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## Synthesis, Structure, Linear and Nonlinear Properties of Tricyanofuran–Terminated Merocyanine Dyes

John P. Tillotson<sup>1\*</sup>, Georgii Bogdanov<sup>2</sup>, Evgheni V. Jucov<sup>2</sup>, Victor N. Khrustalev<sup>2,3</sup>, Sergei Rigin<sup>2</sup>, Joel M. Hales<sup>1</sup>, Joseph W. Perry<sup>1</sup>, Tatiana V. Timofeeva<sup>2\*</sup>

<sup>1</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, 30332 USA
 <sup>2</sup>Department of Chemistry, New Mexico Highlands University, Las Vegas, New Mexico, 87701 USA
 <sup>3</sup>Peoples' Friendship University of Russia (RUDN University), 117198 Moscow, Russia

## ABSTRACT

Structural and spectroscopic characteristics of merocyanine dyes are important because of their potential applications in optoelectronics and sensors. Herein we report synthesis, X-ray diffraction characterization of crystal structure, spectroscopic and NMR studies of four merocyanine dyes which, according to their strong donor-acceptor structure, exhibit a second order polarizability ( $\beta$ ). Crystallographic studies demonstrated an almost planar structure of all molecules and indicated the occurrence of conformational changes in  $\pi$ -conjugated bridge between donor and acceptor. For three homologues similar packing modes, defined mostly by week C-H...N interactions, were found in crystals. Bond length alternation (BLA) values have been evaluated using crystallographic and NMR data and have shown a correlation to their nonlinear optical activity. Second order polarizabilities for all compounds were measured using hyper Rayleigh scattering (HRS) in solution. It was found that the merocyanines studied exhibit very large second order polarizabilities (up to 4.1 10<sup>-27</sup> esu), making them potentially useful for materials for second harmonic generation (SHG). Unfortunately, they do not demonstrate acentric packing of chromophores, which is required for SHG in the crystalline state, but may show promise for other applications such as poled polymer blends or for SHG sensing in biological environments.

Keywords: Nonlinear optical materials, Bond length alternation, Second harmonic generation, Crystal structure

#### **1 INTRODUCTION**

Interest in organic merocyanine dyes, or "push-pull" polymethines, has arisen largely a result of their applications in optoelectronics, for instance, in organic light emitting diodes [1], luminescent sensors [2,3], solid-state lasers [4] and in bioimaging [5], where two-photon excitation offers additional advantages [6]. Optimizing the electrooptic activity of push-pull chromophores requires rational molecular design, analogous to that of other nonlinear optical (NLO) molecules. The photophysical properties of this class of chromophores are largely dependent on three main structural aspects: strength of terminal donor and acceptor groups and length of conjugated chain between them. Recently, organic chromophores with (3-cyano-5,5-dimethyl-2(5H)-furanylidene)malononitrile (so called tricyanofuran, TCF) as an acceptor group have been investigated for their high electrooptic activity and structural characteristics in solid state [6-10]. Different applications in technics, biology and medicine were identified for this group of materials, such as their use for data storage [11], for sensors for gaseous and aqueous alkaline analytes [12,13], antibacterial activity [14] and many others.

Computational estimates of the first hyperpolarizability of a large series of TCF-terminated push-pull chromophores have been carried out using DFT calculations [15]. Authors considered different conformations of polyene chains and different orientations of TCF groups relative to these chains. Absorbance and fluorescence spectra of this group of materials have also been studied before [16,17], and we enriched published data by investigation of these spectra in different solvents. However, to the best of our knowledge, no structural studies of TCF merocyanines with N,N-dimethylaminophenyl (DMAP) donor groups, such as those of this series (see Scheme 1 for a generic DMAP-TCF structure) in crystal, have been published. We are presenting here four DMAP-TCF structures with the polyene bridges containing 1, 2, 3 or 4 - C=C- bonds (TCF[1], TCF[2], TCF[3], and TCF[4], respectively) along with discussion of their conformational peculiarities and interrelations of the molecular and packing characteristics to their properties.



Chemical structure of TCF[n], where n = 1-4

Scheme 1

#### 2 MATERIALS AND METHODS

#### 2.1 Synthesis

Synthetic scheme of described materials is presented below.



Figure 1. Stepwise extension of dimethylaminophenyl-terminated polyenals.



Figure 2. Synthesis of TCF[n] by Knoevenagel condensation.

All materials and reagents were commercially available, purchased from Sigma Aldrich and used as received except where noted. Tetrahydrofuran was dried using a sodium-benzophenone ketyl pot and freshly distilled for each use. ((1,3-Dioxolan-2-yl)methyl)triphenyl phosphonium bromide, while commercially available, was synthesized as described below because it resulted in higher yields. Synthesis details are presented in Supporting Information.

## **2.2 Instrumentation**

**X-Ray:** The single-crystal X-ray diffraction data for TCF[1]-TCF[4] were collected on a Bruker SMART APEX II CCD diffractometer ( $\lambda$ (MoK<sub> $\alpha$ </sub>)-radiation, graphite monochromator,  $\omega$  and  $\varphi$ scan mode) and corrected for absorption using the *SADABS* program [18]. For details, see **Table 1**. The structures were solved by the intrinsic phasing modification of direct methods [19] and refined by a full-matrix least square technique on F<sup>2</sup> in anisotropic approximation for nonhydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters  $[U_{iso}(H) = 1.5U_{eq}(C)$  for the methyl groups and  $1.2U_{eq}(C)$  for the other groups]. All calculations were carried out using the SHELXTL program suite [19].

**NMR:** <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were acquired on one of the following NMR spectrometers: Bruker Avance IIIHD-500 MHz (with Prodigy cryoprobe), a Bruker Avance IIIHD-700 MHz spectrometer, or a Bruker Avance IIIHD-800 MHz spectrometer. Each NMR will list the field strength used. All chemical shifts are indirectly referenced TMS through the residual solvent peaks as reported in the literature [20].

**Spectroscopic characterization:** Linear absorption measurements were performed using either a UV-Vis-NIR scanning spectrophotometer (UV-3101PC, Shimadzu). Steady state fluorescence measurements were conducted using a scanning spectrofluorometer (Flurolog-2, SPEX). All spectra were measured in 1 cm special optical glass cuvettes (SOG, Starna cells).

Hyper-Rayleigh scattering (HRS): measurements were conducted on a home-built Hyper-Rayleigh scattering / two-photon induced fluorescence setup. The light source for the HRS measurements consisted of a Ti:Sapphire regenerative amplifier (Solstice, Spectra-Physics, 800 nm, 3.7 W average power, 100-fs pulse width, 1 kHz repetition rate). The amplified laser is used to pump a computer controlled optical parametric amplifier (OPA, TOPAS-C, Light Conversion). The OPA can be continuously tuned from 1100 - 2600 nm (FWHM 10 - 30 nm) and the second harmonic of the OPA can be used in the range of 550 - 1100 nm (~30 mW average power). The range of excitation energy, at the sample, varies between  $2 - 12.5 \,\mu$ J and is limited below the onset of higher order nonlinear optical effects such as white-light generation. Before entering the sample enclosure, the beam is filtered using appropriate long pass filters (typically 850nm long pass) to remove stray 800 nm light. The beam then passes through two orthogonally oriented cylindrical lenses and into the sample cell (1 cm path length, Special Optical Glass, Starna Cells). The cell holder is attached to a movable stage allowing the cuvette to be positioned such that the focus of the beam is just next to the wall of the cell, in order to minimize reabsorption. The generated light is collected at a right angle by means of a collection lens (focal length = 8.0 mm, KPA016-C, Newport Corporation) and is passed through appropriate short pass filters needed to remove scattered light from excitation beam as well as two-photon fluorescence from the sample. The filtered light is collected by fiber collimators (F810SMA-543, Thorlabs) and sent through a two-leg fiber bundle (13 fibers per bundle oriented in a line, Leoni) to an imaging fiber adapter (FC-446-030, Princeton Instruments) that is coupled to a monochrometer (SpectrPro-150, Acton). The HRS signal is detected on a liquid nitrogen cooled CCD camera (LN/CCD-1100PB, Roper Scientific, controller: ST-133, Roper Scientific).

For HRS measurements, samples were dissolved in spectroscopy grade solvents at concentrations ranging from 1  $\mu$ M to 10 mM. HRS spectra were acquired over long exposure times (50 – 500 s) due to the weak nature of the HRS signal. All samples were stirred with a micro stirbar that was carefully placed below the beam. All hyperpolarizability values were referenced internally to and corrected for the HRS signal and hyperpolarizability of the corresponding solvent as reported by Campo et al<sup>1</sup>. The raw data was processed in MATLAB by first smoothing the data using the built-in smoothing protocol and the robust loess function which is a local regression using a weighted linear least square fit with second degree polynomial model and assigns a lower weight to outliers. The smoothing function was adjusted to exclude cosmic rays, typically spanning 0.5 to 1% of the data. To remove the contribution from multiphoton fluorescence the baseline of the smoothed data was fit by a fifth-order polynomial using manually selected regions of baseline and subtracted from the raw data.

## **3. RESULTS AND DISCUSSION**

## 3.1 X-Ray structure determination

Crystal data and structure refinement results of TCF[1]-TCF[4] are summarized in Table 1.

Table 1. Crystallographic	data and	summary of	data co	ollection	and structure	refinement	for
TCF[1]-TCF[4].							

Identification code	TCF[1]	TCF[2]	TCF[3]	TCF[4]
Empirical formula	C <sub>20</sub> H <sub>18</sub> N <sub>4</sub> O	$C_{22}H_{20}N_4O$	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O	C <sub>26</sub> H <sub>24</sub> N <sub>4</sub> O
Formula weight, g/mol	330.38	356.42	382.45	408.49
Temperature, K	150	100	150	100
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	Pnma	Pnma	$P2_{1}/c$	<i>P</i> -1
<i>a</i> , Å	18.618(3)	17.553(3)	7.0919(10)	7.6501(17)
<i>b</i> , Å	6.9885(13)	6.8670(13)	17.289(2)	17.261(4)
<i>c</i> , Å	13.737(3)	15.561(3)	17.417(3)	18.469(4)
α, °	90	90	90	66.112(3)
β, °	90	90	98.082(2)	87.328(3)
γ, °	90	90	90	85.196(3)
V, Å <sup>3</sup>	1787.3(6)	1875.7(6)	2114.3(5)	2221.9(8)
Ζ	4	4	4	4
$d_{calcd}, g/cm^3$	1.228	1.262	1.201	1.221
$\mu$ , mm <sup>-1</sup>	0.079	0.080	0.076	0.076
F(000)	696	752	808	864
Theta range for data	1.842 to 31.759	4.097 to 30.603	1.668 to 31.868	4.261 to 30.650
collection, °				
Index ranges	$-27 \le h \le 26$ ,	$-25 \le h \le 25$ ,	$-9 \le h \le 10$ ,	$-10 \le h \le 10$ ,
	$-10 \le k \le 9,$	$-9 \le k \le 9,$	$-24 \le k \le 25$ ,	$-24 \le k \le 24,$
	$-20 \le l \le 19$	$-22 \le l \le 22$	$-24 \le 1 \le 25$	$-26 \le l \le 26$
Reflections collected	20316	15371	24461	26728
Independent reflections	3125	3089	6785	13529
	$[R_{\rm int} = 0.0446]$	$[R_{\rm int} = 0.0363]$	$[R_{\rm int} = 0.0574]$	$[R_{\rm int} = 0.0308]$
Data / restraints /	3125/0/151	1999 / 0 / 170	6785 / 0 / 266	13529 / 0 / 567
parameters				
Goodness-of-fit on $F^2$	1.129	1.045	1.011	1.007
Final <i>R</i> indices $[I > 2\sigma(I)]$	0.0680, 0.1819	0.0441, 0.1211	0.0542, 0.1469	0.0511, 0.1219
$R_1, wR_2$				
$R$ indices (all data), $R_1$ ,	0.0899, 0.1976	0.0526, 0.1294	0.0809, 0.1653	0.0839, 0.1372
$wR_2$				

#### 3.2 Structural properties

All molecules studied (Scheme 1, Figures 3, 4) have nearly planar structures. A consideration of the three planar fragments in these molecules – donor (D), acceptor (A) and  $\pi$ -conjugated bridge ( $\pi$ ) demonstrated that TCF[1] and TCF[2] are perfectly planar (in the crystal,

molecules occupy a special position on the mirror plane *m*). In molecule TCF[3], deviations of atoms from the mean plane passed through these three fragments are relatively small – 0.048  $\Box$ . In two symmetrically independent TCF[4] molecules (**A** and **B**), deviations from the total planarity are slightly larger (for **A** – 0.187  $\Box$  and **B** – 0.242  $\Box$ ). The dihedral angles between acceptor and bridge groups (A/ $\pi$ ) and donor and bridge groups (D/ $\pi$ ) are presented in **Table 2**. All the above-mentioned data demonstrate that an increase of length of conjugated bridge makes a molecule slightly less planar, however, these changes are insignificant. Thus, in all molecules TCF[1]-TCF[4], the X-ray studies revealed the presence of extensive conjugated system. It should be noted that, in all molecules, the  $\pi$ -bridge adopts the all-trans (all-*E*-isomeric) configuration of the double bonds.

**Table 2.** Dihedral angles (°) between planar fragments and selected bond lengths (Å) in molecules TCF[1]-TCF[4].

	TCF[1]	TCF[2]	TCF[3]	TCF[4] (A /B)
Dihedral angle Acceptor/	0.0	0.0	3.671(55)	10.698(74)/11.933(57)
<b>π-</b> Bridge				
Dihedral angle Donor/ $\pi$ -	0.0	0.0	3.920(57)	10.022(84)/8.268(83)
Bridge				
C6-C2	1.377(3)	1.3792(17)	1.3736(15)	1.3774(18)/1.3722(18)
C2-C3	1.432(3)	1.4344(17)	1.4323(15)	1.4301(18)/1.4329(18)
C3-C4	1.383(3)	1.3771(17)	1.3728(15)	1.3732(17)/1.3727(17)
C4-C18	1.416(3)	1.4166(17)	1.4202(15)	1.4140(18)/1.4148(18)
C18-C19	1.364(3)	1.3689(17)	1.3575(17)	1.3641(18)/1.3692(18)
C19-C20 (C19-C13)	1.432(3)	1.4200(18)	1.4219(15)	1.4162(18)/1.4177(18)
C20-C21	-	1.3676(17)	1.3555(17)	1.3588(18)/1.3588(18)
C21-C22 (C21-C13)	-	1.4354(18)	1.4217(16)	1.4213(18)/1.4253(18)
C22-C23	-	5	1.3507(17)	1.3552(19)/1.3507(18)
C23-C24 (C23-C13)	-	-	1.4449(15)	1.4249(18)/1.4357(19)
C24-C25	-	-	-	1.3502(18)/1.3470(18)
C25-C26 (C25-C13)	-	-	-	1.4470(18)/1.4510(19)
C13-C14	1.414(3)	1.4086(17)	1.4040(17)	1.4044(18)/1.3960(19)
C14-C15	1.375(3)	1.3798(18)	1.3775(16)	1.3785(19)/1.3775(19)
C15-C10	1.415(3)	1.4204(18)	1.4105(18)	1.4064(20)/1.4019(19)
C10-N10	1.366(3)	1.3647(17)	1.3707(16)	1.3730(18)/1.3673(17)





**Figure 3.** Molecular structures of TCF[1] (a), TCF[2] (b) and TCF[3] (c) with atomic numbering scheme.



Figure 4. Molecular structures of two symmetrically independent TCF[4] molecules with atomic numbering scheme (A – bottom, B – top).

It is important to point out that, in all molecules TCF[1]–TCF[4], the TCF acceptor group contains the internal -C=C-C=C- conjugated chain, which is bound to the conjugated bridge in different ways. In the molecules TCF[1], TCF[2], TCF[3] and TCF[4]-A, the TCF group is oriented in such a way as to continue the all-trans bridge configuration of the double bonds, when talking about polyenes, this is known as *s*-trans configuration, as the double bonds are opposite to one another across the single bond. Conversely, TCF[4]-B exhibits the s-cis type configuration. The differences between the s-cis and s-trans conformers is highlighted in Figure 5. While single bonds generally allow free rotation, in conjugated  $\pi$ -systems, delocalization of electrons across the conjugated chain leads to a configuration less able to freely rotate. Consequently, the two independent molecules A and B of TCF[4] represent different conformers (*atropoisomers*) relative to the A/ $\pi$  fragment. It should be mentioned that, according to quantum DFT computations of TCF[4] carried out by Chafin and Lindsay [21], the s-cis conformer was found to be 1.3 kcal/mol more favorable than the s-trans conformer. However, our previous DFT calculations of the s-cis and s-trans conformers performed for dye FTC [7] give a smaller difference of only 0.3 kcal/mol. Analysis of literature data shows that in solid state the both binding types have been found [7-10]. This mixture of the TCF[4]-A and B states can also be seen by NMR using a nuclear Overhouser effect spectroscopy (NOESY), showing the interactions of protons through space. As is shown in the Figure 5 below, the interaction of the polyene chain protons and the methyl protons of the TCF group can be examined due to their through-space interactions. Integration of the NOESY signals estimates TCF[4]-A makes up about 62% of the sample in  $CD_2Cl_2$ .



**Figure 5.** Schematic representation of the through space interactions yielding NOESY correlations by NMR.

Molecular packing in crystals of TCF[1]–TCF[4] is influenced by two dominant factors: strong dipole moments and electrostatic interactions. First, due to high dipole moments and

elongated conformations, which are common for NLO chromophores, molecules have antiparallel packing. Second factor is intramolecular and intermolecular interactions between the negatively charged N-atoms of the cyano groups and nearby protons of the polyene chains, phenyl ring and methyl groups. These interactions help to form planar layers (**Figure 6**) and superposition of the layers brings to formation of stacks with antiparallel molecular arrangement. Homologues TCF[1] and TCF[2] are packed in the same space groups with close unit cell parameters and have very similar packing modes. In **Figure 6**, only packing of TCF[2] is shown. Molecular packing mode of TCF[3], which has a monoclinic space group, is also similar to molecular packing in TCF[1] and TCF[2]. In crystal structure of TCF[1]–TCF[4] short C-H...N contacts within the layers are in range 2.48-2.67 (**Figures 6-8**, **Table 3**). These data are in good agreement with the average values for C-H...N(sp<sup>2</sup>) contacts presented by Gavezzotti and Presti [**22**] based on approximately 12,000 of such contacts. Molecular layers are packed in TCF[1] along *b* axis with distance between them equal to 3.494, and in TCF[2] with distance 3.434  $\Box$ .



Figure 6. Molecular packing in crystal TCF[2]: (a) molecular layer along b direction; (b) parquet packing of stacks.

In crystal TCF[3] (**Figure 7**) molecular layers are packed parallel to (-101) with the alternating distances between these layers equal to 3.112 and  $3.524 \square$ . Stacks in structures TCF[1]–TCF[3] present parquet motif (**Figures 6b, 7b**).



**Figure 7.** Molecular packing in crystal TCF[3]: (a) molecular layer parallel to (-101); (b) parquet packing of stacks.

In the crystal TCF[4] molecular packing is more complicated since this crystal is built of two symmetrically independent molecules **A** and **B**. Molecules **A** and **B** form ribbons with alternating positions of these molecules (**Figure 8**). As in molecular layers of TCF[1]–TCF[3], molecules in TCF[4] ribbons are connected by the weak C-H...N hydrogen bonds (**Table 3**). Superposition of this ribbons brings to formation of molecular stacks with antiparallel positions of molecules in such way that stacks are formed of just **A** or just **B** molecules (**Figure 8**). These stacks are packed in almost parallel way (**Figure 8b**).



**Figure 8.** Molecular packing in crystal TCF[4]: (a) molecular ribbons connected with C-H...N bonds and (b) parquet packing of molecular stacks.

 Table 3. Hydrogen bonds parameters in TCF[1]-TCF[4].

	C-H, Å	HN, Å	CA, Å	Angle C-HN,°		
TCF[1]: #	1 x,-y+3/2,z	#2 x-1/2,y,-z+3/2	#3 x-1/2,y,-z+1	/2		
C(51)-H(51B)N(8)#2	0.98	2.67	3.526(3)	145.5		
C(16)-H(16B^a)N(9)#3	0.98	2.63	3.489(4)	145.7		
TCF[2	2]: #1 x,-y+1/2,	z #2 x,y,z-1 #3	x-1/2,y,-z+1/2	•		
C(15)-H(15)N(7)#2	0.95	2.55	3.491(2)	169.2		
C(16)-H(16A)N(9)#3	0.98	2.51	3.489(2)	176.8		
TC	F[3]: #1 -x,y+1	/2,-z+1/2 #2 -x+	1,-y+1,-z+1			
C(16)-H(16B)N(9)#1	0.98	2.60	3.572(2)	172.0		
C(17)-H(17A)N(7)#2	0.98	2.67	3.629(2)	165.0		
TCF[4]: #1 -x+1,-y+1,-z #2 -x+2,-y-1,-z+1						
C52B-H52E-N8A	0.98	2.61	3.274(2)	169.4		
C16A-H16A-N7B	0.98	2.48	3.381(2)	153.1		

It should be mentioned that none of crystals studied demonstrate acentric packing that excludes their direct use for NLO devices.

#### 3.3 Bond length alternation

Furthermore, the structures of TFC[1]–TFC[4] suggest delocalization of electron density inside a polyene chain with the bond length alternation (BLA) presented in **Table 2** and **Figure 9**. The BLA distribution in the dimethylaminophenyl donor fragments found in all molecules demonstrates their pronounced quinoid character (**Table 2**). This phenomenon can be presented by combination of two different resonance forms in the molecules TFC[1]–TFC[4] with distribution of single and double bonds in crystals.



**Figure 9.** Bond length alternation, in Å, for the TCF[n] series as measured by X-ray crystallography.

## 3.4 Absorption spectrum

As it is typical with merocyanines, the studied TCF series exhibit an electronic spectrum, which is dominated by a large broad charge transfer band (**Figure 10**). This series also shows a

hypsochromic shift in absorbance with increasing solvent polarity, also called negative solvatochromism (**Table 4**). This is due to differential solvation of the ground and excited states. It is likely that there is better stabilization of molecule in the ground state relative to that of the first excited state as solvent polarity increases. Interestingly, the negative solvatochromic shift becomes larger with increasing chain length.



Figure 10. Normalized absorbance of TCF[n] series in acetonitrile.

 Table 4. Wavelengths of the absorbance peaks (nm) of TCF[n] series in chloroform and acetonitrile.

Chromophore	Solvent	Polyene Chain Length (number of double bonds)					
	Solvent	1	2	3	4		
TCEIn	CHCl <sub>3</sub>	577	612	645	657		
ICI	ACN	569	595	605	611		

#### 3.5 Bond length alternation by NMR

The measurement of bond lengths by crystallography is widely accepted as a direct measurement of bond length alternation [23,24]. A lesser utilized measurement of BLA for molecules in solution comes from the proton coupling constants of adjacent methylene units [25]. This practice makes the assumption that, in solution, the chromophores maintain a planar structure, thereby eliminating the dependence of coupling constants on dihedral angle of vicinal protons as described, famously, by Karplus [26]. Without having to consider an angular dependence of coupling constants, the major remaining influence is the C-C bond distance between the two methylene units [22]. The measurements of BLA by NMR are shown below (Table 5).



Figure 11. Schematic representation of BLA measurement by NMR.

**Table 5.** Vicinal coupling constants and  $\langle \Delta J \rangle$  of TCF[n] series as measured in dichloromethaned<sub>2</sub>

Dye	J <sub>1-2</sub> (Hz)	J <sub>2-3</sub> (Hz)	J <sub>3-4</sub> (Hz)	J <sub>4-5</sub> (Hz)	J <sub>5-6</sub> (Hz)	J <sub>6-7</sub> (Hz)	J <sub>7-8</sub> (Hz)	J <sub>8-9</sub> (Hz)	<ΔJ> (Hz)
TCF[1]	15.91			/					
TCF[2]	15.16	11.21	14.93						3.84
TCF[3]	15.20	11.36	14.24	11.04	15.12				3.65
TCF[4]	n.d.	n.d.	13.42	11.44	14.12	11.50	15.21		$2.78^{\ddagger}$

**‡**: BLA estimate based on incomplete assignment of coupling constants n.d.: not determined because of overlapping/higher order spectrum

The estimation of BLA by NMR is more ambiguous than by crystallography, largely owing to the need to correctly assign each resonance and characterize its relationship to the others. Complicating this measurement is that second order effects which occur when the separation between two resonances  $\Delta v$  (in Hz) is similar in magnitude to the coupling constant between

them. The only major advantage of estimating BLA by NMR over that of crystallography is that the BLA can be estimated in a particular solvent field.



**Figure 12.** 1H NMR spectra of TCF[2] in acetone- $d_6$  (blue trace), DMSO- $d_6$  (red trace), acetonitrile- $d_3$  (green trace), Chloroform-d (purple trace), and dichloromethane- $d_2$  (black trace) as an example of measuring  $\Delta J$ . All spectra were recorded using a Bruker AVIII-HD 700 MHz NMR spectrometer and are referenced to their residual solvent signals.

## 3.6 Hyperpolarizability

This series of DMAP-TCF merocyanines exhibit very large first hyperpolarizabilities, making them potentially useful for second harmonic generation (SHG), electrooptic modulation, and for voltage sensitivity (**Table 6**). Unfortunately, a requirement for SHG in solids is a non-centrosymmetric spatial arrangement of chromophores [**27**], which none of the TCF[n] materials

exhibit in their crystalline forms. That said, in applications leading to alignment of these chromophores and a loss of center of symmetry, such as poled polymer blends and in lipid membranes, their utility for SHG should be quite strong.

**Table 6.** Measured first hyperpolarizabilities ( $\beta$ ) of TCF[1-4] in acetonitrile (ACN) and N,Ndimethylformamide (DMF);  $\beta$  values referenced to ACN and DMF respectively according to Campo et al. [**28**] Error in HRS measurements estimated at ±8%.

Dyo	Solvont	β x 10 <sup>-27</sup>
Dye	Sorvent	[esu]
	CHCl <sub>3</sub>	1.33
<b>TCF</b> [1]	ACN	1.63
	DMF	1.21
	CHCl <sub>3</sub>	2.54
TCF[2]	ACN	2.11
	DMF	3.11
TCF[3]	CHCl <sub>3</sub>	2.31
	ACN	3.06
	DMF	1.97
TCF[4]	CHCl <sub>3</sub>	n.d.
	ACN	4.10
	DMF	n.d.

n.d.: not determined due to degradation



**Figure 13.** First hyperpolarizability of TCF[1]–TCF[4] in chloroform, acetonitrile and N,N-dimethylformamide as measured by HRS.

The HRS measurements in acetonitrile showed the expected trend in  $\beta$ , as the hyperpolarizability increases with chain length. In chloroform and in DMF, the measured  $\beta$  for TCF[2] was a pretty sizable increase over that of both TCF[1] and TCF[3] (**Figure 13**).



#### **4 CONCLUSIONS**

The X-ray diffraction study of four tricyanofuran terminated merocyanine dyes, TCF[n], which crystal structures were never studied before, demonstrate that in the crystalline state these chromophores have almost planar molecular structures with very similar molecular packing modes for members with n=1-3. In TCF[4] coexistence of two conformers in one crystal was found. The observed bond length alternation in these molecules suggests that they should have notable second-order NLO properties. Experimental measurements of their first hyperpolarizabilities ( $\beta$  values) in different solvents revealed that, in acetonitrile, the  $\beta$  values increase with an increase in length of conjugated chain. In chloroform and DMF solutions, however, such trend was not observed. This unusual behavior may either be due to conformational changes in different solvents or large solvent-dependence in the nonlinearities. The suggested solvent-based conformational change is supported by presence of two conformers in crystal TCF[4].

## ASSOCIATED CONTENT

Crystallographic data for TCF[1]-TCF[4] have been deposited with the Cambridge Crystallographic Data Center, CCDC 1884797-1884800. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

## **AUTHOR INFORMATION**

**Corresponding Authors** 

E-mail: tvtimofeeva@nmhu.edu

Address: 1005 Diamond st., Las Vegas, NM 87701 USA

## **Author Contributions**

All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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## Synopsis

Structural and spectroscopic studies of nonlinear optical merocyanine dyes are presented



## Highlights:

- Series of merocyanine dyes with different length of conjugated chain was synthesized and characterized with X-ray diffraction, <sup>1</sup>H NMR, and several spectroscopic methods.
- NLO characteristics of compounds in different solvents have been evaluated using structural, spectroscopic and <sup>1</sup>H NMR data.
- NLO characteristics in solutions demonstrated growth with the increase of the length of conjugated chain between donor and acceptor.

A ALLANDA