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Stable NIR anionic polymethine dyes: structure, photophysical and redox properties.

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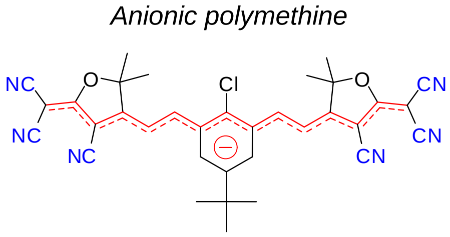
ABSTRACT



The concept of cyanine has been successfully extended to anionic heptamethine dye featuring tricyanofuran (TCF) moieties in terms of structure, reactivity and photophysical properties. Importantly, absorption and emission are red-shifted compared to its classical cationic analog without any cost in term of thermal stability. In addition to its "cyanine" behavior, this molecule exhibits further redox properties: oxidation and reduction led to the reversible formation of radical species whose absorption is in marked contrast with that of cyanines.

Near-infrared (NIR) dyes, *i.e.* molecules featuring both absorption and emission in the 700-1200 nm spectral range, are currently extensively studied for various applications ranging from bio-imaging[1] to photovoltaics[2] and nonlinear optics.[3] In this context, many different families of dyes have been developed such as borondipyrromethene,[4] perylene,[5] porphyrine,[3b] squarines,[2,6] or extended push-pull chromophores.[3a] In this context, a renewal of interest concerns the old polymethine cyanine dyes, owning to their particular photophysical properties, namely extremely intense sharp absorption and emission bands both located in the NIR.[7] As an example, these chromophores were recently used

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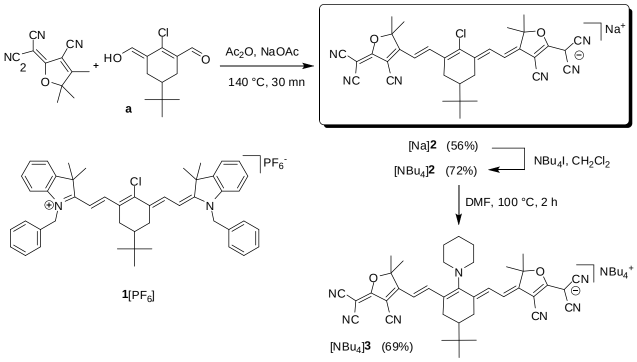
for *in vivo* imaging or sensing applications[8] and as two-photon based optical limiters.[9] These cyanines are generally cationic compounds with the positive charge completely delocalized between two electron-donating groups *via* an odd-number C(sp^2) hydrocarbon skeleton (**1**[PF_6], Scheme 1). In such compounds, a red-shift of the photophysical properties can be achieved by lengthening the π-conjugated backbone; a *c.a.* 100 nm bathochromic shift is usually obtained with every additional vinylene units.[10] This modulation is generally accompanied by a strong decrease of the photochemical or thermal stability limiting the scope of applications. To enhance the stability in the NIR spectral range, fused cyclohexenyl rings and central chloride substitution have been successfully proposed.[11]

Scheme 1. Synthesis of anionic cyanines.



In this work, we take advantage of tricyanofuran (TCF) moities to design an anionic cyanine dye ([Na]**2**, [NBu_4]**2**) also called oxonol,[12] in which the anionic charge is similarly distributed between two strong electron-withdrawing groups. The solid state structure, dynamic and optical properties in solution are reported and compared to that of its cationic analogous. The use of TCF acceptors led to unprecedented heptamethine dye that displays high solubility, strongly red-shifted photophysical properties combined with a short conjugated pathway keeping intact its thermal stability. In addition, we show that the redox behavior of this dye allows the control of the absorption in the NIR range.

Gram scale preparation of [Na]**2**, was readily achieved by a double Knoevenagel condensation between bis-aldehyde **a** and TCF in refluxing acetic anhydride in the presence of sodium acetate and purified by filtration on a silica plug (Scheme 1). The solubility of **2**$^-$ in organic solvent is strongly increased by changing sodium for a lipophilic tetrabutyl ammonium counter-ion. Surprisingly, in spite of the opposite charges, the anionic cyanine [NBu_4]**2** presents the same reactivity towards amine than its cationic counterpart.[13] As example, reaction with piperidine in DMF at 100 °C gave [NBu_4]**3** in good yield (Scheme 1).

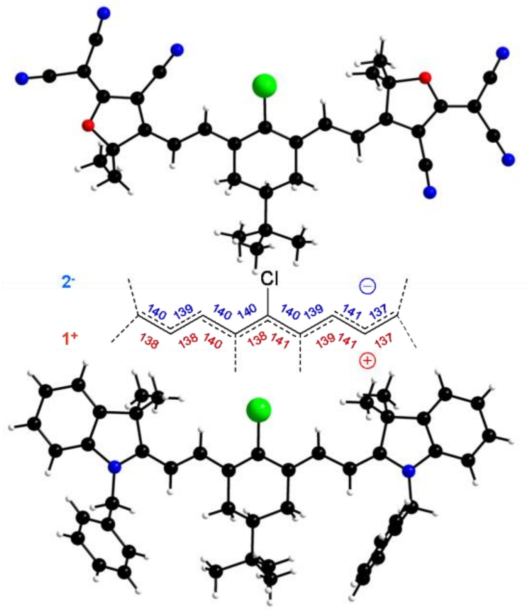


Figure 1. Crystal structures of **1**[PF_6] (bottom) and [Na]**2** (top), counter-ions and solvents molecules being ommited for clarity. Bond lengthes (pm) are reported in the middle scheme.

Single crystals of **1**[PF_6] and [Na]**2**, both featuring metallic shine, were obtained by slow evaporation of chloroform-toluene and methanol-toluene mixtures, respectively. Crystal data, refinements parameters and details of the crystallographic packing are reported in the SI. On the molecular scale (Figure 1), both cyanines present a remarkable planarity without any significant twist of the nine C(sp^2) carbons skeleton (overall tilt angles are 13 and 26° for $\mathbf{1}^+$ and $\mathbf{2}^-$, respectively). This planarity is enforced by the fused central 6-members ring whose conformation is further constrained by the thermodynamically favoured equatorial position of the *tert*-butyl fragment. Contrarily to push-pull polyene, whose conjugated skeleton exhibits a regular alternance of

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single (148 pm) and double (132 pm) C(sp^2)-C(sp^2) bonds, anionic and cationic cyanines present a "polyacetylene-type" π-conjugated backbone with equalized C-C bond lengthes (139±2 pm) intermediate between single and double bonds.[14] This result indicates that, in both cases, the charge is perfectly delocalized between the two distal heterocycles. The most stricking difference between both structures is the molecular conformation: $\mathbf{1}^+$ presents a classical *syn*-type arrangment with the two N atoms on the same side of the methine chain as already observed for other cyanines.[15] On the contrary, $\mathbf{2}^-$ reveals an unexpected *anti* conformation, that could be explained by the formation of linear chains bridged by sodium dimers in the packing (Figure S1).

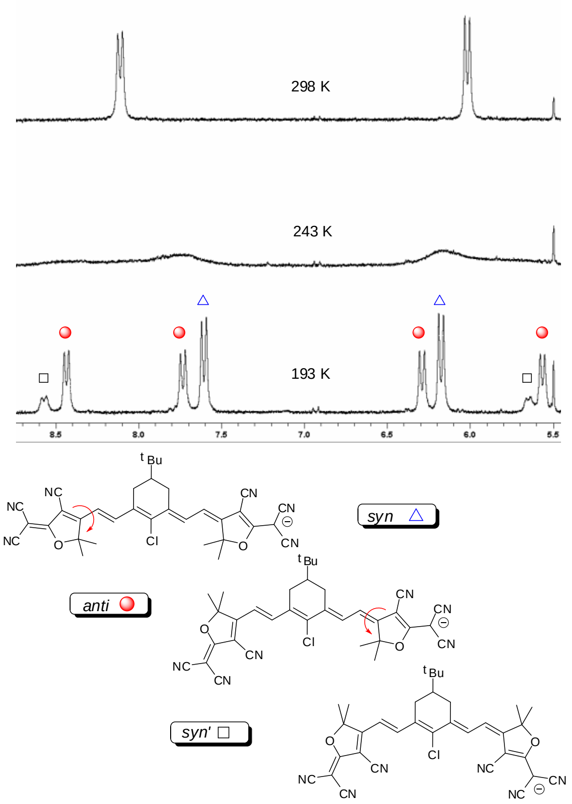

Figure 2. Evolution of the ^{1}H-NMR spectrum aromatic part of [NBu$_4$]**2** with the temperature (499.84 MHz, CD$_2$Cl$_2$) and representation of the three proposed conformers.

This striking difference of conformations in the solid state prompted us to examine the dynamic behavior of cyanines in dichloromethane solution using variable temperature ^{1}H-NMR experiments. In the case of **1**[PF$_6$], lowering the temperature does not result in significant variations of the NMR spectrum. This behavior is in marked contrast with that of the anionic cyanine [NBu$_4$]**2**: the pair of sharp doublets assigned to the vinylic protons observed at 298 K broadens and the coalescence is reached around 243 K (Figure 2). At 193 K, three different sets of well resolved signals are observed, two pairs of doublet and one set of four signals with a 10/35/55 ratio, respectively assigned to the two *syn*/*syn'* and to the non symmetric *anti* conformers. This result unambiguously shows that, at room temperature, a rapid equilibrium occurs between these three conformers by rotation of the TCF moities. This unusual properties already mentioned for push-pull merocyanine chromophores[16] seems to be characteristic of the very strong TCF accepting group. Density Functional Theory calculations carrried out on a model $\mathbf{2}^{-\prime}$ where the *tert*-butyl fragment is replaced by a methyl group allow their rationalization. Indeed, the three conformers have been computed to be energetically close with only a ~5 kcalmol^{-1} energy difference between them (see the computational details and data in SI). It is important to note that whatever the conformer, the polyacetylene-type π-conjugated backbone is reproduced indicating that the conformation has very little influence on the delocalization.

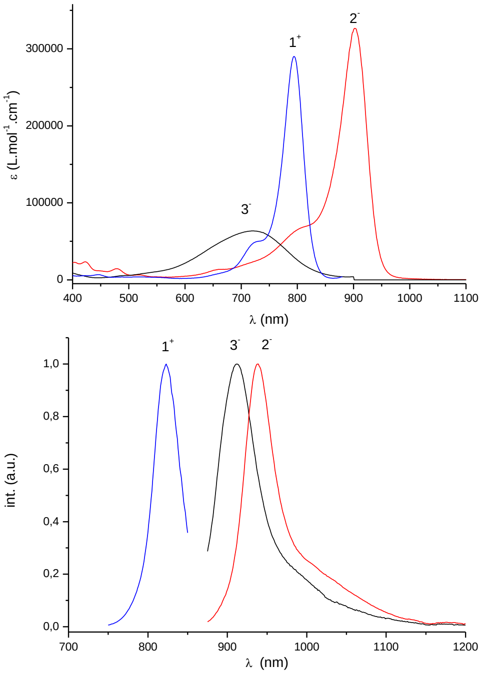

Figure 3. Absorption (up) and emission (down) spectra of **1**[PF$_6$] (blue), [NBu$_4$]**2** (red) and [NBu$_4$]**3** (black) in CH$_2$Cl$_2$.

The photophysical properties were measured in diluted dichloromethane solution (Table S1 and Figure 3). The anionic compound [NBu$_4$]**2** presents the typical cyanine like absorption spectrum with a sharp transition featuring exceptional extinction coefficient (> 300000 L.mol^{-1}.cm^{-1}) located in the infra-red (901 nm) and red-shifted by 110

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nm compare to **1**[PF_6]. The emission band (939 nm) follows the same trend. It is worth noting that the strong red-shifts of the absorption and emission bands for [NBu_4]**2** have been achieved without any chain-length modulation and that this chromophore conserves an excellent thermal stability (Td_{10}= 260 °C) which is of prime importance for further applications. In addition, as already observed for cationic cyanine dyes, substitution of the central chloride atom by amino moities ([NBu_4]**3**) results in a profound blue shift of the absorption band but has only a little influence on the emission.[13] As underlined by Peng and co-workers, amino-substituted cyanines present larger Stokes shift which is a great advantage for bio-imaging applications.[13]

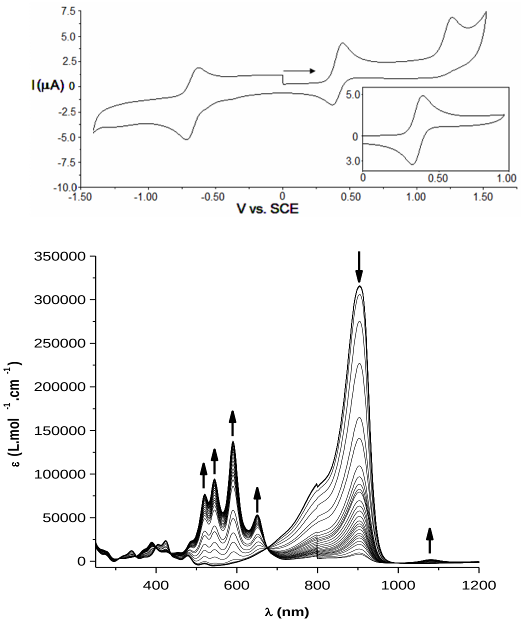

Figure 4. (top) CV traces obtained for [NBu_4]**2** (CH_2Cl_2, 0.2 M Bu_4NPF_6, v = 100 mV.s^{-1}). Inset shows the isolated first oxidation process. (bottom) Electronic absorption spectra obtained upon electrochemical oxidation in an OTTLE cell (CH_2Cl_2, 0.2 M Bu_4NPF_6).

The redox properties of [NBu_4]**2** were investigated by means of cyclic voltammetry (Figure 4). This compound undergoes reversible one electron oxidation at $E°_{ox}$ = 0.44 V vs. SCE (ΔE_p = 60 mV), followed by a second irreversible oxidation at E_{pa} = 1.27 V. A partially reversible reduction is also observed at at $E°_{red}$ = -0.64 V vs. SCE (ΔE_p = 90 mV, $I_{pc}/I_{pa} \approx 0.85$). These properties give the opportunity to generate radical species **2**$^{\cdot}$ and **2**$^{\cdot 2-}$ that may present enough stability to be characterized. Therefore, achieving *in situ* oxidation of [NBu_4]**2** with acetylferricinium in a THF solution (E = 0.77 V vs SCE) into a capped EPR tube allows a direct observation of the generated radical species **2**$^{\cdot}$. At room temperature, the oxidized species presents a broad isotropic signal (g = 2.0035), with a complex hyperfine structure due to the coupling of the unpaired electron with the magnetically different nitrogen and hydrogen atoms of the cyano moieties and vinylic backbone, respectively (Figure S3). This coupling indicates that the unpaired electron is probably delocalized along the complete conjugated chain as already observed for related electron acceptors like tetracyanoethylene or tetracyanoquinodimethane.[17]

Finally, the optical properties of **2**$^{\cdot}$ were investigated by means of UV/Vis/NIR spectro-electrochemistry. On one electron oxidation, the intense cyanine absorption band at λ_{max} = 901 nm vanishes, and weaker absorptions concomitantly show up at λ = 1082, 650, 590, 544 and 520 nm (Figure 4). The presence of a single isobestic point allows assigning the new transitions to the radical species. At the end of the experiment, the original material could be cleanly regenerated by reduction with ca 100% optical yield, and the recovered sample displays in the spectral region of interest no features other than those of the parent material. An analogous behavior is observed in reduction with the formation of a second radical species **2**$^{\cdot 2-}$ (Figure S4). The reversibility of the process is lower (85%) than in oxidation in agreement with the cyclic voltametry indicating that second radical species is less stable than the first one. In all cases, it is important to note that the characteristic transition of cyanines observed for both cationic and anionic derivatives completely desappears in the case of the radical species indicating a profound modification of the electronic structure.

In conclusion, we reported the synthesis of a new anionic polymethine cyanine dye featuring tricyanofuran end groups. This chromophore presents the characteristic structure and reactivity of cyanine dyes which expands the concept of cyanine to anionic odd carbon number derivatives. Its photophysical properties were significantly red-shifted compared to its cationic analog, keeping intact its thermal stability which makes it very attractive for bio-imaging applications. In addition to its "cyanine" behavior, this molecule exhibits redox properties associated to the TCF end group: one electron oxidation and reduction lead to the formation of a radical species whose absorption properties are completely different to that of usual cyanine dyes. Further studies are in progress to explain the profound perturbations in the delocalization and to take benefit of this new optical redox-switch.

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Supporting Information Available Synthetic procedures, complete characterisations, crystollographic and computational details are available in Supporting Information.

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