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Pierre-Antoine Bouit, Emmanuel Di Piazza, Stéphane Rigaut, Boris Le Guennic, Christophe Aronica, et al.. Stable Near-Infrared Anionic Polymethine Dyes: Structure, Photophysical, and Redox Properties. *Organic Letters*, 2008, 10 (19), pp.4159-4162. 10.1021/ol801416n . hal-00369219

HAL Id: hal-00369219

<https://hal.science/hal-00369219v1>

Submitted on 26 Nov 2019

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

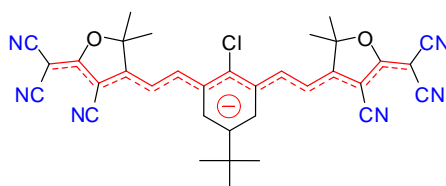
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ABSTRACT

Anionic polymethine



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-imaging¹ to photovoltaics² 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, owing 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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¹ Ghorroghchian, P.P.; Frail, P.R.; Susumu, K.; Blessington, D.; Brannan, A.; Bates, F.S.; Chance, B.; Hammer, D.A.; Therien, M.J. *Proc. Nat. Ac. Sci.* **2005**, *102*, 2922-2927.

² Burke, A.; Schmidt-Mende, L.; Ito, S.; Grätzel, M. *Chem. Commun.* **2007**, 234-236.

³ a) Beverina, L.; Fu, J.; Leclercq, A.; Zojer, E.; Pacher, P.; Barlow, S.; Van Stryland, E.W.; Hagan, D.J.; Brédas, J.-L.; Marder, S.R. *J. Am. Chem. Soc.* **2005**, *127*, 7282-7283; b) Kurotobi, K.; Kim, K.S.; Noh, S.B.; Kim, D.; Osuka, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 3944-3947.

⁴ a) Umezawa, K.; Nakamura, Y.; Makino, H.; Citterio, D.; Suzuki, K. *J. Am. Chem. Soc.* **2008**, *130*, 1550-1551; b) Zhao, W.; Carreira, E.M. *Angew. Chem. Int. Ed.* **2005**, *44*, 1677-1679;

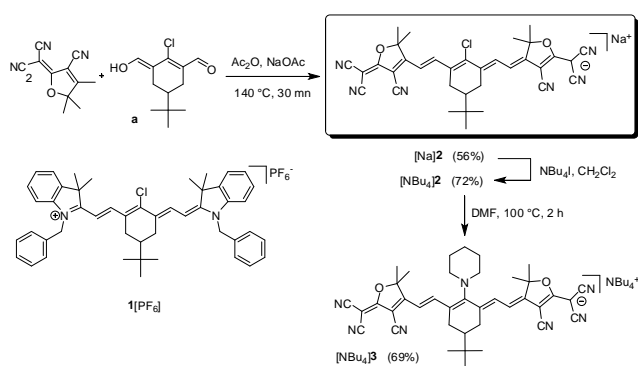
⁵ Pschirer, N.G.; Kohl, C.; Nolde, C.; Qu, J.; Müllen, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 1401-1404.

⁶ For a review, see: Sreejith, S.; Carol, P.; Chithra, P.; Ajayagosh, A. *J. Mater. Chem.* **2008**, *18*, 264-274.

⁷ Mishra, A.; Behera, R.K.; Behera, P.K.; Mishra, B.K.; Behera, G.B. *Chem. Rev.* **2000**, *100*, 1973-2011.

for *in vivo* imaging or sensing applications⁸ 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**[PF₆], 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) moieties to design an anionic cyanine dye ([Na]**2**, [NBu₄]**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 analogues. The use of TCF acceptors led to unprecedented heptamethine dye that displays high solubility, strongly red-shifted photophysical properties combined with a short

8 For selected examples: a) Leevy, W.M.; Gammon, S.T.; Jiang, H.; Robinson, J.R.; Maxwell, D.J.; Jackson, E.N.; Marquez, M.; Piwnicka-Worms, D.; Smith, B.D. *J. Am. Chem. Soc.* **2006**, *128*, 16476-16477; b) Li, C.; Greenwood, T.R.; Bhujwalla, Z.M.; Glunde, K. *Org. Lett.* **2006**, *8*, 3623-3626; c) Ye, Y.; Bloch, S.; Jeffery Kao, J.; Achilefu, S. *Bioconjugate Chem.* **2005**, *16*, 51-61.

9 Bouit, P.-A.; Wetzal, G.; Berginc, G.; Toupet, L.; Feneyrou, P.; Bretonnière, Y.; Maury, O.; Andraud, C. *Chem. Mater.* **2007**, *19*, 5325-5335.

10 Asato, A.E.; Watanabe, D.T.; Liu, R.S.H. *Org. Lett.* **2000**, *2*, 2559-2562.

11 Chen, X.; Peng, X.; Cui, A.; Wang, B.; Wang, L.; Zhang, R. *J. Photochem. Photobiol. A* **2006**, *181*, 79-85 and references therein.

12 Kulinich, A.V.; Derevyanko, N.A.; Ishchenko, A.A. *J. Photochem. Photobiol. A* **2007**, *188*, 207-217; b) Tatikolov, A.S.; Costa, S.M.B. *Chem. Phys. Lett.* **2007**, *440*, 73-78; c) Inagaki, Y.; Morishima, S.I.; Wariishi, K.; Akiba, M. *J. Mater. Chem.* **2006**, *16*, 345-347; d) Hales, J.M.; Zheng, S.; Barlow, S.; Marder, S.R.; Perry, J.W. *J. Am. Chem. Soc.* **2006**, *128*, 11362-11363; d) Halik, J.W.; Hartmann, M. *Chem. Eur. J.* **1999**, *5*, 2511-2517.

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 [NBu₄]**2** presents the same reactivity towards amine than its cationic counterpart.¹³ As example, reaction with piperidine in DMF at 100 °C gave [NBu₄]**3** in good yield (Scheme 1).

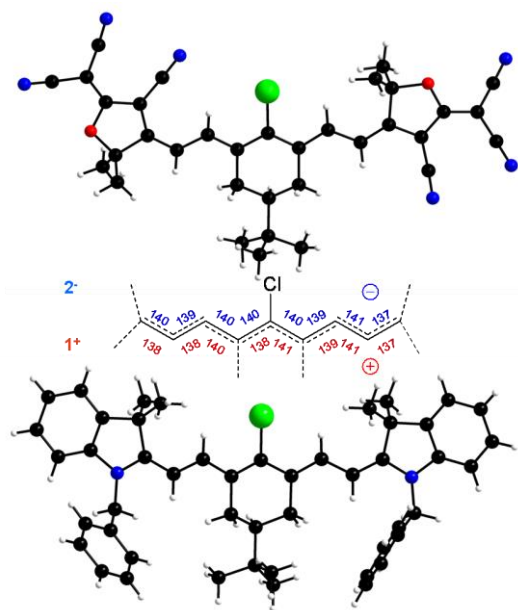


Figure 1. Crystal structures of **1**[PF₆] (bottom) and [Na]**2** (top), counter-ions and solvents molecules being omitted for clarity. Bond lengths (pm) are reported in the middle scheme.

Single crystals of **1**[PF₆] 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 **1**⁺ and **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

13 Peng, X.; Song, F.; Lu, E.; Wang, Y.; Zhou, W.; Fan, J.; Gao, Y. *J. Am. Chem. Soc.* **2005**, *127*, 4170-4171.

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 lengths (139 \pm 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 striking difference between both structures is the molecular conformation: **1**⁺ presents a classical *syn*-type arrangement with the two N atoms on the same side of the methine chain as already observed for other cyanines.¹⁵ On the contrary, **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).

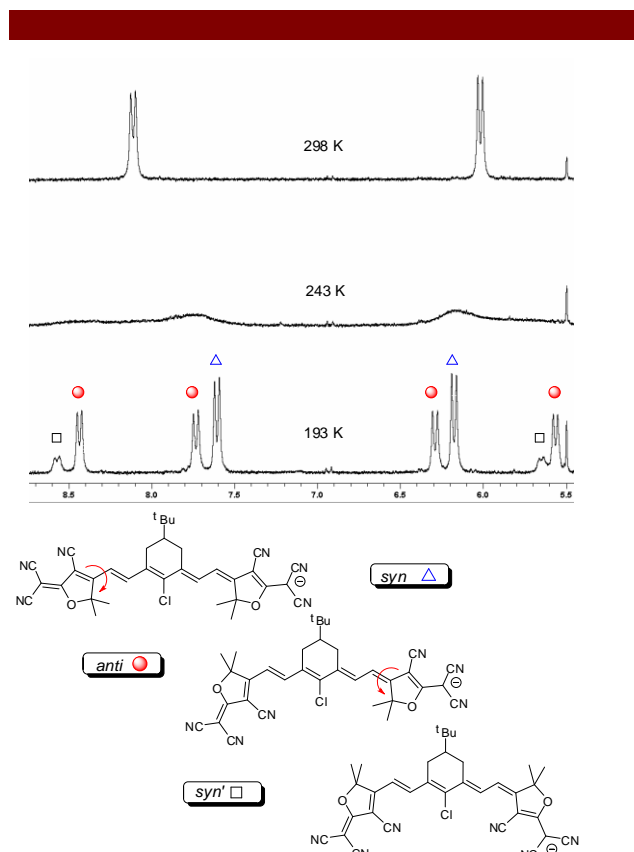


Figure 2. Evolution of the ¹H-NMR spectrum aromatic part of [NBu₄]**2** with the temperature (499.84 MHz, CD₂Cl₂) and representation of the three proposed conformers.

This striking difference of conformations in the solid state prompted us to examine the dynamic behavior of cyanines in dichloromethane solution using variable temperature ¹H-NMR experiments. In the case of **1**[PF₆], 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 [NBu₄]**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 moieties. This unusual properties already mentioned for push-pull merocyanine chromophores¹⁶ seems to be characteristic of the very strong TCF accepting group. Density Functional Theory calculations carried out on a model **2**' 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.

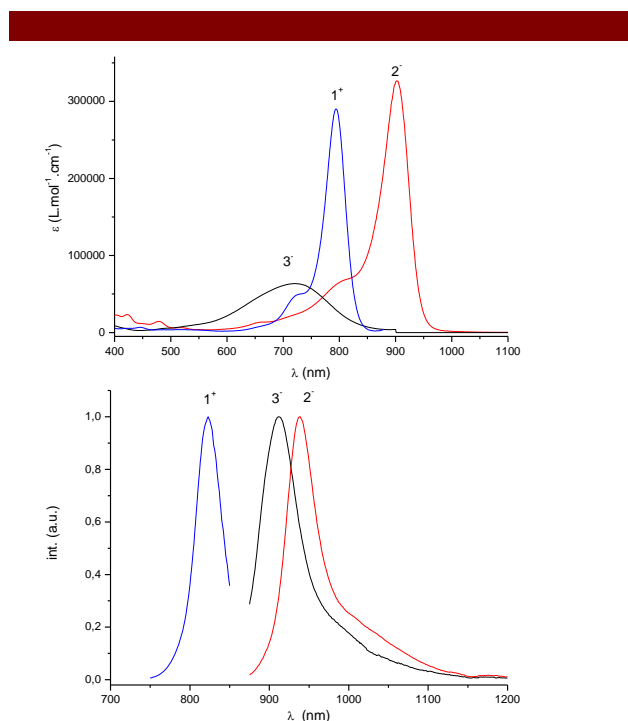


Figure 3. Absorption (up) and emission (down) spectra of **1**[PF₆] (blue), [NBu₄]**2** (red) and [NBu₄]**3** (black) in CH₂Cl₂.

The photophysical properties were measured in diluted dichloromethane solution (Table S1 and Figure 3). The anionic compound [NBu₄]**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

¹⁴ Tolbert, L.R.; Zhao, X. *J. Am. Chem. Soc.* **1997**, *119*, 3253-3258.

¹⁵ a) Nagao, Y.; Sakai, T.; Kozawa, K.; Urano, T. *Dyes Pigm.* **2007**, *73*, 344-352; b) Dai, Z.F.; Peng, B.X.; Chen, X.A. *Dyes Pigm.* **1999**, *40*, 219-223.

¹⁶ Kay, A.J.; Woolhouse, A.D.; Zhao, Y.; Clays, K. *J. Mater. Chem.* **2004**, *14*, 1321-1330.

nm compare to **1**[PF₆]. 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 [NBu₄]**2** have been achieved without any chain-length modulation and that this chromophore conserves an excellent thermal stability (T_{d10} = 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 moieties ([NBu₄]**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

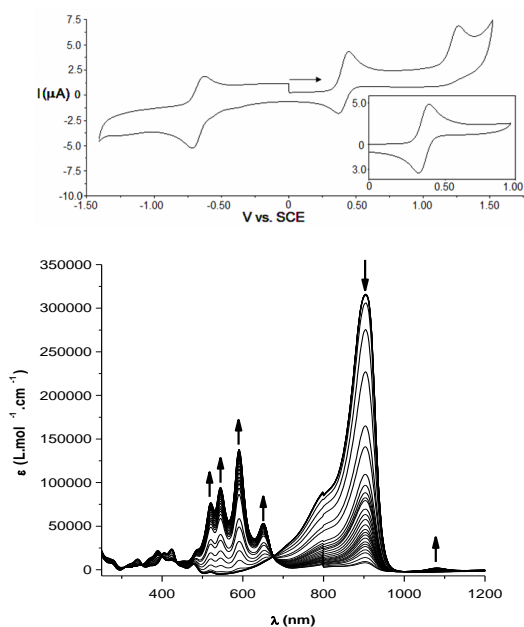


Figure 4. (top) CV traces obtained for [NBu₄]**2** (CH₂Cl₂, 0.2 M Bu₄NPF₆, $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$). Inset shows the isolated first oxidation process. (bottom) Electronic absorption spectra obtained upon electrochemical oxidation in an OTTE cell (CH₂Cl₂, 0.2 M Bu₄NPF₆).

The redox properties of [NBu₄]**2** were investigated by means of cyclic voltammetry (Figure 4). This compound undergoes reversible one electron oxidation at $E^{\circ}_{\text{ox}} = 0.44 \text{ V vs. SCE}$ ($\Delta E_p = 60 \text{ mV}$), followed by a second irreversible oxidation at $E_{\text{pa}} = 1.27 \text{ V}$. A partially reversible reduction is also observed at $E^{\circ}_{\text{red}} = -0.64 \text{ V vs. SCE}$ ($\Delta E_p = 90 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 0.85$). These properties give the opportunity to generate radical species **2**[•] and **2**²⁻ that may present enough stability to be characterized. Therefore, achieving *in situ* oxidation of [NBu₄]**2** with acetylferricinium in a THF solution ($E = 0.77 \text{ V vs SCE}$) into a capped EPR tube allows a direct observation of the generated radical species **2**[•]. 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**[•] were investigated by means of UV/Vis/NIR spectro-electrochemistry. On one electron oxidation, the intense cyanine absorption band at $\lambda_{\text{max}} = 901 \text{ nm}$ vanishes, and weaker absorptions concomitantly show up at $\lambda = 1082, 650, 590, 544$ 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**²⁻ (Figure S4). The reversibility of the process is lower (85%) than in oxidation in agreement with the cyclic voltammetry 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 disappears 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.

Acknowledgments. Authors thank the Direction Generale des Armées (DGA) for a grant to PAB. We are also grateful to L. Bonneviot, B. Albela and J.P. Dutasta of university of Lyon for assistance in EPR, and NMR spectroscopy respectively, and to the Centre de Diffraction H. Longchambon of the university of Lyon for X-rays diffraction facilities.

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