The mixture was then stirred at room temperature until the starting materials had disappeared as juged by TLC (few hours). The mixture was poured into an aqueous solution of $NaHCO_3$ (2 mol%). The mixture was stirred at room temperature for 1 hour. The solid was filtrated and washed with dichloromethane and the filtrate was concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography.

Procedure B for Suzuki-Miyaura cross-coupling reaction: Into a Schlenk-flask were placed the halogenated compound (1.0 eq, 0.06 M), toluene and the tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ (2.5 mol% per substitution) under argon. The reaction mixture was stirred at room temperature for 15 minutes and then were added the solutions of boronic acid (1.1 eq per substitution, 1.6 M) in methanol and Na_2CO_3 (2.0 eq per substitution, 2.0 M) in distilled water. The reaction mixture was stirred at 80 °C until the halogenated compound had disappeared as juged by TLC (around one day). The reaction mixture was cooled to room temperature and a saturated aqueous NH_4Cl solution was added. The medium was extracted with dichloromethane, dried over anhydrous Na_2SO_4, filtered and concentrated under

reduced pressure. The crude product was purified by a silica gel column chromatography.

Procedure C for bromination in para positions of a triphenylamine derivative: In a round-bottom-flask were placed triphenylamine derivative (1.0 eq, 0.07 M), dimethylformamide and recrystallized *N*-bromosuccinimide (2.2 eq). Reaction mixture was stirred at room temperature without light until the triphenylamine derivative had disappeared as juged by TLC (few hours). The reaction mixture was cooled to room temperature and distilled water was added. It was extracted with diethylether, washed with saturated solution of NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography.

Procedure D for deprotection of alcohol protected with THP: In a round-bottom-flask were placed protected alcohol (1.0 eq) and *p*-toluenesulfonic acid (0.1 eq) in a mixture of solvents chloroform/methanol (1:1, 0.02 M). The reaction mixture was then stirred at room temperature until the starting materials had disappeared as juged by TLC (few hours). Volatile compounds were removed concentration under reduced pressure and Na_2CO_3 solution was added. It was extracted with dichloromethane, washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography.

Procedure E for SN_{Ar} on 3,6-dichloro-*s*-tetrazine $TzCl_2$: To a solution of alcohol compound (1.0 eq, 0.05 M) in anhydrous CH_2Cl_2 were added 3,6-dichloro-*s*-tetrazine (1.0 eq), and 2,4,6-collidine (1.0 eq). The mixture was stirred at room temperature for 1 hour then concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography.

3-chloro-6-([4''-([4'''-(dimethoxy)-1,1'-biphenyl]amine)-1',1''-biphenyl]ethoxy)-*s*-tetrazine (1) : The procedure E was applied using *N,N*-di-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-ethanol]biphenyl)amine **5** (230 mg, 0.296 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 3/7 to petroleum ether/CH_2Cl_2: 5/5) to give a purple solid (143 mg, 83%). m.p.: 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.57-7.42 (m, 12H), 7.37 (d, J=8,2 Hz, 2H), 7.23-7.20 (m, 6H), 6.98 (d, J=8.2 Hz, 4H), 4.87 (t, J=6,9 Hz, 2H), 3.85 (s, 6H), 3.27 (t, J=6,9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.7, 164.4, 159.0, 147.2, 146.4, 139.6, 135.5, 135.3, 134.8, 133.3, 129.7, 127.9, 127.6, 127.1, 124.8, 124.2, 114.4, 71.2, 55.5, 34.8; IR (cm^{-1}): 1601, 1494, 1453, 1344, 1326, 1281, 1248, 1178, 1040, 999, 819; HRMS-ESI: calcd. for M=$C_{42}H_{34}N_5O_3Cl$ 691.2350 (100%), 692.2384 (45%), 693.2321 (49%), found 691.2364 (100%), 692.2396 (52%), 693.2365 (48%); UV-vis (CH_3CN): λ_{max} (ε) = 345 (68600 $L.cm^{-1}.mol^{-1}$), 520 (690 $L.cm^{-1}.mol^{-1}$), λ_{em} (Φ_F) = 418 (0.004) in CH_3CN, τ = 1.63, 0.001 ns; E° (C, CH_2Cl_2) *vs* ferrocene: -0.97 V, 0.39 V

3-[2'-(4''-[*N*-bromophenyl-*N*-(4'''-methoxy-1''',1''''-biphenyl)amine]-1',1''-biphenoxy)ethoxy]-6-chloro-*s*-tetrazine (2) : The procedure E was applied using *N*-(4-bromophenyl)-*N*-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-ethoxy]-1',1''-biphenoxy)amine **6** (360 mg, 0.635 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 3/7) to give a purple solid (298 mg, 69%). m.p.: 165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52 (d, J=8.7 Hz, 2H), 7.51 (d, J=8.7 Hz, 2H), 7.46 (d, J=8.7 Hz, 2H), 7.45 (d, J=8.7 Hz, 2H), 7.36 (d, J=9.2 Hz, 2H), 7.16 (d, J=8.2 Hz, 2H), 7.15 (d, J=8,7 Hz, 2H), 7.03 (d, J=8,7 Hz, 2H), 6.99 (d, J=8.7 Hz, 2H), 6.97 (d, J=9.2 Hz, 2H), 5.02 (t, J=4.6 Hz, 2H), 4.48 (t, J=4.6 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.7, 164.7, 159.0, 157.5, 146.9, 146.3, 146.0, 135.8, 135.4, 134.0, 133.1, 132.3, 127.9, 127.8, 127.6, 127.6, 125.4, 124.7, 124.6, 115.1, 115.0, 114.3, 68.9, 65.5, 55.4; IR (cm^{-1}): 1607, 1583, 1485, 1461, 1442, 1375, 1345, 1319, 1280, 1246, 1198, 1039**,** 930**,** 818**;** HRMS-ESI: calcd. for M= $C_{35}H_{27}N_5O_3ClBr$ $[M+H]^+$ 680.1064, found 680.1035; UV-vis (CH_3CN): λ_{max} (ε) = 257 (30200 $L.cm^{-1}.mol^{-1}$), 326 (55000 $L.cm^{-1}.mol^{-1}$), 511 (690 $L.cm^{-1}.mol^{-1}$), λ_{em} = 412 in CH_3CN, τ = 1.18, 0.018 ns; E° (C, CH_2Cl_2) *vs* ferrocene: -0.82, 0.54, 1.40 V

3-chloro-6-[2'-(4''-[*N*,*N*-di-(4'''-methoxy-1''',1''''-biphenyl)amine]-1',1''-biphenoxy)ethoxy]-*s*-tetrazine (3): The procedure E was applied using *N,N*-(4-methoxy-1',1''-biphenyl)-*N*-[4-(2'-ethoxy)-1',1''-biphenoxy]amine **7** (44 mg, 0.074 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 2/8) to give a purple solid (42 mg, 81%). m.p.: 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52 (m, 6H), 7.47 (d, J=8.7 Hz, 4H), 7.46 (d, J=8.7 Hz, 2H), 7.20 (m, 6H), 6.99 (d, J=8.7 Hz, 2H), 6.97 (d, J=8.7 Hz, 4H), 5.01 (t, J=4,6 Hz, 2H), 4.47 (t, J=4,6 Hz, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.7, 164.7, 159.0, 157.5, 146.7, 146.4, 135.3, 134.9, 134.2, 133.3, 127.9, 127.8, 127.5, 124.6, 124.4, 115.0, 114.3, 68.9, 65.5, 55.4; IR (cm^{-1}): 2916, 2850, 1602, 1493, 1381, 1327, 1246, 1197, 932, 821; HRMS-ESI: calcd. for M= $C_{42}H_{34}N_5O_4Cl$ $[M]^{\bullet+}$ 707.2299 (100%), 708,2333 (45%), found 707.2313 (100%), 708.2362 (48%); UV-vis (CH_3CN): λ_{max} (ε) = 260 (36500 $L.cm^{-1}.mol^{-1}$), 336 (58400 $L.cm^{-1}.mol^{-1}$), 511 (710 $L.cm^{-1}.mol^{-1}$), λ_{em} (Φ_F) = 418 (0.01) in CH_3CN, τ = 1.61, 0.015 ns; E° (C, CH_2Cl_2) *vs* ferrocene: -0.96, 0.31, 1.15 V

3-chloro-6-[4''-(*N*,*N*-di-[4'''-(dimethylamino)-1,1'-biphenyl]amine)-1',1''-biphenoxy]ethoxy)-*s*-tetrazine (4): The procedure E was applied using 2-[4''-(*N*,*N*-di-[4'''-(dimethylamino)-1,1'-biphenyl]amine)-1',1''-biphenoxy]ethanol **8** (25 mg, 0.040 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 3/7 to CH_2Cl_2/EtOH : 9,9/0,1) to give a purple solid (13 mg, 43%). m.p.: 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52-7.45 (m, 12H), 7.26-7.20 (m, 6H), 6.99 (d, J=8.7 Hz, 2H), 6.90 (d, J=8.2 Hz, 4H), 5.03 (t, J=4.4 Hz, 2H), 4.49 (t, J=4.4 Hz, 2H), 3.01 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.7, 164.7, 157.4, 146.8, 146.0, 134.6, 134.3, 133.9, 128.0, 127.9, 127.5, 127.1, 124.6, 124.2, 115.0, 114.9, 68.9, 65.5, 41.2; IR (cm^{-1}): 2917, 2850, 1607, 1494, 1344, 1323, 1197, 1113, 1041, 946, 813; HRMS-ESI: calcd. for M=$C_{44}H_{40}N_7O_2Cl$ $[M]^{\bullet+}$ 733.2932 (100%), 734.2966 (47%), 735.2903 (32%), 736.2936 (15%), found 733.2949 (100%),

734.3003 (47%), 735.2972 (44%), 736. 2966 (24%); UV-vis (CH_3CN): λ_{max} (ε) = 345 (43500 L.cm^{-1}.mol^{-1}), 504 (690 L.cm^{-1}.mol^{-1}), λ_{em} (Φ_F) = 426 (0.06) in CH_3CN, E° (C, CH_2Cl_2) *vs* ferrocene: -1.27, 0.13, 0.48, 0.66 V

***N,N*-di-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-ethanol]biphenyl)amine (5):** The procedure D was applied using *N,N*-di-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-(tetrahydro-2H-pyran-2''-yloxy)ethyl]biphenyl)amine **16** (264 mg, 0.400 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/EtOH: 9.9/0.1) to give a white solid (172 mg, 74%). m.p.: <50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.55-7.47 (m, 14H), 7.30 (d, J=8.2 Hz, 2H), 6.97 (m, 8H), 3.91 (t, J=3.5 Hz, 1H), 3.85 (s, 6H), 2.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 146.9, 146.3, 138.9, 137.2, 135.3, 135.0, 133.2, 129.6, 127.8, 127.5, 126.9, 124.6, 124.1, 114.3, 63.7, 55.4, 38.9

***N*-(4-bromophenyl)-*N*-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-ethoxy]-1',1''-biphenoxy)amine (6):** The procedure D was applied using *N*-(4-bromophenyl)-*N*-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-(tetrahydro-2H-pyran-2''-yloxy)ethoxy]biphenyl)amine **17** (400 mg, 0.615 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/EtOH: 9.5/0.5) to give a white solid (347 mg, quant). m.p.: 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52 (d, J=8.7 Hz, 4H), 7.47 (d, J=8.7 Hz, 4H), 7.36 (d, J=9.2 Hz, 2H), 7.16 (d, J=8.7 Hz, 4H), 7.03 (d, J=8.7 Hz, 2H), 7.00 (d, J=8,7 Hz, 2H), 6.98 (d, J=8.7 Hz, 2H), 4.13 (t, J=4.6 Hz, 2H), 4.00 (t, J=4.6 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 157.9, 146.7, 146.0, 145.9, 135.6, 135.5, 133.3, 132.9, 132.2, 127.8, 127.7 (2 signals), 127.5, 125.2, 124.5, 124.5, 114.9, 114.2, 69.2, 61.3, 55.3; IR (cm^{-1}): 2950, 1608, 1585, 1493, 1485, 1316, 1285, 1251, 1177, 1162, 1136, 1071, 1034, 969, 925; UV-vis (CH_3CN): λ_{max} (ε) = 256 (22600 L.cm^{-1}.mol^{-1}), 327 (39400 L.cm^{-1}.mol^{-1}), λ_{em} (Φ_F) = 411 (0.06) in CH_3CN, τ = 1.20, 0.023 ns

***N,N*-(4-methoxy-1',1''-biphenyl)-*N*-[4-(2'-ethoxy)-1',1''-biphenoxy]amine (7):** The procedure D was applied using *N,N*-di-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-(tetrahydro-2H-pyran-2''-yloxy)ethoxy]biphenyl)amine **18** (195 mg, 0.288 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/EtOH: 9.9/0.1) to give a white solid (44 mg, 26 %). m.p.: <50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.53 (m, 6H), 7.47 (m, 6H), 7.21 (m, 6H), 6.99 (d, J=8.7 Hz, 2H), 6.98 (d, J=8,7 Hz, 4H), 4.12 (t, J=4.4 Hz, 2H), 4.00 (t, J=4.4 Hz, 2H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 158.0, 146.6, 146.4, 135.3, 135.0, 133.8, 133.3, 127.9, 127.8, 127.5, 124.5, 124.4, 115.0, 114.3, 69.4, 61.6, 55.4; IR (cm^{-1}): 1602, 1494, 1245, 1176

2-[4''-(*N,N*-di-[4'''-(dimethylamino)-1,1'-biphenyl]amine)-1',1''-biphenoxy]ethanol (8) : The procedure D was applied using *N,N*-di-[4''-(*N',N'*-dimethyl)-1',1''-biphenyl]-*N*-(4''-(2-(tetrahydro-2H-pyran-2-yloxy)ethoxy)-1',1''-biphenyl)amine **19** (81 mg, 0.12 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/EtOH: 9.9/0.1) to give a white solid (15 mg, 21 %). m.p.: <50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.53-7.45 (m, 12H) ; 7.21-7.18 (m, 6H) ; 6.98 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 4H), 4.13 (t, J = 4.6 Hz, 2H), 4.00 (t, J = 4.6 Hz, 2H), 3.00 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.9, 149.7, 146.8, 146.0, 135.8, 134.7, 133.9, 132.3, 127.8, 127.4, 127.1, 124.6, 124.1, 115.0, 113.1, 68.9, 65.5, 41.2

2-(4'-bromophenylethoxy)tetrahydro-2H-pyran (9): The procedure A was applied using 4-bromophenylethanol (1.00 g, 4.97 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 2/8) to give a colorless liquid (1.41 g, quant). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.40 (d, J=8.7 Hz, 2H), 7.12 (d, J=8.7 Hz, 2H), 4.57 (t, J=3.2 Hz, 1H), 3.95-3.50 (m, 6H), 2.86 (t, J=6.9 Hz, 2H), 1.80-1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 138.4, 131.4, 130.9, 120.1, 98.9, 68.0, 62.3, 35.9, 30.8, 25.5, 19.6; IR (cm^{-1}): 2941, 2869, 1487, 1352, 1199, 1135, 1120, 1081, 1072, 1011, 972, 907, 870, 814

2-(2'-bromoethoxy)tetrahydro-2H-pyrane (10): The procedure A was applied using bromoethanol (4,80 mL, 68,2 mmol, 1,0 éq). The crude product was purified by a silica gel column chromatography (cyclohexane/AcOEt: 9/1) to give a colorless liquid (12.0 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.66 (t, J=3.4 Hz, 1H), 4.01 (t, J=5.5 Hz, 2H), 3.98 (t, J=5.5 Hz, 2H), 3.87 (td, J=8.7, 3.7 Hz, 2H), 3.76 (tt, J=6.4, 6.4 Hz, 2H), 3.74 (tt, J=6.4, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 99.0, 67.6, 62.4, 30.1, 30.5, 25.5, 19.4; IR (cm^{-1}): 2971, 2912, 2850, 1454, 1438, 1183, 1120, 1068, 930, 907, 883, 869, 852, 837, 814

2-[2'-(4''-iodophenoxy)ethoxy]tetrahydro-2H-pyrane (11): : In a round-bottom-flask were placed the 2-(2'-bromoethoxy)tetrahydro-2H-pyrane **10** (2.14 g, 10.2 mmol, 1.1 eq), dimethylformamide (100 mL), the 4-iodophenol (2.02 g, 9.18 mmol, 1.0 eq) and the potassium carbonate (1.54 g, 11.1 mmol, 1.2 eq). The reaction mixture was then stirred at 65 °C for 20 hours. Volatile compounds were removed by concentration under reduced pressure and distilled water (100 mL) was added. The medium was extracted with dichloromethane (4*100 mL), washed with saturated solution of sodium chloride (500 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give a colorless oil (3.18 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.54 (d, J=9.2 Hz, 2H) ; 6.71 (d, J=8.7 Hz, 2H) ; 4.69 (t, J=3.4 Hz, 1H) ; 4.12-3.52 (m, 6H) ; 1.85-1.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 138.3, 117.3, 99.2, 83.3, 67.7, 65.8, 62.4, 30.6, 25.5, 19.5; IR (cm^{-1}): 2939, 2871; 1586, 1573; 1484, 1452; 1282, 1242, 1200, 1138, 1124; 1077; 1032, 1020; 985, 871, 815

2-[4'-(4''-triphenylamine)phenylethoxy]tetrahydro-2H-pyran (12): The procedure B was applied using 2-(4'-bromophenylethoxy)tetrahydro-2H-pyran **9** (889 mg, 3.12 mmol, 1.1 eq) and 4-(*N,N*-diphenylamino)phenylboronic acid (800 mg, 2.77 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 2/8 to CH_2Cl_2) to give a colorless oil (1.05 g,

84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.49 (d, J=8.2 Hz, 2H), 7.46 (d, J=8.7 Hz, 2H), 7.30-7.24 (m, 6H), 7,13 (m, 6H), 7.03 (dd, J=7.3, 7.3 Hz, 2H), 4.62 (t, J=3.4 Hz, 1H), 4.00-3.48 (m, 4H), 2.95 (t, J=7.3 Hz, 2H), 1,83-1,51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 147.9, 147.1, 138.7, 137.9, 135.2, 129.5, 129.4, 127.8, 126.7, 124.5, 124.1, 123.0, 98.9, 68.4, 62.4, 36.1, 30.8, 25.6, 19.7; IR (cm^{-1}): 3029, 2940, 1591, 1492, 1325, 1276, 1135, 1120, 1077, 1030, 972, 870, 839, 816

2-(2'-[4''-(4'''-triphenylamine)phenoxy]ethoxy)tetrahydro-2H-pyrane (13): The procedure B was applied using 2-[2'-(4''-iodophenoxy)ethoxy]tetrahydro-2H-pyrane **11** (1.67 g, 4.79 mmol, 1.1 eq) and 4-(*N*,*N*-diphenylamino)phenylboronic acid (1.26 g, 4.35 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 7/3 to CH_2Cl_2) to give a white solid (1.84 g, 91%).m.p.: < 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.51 (d, J=8.7 Hz, 2H), 7.45 (d, J=8.7 Hz, 2H), 7.28 (dd, J=8.7, 7.3 Hz, 4H), 7,15 (m, 6H), 7.05-7.00 (m, 4H), 4.75 (t, J=3.7 Hz, 1H), 4.23-3.52 (m, 6H), 1.92-1.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.3, 147.9, 146.7, 135.1, 133.5, 129.4, 127.8, 127.4, 124.3, 122.9, 115.1, 99.1, 67.6, 66.0, 62.3, 30.6, 25.5, 19.5; IR (cm^{-1}): 2951; 1586; 1488, 1456; 1316, 1284, 1252; 1162, 1137, 1119; 1070, 1034; 986, 926, 885, 842, 818

2-[2'-(4''-[4'''-*N*,*N*-di-(4''''-bromophenyl)aniline]phenyl)ethoxy]tetrahydro-2H-pyrane (14): The procedure C was applied using 2-[4'-(4''-triphenylamine)phenylethoxy]tetrahydro-2H-pyran **12** (1.04 g, 2.23 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 3/7) to a give a beige solid (1.39 g, quant). m.p.: < 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =: 7.50 (d, J=8.2 Hz, 2H), 7.48 (d, J=8.7 Hz, 2H), 7.36 (d, J=9.2 Hz, 4H), 7.31 (d, J=8,2 Hz, 2H), 7.11 (d, J=8.7 Hz, 2H), 6.98 (d, J=8.7 Hz, 4H), 4.63 (t, J=3,6 Hz, 1H), 4.00-3.48 (m, 4H), 2.96 (t, J=7,1 Hz), 1.86-1.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 146.5, 146.0, 138.3, 138.2, 136.3, 132.5, 129.6, 128.0, 126.7, 125.6, 124.6, 115.7, 98.9, 68.3, 62.3, 36.1, 30.8, 25.6, 19.6; IR (cm^{-1}): 2940, 1578, 1484, 1313, 1284, 1135, 1120, 1071, 1030, 1006, 816

2-[2'-(4''-[4'''-*N*,*N*-di-(4''''-bromophenyl)aniline]phenoxy)ethoxy]tetrahydro-2H-pyrane (15): The procedure C was applied using 2-(2'-[4''-(4'''-triphenylamine)phenoxy]ethoxy)tetrahydro-2H-pyrane **13** (1.80 g, 3.87 mmol, 1.0 eq). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to a white solid (1.29 g, 56%). m.p.: < 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =:7.52 (d, J=8.7 Hz, 2H), 7.48 (d, J=8.2 Hz, 2H), 7.38 (d, J=9.2 Hz, 4H), 7.12 (d, J=8.2 Hz, 2H), 7.04 (d, J=8.7 Hz, 2H), 7.00 (d, J=9.2 Hz, 4H), 4.78 (t, J=3.7 Hz, 1H), 4.24-3.58 (m, 6H), 1.92-1.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.3, 146.4, 145.5, 132.9, 132.3, 127.63, 127.60, 125.4, 124.7, 115.5, 115.0, 98.9, 67.5, 65.8, 62.1, 30.5, 25.4, 19.4; IR (cm^{-1}): 2941, 1607, 1579, 1484, 1455, 1313, 1284, 1268, 1248, 1201, 1176, 1125 , 1071, 1035, 1007, 988, 819

***N*,*N*-di-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-(tetrahydro-2H-pyran-2''-yloxy)ethyl]biphenyl)amine (16):** The procedure B was applied using 2-[2'-(4''-[4'''-*N*,*N*-di-(4''''-bromophenyl)aniline]phenyl)ethoxy]tetrahydro-2H-pyrane **14** (402 mg, 0.662 mmol, 1.0 eq) and 4-methoxyphenylboronic acid (245 mg, 1.61 mmol, 2.4 eq). The crude product was purified by a silica gel column chromatography (petroleum ether/CH_2Cl_2: 6/4 to CH_2Cl_2) to give a white solid (380 mg, 87%). m.p.: 126 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.55-7.47 (m, 14H), 7.31 (d, J=8.2 Hz, 2H), 7.21 (d, J=8.7 Hz, 4H), 6.98 (d, J=8.7 Hz, 4H), 4.64 (t, J=3.5 Hz, 1H), 3.86 (s, 6H), 4.02-3.50 (m, 4H), 2.97 (t, J=7.1 Hz, 2H), 1.90-1.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 146.9, 146.4, 138.6, 137.9, 135.3, 135.3, 133.3, 129.5, 127.8, 127.5, 126.6, 124.6, 124.3, 114.3, 98.9, 68.4, 62.4, 55.4, 36.1, 30.8, 25.6, 19.6; IR (cm^{-1}): 2919, 1601, 1494, 1247, 1177, 1040, 818

***N*-(4-bromophenyl)-*N*-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-(tetrahydro-2H-pyran-2''-yloxy)ethoxy]biphenyl)amine (17)** and ***N*,*N*-di-(4-methoxy-1',1''-biphenyl)-*N*-(4-[2'-(tetrahydro-2H-pyran-2''-yloxy)ethoxy]biphenyl)amine (18):** The procedure B was applied using 2-[2'-(4''-[4'''-*N*,*N*-di-(4''''-bromophenyl)aniline]phenoxy)ethoxy]tetrahydro-2H-pyrane **15** (510 mg, 0.818 mmol, 1.0 eq) and 4-methoxyphenylboronic acid (279 mg, 1.84 mmol, 2.2 eq). The crude product was purified by a silica gel column chromatography (cyclohexane/AcOEt: 1/9) to give two white solids **17** (241 mg, 45%) and **18** (194 mg, 21%). Properties of **17**: m.p.: < 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.59 (d, J=8.7 Hz, 2H), 7.58 (d, J=8.7 Hz, 2H), 7.54 (d, J=8.7 Hz, 2H), 7.53 (d, J=8.7 Hz, 2H), 7.43 (d, J=8.7 Hz, 2H), 7.22 (d, J=8.2 Hz, 4H), 7.10 (d, J=8.7 Hz, 2H), 7.08 (d, J=8.7 Hz, 2H), 7,05 (d, J=8.7 Hz, 2H), 4.84 (t, J=3,4 Hz, 2H), 4.29-3.62 (m, 6H), 3.91 (s, 3H), 2.00-1.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 158.3, 146.8, 146.5, 145.9, 135.6, 133.1, 133.0, 132.2, 127.7, 127.6, 127.6, 127.5, 125.2, 124.6, 124.3, 115.0, 114.9, 114.2, 99.0, 67.5, 65.9, 62.1, 55.3, 30.5, 25.5, 19.4; IR (cm^{-1}): 1493, 1483, 1313, 1274, 1268, 1248, 1071, 1034, 847, 823, 817. Properties of **18**: m.p.: < 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.53 (d, J=8.7 Hz, 4H), 7.52 (d, J=8,7 Hz, 2H), 7.47 (m, 6H), 7.20 (m, 6H), 7,00 (d, J=8,7 Hz, 2H), 6,97 (d, J=8,7 Hz, 4H), 4,74 (t, J=3,7 Hz, 1H), 4,22-3,54 (m, 6H), 3,85 (s, 6H), 1,87-1,53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.9, 158.3, 146.5, 135.2, 133.4, 133.3, 127.8, 127.7, 127.5, 124.5, 115.1, 114.3, 99.1, 67.6, 65.9, 62.3, 55.4, 30.6, 25.5, 19.5; IR (cm^{-1}): 1602, 1493, 1281, 1246, 1176, 1039, 846, 835, 820

***N*,*N*-di-[4''-(*N'*,*N'*-dimethyl)-1',1''-biphenyl]-*N*-(4''-(2-(tetrahydro-2H-pyran-2-yloxy)ethoxy)-1',1''-biphenyl)amine (19):** The procedure B was applied using 2-[2'-(4''-[4'''-*N*,*N*-di-(4''''-bromophenyl)aniline]phenoxy)ethoxy]tetrahydro-2H-pyrane **15** (510 mg, 0.818 mmol, 1.0 eq) and 4-(*N*,*N*-dimethylamino)phenylboronic acid (297 mg, 1.80 mmol, 2.2 eq). The crude product was purified by a silica gel column chromatography (cyclohexane/AcOEt: 1/9) to give a white solid (81 mg, 14%). m.p.: < 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52-7.47 (m, 12H), 7.22-7.19 (m, 6H), 7.00 (d, J=8.7 Hz, 2H), 6.82 (d, J=8.7 Hz, 4H), 4.75 (t, J=3,4 Hz, 1H), 4.20-3.86 (m, 6H), 3.00 (s, 12H), 1.67-1.45 (m, 6H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.2, 149.7, 146.7, 146.0, 135.7, 134.8, 133.6, 129.1, 127.7, 127.6, 127.4, 127.0, 124.6, 124.1, 115.1, 113.0, 99.1, 67.6, 66.0, 62.3, 41.2, 30.6, 25.5, 19.5; IR (cm^{-1}): 1608, 1494, 1249, 1177, 989, 869

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Notes and references

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1. G. Clavier and P. Audebert, *Chem. Rev.*, 2010, **110**, 3299-3314.
2. P. Audebert, S. Sadki, F. Miomandre and G. Clavier, *Electrochemistry Communications*, 2004, **6**, 144-147.
3. P. Audebert, S. Sadki, F. Miomandre, G. Clavier, M. Claude Vernieres, M. Saoud and P. Hapiot, *New J. Chem.*, 2004, **28**, 387-392.
4. P. Audebert, F. Miomandre, G. Clavier, M.-C. Vernières, S. Badré and R. Méallet-Renault, *Chem. Eur. J.*, 2005, **11**, 5667-5673.
5. Y. H. Gong, F. Miomandre, R. Méallet-Renault, S. Badré, L. Galmiche, J. Tang, P. Audebert and G. Clavier, *Eur. J. Org. Chem.*, 2009, 6121-6128.
6. C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, G. Clavier and P. Audebert, *Chem. Eur. J.*, 2015, **21**, 2230-2240.
7. C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, G. Clavier and P. Audebert, *RSC Advances*, 2014, **4**, 34332-34342.
8. Y. Kim, E. Kim, G. Clavier and P. Audebert, *Chem. Commun.*, 2006, 3612-3614.
9. Y. Kim, J. Do, E. Kim, G. Clavier, L. Galmiche and P. Audebert, *J. Electroanal. Chem.*, 2009, **632**, 201.
10. F. Miomandre, E. Lépicier, S. Munteanu, O. Galangau, J. F. Audibert, R. Méallet-Renault, P. Audebert and R. B. Pansu, *ACS Appl. Mater. Interfaces*, 2011, **3**, 690-696.
11. C. Dumas-Verdes, F. Miomandre, E. Lépicier, O. Galangau, T. T. Vu, G. Clavier, R. Méallet-Renault and P. Audebert, *Eur. J. Org. Chem.*, 2010, **2010**, 2525-2535.
12. A. C. Benniston, G. Copley, K. J. Elliott, R. W. Harrington and W. Clegg, *Eur. J. Org. Chem.*, 2008, 2705-2713.
13. C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, G. Clavier, F. Miomandre and P. Audebert, *Eur. J. Org. Chem.*, 2012, 1394-1403.
14. C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre and P. Audebert, *Electrochim. Acta*, 2013, **110**, 693-701.
15. H. G. Zhang, X. T. Tao, K. S. Chen, C. X. Yuan, S. N. Yan and M. H. Jiang, *Chinese Chemical Letters*, **22**, 647-650.
16. Z. Qing, P. Audebert, G. Clavier, F. Miomandre, J. Tang, T. T. Vu and R. Méallet-Renault, *J. Electroanal. Chem.*, 2009, **632**, 39.
17. Q. Zhou, P. Audebert, G. Clavier, R. Méallet-Renault, F. Miomandre, Z. Shaukat, T.-T. Vu and J. Tang, *J. Phys. Chem. C*, 2011, **115**, 21899-21906.
18. E. Jullien-Macchi, V. Alain-Rizzo, C. Allain, C. Dumas-Verdes and P. Audebert, *RSC Adv.*, 2014, **4**, 34127-34133.
19. A. J. Wain, I. Streeter, M. Thompson, N. Fietkau, L. Drouin, A. J. Fairbanks and R. G. Compton, *J. Phys. Chem. B*, 2006, **110**, 2681-2691.
20. S. Barlow, C. Risko, S. A. Odom, S. Zheng, V. Coropceanu, L. Beverina, J.-L. Brédas and S. R. Marder, *J. Am. Chem. Soc.*, 2012, **134**, 10146-10155.
21. A. Petr, C. Kvarnström, L. Dunsch and A. Ivaska, *Synth. Met.*, 2000, **108**, 245-247.
22. A.-D. Bendrea, L. Vacareanu and M. Grigoras, *Polym. Int.*, 2009, **59**, 624-629.
23. R. Suzuki, T. Matsumoto, K. Tanaka, Y. Takeuchi and T. Taketomi, *J. Organomet. Chem.*, 2001, **636**, 108-123.
24. N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage and B. Ventura, *J. Am. Chem. Soc.*, 1999, **121**, 4397-4408.
25. Y. Lin, P. Cheng, Y. Li and X. Zhan, *Chem. Commun.*, 2012, **48**, 4773-4775.
26. N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
27. G. Zhou, W.-Y. Wong, B. Yao, Z. Xie and L. Wang, *Angew. Chem. Int. Ed.*, 2007, **46**, 1149-1151.
28. H. Yu, C. Shen, M. Tian, J. Qu and Z. Wang, *Macromolecules*, 2012, **45**, 5140-5150.
29. W. Wenseleers, F. Stellacci, T. Meyer-Friedrichsen, T. Mangel, C. A. Bauer, S. J. K. Pond, S. R. Marder and J. W. Perry, *J. Phys. Chem. B*, 2002, **106**, 6853-6863.
30. D. Simoni, F. P. Invidiata, M. Eleopra, P. Marchetti, R. Rondanin, R. Baruchello, G. Grisolia, A. Tripathi, G. E. Kellogg, D. Durrant and R. M. Lee, *Bioorg. Med. Chem.*, 2009, **17**, 512-522.
31. J. M. Moszynski and T. M. Fyles, *J. Am. Chem. Soc.*, 2012, **134**, 15937-15945.
32. D. E. Chavez and M. A. Hiskey, *J. Heterocycl. Chem.*, 1998, **35**, 1329.
33. D. E. Chavez and M. A. Hiskey, *J. Energ. Mater.*, 1999, **17**, 357.
34. M. D. Coburn, G. A. Buntain, B. W. Harris, M. A. Hiskey, K. Y. Lee and D. G. Ott, *J. Heterocycl. Chem.*, 1991, **28**, 2049.
35. Y. H. Gong, P. Audebert, J. Tang, F. Miomandre, G. Clavier, S. Badré, R. Méallet-Renault and J. Marrot, *Journal of Electroanalytical Chemistry*, 2006, **592**, 147-152.
36. Y.-H. Gong, P. Audebert, G. Clavier, F. Miomandre, J. Tang, S. Badré, R. Méallet-Renault and E. Naidus, *New J. Chem.*, 2008, **32**, 1235-1242.
37. Z. Qing, P. Audebert, G. Clavier, R. Meallet-Renault, F. Miomandre and J. Tang, *New Journal of Chemistry*, 2011, **35**, 1678-1682.
38. J. Malinge, C. Allain, A. Brosseau and P. Audebert, *Angew Chem Int Ed Engl*, 2012, **51**, 8534-8537.
39. J. Malinge, C. Allain, L. Galmiche, F. Miomandre and P. Audebert, *Chem. Mater.*, 2011, **23**, 4599-4605.
40. D. E. Chavez, S. K. Hanson, J. M. Veauthier and D. A. Parrish, *Angew Chem Int Ed Engl*, 2013, **52**, 6876-6879.
41. G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991-1024.

42. C.-C. Chang, H. Yueh and C.-T. Chen, *Org. Lett.*, 2011, **13**, 2702-2705.
43. K. Sreenath, C. V. Suneesh, K. R. Gopidas and R. A. Flowers, *J. Phys. Chem. A*, 2009, **113**, 6477-6483.
44. K. Sreenath, C. V. Suneesh, V. K. Ratheesh Kumar and K. R. Gopidas, *J. Org. Chem.*, 2008, **73**, 3245-3251.
45. M. Voicescu, D. Rother, F. Bardischewsky, C. G. Friedrich and P. Hellwig, *Biochemistry*, **50**, 17-24.

