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# Design of Near-Infrared-Absorbing Unsymmetrical Polymethine Dyes with Large Quadratic Hyperpolarizabilities

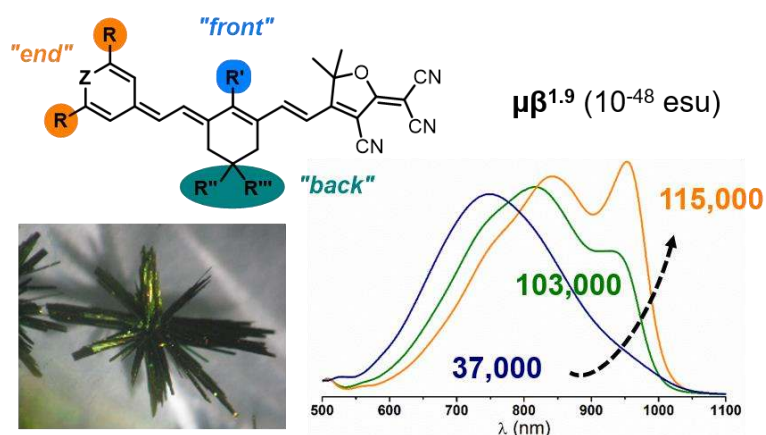
Simon Pascal,<sup>\*,†,‡</sup> Yulia A. Getmanenko,<sup>‡</sup> Yadong Zhang,<sup>‡</sup> Iryna Davydenko,<sup>‡</sup> Minh Hoang Ngo,<sup>§</sup> Guillaume Pilet,<sup>||</sup> Sébastien Redon,<sup>†</sup> Yann Bretonnière,<sup>†</sup> Olivier Maury,<sup>†</sup> Isabelle Ledoux-Rak,<sup>§</sup> Stephen Barlow,<sup>‡</sup> Seth R. Marder<sup>\*,‡</sup> and Chantal Andraud<sup>\*,†</sup>

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## ABSTRACT

Abstract: Fifteen heptamethine dyes in which a tricyanofuran acceptor is linked to donors of different strength were synthesized, and their absorption, thermal, electrochemical, and second-order nonlinear optical properties were investigated. While the variation of the peripheral bulky substituents allowed a decrease of the intermolecular interactions in the solid state, subtle engineering of the heterocyclic donor provided dyes with electronic structures that varied between dipolar and cyanine-like (i.e. with little bond length alternation and with ground and excited states having similar dipole moment) and remarkably high quadratic hyperpolarizabilities ( $\mu\beta^{1.9}$ ) of up to  $115,000 \times 10^{-48}$  esu.

## INTRODUCTION

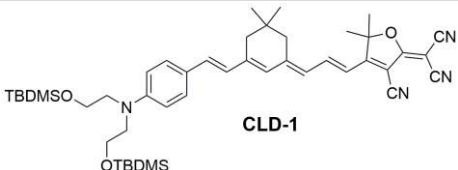
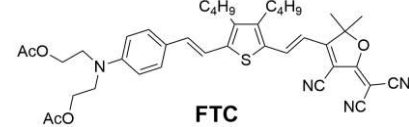
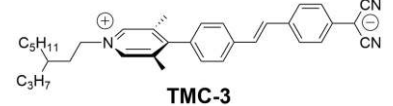
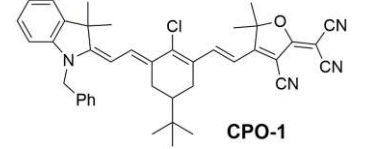
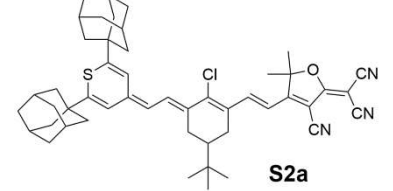
Organic second-order nonlinear optical (NLO) chromophores have been widely investigated for electro-optical (EO) applications;<sup>1-3</sup> EO modulators based upon organic molecules can be modulated at very high frequency giving extraordinary bandwidths. The flexibility of organic synthesis enables the incorporation of subtle structure modifications and, therefore, the ability to tune the electronic structure so as to optimize the NLO response at the microscopic level and, to some extent, control chromophore-chromophore interactions in the solid state. The main factors that facilitate the design, synthesis, and processing of efficient materials for EO modulation are: (i) high quadratic hyperpolarizability  $\beta$ , (ii) good thermal and chemical stability, (iii) possible large scale synthesis of the dye, and (iv) adequate solubility for further incorporation into devices.

Among the numerous organic molecules developed for the second order NLO applications, “push-pull” chromophores have been extensively investigated,<sup>4</sup> including those using the strong tricyanofuran (TCF) acceptor, which also enables dyes

with good solubility to be obtained. Well-known examples of molecules bearing TCF are **CLD-1** and **FTC** (Table 1), which possess the required characteristics for EO applications, e.g. high second-order NLO response at a wavelength of 1.9  $\mu\text{m}$ ,  $\mu\beta^{1.9}$  ( $\mu$  being the permanent dipole moment of the molecule and  $\beta$  the second-order molecular polarizability), of around  $20,000 \times 10^{-48}$  esu, good solubility in the solvents used for the fabrication of EO devices, and suitable thermal stability.<sup>5-7</sup> Importantly, the structure of **CLD-1** has been optimized using TCF-CF<sub>3</sub> moieties which led to large  $\beta^{1.9}$  values of  $7,600 \times 10^{-30}$  esu and remarkable EO properties following chemical engineering with bulky substituents.<sup>8-10</sup>

The **TMC-3** dye (Table 1), featuring a strong intramolecular charge transfer is one of the most promising chromophores for EO applications.<sup>11-13</sup> Its giant  $\mu\beta$  value, up to  $-488,000 \times 10^{-48}$  esu is a consequence of a ground state zwitterionic electronic structure, resulting in a very large dipole moment. A major challenge for using highly dipolar chromophores in poled polymers, however, is aggregation, which can occur at high chromophore concentrations. Typically, this aggregation leads to the formation of centrosymmetric dimers or multichromophore aggregates, and consequentially a dramatic decrease of the nonlinear response.

**Table 1.** Structures and second-order nonlinearities of the known **CLD-1**, **FTC**,<sup>5-7</sup> **TMC-3**<sup>11-13</sup> and **CPO-1**<sup>14-16</sup> dipolar chromophores and of the new dye **S2a** described in this study.  $\mu\beta^{1.9}$  values are measured using the EFISH technique,  $\beta^{1.9}$  values are measured by HRS at 1907 nm.

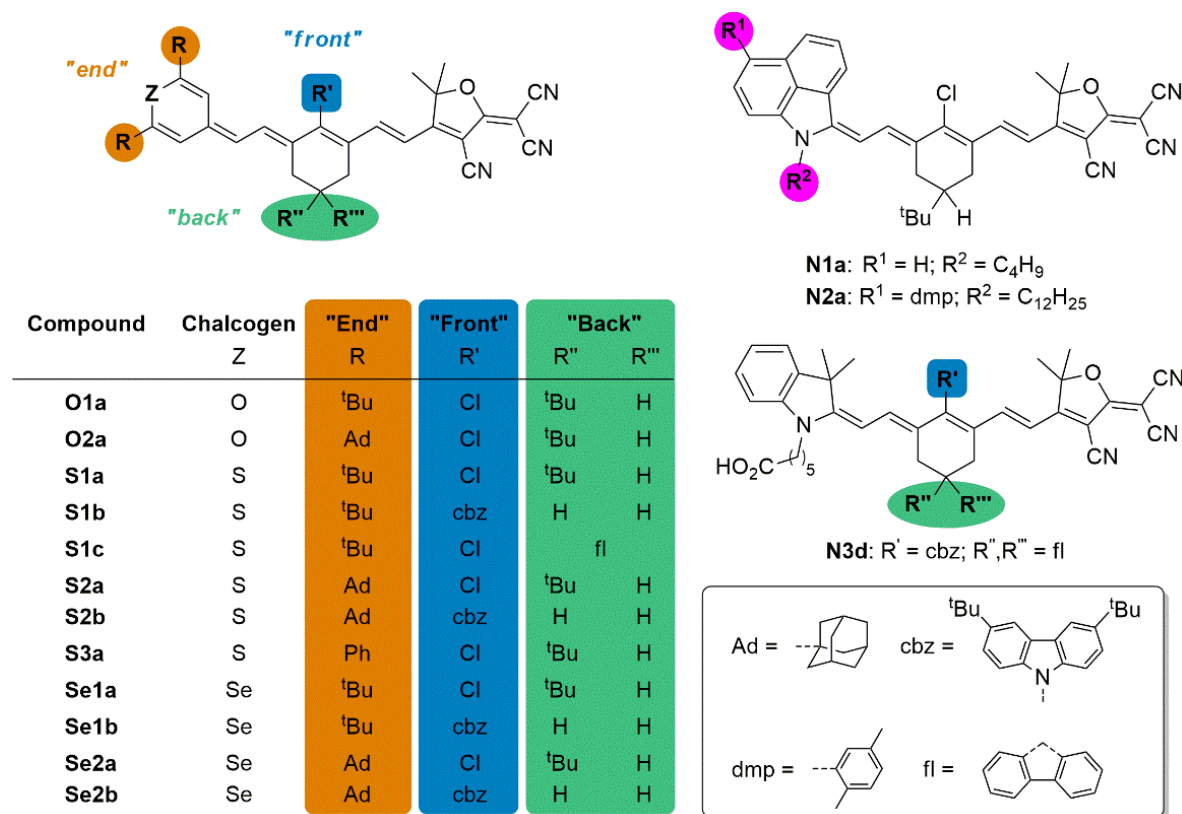
Structure	$\mu\beta^{1.9} \times 10^{48}$ / esu	$\beta^{1.9} \times 10^{30}$ / esu	$T_d$ / °C
	14,100	445	271
	17,600	–	312
	-488,000	9,800	330
	29,500	5,000	250
	115,000	2,680	305

Recently, the gram-scale preparation of the unsymmetrical **CPO-1** polymethine and an evaluation of its NLO properties were reported (Table 1).<sup>14-16</sup> This dye is readily obtained following five synthetic steps with a ca. 79% overall yield and exhibits good thermal stability, high quadratic hyperpolarizability ( $\mu\beta^{1.9}$ ) and promising EO response.

Given the promising characteristics of **CPO-1**, the present study is focused on systematic modification of its chemical structure in order to further increase the thermal stability and the quadratic hyperpolarizability of the chromophore. Inspired by recent work on near-infrared (NIR) symmetrical cationic polymethines,<sup>17-18</sup> fifteen new unsymmetrical heptamethines incorporating a TCF acceptor and chalcogenopyran or benzoindoline donors were prepared (Figure 1) to investigate effect on optical and electronic properties. To reduce detrimental chromophore-chromophore interactions in the solid

state incorporation of the “front” and “back” groups using moderate to large steric bulkiness was examined.

A wide range of pyran, thiopyran, selenopyran, benzoindoline or indoline derivatives investigated by UV-vis-NIR absorption spectroscopy and cyclic voltammetry demonstrates the strong influence of the donor fragments on their optical and electronic properties. Absorption solvatochromism experiments indicates a progressive establishment of a highly delocalized cyanine-like electronic structure in polar solvents. This observation is quite significant since the polyene-like and cyanine-like polymethines respectively display positive and null bond length alternation (BLA), a parameter directly related to the second order hyperpolarizability.<sup>19-22</sup> High quadratic hyperpolarizabilities  $\mu\beta^{1.9}$  are recorded in solution for the present scope of polymethines, as illustrated by **S2a** in Table 1.



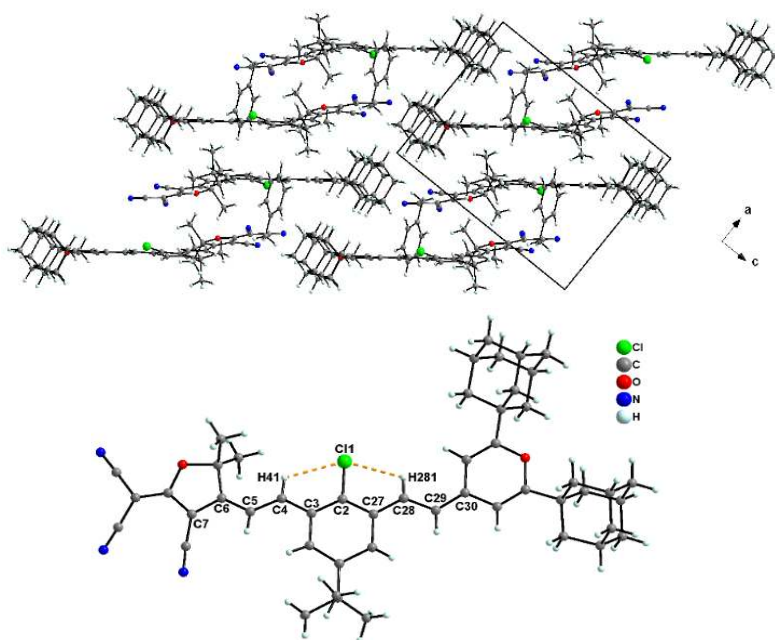
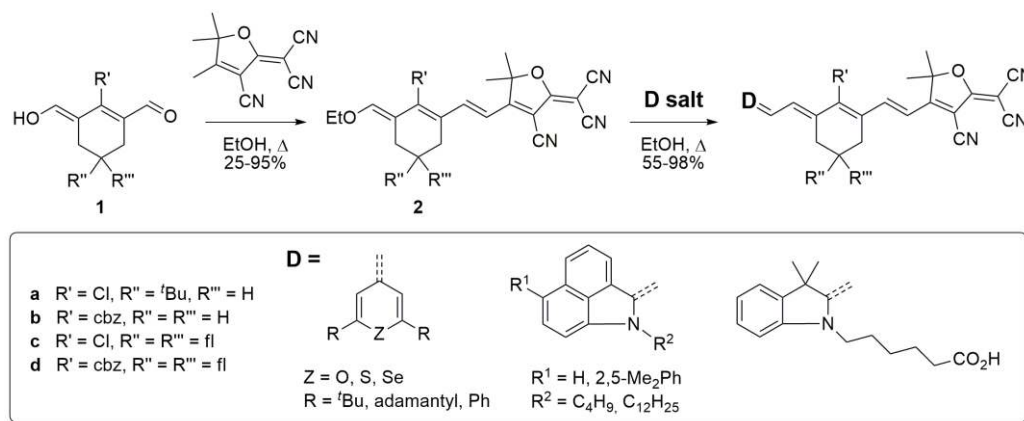
**Figure 1.** Structures of unsymmetrical polymethine dyes studied here.

## RESULTS AND DISCUSSION

**Synthesis.** The target dyes were obtained by two consecutive condensations, as depicted in Scheme 1.<sup>14, 16</sup> First, the “bisaldehyde-like” precursors **1a-d** with different “front”/“end” groups combinations ((**a**): Cl/<sup>t</sup>butyl,H; (**b**): cbz/H,H; (**c**): Cl/fl; and (**d**) cbz/fl) were reacted with a TCF derivative to give corresponding adducts **2** in moderate to good yields. With these four intermediates **2a-d** in hand, formation of the unsymmetrical polymethines was accomplished by a second high-yield condensation with pyrylium, thiopyrylium, selenopyrylium, benzoindolenium or indolenium salts. The final dyes depicted in Figure 1 incorporate chalcogenopyran moieties with <sup>t</sup>butyl (dyes **O1**, **S1**, **Se1**), adamantyl (dyes **O2**, **S2**, **Se2**) or phenyl (dye **S3**) “end” groups and benzoindoline

donors with a butyl chain (dye **N1**) or a long dodecyl chain with additional 2,5-dimethylphenyl substituent (dye **N2**). Polymethine **N3d**, an analogue of **CPO-1** with di-<sup>t</sup>Bu-carbazole “front” and fluorene “back” substituents, was prepared in order to examine the changes in the thermal stability brought about by bulky groups. The new compounds were characterized by high-resolution mass spectrometry (HRMS), and NMR spectroscopy (spectra provided in the ESI). All final chromophores exhibit a metallic green luster in the solid state, characteristic of several strongly absorbing far-red to NIR polymethine dyes. The <sup>1</sup>H NMR spectra are consistent with all-*trans* configurations for the polymethine bridge, but with BLA reduced from that seen in simple polyenes (<sup>3</sup>*J* = 12-13 Hz).

**Scheme 1.** General synthesis of the new unsymmetrical polymethine dyes with chalcogenopyran, benzoindoline and indoline donor groups.



**Figure 2.** Left: crystal packing of **O2a**•toluene in columns running along the a-axis of the unit-cell. Right: Crystal structure of **O2a** with labeled polymethine bridge atoms. Orange dashed lines represent hydrogen bonds. A co-crystallized toluene solvent molecule has been omitted for clarity.

**X-ray crystallography.** An X-ray quality crystal of compound **O2a** was obtained by slow evaporation of a toluene solution over 2 weeks. The X-ray data were collected immediately to avoid any solvent loss from the crystal (see ESI for details on the data collection and the refinement results). The final refined formula is **[O2a•(toluene)]** where one molecule of toluene co-crystallizes with one **O2a** molecule in the unit-cell. The crystal packing can be viewed as columns of **O2a** molecules running along the *a*-axis of the unit-cell (Figure 2, left). Within the column, molecules stack in a head to tail mode and the average plane-to-plane distance between two neighboring molecules is equal to 3.93(1) Å. Toluene co-crystallized solvent molecules are inserted between dye molecules and columns. The whole crystal packing is then ensured by weak interactions.

**Table 2. Important bond lengths within crystal structure of O2a.**

Bond	Bond length / Å	Bond	Bond length / Å
C6-C5	1.398(6)	C5-C4	1.374(6)
C4-C3	1.411(6)	C3-C2	1.372(6)
C2-C27	1.430(5)	C27-C28	1.383(6)
C28-C29	1.401(5)	C29-C30	1.380(5)

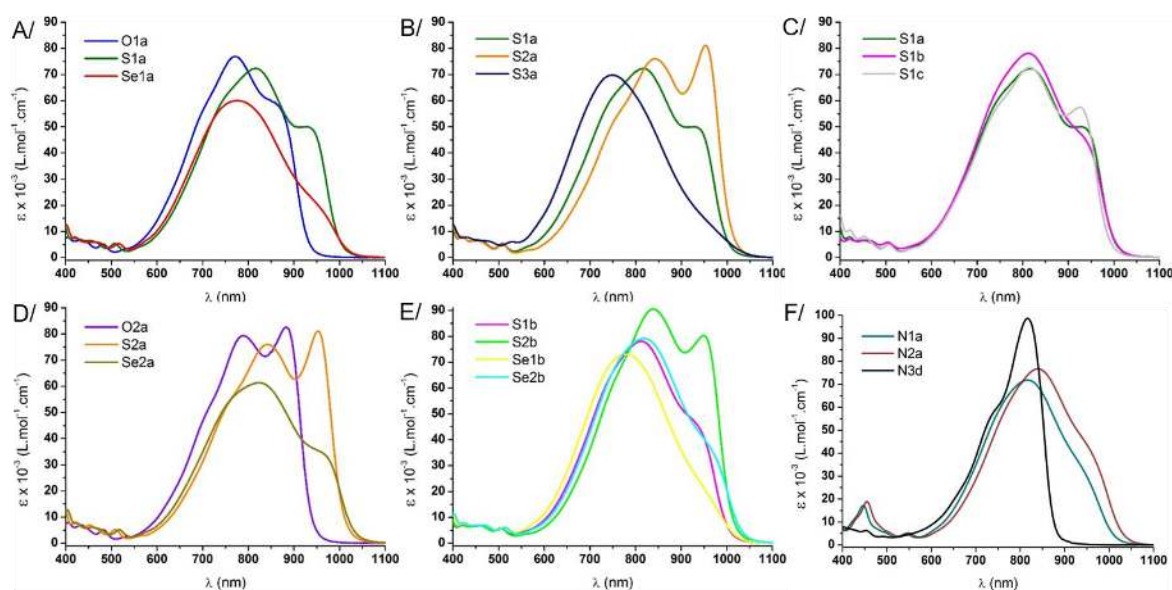
The crystallographically determined molecular structure (Figure 2, right) revealed a *trans* configuration of the polymethine bridge without any large twist of the 14 sp<sup>2</sup> carbon-skeleton. The geometry of the molecule is influenced by hydrogen...halogen weak interactions (C4-H41...Cl1 and C28-H281...Cl1, 2.41(1) and 2.51(5) Å respectively). The conjugated C<sub>6</sub>-C<sub>30</sub> carbon chain is constituted of alternating long (average bond length: 1.410(6) Å) and short (average bond length: 1.377(8) Å) C(sp<sup>2</sup>)-C(sp<sup>2</sup>) bonds, with a BLA value of 0.03(3) Å within the central heptamethine bridge (see Table 2). This

value is lower than that seen in the crystal structure of polymethine **CPO-1** (BLA = 0.06 Å),<sup>14</sup> indicating an increased contribution from the zwitterionic resonance structure for **O1a**, resulting in a somewhat more cyanine-like structure (*vide infra*), at least in its crystals.<sup>23</sup>

**Thermogravimetric analysis.** The thermal stability of the dyes was evaluated by thermogravimetric analysis under inert atmosphere, and the decomposition temperatures corresponding to a 10% weight loss (T<sub>d10</sub>) are summarized in Table 3. All dyes possess good to excellent thermal stability with decomposition temperatures between 255 °C for **Se2a** and 370 °C for **Se2b**. It is important to note that the introduction of a di-*t*-Bu-carbazole “front” functional group in place of chlorine significantly improves thermal stability, especially in the case of the **N3d** dye, for which T<sub>d10</sub> is increased by 50 °C in comparison to its chloro-substituted analogue **CPO-1**.

**Absorption spectroscopy.** The UV-vis-NIR absorption properties of the fifteen dyes were recorded at room temperature in dichloromethane solution (ca. 10<sup>-5</sup> M) and the data are summarized in the Table 3. The absorption spectra presented in Figure 3 show the dependence of these spectra on the nature of chalcogen in the chalcogenopyran dyes (Figure 3, A/ and D/), of the “end” moieties of thiopyran dyes (Figure 3, B/), of the “front” or “back” substituents of chalcogenopyrans (Figure 3, C/ and E/), and of the various structural features of the (benzo)indoline-based derivatives (Figure 3, F/).

All these unsymmetrical polymethines display relatively broad and strong absorption bands centered in the red to NIR spectral range (600-1000 nm), molar extinction coefficients (ε) ranging from 60,000 (**Se1a**) to 100,000 M<sup>-1</sup>cm<sup>-1</sup> (**N3d**), and full widths at half-maximum (FWHMs) ranging from 2,200 (**N3d**) to 4,300 cm<sup>-1</sup> (**S2a**). In most cases, absorption spectra consist of a relatively broad high-energy component, in some cases with poorly resolved, presumably vibronic, structure, and a lower energy relatively narrow feature, which varies from the most



**Figure 3.** Comparative absorption spectra, in dichloromethane solutions (ca. 10<sup>-5</sup> M), of the polymethines studied in this work.

strongly absorbing feature in the spectrum for some compounds (e.g., **S2a**) to a barely discernible shoulder for others (**S3a**). The absorption spectra of the O-, S-, Se-pyrylium-terminated polymethines (Figure 3, A/ and D/) reveal a 40 nm (ca. 700  $\text{cm}^{-1}$ ) red-shift of the most prominent transition for dye **S1a** compared to **O1a** and **Se1a**. A similar trend is observed for **S2a** compared to **O2a** and **Se2a**. The influence of the “end” substituents is evaluated for the thiopyran derivatives **S1-3a** (Figure 3, B/). The phenyl-containing polymethine **S3a** exhibits the most blue-shifted absorption band, featuring a particularly structureless profile. The absorption of ‘butyl and adamantyl-containing dyes **S1a** and **S2a** are red-shifted and show a more well-defined sharp low-energy feature, which is centered at 950 nm. Such a comparison suggests that the lower energy band intensity is correlated with the increasing electron-rich character of the thiopyran extremity, as indicated by cyclic voltammetry (*vide infra*). The possible origin of the broad and sharp features is discussed below in the context of the solvatochromism of these compounds.

Not surprisingly, the “front” and “back” substituents in the **S1a-c** series (Figure 3, see C/ and E/) have relatively little influence on the absorption bands. Corresponding absorption profiles are almost superimposable, with largest differences in the low energy transition. Benzoindoline-containing polymethines **N1a** and **N2a** display comparable almost structureless absorption bands (Figure 3, F/). The noticeable absorption red-shift compared to that of the **N3d** indoline-containing dye is explained by the conjugation extension brought by the additional benzene ring in **N1a** and **N2a**. Polymethine **N3d** exhibits the most pronounced contribution of the low energy band within the whole series.

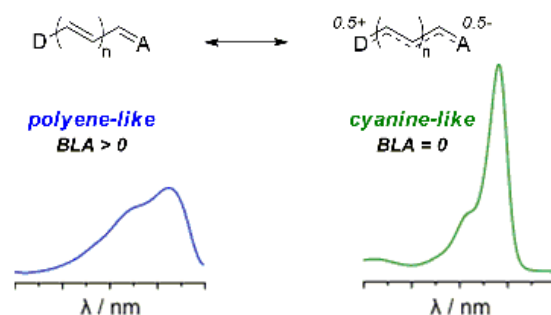
**Table 3. Linear optical and thermal data for polymethines.**

Compound	$\lambda_{\text{max}} / \text{nm}$ ( $\epsilon_{\text{max}} \times 10^{-3} / \text{M}^{-1}\text{cm}^{-1}$ ) [a]	$\lambda_{\text{em}} / \text{nm}$ [a]	$T_{\text{d}10} / \text{°C}$ [b]
<b>O1a</b>	771 (77)	931	280
<b>O2a</b>	789 (79), 882 (82)	932	270
<b>S1a</b>	816 (72)	986	285
<b>S1b</b>	812 (78)	988	325
<b>S1c</b>	816 (73)	974	275
<b>S2a</b>	842 (76), 953 (81)	993	305
<b>S2b</b>	839 (91), 949 (80)	n.d.	n.d.
<b>S3a</b>	748 (69)	1068	300
<b>Se1a</b>	775 (60)	1008	300
<b>Se1b</b>	779 (73)	1012	340
<b>Se2a</b>	824 (61)	1016	255
<b>Se2b</b>	819 (80)	1017	370
<b>N1a</b>	817 (72)	1008	260
<b>N2a</b>	840 (77)	1022	285
<b>N3d</b>	816 (100)	862	300

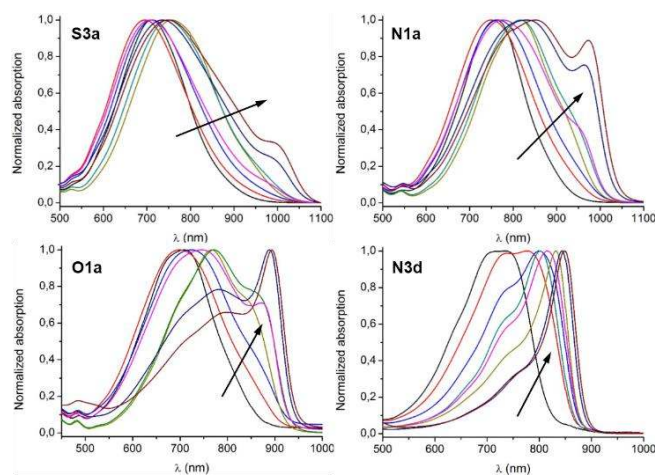
[a] In dichloromethane. [b] Decomposition temperature with 10% weight loss measured by TGA.

This particularly sharp (FWHM  $\sim 2,000 \text{ cm}^{-1}$ ) and strong ( $\epsilon = 100,000 \text{ M}^{-1}\text{cm}^{-1}$ ) absorption is accompanied by a high energy shoulder, possibly vibronic in origin, and is reminiscent of the transitions commonly observed for symmetrical cyanines and cyanine-like polymethines (*vide infra*).<sup>24</sup>

**Absorption solvatochromism.** According to previous studies<sup>25-35</sup> the balance of the electron-donating/withdrawing strengths at the extremities of a push-pull polymethine can modulate the low-energy band between relatively broad charge-transfer-like band shapes and a very sharp feature with much higher peak absorptivity. A narrow band shape indicates that polymethine has a cyanine-like electronic structure, characterized by a near-zero BLA (Figure 4), which can be thought of as arising from equal contributions of neutral and zwitterionic resonance structures. Unsymmetrical polymethines are known to be sensitive to their environment: a polar solvent will favor more strongly dipolar structures and so can drive a structure from polyene-like to cyanine-like, or from cyanine-like to zwitterionic.<sup>16, 36</sup>



**Figure 4.** Representation of the *polyene*-like and *cyanine*-like electronic structures of polymethine dyes and of their corresponding absorption profiles.



**Figure 5.** Absorption solvatochromism for polymethines **S3a**, **N1a**, **O1a** and **N3d** in toluene (black), ethyl acetate (red), tetrahydrofuran (blue), chloroform (dark yellow), dichloromethane (cyan), acetone (magenta), *N,N*-dimethylformamide (navy), dimethylsulfoxide (wine).

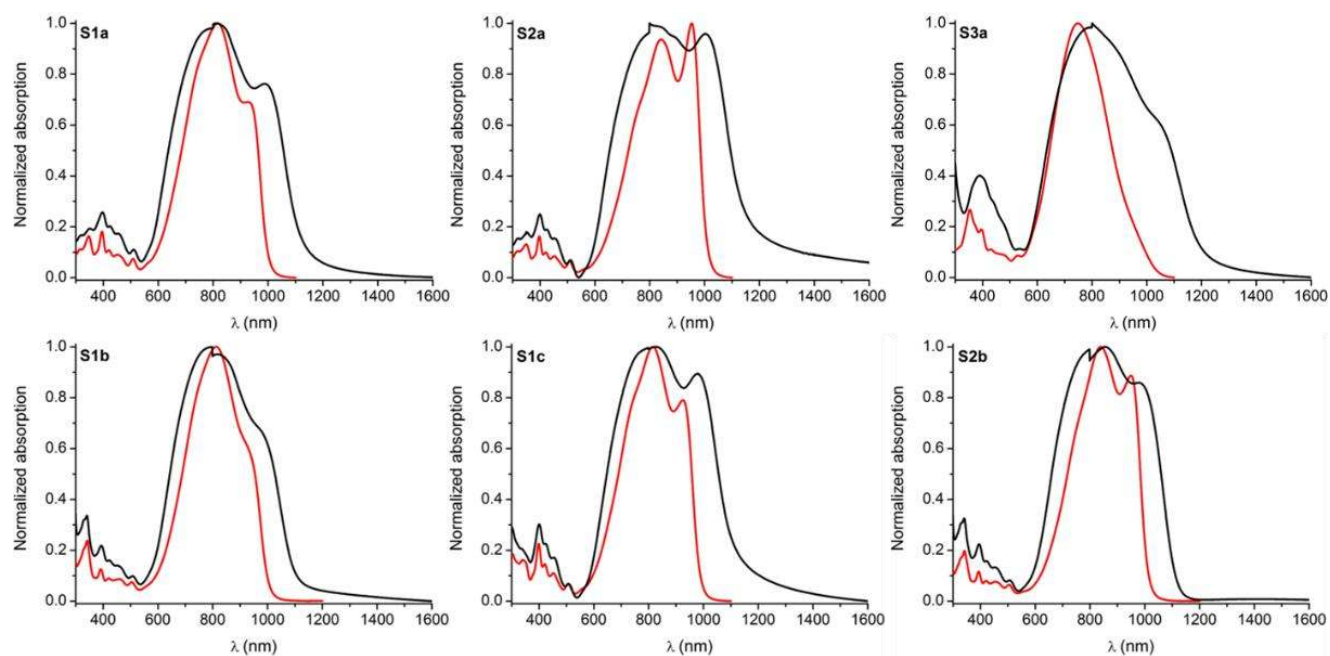
The behavior of the present series of polymethines was further investigated by studying the absorption solvatochromism of selected compounds in a wide range of



medium polarity. Most of the molecules feature a broad near-Gaussian band in less polar solvents (Figures 5 and S67). The solvatochromism of polymethine **N3d** is perhaps the most straightforward, and is similar to that of its **CPO-1** analogue.<sup>16</sup> The spectrum is red-shifted and increasingly cyanine-like as the solvent polarity is increased, consistent with expectations of a more polar solvent on the BLA. In contrast, the spectra of **S3a** and **N1a** display a progressive red-shift of the absorption maxima with increasing polarity and reveal the appearance of a relatively sharp low-energy peak at 950 nm in the most polar solvents (DMF and DMSO). In the case of **O1a**, the solvent polarity has a more dramatic influence on the shape of the absorption bands. The growing feature centered at 900 nm becomes stronger than the broad band with  $\lambda_{\text{max}}$  at around 750 nm and is weakly shifted upon increasing polarity. Such a behavior is more pronounced than that seen in other donor-acceptor polyenes in that, in the more polar solvents, apparently cyanine-like and polyene-like features are simultaneously present. These spectra (including many of the CH<sub>2</sub>Cl<sub>2</sub> spectra shown in Figure 3) are reminiscent of what is seen for certain long-chain nominally symmetrical cyanine-like ionic polymethines.<sup>37,23, 38-42</sup> The origin of such spectra are not

entirely clear, but may reflect the coexistence of polyene-like and cyanine-like structures, perhaps arising from different local solvation spheres.<sup>43-44</sup>

**Thin film absorption.** The absence of aggregation is beneficial for the fabrication of NLO devices that require high concentration of the material without significant alteration of its optical properties. To examine the extent to which the spectra of dyes in this study are perturbed upon going from dilute solution to high-concentration thin films, we prepared films with 100 wt % dye loading by spincoating solutions of the dyes in dichloromethane (10 mg/mL) on glass substrates. The corresponding absorption spectra shown in Figure 6 and S66 exhibit much greater similarities between solution and thin film absorption profiles than those for previously reported symmetrical cationic polymethine analogues.<sup>17-18, 45</sup> For example in the thiopyran derivative **S1a** the absorption maxima in solution and thin film are fairly similar, with a slight broadening of the high and low energy edges. Replacement of 'butyl with adamantyl "end" group (**S2a**) results in a more significant perturbation of the shape of the spectra together with



**Figure 6.** Normalized absorption spectra in dichloromethane solutions (red, *ca.*  $10^{-5}$  M) and films of 100 wt % dye (black).

a noticeable shift of the onset of absorption and/or scattering to beyond 1600 nm. Polymethine **S3a** reveals the most pronounced broadening of absorption towards low energy. The spectrum suggests the formation of a new aggregate transition, the terminal phenyl groups being inefficient at preventing intermolecular interactions in the solid state (consistent with what is seen in bis(chalcogenopyrylium)-terminated heptamethines<sup>18</sup>). Introduction of the fluorenyl moiety in the “back” position (**S1c**) provides no significant change of absorption profile compared to **S2a**, whereas the di-<sup>t</sup>Bu-carbazole substituent in **S1b** affords the smallest shifts in the red absorption edge. The combination of bulky adamantyl “end” and di-<sup>t</sup>Bu-carbazole “back” groups (**S2b**) leads to the spectra that show the least difference between the solution and solid states, the solid-state spectra exhibiting a well-defined low-energy cut-off at 1150 nm. These results demonstrate that the combination of selected bulky substituents provides a control of the absorption properties in the solid state, as recently observed for Pd-substituted polymethines.<sup>46</sup> However, the quasi-suppression of aggregation evidenced here does not prevent an antiparallel alignment (hence centrosymmetric) of neighboring dipolar molecules, as found in the crystal structure of **O1a**.

**Cyclic voltammetry.** To gain insight into the relative strength of the various electron-donating extremities, the redox properties of selected compounds were investigated by cyclic voltammetry in dichloromethane (Table 4). The  $\pi$ -donor strength of the chalcogenopyran moieties can be compared by examining the reduction potentials of polymethines **O1a**, **S1a** and **Se1a**. The compounds become increasingly easier to reduce from O- to S- to Se-containing dyes (−1.03, −0.99, −0.95 V respectively). This suggests that the  $\pi$ -donor strength decreases in the order pyran > thiopyran > selenopyran, leading to a decreased contribution from the zwitterionic resonance structure and to moving the electronic structure of the dyes away from the cyanine limit (consistent with the relative importance of the sharp low-energy transition in absorption spectra seen in Figure 3, A).<sup>47</sup>

**Table 4. Redox potentials vs. FeCp<sub>2</sub><sup>+0</sup> in dichloromethane / 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> for selected unsymmetrical polymethines.**

Compound	E <sub>1/2</sub> <sup>+0</sup> / V	E <sub>1/2</sub> <sup>0-</sup> / V
<b>O1a</b>	+0.14	−1.03
<b>S1a</b>	+0.06	−0.99
<b>Se1a</b>	+0.15	−0.95
<b>S2a</b>	+0.06	−1.00
<b>S3a</b>	+0.17	−0.92
<b>N1a</b>	+0.18	−0.96

As expected, the adamantyl-substituted compound (**S2a**) has redox potentials similar to its <sup>t</sup>butyl analogue (**S1a**). The phenyl-based thiopyran (**S3a**) appears to be a slightly weaker donor than its alkyl analogues with reduction occurring at −0.92 V. The phenyl groups presumably act themselves as mild  $\pi$ -acceptors, thereby decreasing the donor's electron-density. This observation correlates with the absorption shift observed in Figure 3 (B/),

where the alkyl end groups induce a red-shift of the absorption maxima. The polymethine **N1a** shows similar reduction potential to **Se1a**, which is consistent with the comparable structure of their absorption spectra.

**Fluorescence spectroscopy.** Luminescence measurements in dichloromethane solution (Table 3 and Figure S68) show that these polymethines display detectable fluorescence in the NIR with lifetimes < 0.4 ns. The emission bands are characterized by a sharp profile (FWHM generally ~ 1500-2000 cm<sup>-1</sup>), especially in the case of the **N3d** dye (FWHM ~ 700 cm<sup>-1</sup>). It is worth noting that **N3d** presents the smallest Stokes shift, consistent with its more cyanine-like absorption spectrum (Figure S69).

**Second-order nonlinear optical properties.** The quadratic hyperpolarizabilities of the new chromophores were determined by Electric Field Induced Second Harmonic (EFISH)<sup>48-49</sup> and Hyper Rayleigh Scattering (HRS)<sup>50-51</sup> measurements at 1907 nm in chloroform solution, and results are summarized in Table 5. Due to the high absorption of our molecules at the second harmonic wavelength at 955 nm,  $\mu\beta^{1.9}$  values were inferred from experimental second-harmonic intensity values corrected according to the Beer–Lambert law of solution absorption using a 10<sup>6lc</sup> factor where  $\epsilon$  is the molar extinction coefficient of the sample at 955 nm,  $l$  the thickness of the solution, and  $c$  its concentration. Measurements were carried out at low concentrations not exceeding 10<sup>-4</sup> M in order to minimize this correction factor (10<sup>6lc</sup> < 3).

With that said, high to exceptionally high quadratic hyperpolarizabilities were recorded by EFISH for all these polymethines. Compounds **O1a** and **O2a** with the pyran donor show large  $\mu\beta^{1.9}$  values of 26,000×10<sup>-48</sup> esu and 36,600×10<sup>-48</sup> esu, respectively. The thio- and selenopyran-containing derivatives display higher  $\mu\beta^{1.9}$  values between 86,300×10<sup>-48</sup> esu (**S1b**) and 115,000×10<sup>-48</sup> esu (**S2a**), with the exception of dye **S3a** with Ph “end” groups, which displays a  $\mu\beta^{1.9}$  of 37,000×10<sup>-48</sup> esu. Dyes **N1a** and **N2a** with benzoindoline donor display hyperpolarizabilities of the order of 100,000×10<sup>-48</sup> esu, whereas **N3d** response is more modest, with 28,000×10<sup>-48</sup> esu. This latter value is consistent with the one obtained for **CPO-1** with similar conjugated backbone,<sup>16</sup> and with their more cyanine-like absorption spectra. The influence of the “front” and “back” substituents is weak, with  $\mu\beta^{1.9}$  in the range of 90,000-100,000×10<sup>-48</sup> esu for the **S1a-c** series, in agreement with the tendency observed for linear absorption (Figure 3, C/).

Interestingly, polymethines **O1a**, **O2a**, **S3a** and **N3a** have the smallest nonlinear responses in the series, which can be correlated to their low absorption intensity at 955 nm corresponding to a weaker resonance with the incident light harmonic. Dyes **Se1a** and **Se1b** have similar quadratic hyperpolarizabilities, with 53,000×10<sup>-48</sup> esu and 67,000×10<sup>-48</sup> esu respectively. The quadratic hyperpolarizabilities were also evaluated by HRS and show reasonable values ranging from about 2,600×10<sup>-30</sup> (**S1b**) to 6,500×10<sup>-30</sup> esu (**Se2b**). These results are among the highest responses measured for organic dyes. It must be pointed-out that HRS results do not necessarily follow the trends observed for  $\mu\beta$  values inferred by EFISH, as  $\beta_{\text{HRS}}$  values contain, not only the

dipolar contribution to the  $\beta$  values, but also potentially non-negligible octupolar contribution that are not correlated to its dipolar counterpart.<sup>52</sup>

**Table 5. Quadratic hyperpolarizabilities of polymethines in chloroform.  $\mu\beta^{1.9}$  measured by EFISH at 1907 nm and  $\beta^{1.9}$  measured by HRS at 1907 nm.**

Compound	$\mu\beta^{1.9}_{\text{EFISH}} / 10^{-48}$ esu	$\beta^{1.9}_{\text{HRS}} / 10^{-30}$ esu
O1a	26,000	n.d.
O2a	36,600	n.d.
S1a	103,000	3,320
S1b	86,300	2,600
S1c	87,500	4,880
S2a	115,000	2,680
S3a	37,000	3,010
Se1a	53,000	4,100
Se1b	67,000	2,370
Se2a	85,400	2,730
Se2b	78,500	6,540
N1a	99,200	3,070
N2a	94,100	2,960
N3d	28,000	n.d.

## CONCLUSION

In summary, a series of fifteen new TCF-based unsymmetrical polymethines has been synthesized. The introduction of bulky groups led to an increase of the thermal stability and a decrease of the effect of chromophore-chromophore interactions in films of pure dyes. The synthetic pathway enables the incorporation of selected heterocyclic donors having a direct influence on the electronic properties of the dyes. Solvatochromism experiments evidenced that the series of dyes tend to stabilize under a cyanine electronic structure in polar solvents. Finally, the combination of high intrinsic hyperpolarizability coupled with a large static dipolar moment results in excellent values of  $\mu\beta$  for pyran-, thiopyran-, selenopyran- and benzoindoline-containing polymethines. From that point of view, these dyes are particularly promising for electro-optical modulation.

## ASSOCIATED CONTENT

Additional spectroscopic details, thermogravimetric analysis, single-crystal X-ray diffraction data, synthetic details and characterizations, including NMR spectra are provided. This material is available free of charge via the Internet at <https://doi.org/10.1021/acs.chemmater.8b00960>

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## Notes

The authors declare no competing financial interest.

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