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A comprehensive study of tetracyanobutadiene push-pull chromophores derived from γ -pyranylidene



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ABSTRACT

A new class of push-pull 1,1,4,4-tetracyanobutadienes (TCBDs) chromophores bearing a γ -pyranylidene as a pro-aromatic donor group have been developed, characterized and studied for their electrochemical, photophysical and second-order nonlinear optical (NLO) properties. [2 + 2] Cycloaddition-retroelectrocyclizations (CA-RE) with tetracyanoethylene (TCNE) allowed the formation of new TCBDs by taking advantage of the electron-donating ability of γ -pyranylidene functional groups. The limits of the reaction between TCNE and the corresponding alkynes have been investigated, both in terms of reactivity and solubility. Electrochemical studies of pyranylidene-TCBD **1a-1j** revealed two reversible reduction waves typical of TCBDs, and two oxidation waves originating from the γ -pyranylidene moiety. More complex electrochemical signals have been recorded when studying chromophores bearing multiple TCBD and/or γ -pyranylidene units. All pyranylidene-TCBDs showed panchromatic absorption properties, extending to the NIR in some cases. Changes made around the electron-withdrawing TCBD units significantly affected the ICT performance of the push-pull chromophores. Computational studies have been performed on this series of compounds to rationalize the origin of their optical properties. TD-DFT calculations confirmed that the synthesized pyranylidene-TCBDs are potential NLOphores. The second-order NLO properties of all chromophores were determined by the Electric Field-Induced Second Harmonic generation (EFISH) technique, and all systems exhibited valuable NLO properties with large $\mu\beta_{\text{EFISH}}$ values for purely organic compounds, up to $5700 \cdot 10^{-48}$ esu.

1. Introduction

1,1,4,4-Tetracyanobutadienes (TCBDs) received considerable attention over the last two decades [1–3]. They were first synthesized from transition metal alkynides and tetracyanoethylene (TCNE) in the early 80's [4], but the first occurrence of a purely organic TCBD was reported in the late 90's [5]. In 2005, Diederich and coworkers reported a seminal paper where they described the high-yield synthesis of TCBDs from *para*-aniline substituted alkynes [6]. Their intense third-order nonlinear absorption was also described in the same study. Since then, a wide panel of peculiar optical properties was observed in this family of compounds,

with applications in several fields like photovoltaics [7–10], emissive materials [11–13], or chiral chromophores [14–16].

As attested by the numerous papers describing organic TCBDs, their synthesis requires the use of an electron-rich alkyne to make them react with TCNE according to a stepwise sequence of [2 + 2]cycloaddition-retroelectrocyclization (CA-RE) to afford a TCBD [17–19]. The yield of the reaction depends on the substrates but since no additive is required (Lewis or Brønsted acid, catalyst, salt, ...), the functional tolerance of this [2 + 2]CA-RE is high, which likely explains why it became so popular.

The nature of the electron-donating group that enriches the $\text{C}\equiv\text{C}$ triple bond to make it reactive with TCNE dramatically influences the

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optoelectronic properties of the TCBDs. For instance, while *para*-aniline substituted TCBDs are poorly fluorescent, we recently observed that TCBDs derived from ynamides were able to emit light from the visible to the near-infrared (NIR) range, especially in apolar media [13,18,20]. Independently, Jayamurugan and coworkers also found that *para*-urea-phenyl substituted TCBDs were able to emit light, but in totally different conditions from what we observed with ynamide-derived TCBDs [12]. This is the reason why finding new electron-donating groups able to initiate this [2 + 2]CA-RE might in principle open new horizons.

Among potentially interesting electron-donating groups, we thought of the proaromatic γ -pyranylidene fragments. Their electron-donating ability is based on the formation of an aromatic pyrylium fragment resulting from an intramolecular charge transfer process. In previous studies, the γ -pyranylidene moiety has been incorporated as an electron-donating group in various platinum- and ruthenium-based

organometallic complexes as well as in organic molecules for the preparation of push-pull structures with large second-order Non-Linear Optical (NLO) properties [21–27] or valuable behavior in Dyes Synthesized Solar Cells (DSSCs) [28–36].

We report herein the synthesis of new TCBDs **1a–1j** and **2–7** substituted with γ -pyranylidene group (Fig. 1). Apart from the evaluation of the scope and limitations of this methodology, we also characterized the electronic and optical properties of these compounds. In particular, we showed that the insertion of 1,1,4-tetracyanobutadiene unit in the D- π -A or D- π -D structures has a dramatic effect on their NLO responses as given by the Electric-Field-Induced Second Harmonic (EFISH) method, increasing the $\mu\beta_{\text{EFISH}}$ values by one order of magnitude. In addition to the NLO properties, theoretical studies were also conducted to support the experimental data and to correlate the chromophore structures to their electronic properties.

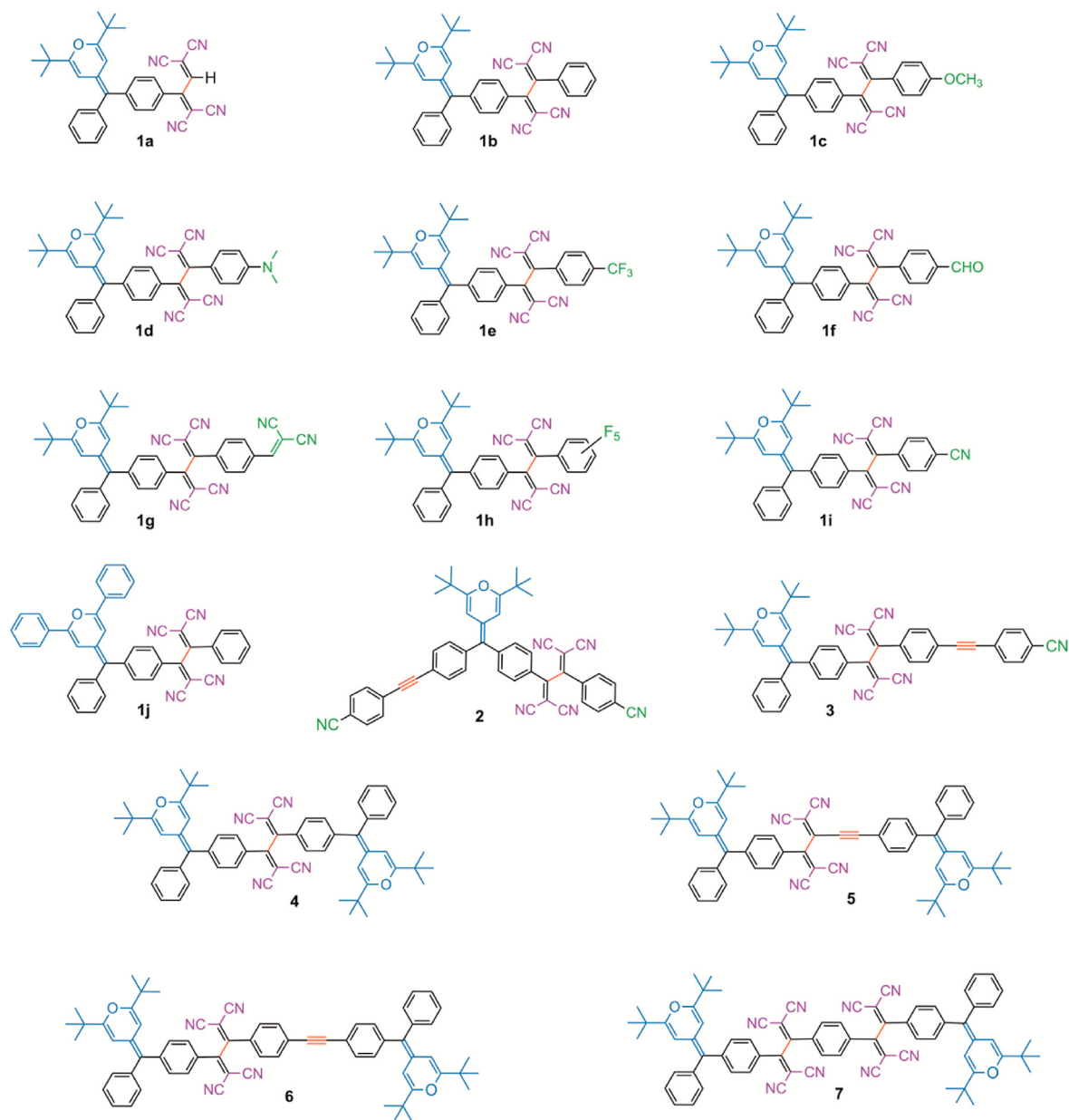


Fig. 1. Chemical structures of γ -pyranylidene-TCBD derivatives **1a–j**, and **2–7**.

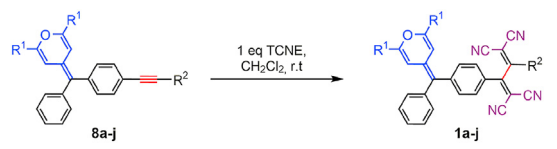
2. Results and discussion

2.1. Synthesis

In the past, we observed that all electron-donating groups conjugated to a $\text{C}\equiv\text{C}$ triple bond were not able to afford TCBDs by reaction with TCNE [37–39]. For instance, in the family of compounds bearing a $\text{C}\equiv\text{C}$ triple bond directly connected to a nitrogen, while ynamides [40] as well as some arylamines [41] and alkynyltriazenes [42] are reactive substrates with TCNE thanks to the polarization of the triple bond, ynehydrazides, which possess a similar structure, are not reactive at all [40]. In contrast, alkynylamines quickly react with TCNE at room temperature but not selectively, yielding numerous colored products [43]. Therefore, it was necessary to first evaluate the reactivity of a $\text{C}\equiv\text{C}$ triple bond enriched by a γ -pyranilidene fragment with TCNE. To this end, alkynyl γ -pyranilidene **8a** was used as a key compound to generate several γ -pyranilidene derivatives by Sonogashira couplings with different bromobenzenes [31]. The corresponding functionalized compounds **8b–i** were thus isolated in good yields (70–90%) (see the Supporting Information for synthetic details).

We started this investigation by reacting **8a** with TCNE. We were delighted to obtain the corresponding TCBD **1a** in 69% yield (Table 1, entry 1). When the γ -pyranilidene was functionalized with a phenyl (**8b**), a *para*-methoxyphenyl (**8c**), a *para*-dimethylaniline (**8d**) and a *para*-trifluoromethylphenyl group (**8e**), the yield exceeded 50% (54–83%, entries 2–5). When the phenyl moiety was substituted with an aldehyde (**8f**) or a dicyanovinyl (**8g**) group, the corresponding TCBDs were obtained in 37 and 41% yields (entries 6–7). When using a perfluorinated phenyl (**8h**) or a *para*-cyanophenyl group (**8i**), the yields significantly dropped to 19 and 21% respectively (entries 8–9). This is explained by the strong electron-withdrawing effect of these two substituents. In the latter case, one notices that the yield increased to 36% when using 3 equivalents of

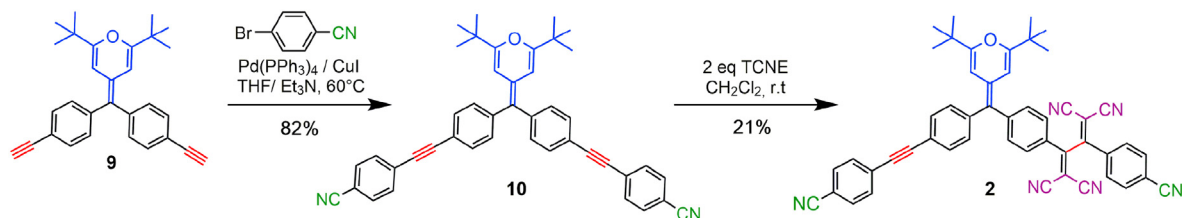
Table 1
Reactivity of γ -pyranilidene derivatives **8a–j** with TCNE to afford TCBD **1a–j**.



| Entry | γ -pyranilidene | R ¹ | R ² | TCBD | Yield (%) |
|-------|------------------------|----------------|---|-----------|-----------------|
| 1 | 8a | <i>t</i> -Bu | H | 1a | 69 |
| 2 | 8b | <i>t</i> -Bu | Ph | 1b | 58 |
| 3 | 8c | <i>t</i> -Bu | <i>p</i> -OMe-C ₆ H ₄ | 1c | 54 |
| 4 | 8d | <i>t</i> -Bu | <i>p</i> -NMe ₂ -C ₆ H ₄ | 1d | 83 |
| 5 | 8e | <i>t</i> -Bu | <i>p</i> -CF ₃ -C ₆ H ₄ | 1e | 63 |
| 6 | 8f | <i>t</i> -Bu | <i>p</i> -CHO-C ₆ H ₄ | 1f | 37 |
| 7 | 8g | <i>t</i> -Bu | <i>p</i> -CHC(CN) ₂ -C ₆ H ₄ | 1g | 41 |
| 8 | 8h | <i>t</i> -Bu | Ph | 1h | 19 |
| 9 | 8i | <i>t</i> -Bu | Ph | 1i | 21 ^a |
| 10 | 8j | Ph | Ph | 1j | 51 ^b |

^a The yield could be increased to 36% using 3 equivalents of TCNE.

^b 5 equivalents of TCNE were used.



Scheme 1. Synthesis of TCBD **2**.

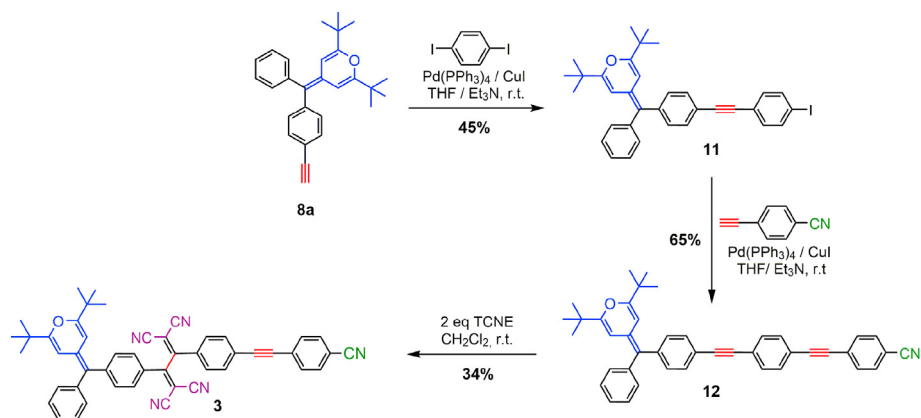
TCNE. This study on simple γ -pyranilidene derivatives was completed by changing the R¹ substituent to a phenyl instead of a *tert*-butyl moiety, with a phenyl at R² (**8j**). In this case, the corresponding TCBD **1j** was isolated in 51% yield but 5 equivalents of TCNE were required to reach complete conversion (entry 10). In addition, the use of phenyl groups in R¹ significantly decreased the solubility of the corresponding TCBD **1j**, making the purification by silica chromatography much more tedious than in previous cases. Therefore, only *tert*-butyl groups in the R¹ position were chosen to avoid solubility problems for the rest of the study.

Next, we evaluated the applicability of this methodology to more complex systems, *i.e.* more extended systems with two $\text{C}\equiv\text{C}$ triple bonds and/or two γ -pyranilidenes. Thus, we applied the same synthetic route to consider introducing TCBD units on a single V-shaped γ -pyranilidene-based core **10** [23]. The synthetic approach followed for the preparation of compound **10**, shown in Scheme 1, is based on the double Sonogashira coupling reaction with 1-bromo-4-cyanobenzene and compound **9** in 82% yield [22]. The CA-RE reaction of V-shaped compound **10** with two equivalents of TCNE at room temperature for 24 h resulted in the exclusive isolation of mono-TCBD **2** in 21% yield. Only traces of the expected double TCBD adduct were observed but could not be isolated, even using 5 equivalents of TCNE. This suggests that the formation of one TCBD dramatically decreases the donating ability of the γ -pyranilidene, which precludes the reaction of the second $\text{C}\equiv\text{C}$ triple bond with TCNE.

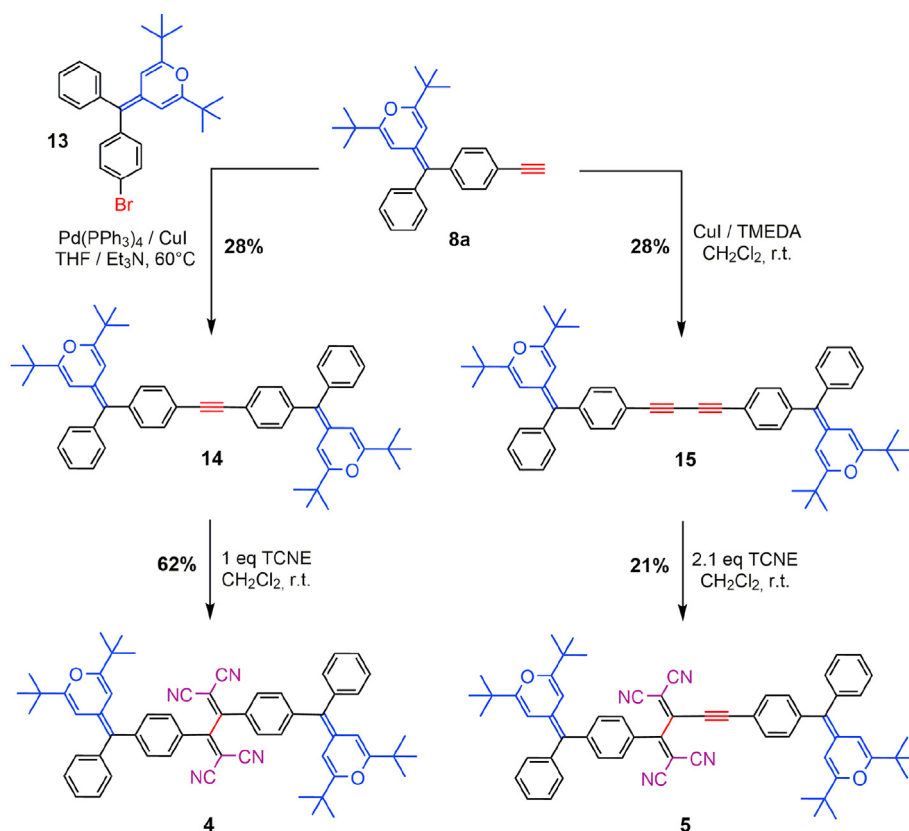
A second substrate possessing two $\text{C}\equiv\text{C}$ triple bonds and one nitrile function was then synthesized (Scheme 2). Compound **8a** was submitted to a statistical Sonogashira coupling with 1,4-diiodobenzene to afford compound **11** in 45% yield. The latter was submitted to a second Sonogashira coupling with 4-ethynylbenzotrile to give substrate **12** in 65% yield. Compound **12** contains two acetylenes in the π -spacer groups bridging the pyranilidene donor to the cyanobenzene acceptor. When **12** was reacted with 2 equivalents of TCNE at room temperature for 18 h, TCBD **3** was obtained in 34% yield. It is likely that this disappointing yield is related to the presence of an additional electron-withdrawing group that significantly deactivates the reactive $\text{C}\equiv\text{C}$ triple bond. Nevertheless, the reaction was completely selective for the triple bond adjacent to the pyranilidene, as expected.

We also synthesized various bis-pyranilidene conjugated with acetylene bridges **14** and **15** in order to evaluate their reactivity with TCNE (Scheme 3). To this end, compound **8a** was submitted to a Sonogashira coupling (Pd(PPh₃)₄/CuI/Et₃N) with compound **13** to obtain substrate **14** encompassing two γ -pyranilidenes separated by one $\text{C}\equiv\text{C}$ triple bond (28% yield). Substrate **15** comprising two conjugated $\text{C}\equiv\text{C}$ triple bonds instead of one was prepared using a Hay coupling (CuI/TMEDA) of compound **8a** (28% yield). Substrate **14** was reacted with one equivalent of TCNE to afford TCBD **4** in a satisfying 62% yield. Concerning substrate **15**, two equivalents of TCNE were necessary to give the corresponding TCBD **5** in 21% yield. No traces of the double adduct could be observed, which is unsurprising considering the strong electron-withdrawing ability of the adjacent TCBD unit that deactivates the second $\text{C}\equiv\text{C}$ triple bond, as already observed by others [44].

Finally, substrate **16** containing two pyranilidenes separated by a 1,4-diethynylphenyl bridge was synthesized from compound **8a** with the help of a double Sonogashira coupling with 1,4-diiodobenzene. When compound **16** was reacted with 2.4 equivalents of TCNE, mono-TCBD **6**



Scheme 2. Synthesis of TCBD 3.



Scheme 3. Synthesis route of TCBDs 4 and 5.

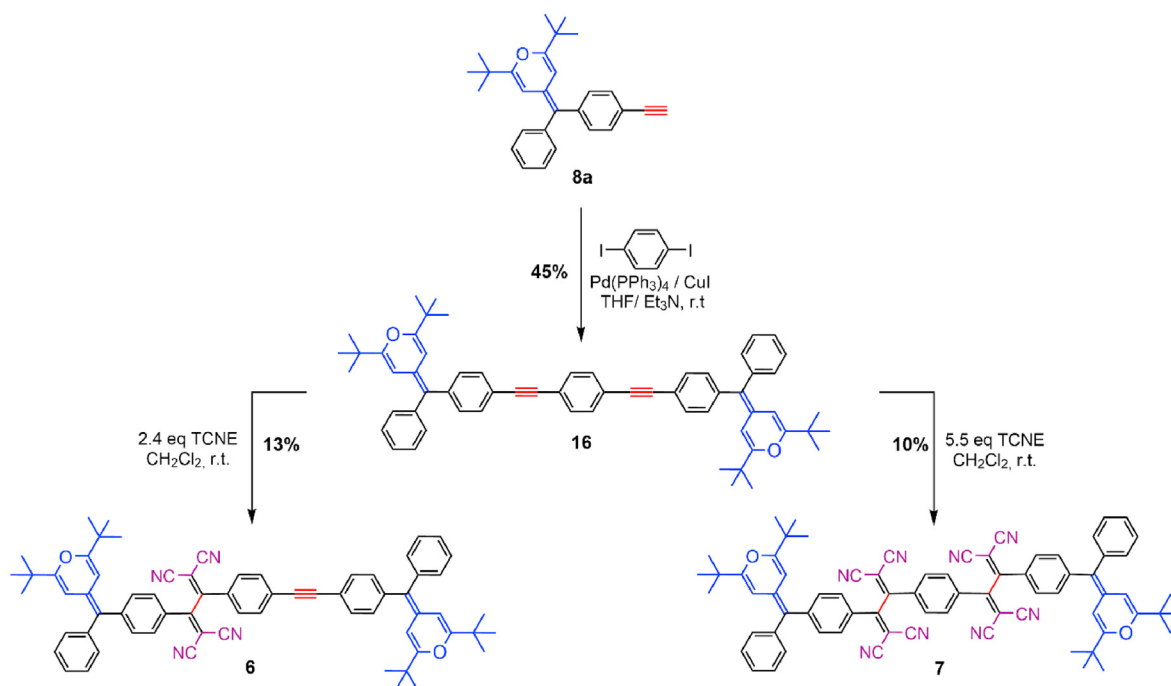
could be isolated in 13% yield. Traces of the double adduct were observed but could not be isolated. In contrast, when using 5.5 equivalents of TCNE, double adduct 7 was isolated in 10% yield while mono-adduct 6 was observed but could not be isolated (Scheme 4).

The newly synthesized pyranilidene-TCBDs 1a–j, 2 and 3 and bis-pyranilidene-TCBDs 4–7 were characterized by ^1H and ^{13}C NMR spectroscopy, and by HRMS (Supporting Information). The characterization data were found to be in complete agreement with the proposed structures.

3. Electrochemistry

Most of the above-mentioned TCBDs were characterized by cyclic voltammetry (Table 2), and they all display two reversible reduction

waves typical of TCBDs (see Fig. 2 for compound 1b), except for compound 7 that shows four well-resolved reduction waves since it possesses two TCBD groups (Fig. S88). The potential where the reduction occurs strongly depends on the R^2 group (Table 1). The more electron-donating are these groups, the lower the potentials; the more electron-withdrawing, the higher the potentials. Therefore, the reduction potentials are comprised between -0.50 (1h that bears a pentafluorophenyl group) and -0.95 V vs Fc^+/Fc (1d that bears a *para*-dimethylaniline group) for the first reduction, and between -1.01 and -1.26 V vs Fc^+/Fc for the second one. An exception is observed with the fourth reduction wave of compound 7, for which the fourth electron is obviously more difficult to add in the structure for coulombic reasons (-1.31 V vs Fc^+/Fc). These values overall fit with the data obtained previously for other TCBDs [41,45,46]



Scheme 4. Synthesis route of TCBDs 6 and 7.

Table 2

Electrochemical data extracted from cyclic voltammetry in dichloromethane (+0.1 M of NBu_4PF_6); potentials are given versus the ferrocene/ferrocenium redox couple. Scan rate: 0.1 V s^{-1} .

| TCBD | $E_{1/2}^a$ | E_p^b |
|------|--|----------------|
| 1a | N/A | N/A |
| 1b | +0.336; -0.779; -1.171 | +0.809 |
| 1c | +0.311; -0.833; -1.210 | +0.792 |
| 1d | +0.907; +0.308; -0.947; -1.265 | +0.831 |
| 1e | +0.326; -0.689; -1.114 | +0.797 |
| 1f | +0.312; -0.675; -1.078 | +0.765 |
| 1g | +0.319; -0.636; -1.007 | +0.830 |
| 1h | +0.331; -0.502; -1.072 | +0.810 |
| 1i | +0.317; -0.642; -1.066 | +0.778 |
| 1j | +0.382; -0.754; -1.178 | +0.814 |
| 2 | +0.338; -0.631; -1.070 | +0.794 |
| 3 | +0.311; -0.722; -1.117 | +0.777 |
| 4 | +0.308; -0.837; -1.212 | +0.808 |
| 5 | +0.289; -0.639; -1.127 | +0.649 |
| 6 | +0.317; +0.193; -0.746 | +0.764; +0.662 |
| 7 | +0.309; -0.601; -0.822; -1.155; -1.308 | +0.802 |

^a $E_{1/2} = (E_{pc} + E_{pa})/2$, in which E_{pc} and E_{pa} correspond to the cathodic and anodic peaks, respectively; this potential is calculated when the electron transfer is reversible.

^b E_p = potential peak; this potential is calculated when the electron transfer is irreversible.

On the anodic side, two oxidation waves are generally observed. The first one is reversible while the second one is irreversible. They are attributed to two successive one-electron oxidations of the pyranilidene core, leading thus to the cationic and dicationic species as already described [31]. In contrast with the reduction waves, the potentials are quite insensitive to the nature of the R^2 group, as long as the pyranilidene core is directly connected to a TCBD (for the sake of comparison, the CVs of precursors **8i**, **8b**, **10** and **12** are displayed in Figs. S70–S73). The potentials of the first oxidation are comprised between +0.29 (**5**) and +0.34 (**1b**) vs Fc^+/Fc if we except **1j** that bears phenyl instead of *tert*-butyl groups in R^1 (a 46 mV shift when comparing compounds **1b** and **1j**). In the series of compounds bearing only one pyranilidene core (compounds **1b–1j**, **2** and **3**), the peak potentials of the

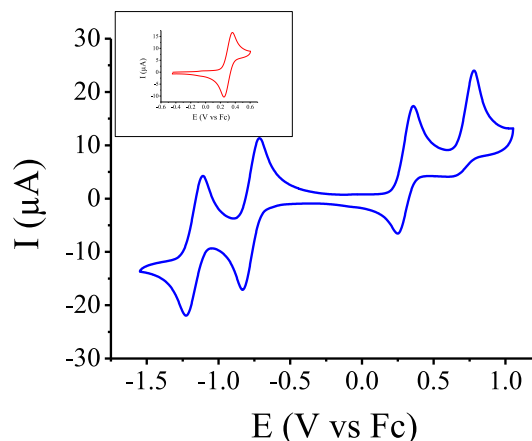


Fig. 2. Cyclic voltammogram in a dichloromethane solution containing 0.1 mol L^{-1} of tetrabutylammonium hexafluorophosphate (nBu_4NPF_6) and $10^{-3} \text{ mol L}^{-1}$ of compound **1b**. Scan rate: 100 mV s^{-1} . All potentials are indicated versus ferrocene/ferrocenium redox couple used as an internal reference. Insert: Focus on the first oxidation process that is reversible when not applying excessive anodic potential (not going to the second irreversible oxidation).

second oxidation wave are comprised between 0.76 and 0.83 vs Fc^+/Fc . An additional reversible oxidation wave at 0.907 V vs Fc^+/Fc is observed for compound **1d** because of the presence of the dimethylaniline. Additional oxidation waves may be observed when the compound possesses two pyranilidene cores and is unsymmetrical (compounds **5** and **6**) [47].

A typical cyclic voltammogram of a TCBD derived from γ -pyranilidene is exhibited in Fig. 2 (compound **1b**), with two reversible reduction waves and two oxidation waves, one reversible and one irreversible. All the recorded CVs can be found in the supporting information (Figs. S70–S88).

4. UV-visible spectroscopy

UV-visible absorption spectra of γ -pyranilidene-TCBD derivatives

1a–j, **2–7** and γ -pyranylidene precursors **8a–i**, **10**, **12**, **14–16** recorded in diluted dichloromethane ($1.0\text{--}3.0 \times 10^{-5}$ M), are shown in Figs. 3 and 4, and S1–S4, whereas the corresponding spectroscopic data are collected in Tables 3 and S1.

The absorption spectra of γ -pyranylidene precursors **8a–j**, **10**, **12** show multiple absorption bands in the 290–470 nm region. The absorption bands in the shorter wavelength region result from localized $\pi\text{--}\pi^*$ transitions whereas the absorption band in the longer wavelength region may be attributed to an internal charge transfer (ICT) from the pyranylidene donor unit to the acceptor fragments, by analogy with analyses performed on similar structures [33,34]. This is consistent with the effects of substitution, with bathochromic shifts associated to an increase of the strength of the electron-withdrawing moiety. For instance, in chromophores **8b–j**, the wavelength of the ICT band is tuned from 370 nm (**8c**, OMe substituent) to 468 nm (**8g**, dicyanovinyl substituent). The V-shaped compound **10** bearing two electron-withdrawing cyano substituents, displays a maximum absorption at 401 nm similar to that of the linear compounds **8i** (402 nm) and **12** (397 nm), its molar extinction coefficient ($\epsilon_{\text{max}} = 4.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) being about twice that of **8i** ($\epsilon_{\text{max}} = 2.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 3). As shown by the spectra in Fig. 4, the extension of the π -conjugation by one $\text{C}\equiv\text{C}$ triple bond in **15** compared to compound **14** induces a redshifted $\pi\text{--}\pi^*$ transition (410 versus 392 nm). The molar extinction coefficients of chromophores **15** and **16** are significantly larger than that of chromophore **14**, and

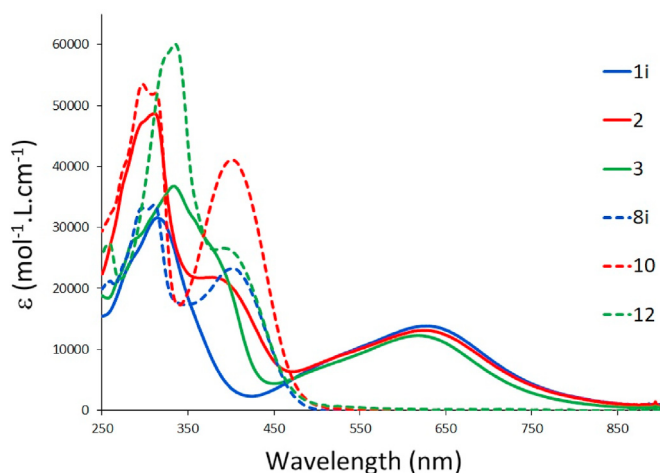


Fig. 3. UV-visible absorption spectra of compounds **1i**, **2**, **3**, **8i**, **10**, and **12** in dichloromethane.

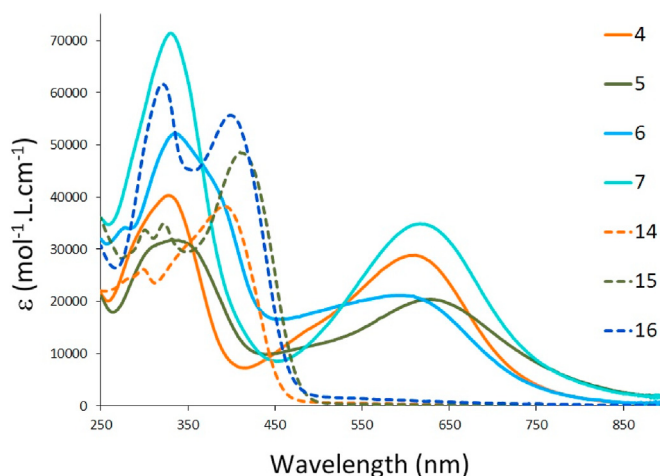


Fig. 4. UV-visible absorption spectra of compounds **4–7** and **14–16** in dichloromethane.

respectively attain $5.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 399 nm and $4.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 410 nm, while the chromophore **14** extinction coefficient is $3.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 392 nm. These stronger absorptions in **15** and **16** can be explained by the significant contribution of the ethynyl linkers in the electron delocalization (see calculations below).

The presence of a TCBD acceptor results in the appearance of intense ICT bands (Figs. 3 and 4). The simplest molecule **1a** displays a strong absorption in the visible region centered at 703 nm and extending into the NIR region, beyond 900 nm. This can be attributed to the presence of an ICT from the pyranylidene to the strong electron-withdrawing TCBD unit (Figs. S1 and S3). As illustrated in Fig. 3, the TCBD-substituted chromophores **1i**, **2**, and **3** show redshifted ICT bands centered at 622, 627, and 619 nm, respectively, compared to their precursors (**8i**, **10**, and **12**). TCBDs **4** and **5** show the presence of an ICT band in the visible region centered at 607 and 628 nm, respectively, due to the positioning of an attracting TCBD unit in the symmetric structure of their precursors **14** and **15** (D- π -D).

Finally, the introduction of TCBD moieties induces a dramatic effect on the UV/Vis spectra of both mono- and bis-adducts **6** and **7** when compared to diyne **16**, with a redshift of 198–218 nm (Fig. 4). Indeed, broader bands localized at the lower-energy part of the spectrum appeared (centered at 597 nm for **6** and 617 nm for **7**). Bis-TCBD **7** show a significant bathochromic shift and strong hyperchromic effect in absorption, similarly to recently reported symmetrical TCBD derivatives [13]. Compounds **4–7** exhibit particularly high extinction coefficients ϵ in a range going from 2.1×10^4 to $3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. All the TCBDs described here possess a broad low-energy absorption extending beyond 800 nm in the NIR region.

In addition, we studied the solvatochromism on compound **1j**. To do so, we recorded its UV-visible spectra in toluene, chloroform, acetone and acetonitrile (Fig. S5). We observed a color change even by naked eye upon changing the solvent. Actually, the absorption maximum of the lowest-energy band is strongly impacted by the polarity: 617 nm in chloroform, 604 nm in dichloromethane, 599 nm in toluene, 567 nm in acetonitrile and 560 nm in acetone. On the whole, the absorption is blueshifted when increasing the solvent polarity, which corresponds to a negative solvatochromism. This observation may be explained by the pro-aromatic nature of the pyranylidene and the strong acceptor ability of the TCBD. Therefore, these kinds of TCBDs seem to be better described as zwitterionic species in the ground state, with a positively charged pyranylidene and a negatively charge TCBD moiety.

5. NLO properties

In order to investigate the second-order NLO properties of the pyranylidene-TCBDs **1b–i**, **2–7** and their precursors **8i**, **10**, **12**, and **15** the EFISH method has been used as it can provide direct information on the intrinsic dipolar molecular second-order NLO properties [48–52]. The $\mu\beta_{\text{EFISH}}$ values were measured in chloroform solution (concentration = 10^{-2} – 10^{-3} M) using a Raman shifted Nd:YAG laser source with $\lambda = 1907$ nm. The values obtained are reported in Table 3. The $\mu\beta_{\text{EFISH}}$ values of compounds **1b–i**, **2–7**, **8i**, **10**, **12** and **15** are positive, indicating the excited states are more polarized than the ground state ($\mu_e > \mu_g$). In addition, this implies that the ground and excited states are polarized in the same direction. This observation is in agreement with the above-mentioned ICT from the pyranylidene to the TCBD unit.

The $\mu\beta_{\text{EFISH}}$ values observed for the precursors **8i**, **10**, **12** and **15** ($\mu\beta_{\text{EFISH}} = 100\text{--}660 \times 10^{-48}$ esu) are of the same order of magnitude as Disperse Red 1 ($\mu\beta_{\text{EFISH}} = 500 \times 10^{-48}$ esu), a typical benchmark for EFISH [53]. However, the NLO responses are dramatically enhanced when a TCBD fragment is included in the π -conjugated structures. For example, the value obtained for compound **1i** is almost ten times higher than the one obtained for compound **8i**, indicating a positive effect of the TCBD (3300×10^{-48} esu versus 380×10^{-48} esu). For pyranylidene-TCBDs **1b–i**, the $\mu\beta_{\text{EFISH}}$ values range between 1200 and 3300×10^{-48} esu. Pyranylidene-TCBDs **2** and **3** also exhibit significantly

Table 3

Absorption data for compounds **1a–j**, **2–7**, **8i**, **10**, **12**, **14–16** measured in CH₂Cl₂ solution. The corresponding molar absorption coefficients are indicated between parentheses. Measured $\mu\beta_{\text{EFISH}}$ values for compounds **1b–i**, **2–7**, **8i**, **10**, **12**, and **15** in CHCl₃ solution.

| | $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mM}^{-1}\cdot\text{cm}^{-1}$) | $\mu\beta_{\text{EFISH}}^a$ |
|-----------|---|-----------------------------|
| 1a | 303 (23); 389 (15), 703 (4) | – |
| 1b | 325 (10); 614 (5) | 2000 |
| 1c | 334 (22); 606 (11) | 2500 |
| 1d | 324 (22); 467 (30); 575 (18) | 1800 |
| 1e | 312 (22); 624 (19) | 3500 |
| 1f | 319 (44); 621 (19) | 3250 |
| 1g | 345 (29); 614 (10) | 3100 |
| 1h | 307 (19); 485 (8); 685 (5) | 1200 |
| 1i | 313 (32); 622 (14) | 3300 |
| 1j | 337 (12); 604 (6) | – |
| 2 | 311 (49); 386 (22); 627 (13) | 2350 |
| 3 | 334 (37); 619 (12) | 2350 |
| 4 | 328 (40); 607 (29) | 3000 |
| 5 | 333 (32); 628 (20) | 5700 |
| 6 | 336 (52); 597 (21) | 3400 |
| 7 | 330 (71); 617 (35) | 4700 |
| 8i | 297 (33); 313 (33); 402 (23) | 380 |
| 10 | 297 (54); 311 (52); 401 (41) | 660 |
| 12 | 335 (60); 397 (26) | 420 |
| 14 | 299 (26); 392 (38) | – |
| 15 | 301 (34); 322 (35); 410 (49) | 100 |
| 16 | 321 (62); 399 (56) | – |

^a $\mu\beta_{\text{EFISH}}(2\omega)$ at 1907 nm. Molecular concentration used for the measurements were in the range 10^{-3} to 10^{-2} M. $\mu\beta_{\text{EFISH}} \pm 10\%$.

higher NLO responses (2300×10^{-48} esu and 2350×10^{-48} esu, respectively) than their pyranilidene analogues **10** and **12** (660×10^{-48} esu and 420×10^{-48} esu, respectively). A similar trend may be observed for bis-pyranilidene-TCBDs **4–7** which show high NLO responses ($\mu\beta_{\text{EFISH}} = 3000\text{--}5700 \times 10^{-48}$ esu). Finally, the highest $\mu\beta_{\text{EFISH}}$ value of the series is obtained for bis-pyranilidene-TCBD **5** which is dramatically increased with regard to its symmetrical precursor **15** (5700×10^{-48} esu versus 100×10^{-48} esu). When comparing measurements made by the EFISH technique in recent literature, γ -pyranilidene-TCBDs **1b–i**, **2–7** show significantly better NLO responses compared to donor-acceptor-donor-type TCBD-NLOphores containing dialkylated triazene and aniline groups [54]. Indeed, even if the γ -pyranilidene group is a weaker electron donor group than dialkynaniline, the NLO results show $\mu\beta_{\text{EFISH}}$ values up to 5 times higher.

6. Theoretical calculations

To obtain more information on the nature of the excited states involved in these systems, we performed TD-DFT calculations with a protocol detailed in the SI. As above mentioned (Fig. 3), the UV/Vis absorption of **8i**, **10**, and **12** all show a strong absorption band at ca. 400 nm. Although caution should be taken when comparing vertical TD-DFT energies and experimental λ_{max} , it is reassuring that theory provides

similar results (Table S2). This band corresponds to the lowest absorption that is very strongly dipole-allowed with, e.g., an oscillator strength of 1.38 for **8i**. Illustratively, we show in Fig. 5 the density difference plot describing the density reorganization induced by photon absorption at 400 nm for **8i** (see the SI for other compounds). The ICT character of the transition is crystal-clear, the pyranilidene playing the role of the donor (in blue) and the cyano-substituted ethynyl-phenyl moiety the role of the acceptor (in red). Quantitatively, Le Bahers' model [55] returns a transfer of 0.73 electron over 4.48 Å, which can be clearly considered as a significant ICT effect. When switching to the corresponding TCBD **1i**, the experimental visible band is strongly redshifted to 622 nm, an effect reproduced by the calculations that yield 604 nm for the vertical transition. Interestingly, the global topology of the excited state is conserved, though the accepting character is increased thanks to the TCBD (Fig. 5). The ICT is now of 0.98 electron (almost quantitative) over 4.24 Å. The reason why **1i**, **2**, and **3** have very similar optical signatures, although the two latter compounds present extended conjugated arms (see Table 1), can be explained by the electron density difference (EDD) provided in Fig. 5. Actually, the nature of the excited state is unchanged by the addition of an extra arm, the additional groups (as compared to **1i**) playing no role in the lowest electronic transition. As a specific note, the presence of an ICT band at 703 nm in the compact **1a** dye is well reproduced by theory (710 nm, see Table S2).

It is also insightful to compare compounds **14–16** with their corresponding TCBDs **4–7**, for which the experimental spectra are displayed in Fig. 4. For the former, the first absorption band appears in the 392–410 nm domain (Table 3), and theory again reproduced this outcome with great accuracy (395–416 nm). As shown in the EDD plot displayed in Fig. 6, the excited state now acquires a local $\pi-\pi^*$ character, which is confirmed by Le Bahers' metric that returns the charge-transfer is insignificant ($d^{\text{CT}} = 0.43$ Å, see the SI). In **4**, however, a clear CT from the periphery to the core can clearly be seen, and this is logically accompanied by a strong redshift (575 nm in theory, 607 nm experimentally). These global trends pertain for the other member of these two series.

We have also used DFT, in its coupled-perturbed formalisms to estimate the molecular polarizabilities and hyperpolarizabilities (see the SI for computational details and full results). The DFT computed $\beta(-2\omega;\omega,\omega)$ values at 1907 nm are 418.5×10^{-30} , 668.0×10^{-30} , 683.1×10^{-30} , and 34.8×10^{-30} esu for **2**, **5**, **7**, and **15**, respectively. These data obviously follow the measured trends, with the largest response obtained for **5** and **7**.

7. Conclusion

We disclose the possibility to generate new TCBDs by taking advantage of the electron-donating ability of γ -pyranilidene functional groups. The scope and limitations of the reaction between TCNE and the corresponding alkynes was assessed. Rather complex push-pull chromophores were isolated and studied. For the simplest ones **1a–1j**, electrochemical studies revealed two reversible reduction waves typical of TCBDs, and two oxidation waves coming from the γ -pyranilidene fragment. More

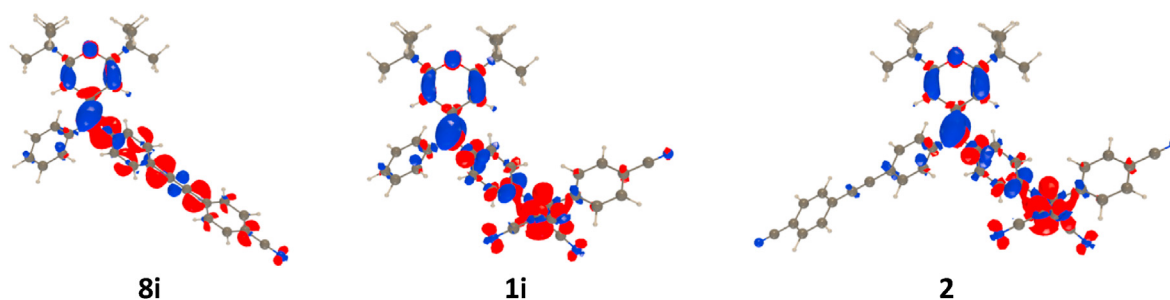


Fig. 5. EDD plot for **8i**, **1i**, and **2i**: the blue and red lobes represent regions of decrease and increase of density upon photoabsorption, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

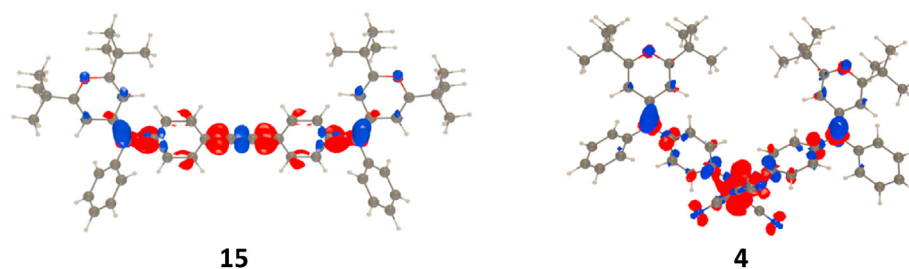


Fig. 6. EDD plot for **15** and **4**: the blue and red lobes represent regions of decrease and increase of density upon photoabsorption, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

complex electrochemical signals were recorded when studying further functionalized compounds bearing several donor or acceptor moieties. All compounds showed panchromatic absorption properties, some of them developing strongly redshifted absorption, extending towards the NIR. They also showed valuable NLO properties with $\mu\beta_{\text{EFISH}}$ values reaching up to $5700 \cdot 10^{-48}$ esu. The optical properties of this series of compounds were rationalized with the help of TD-DFT calculations. We trust that this study disclosing new TCBDs with original linear and nonlinear optical properties could pave the way towards the elaboration of new chromophores in the fields of photovoltaics or biomedical therapy, by using photothermal effects, for instance [56]. Both directions will be investigated by our team in the near future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tchem.2023.100036>.

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