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Synthesis and photophysical properties of 1,1,4,4-tetracyanobutadienes derived from ynamides bearing fluorophores

Clotilde Philippe,^[a] Anh Thy Bui,^[a,b] Maxime Beau,^[a] Hugo Bloux,^[a] François Riobé,^[c] Olivier Mongin,^[a] Thierry Roisnel,^[a] Marie Cordier,^[a] Frédéric Paul,^[a] Loïc Lemiègre,^{[a]*} Yann Trolez^{[a]*}

^[a] Dr. C. Philippe, Dr. A. T. Bui, Dr. M. Beau, H. Bloux, Dr. O. Mongin, Dr. T. Roisnel, M. Cordier, Dr. F. Paul, Dr. L. Lemiègre, Dr. Y. Trolez

Loïc Lemiègre : loic.lemiegre@ensc-rennes.fr ; Yann Trolez : yann.trolez@ensc-rennes.fr

Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France

^[b] Dr. A. T. Bui

Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France

^[c] Dr. F. Riobé

Université de Lyon, Ecole Normale Supérieure de Lyon, CNRS UMR 5182, Laboratoire de Chimie, 46 allée d'Italie, F69364 Lyon, France

Abstract

1,1,4,4-Tetracyanobutadienes (TCBDs) bearing a large diversity of fluorophores were prepared following a multi-step synthesis. In a crucial last step, all compounds were obtained from the corresponding ynamides, which were particularly suitable for the formation of the TCBDs in the presence of tetracyanoethylene via a [2+2] cycloaddition/retroelectrocyclization step (CA-RE). Several fluorenyl derivatives in addition to phenanthrenyl and terphenyl ones provided ynamide-based TCBDs affording remarkable emission properties covering a large range of wavelengths. Those compounds emit both in solid state and in solution from the visible region to the NIR range, depending on the molecular structures. Quantum yields in cyclohexane reached unforeseen values for such derivatives, up to 7.8%. A huge sensitivity to the environment of the TCBDs has also been unraveled for most of the compounds since we observed a dramatic fall of the quantum yields when changing the solvent from cyclohexane to toluene, while they are almost non-emissive in dichloromethane.

Keywords: cycloaddition, fluorescence, tetracyanobutadiene, ynamide

Introduction. The strong electron-accepting 1,1,4,4-tetracyanobutadiene (TCBD) unit has been introduced in numerous push-pull systems^[1–12] since the first examples described by Bruce and coworkers in 1981.^[13] Indeed, beyond their ease of synthesis, TCBDs are particularly relevant for the conception of linear and non-linear absorbers.^[14–18] In contrast, the luminescence properties of TCBD derivatives have barely been explored as they are generally considered non-emissive due to intrinsically rapid nonradiative deactivations.^[19] However, some examples of luminescent TCBDs in solution or in the solid state have recently emerged,^[20–34] although often with very low quantum yields at room temperature that hardly exceed 1%, except for a work from Jayamurugan *et al.*^[27] where the authors claimed quantum yields up to 4.3% at room temperature in acetonitrile. We also reported TCBDs bearing triphenylamine and fluorenyl units that showed quantum yields comprised between 2 and 6% in rigid media at room temperature.^[16]

Within this context, our research group recently demonstrated that TCBDs synthesized from ynamides conjugated to a fluorescent motif could display low-energy emissions. Especially, when

pyrene, perylene and anthracenes were appended with the resulting sulfonamide-TCBD moiety, the compounds showed emission in the solid state as well as in rigid matrices in the NIR region (up to 1550 nm).^[35,36] Interested by the potential of this TCBD family, we thus decided to undertake a systematic study on this type of derivatives. In the light of the previously obtained results, the fluorene motif was selected as an exemplar and most of the structures presented herein were based on a dimethylfluorene core (**1a**). Electronic effects were inspected through 2,7- and 9-substitutions: the fluorene core was equipped with additional electron withdrawing groups (ketone, bis-TCBD **1b,e**), electron donating groups (hexyloxy, ynamide **1c,d**), as well as aromatic rings (**1f,g,h**) and oxo substituent in place of the two methyl groups (**1j**). The general scope of the TCBD-functionalized polyaromatic hydrocarbons series was finally expanded using two other tricyclic moieties, phenanthrenyl (**1i**) and terphenyl (**1k**). Dibutylfluorene TCBD **1l**, which has already been described by our research group, was chosen as a reference within the photophysical studies.^[37] Overall, we report here on the synthesis and characterization of 11 new TCBD-bearing fluorophores, derived from homologous methyltosyl-ynamides (Figure 1). Along with the description of their synthesis, the absorption and emission properties of all compounds are reported, both in solution and in solid state. The variety of fluorophores envisaged in this study permitted to reach photophysical properties within a relatively large range of wavelengths. It also confirms the potential of TCBD derivatives as luminescent small molecules with improved quantum yields, in solution at room temperature, and it provides important clues on the impact of an ynamide-based TCBD group on the optical properties of such compounds.

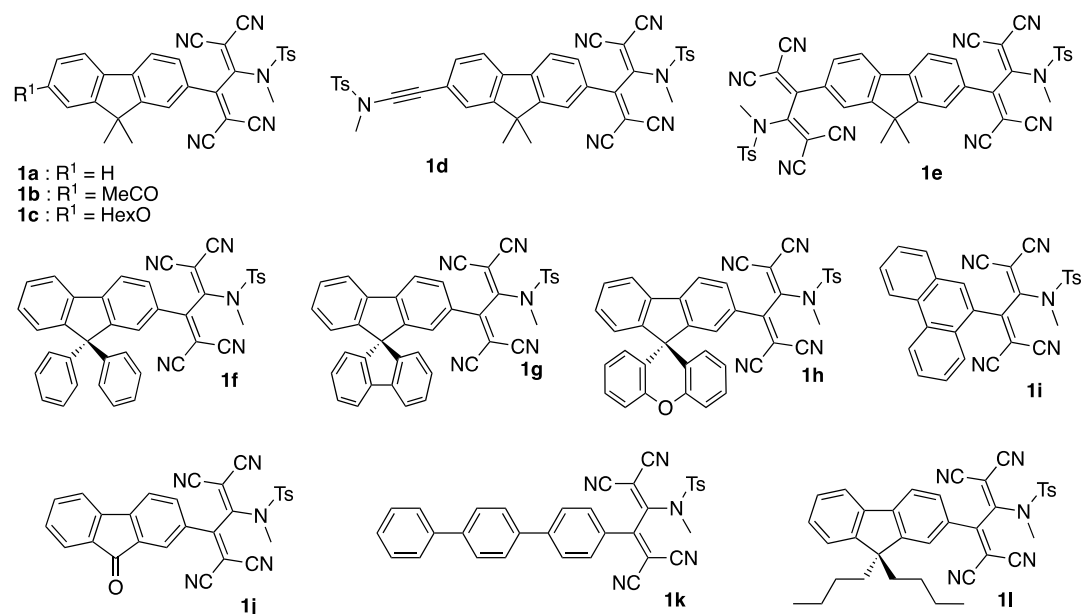
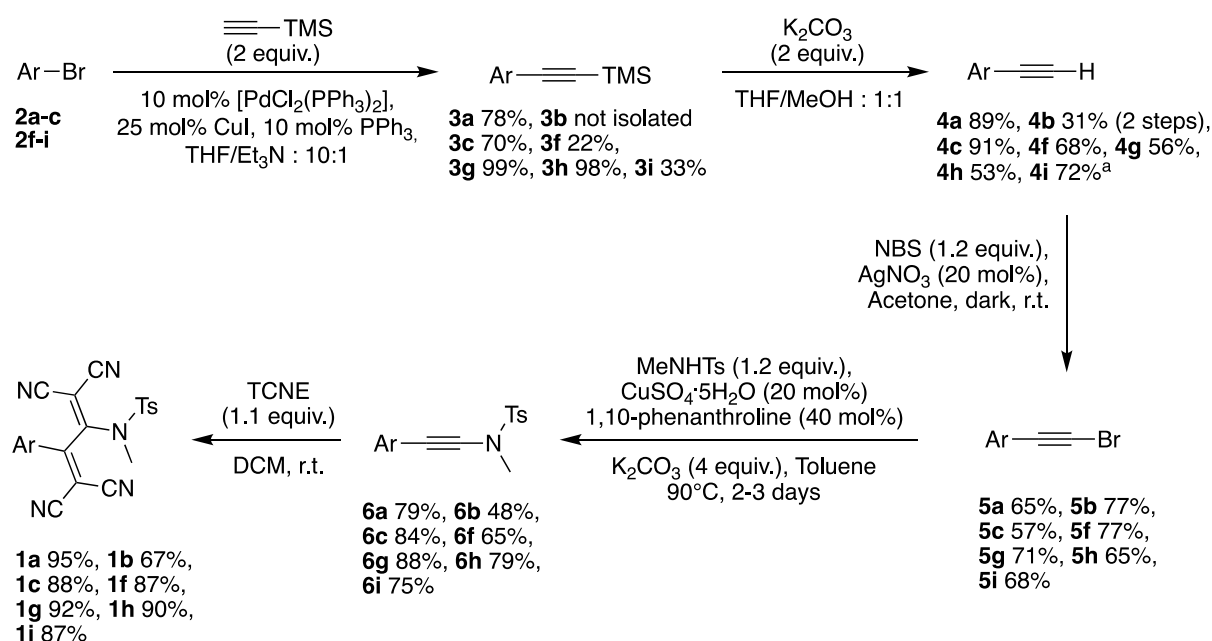


Figure 1. Ynamide-based TCBD derivatives bearing various fluorophores

Synthesis. The synthetic strategies used for the preparation of compounds **1a-b** and **1f-i** were very similar whatever the target compounds. The last step was based on the final [2+2] cycloaddition/retro-electrocyclization between tetracyanoethylene (TCNE) and the corresponding ynamides. The latter were obtained from the bromoalkyne compounds using reaction conditions developed by Hsung.^[38] The key starting materials in this strategy were brominated aryls from which the introduction of the triple bond was achieved through a Sonogashira coupling followed by the bromination of the alkyne. Most of the aryl bromines **2a-i** were commercially available except **2b-c** for which the synthesis was easily adapted from the literature^[39-41] (see Supporting Information for details). In general, the 5-step synthetic scheme described here provided a clean and easy access to this TCBD family (Scheme 1). In detail, the introduction of the protected alkyne moiety was achieved

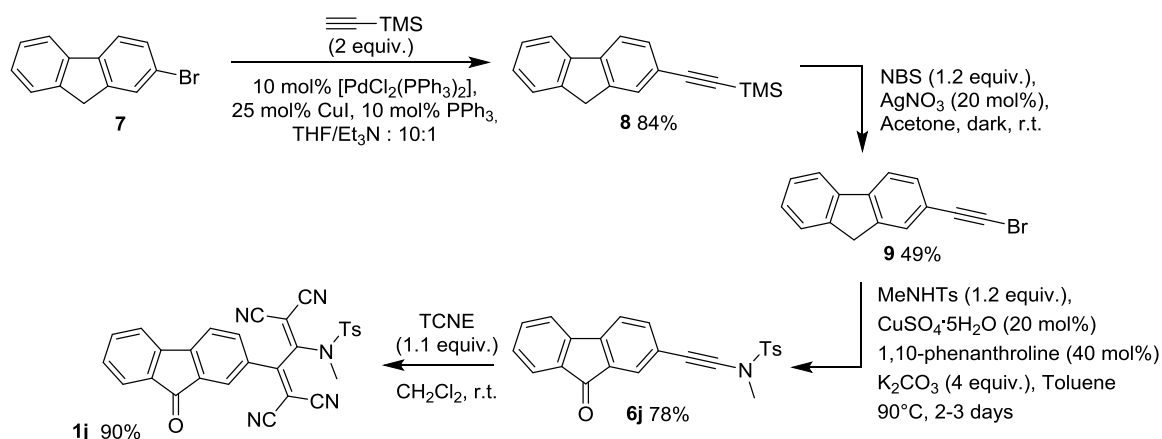
by using classic Sonogashira conditions ($\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}/\text{Et}_3\text{N}$) in the presence of 2 equivalents of trimethylsilylacetylene at reflux (THF). Completion of the reaction required 15 to 60 h, providing after flash chromatography all compounds with moderate to excellent yields (22% to 99 %). Relatively low yields originated from purification difficulties due to such compounds being particularly apolar. The purification of the aceto-dimethyl fluorene derivative **3b** was especially tedious, and proved unsuccessful. The formation of this compound was confirmed by ^1H NMR and it was engaged in the deprotection step which permitted to isolate the terminal alkyne **4b** in 31% yield (2 steps). Regarding the deprotection of the alkyne moiety, the treatment of compounds **3** with potassium carbonate in THF/MeOH induced the removal of the silyl group, providing the terminal alkynes **4** in 53% to 90% yields. Surprisingly, one example (**3i**) did not proceed well under these classic conditions and required the addition of KF to achieve a complete removal of the TMS group; compound **4i** was thus obtained with 72% yield. *N*-Bromosuccinimide was found to be a suitable brominating agent for the terminal alkynes in the presence of a catalytic amount of silver nitrate (20 mol%). Indeed, under dark conditions at room temperature, the bromination of the acetylenic group was achieved in good yields (57% to 77%). Next step involved the formation of ynamides **6**. We selected the conditions described by Hsung^[38] which provided very good results with our compounds. Indeed, a slight excess of *N*-methyl-*p*-toluenesulfonamide (1.2 equiv.) reacted at 90°C in toluene, in the presence of phenanthroline and copper sulfate pentahydrate, affording the displacement of the bromine atom and therefore the formation of the corresponding ynamides. All compounds **5a-c** and **5f-i** reacted the same way in satisfactory to excellent yields (48-88%) after 48 to 72 h of reaction. Those electron rich alkynes were then ready for the final [2+2]cycloaddition-retroelectrocyclization sequence with TCNE. The particularly reactive triple bond reacted smoothly with TCNE at room temperature, and 1.1 equivalents of alkene proved sufficient to reach completion. The TCBDs **1a-c** and **1f-i** were then isolated by flash column chromatography on silica gel in excellent yields (67-95%).



Scheme 1. General synthesis of TCBDs **1a-c** and **1f-i**. ^aDeprotection was achieved after addition of KF in the reaction medium.

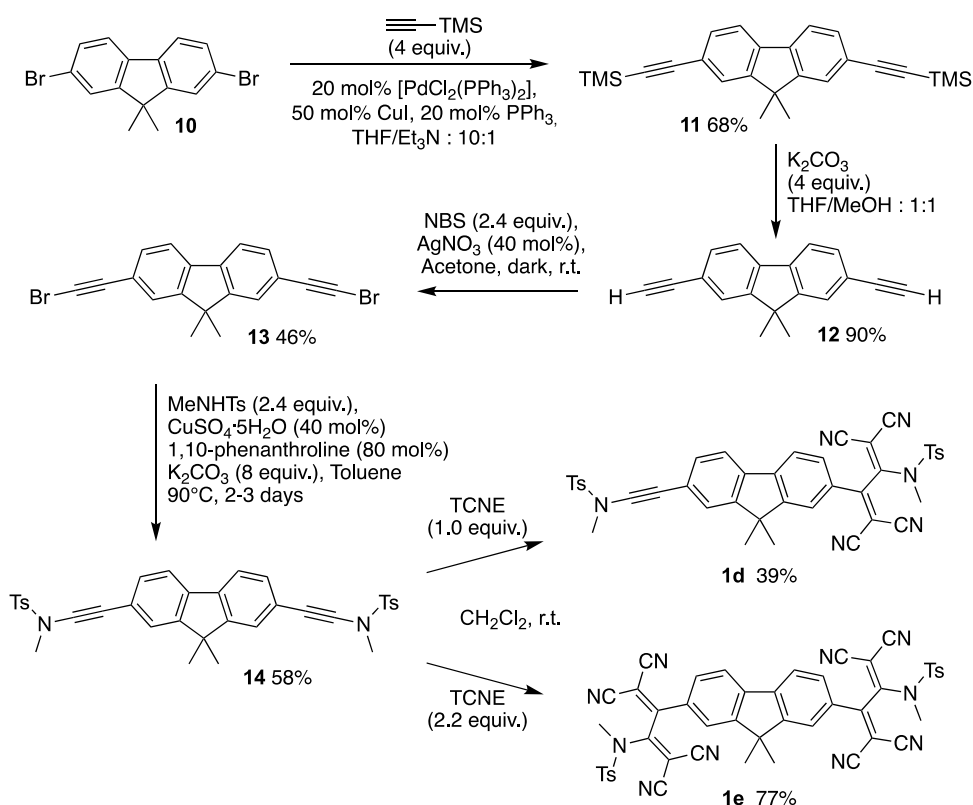
When attempting to synthesize the simpler unsubstituted fluorene-TCBD derivative, we engaged the bromofluorene **7** in a similar synthetic scheme (Scheme 2). The Sonogashira coupling permitted the clean introduction of the trimethylsilylacetylene uneventfully (84% yield). During our investigations,

we also considered to carry out this bromination step from the TMS protected alkynes, shortening by one step this synthetic scheme. As an example, this direct bromination was successfully applied to fluorene derivative **8**, providing the corresponding brominated compound **9** in a reasonable yield (49%). Surprisingly, the reaction conditions previously used for the formation of the other ynamides induced an additional oxidation when applied to the fluorene bromoalkyne **9**. Indeed, the methylene unit of the fluorene was converted into the corresponding ketone, probably because of its high sensitivity to molecular oxygen during the purification process.^[42] This unexpected oxidation did not permit to reach the initially envisaged fluorene-TCBD derivative, but we decided at this point to continue the synthesis toward the formation of the TCBD with this interesting fluorenone **6j** instead. The CA-RE proceeded in the presence of 1.1 equivalents of TCNE and provided the fluorenone-TCBD **1j** in 90% yield.



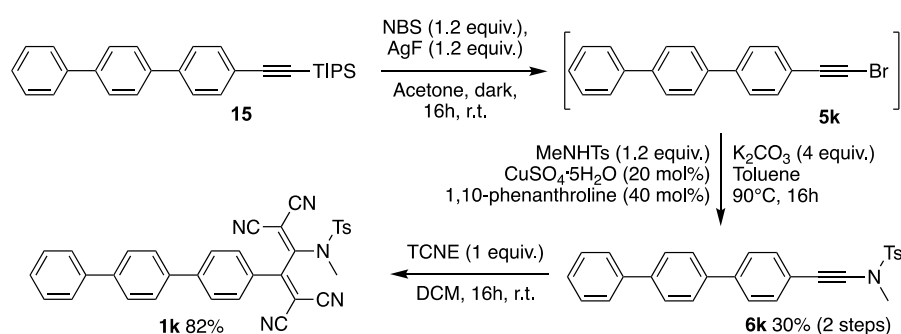
Scheme 2. Preparation of fluorenone TCBD **1j**.

In an even more challenging synthetic scheme, we envisaged to introduce two TCBD units on a single dimethylfluorene core. Starting from the commercially available dibromofluorene **10**, we reproduced the same synthetic sequence but using double quantities of reactants and catalysts (Scheme 3). The double Sonogashira coupling permitted to equip the dimethylfluorene with two trimethylsilyl acetylene units (**11**) in 68% yield. The deprotection step toward the formation of the terminal alkynes was carried out with potassium carbonate, providing **12** in 90% yield. Then, the double bromination as well as the formation of the bis-ynamide **14** proceeded in good yields, considering the additional complexity of these double reactions (46% and 58% respectively). The double CA-RE between bis-ynamide **14** and 2.2 equivalents of TCNE provided the desired double-TCBD **1e** in good yield after 18h of reaction (77%). The mono-TCBD **1d** was also synthesized by reducing both the TCNE quantity (1 equivalent) and the reaction time (2h). Unfortunately, **1d** was poorly stable on silica gel, leading to a disappointing yield (39%).



Scheme 3. Synthesis of bis-TCBDs **1e**.

The terphenyl-TCBD derivative **1k** was prepared from the already described TIPS protected alkyne **15**^[23] (Scheme 4). We took advantage of the direct bromination of this protected alkyne, *N*-bromosuccinimide and silver fluoride then providing the bromoalkyne **5k**. As all attempts to isolate this compound were unsuccessful, the crude material was engaged in the ynamide formation step. As for the other ynamides of the series, Hsung conditions were suitable for the conversion of **5k** into the methyl-tosyl ynamide **6k** in 30% yield for the two steps. Then the CA-RE sequence proceeded in the presence of 1 equivalent of TCNE, leading to TCBD **1k** in an excellent yield (82%).



Scheme 4. Synthesis of TCBD **1k** bearing a terphenyl unit.

Crystallization by slow diffusion of cyclohexane in a dichloromethane solution afforded monocrystals suitable for an X-Ray analysis of TCBDs **1i-k** (Figure 2). These structures, crystallizing in *P*-1 (**1i-j**) or *C*2/*c* (**1k**) space groups, revealed very similar orientation of the TCBD unit for **1i** and **1k** with dihedral angles of 52° (**1i**) and 62° (**1k**) meaning that the butadiene adopted a cisoid conformation. The aromatic cores were oriented towards the methyl of the sulfonamide and a slightly different orientation of the tolylsulfonamide was observed. The fluorenone derivative **1j** adopted, in the crystalline state, a different shape with a more transoid conformation of the TCBD unit (dihedral

angle of 122°) which led to a completely different orientation of both the aromatic core and the sulfonamide group.

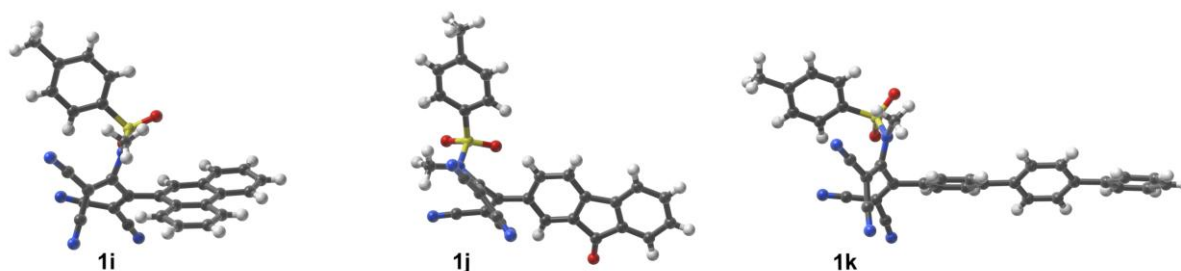


Figure 2. X-ray structure of compounds **1i-k** (solvent molecules were omitted for clarity).

Electrochemical properties. The cyclic voltammetry of some representative TCBDs (**1a**, **1c**, **1e** and **1j**) was recorded in order to gain insight into their electronic properties (Figures S41-S44). As expected, TCBDs **1a** and **1j** exhibit two monoelectronic reversible reductions, as usually observed with TCBDs.^[43] However, the reduction waves of **1j** ($E_{1/2}^1 = -0.53$ V vs Fc; $E_{1/2}^2 = -1.05$ V vs Fc) are shifted towards more positive potentials compared to **1a** ($E_{1/2}^1 = -0.68$ V vs Fc; $E_{1/2}^2 = -1.19$ V vs Fc), probably due to the additional electron-withdrawing group of the fluorenone. The reduction waves of **1c** ($E_{1/2}^1 = -0.65$ V vs Fc; $E_{1/2}^2 = -1.16$ V vs Fc) are in line with those of **1a**. In addition, because of the presence of electron-donating group, one quasi-reversible oxidation ($E_{1/2}^{\text{ox}} = 1.09$ V vs Fc) is observed close to the solvent wall, while no oxidation was observed with **1a** and **1j**. Compound **1e** exhibit two two-electron reductions ($E_{1/2}^1 = -0.60$ V vs Fc; $E_{1/2}^2 = -1.18$ V vs Fc) due to the presence of two TCBD units. Since the first reduction of one TCBD makes the first reduction of the second TCBD slightly more difficult, a shoulder is observed in the first reduction wave. This effect is less important in the second reduction wave while still visible with the enlargement of the signal. No oxidation was observed as for **1a** and **1j**.

Absorption and emission properties. UV-vis spectra of all the TCBDs were recorded in dichloromethane at room temperature (Figure 3 and S45). They all display a strong absorption in the visible region, with absorption coefficients of the lowest-energy band ranging from 3.3×10^3 mol⁻¹.L.cm⁻¹ for phenanthrene derivative **1i** to 2.6×10^4 mol⁻¹.L.cm⁻¹ for bis-TCBD **1e** (Table 1). This band may be attributed to an internal charge transfer (ICT) from the fluorophore to the TCBD unit, by analogy with previous calculations performed on similar structures^[44]. This is consistent with the effects of substitution, with bathochromic shifts associated to an increase of the donor strength of the appended group in the examined positions. For instance, in **1a-d**, the wavelength at absorption maximum of the ICT band was tuned from 423 nm (**1b**, electron-withdrawing acetyl substituent) to 489 nm (**1c**, electron-donating hexyloxy substituent). While aromatic groups and spiro conjugation at the 9-position (**1f-h**) had minimal influence on the energy of this band, a bathochromic shift was observed in compound **1l** ($\lambda_{\text{abs}} = 446$ nm, dibutyl) and a hypsochromic shift was obtained with fluorenone **1j** ($\lambda_{\text{abs}} = 415$ nm) with respect to **1a** ($\lambda_{\text{abs}} = 437$ nm, dimethyl). Bis-TCBD **1e** did not show a significant shift in absorption but demonstrated a strong hyperchromic effect, similarly to recently reported symmetrical TCBD derivatives,^[12,33] doubling the molar absorptivity value (from 1.2×10^4 mol⁻¹.L.cm⁻¹ in **1a**, to 2.6×10^4 mol⁻¹.L.cm⁻¹ in **1e**). Lastly, tricyclic derivatives **1i** and **1k** seemed to confirm these trends, their ICT band shifting according to the conjugation of the molecule. **1i** notably underwent an additional hypochromic effect, presumably pertaining to the position where the phenanthrene core is functionalized as the K-region is more olefinic than aromatic in nature, although the resulting properties were comparable with previously reported anthracene-TCBD ($\epsilon = 4.3 \times 10^3$ mol⁻¹.L.cm⁻¹ at 557 nm).^[36]

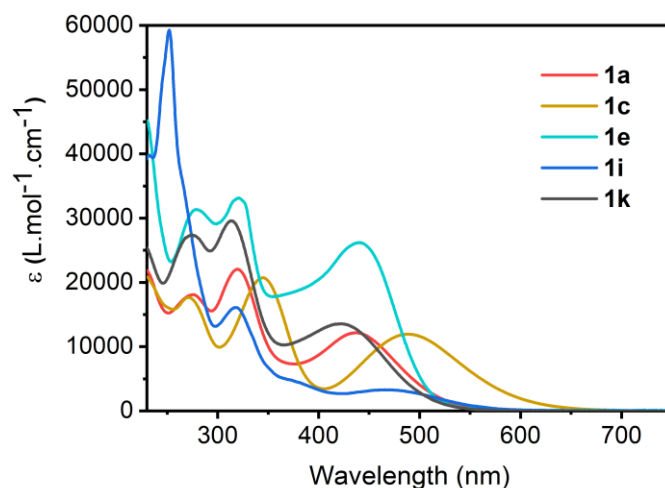


Figure 3. UV-visible absorption spectra of compounds **1a**, **1c**, **1e**, **1i** and **1k** in dichloromethane.

Table 1. Molar absorption coefficients of compounds **1a–l** at the different absorption maxima in dichloromethane. The corresponding wavelengths are indicated between parentheses.

	ϵ [L.mol ⁻¹ .cm ⁻¹] (λ_{abs} [nm])
1a	1.8×10^4 (276), 2.2×10^4 (320), 1.2×10^4 (437)
1b	1.5×10^4 (281), 2.2×10^4 (321), 8.8×10^3 (423)
1c	1.8×10^4 (271), 2.1×10^4 (344), 1.2×10^4 (489)
1d	2.0×10^4 (276), 2.7×10^4 (341), 1.2×10^4 (466)
1e	3.1×10^4 (278), 3.3×10^4 (321), 2.6×10^4 (440)
1f	1.8×10^4 (264), 1.9×10^4 (323), 1.0×10^4 (441)
1g	2.3×10^4 (258), 1.9×10^4 (282), 1.8×10^4 (292), 2.2×10^4 (321), 1.1×10^4 (439)
1h	2.9×10^4 (265), 3.0×10^4 (273), 2.2×10^4 (296), 2.4×10^4 (308), 1.9×10^4 (326), 9.4×10^3 (442)
1i	5.9×10^4 (252), 1.6×10^4 (318), 3.3×10^3 (466)
1j	4.0×10^4 (278), 9.8×10^3 (385), 9.2×10^3 (415)
1k	2.7×10^4 (275), 3.0×10^4 (314), 1.4×10^4 (422)
1l	2.0×10^4 (273), 2.6×10^4 (321), 1.3×10^4 (446) 1.3×10^4 (446)

Fluorescence properties in the visible range (450–800 nm) were then investigated in solution at room temperature. **1d** turned out to be too unstable to generate reproducible results, thus this compound was discarded from the study. For comparison, TCBD **1l**, whose synthesis has already been reported,^[37] was added to the series. First, though dichloromethane was the choice solvent in steady-state UV-vis absorption analyses for solubility reasons, almost no emission could be recorded in this medium, with the notable exception of fluorenone **1j** with a quantum yield of 1.6 % (Table S1). Considering the solvatochromic nature of ICT bands, less polar solvents were then tested. In toluene (see Figures S47, S48 and Table S2 for complementary information), most of the compounds exhibit quantum yields above 1%, except for **1a**, **1c** and **1i**. Noteworthy are the quantum yields of **1b** and **1e** that reach 3.2% and 4.2% respectively. These higher values correlate with the lower emission wavelength in these two compounds (653 and 620 nm respectively), consistently with the energy gap law.^[45] Decreasing the polarity further enhances the fluorescence intensity, sometimes dramatically. Indeed, in cyclohexane (Figures 4a, S49 and Table S3), the quantum yields of some compounds such as **1a** and **1i** are increased by an order of magnitude (from 0.7 to 6.1 % and from 0.1 to 1.6 % respectively). However, the solubility of all the dyes is lower in this solvent, even precluding any

measurements with **1e**. The strong dependence on the nature of solvent on emission features is reminiscent of a solvatochromism that might be explained by the super-accepting property of the TCBD unit that is potentially balanced by adding another electron-withdrawing group like a ketone or another TCBD. A likely mechanism for the drastic deactivation of the excited state when increasing the polarity of the solvent is the formation of TICT (Twisted Intramolecular Charge Transfer) states, in accordance with other studies from the group of Diederich and Armaroli.^[19] This point will be further investigated in the future.

The photophysical properties in cyclohexane were then examined in more detail. As one could anticipate from the absorption properties, the emission maximum strongly depends on the nature of the fluorophore attached to the TCBD moiety, mirroring the trends observed in UV-vis spectroscopy with rather large Stokes shifts that remain similar (6500–7500 cm⁻¹) across the entire family of molecules (Table S3). **1k** shows the largest energy difference (7830 cm⁻¹), possibly due to the additional torsional motions between the phenyl rings. The measured amplitude-weighted fluorescence lifetimes are also presented in Table 2. From the multiexponential analyses (discussed in SI), we could hypothesize that excited-state dynamics lead to emissive species with different conformations, and that their ratios are intricately connected with the resulting fluorescence intensities. More in-depth studies will be required to unveil the nature of these states. Nonetheless, it is interesting to note that the fluorescence quantum yield of **1k** is 7.8 % in cyclohexane, which is, to the best of our knowledge, the highest value ever recorded for a TCBD in solution at room temperature.

Emission spectra in the solid state were also recorded (Figure 4b, S51 and S52). The emission maximum is spread over a large area, going from 588 nm for compound **1e** to 820 nm for **1c** (Table 2). Unsurprisingly, the quantum yields drop when approaching the near-IR region. The most red-shifted emissive compound (**1c**) displays the lowest quantum yield, below 0.1%. The highest quantum yield is provided by compound **1a** (7.5%). Except these extrema, the quantum yields of the other compounds are comprised between 1.2% (**1h** and **1k**) to 6.6% (**1j**). These quantum yields do not follow exactly the same trend as what was observed in solution probably because of complex intermolecular interactions between TCBD molecules in the solid state. Nevertheless, most of these compounds are significantly emissive in powders

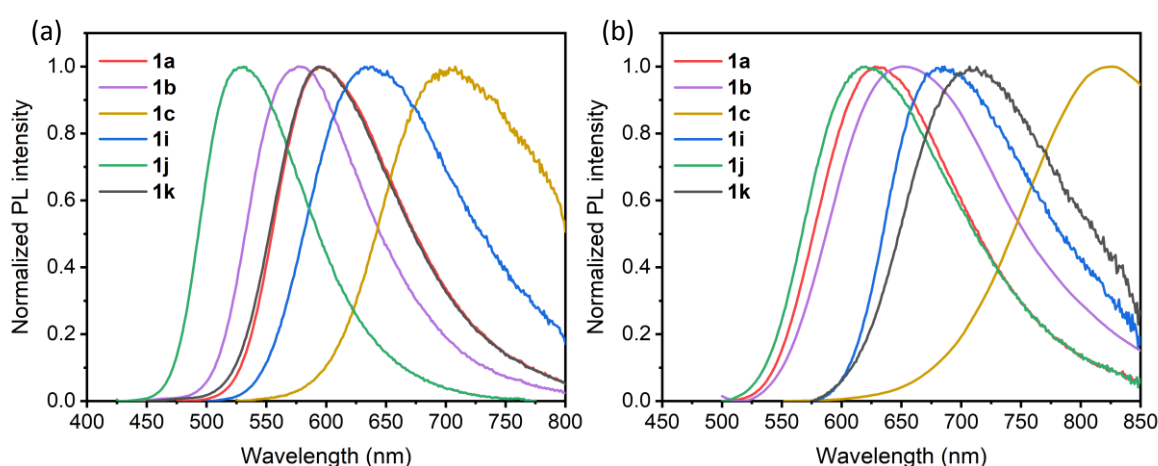


Figure 4. Photoluminescence spectra of compounds **1a**, **1b**, **1c**, **1i**, **1j** and **1k** (a) in cyclohexane (λ_{exc} = 415, 405, 485, 430, 375 and 390 nm, respectively) and (b) in powders (λ_{exc} = 475, 420, 488, 550, 480 and 525 nm, respectively). The weak signals for **1b** and **1c** produced noisy data that were smoothed using a Savitzky-Golay filter to facilitate their reading.

Table 2. Photoluminescence data of compounds **1a–l** in cyclohexane, toluene and powders.

	Cyclohexane			Toluene		Powder	
	λ_{em} (nm)	ϕ (%)	$\langle\tau\rangle$ (ns) ^a	λ_{em} (nm)	ϕ (%)	λ_{em} (nm)	ϕ (%)
1a	596	6.1 ^b	n.d.	699	0.7 ^c	660	7.5
1b	578	4.3 ^b	1.4	653	3.2 ^d	638	2.4
1c	708	0.4 ^c	n.d.	n.d.	< 0.1 ^e	820	< 0.1
1d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1e	n.d.	n.d.	n.d.	620	4.2 ^c	588	4.7
1f	595	7.5 ^b	3.3	679	1.9 ^c	682	5.6
1g	603	5.6 ^b	3.6	684	1.3 ^c	702	1.8
1h	591	3.9 ^b	2.3	669	1.1 ^d	676	1.3
1i	639	1.6 ^b	2.1	729	< 0.1 ^d	686	1.3
1j	531	2.2 ^b	1.0	645	1.3 ^c	640	6.6
1k	594	7.8 ^b	2.3	712	1.5 ^d	707	1.2
1l	612	6.9	3.2	619	0.8 ^c	n.d.	n.d.

^a Amplitude-weighted lifetimes $\langle\tau\rangle = \sum A_i \tau_i / \sum A_i$ (see SI); ^b **1l** in cyclohexane used as a reference (value determined to be 6.9%, see SI); ^c Fluorescein in water used as a reference (69%); ^d **1j** in toluene used as reference (1.3%). ^e **1l** in toluene used as reference (0.8%); n.d. = not determined.

Conclusion. To conclude, we described the synthesis of 11 new TCBDs derived from ynamides and bearing various fluorophores. Their optical properties were investigated by absorption and fluorescence spectroscopies. Noteworthy is their significant emission in apolar solvents such as toluene and cyclohexane with quantum yields up to 7.8 %, an unprecedented value for TCBDs in solution. Emission in the solid state was also observed and quantified. In contrast, the fluorescence signal was rapidly quenched as the polarity of the solvent is increased, with virtually no emission observed in dichloromethane, thus revealing a strong dependence of these dyes on their environments. All these observations bring a new insight in the optoelectronic properties of this family of TCBDs and pave the way to the synthesis of more efficient emitters of this kind.

X-Ray Crystallography

Deposition Numbers CCDC 2127295 (**5h**), 2112157 (**1i**), 2113145 (**1j**) and 2112158 (**1k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Conflicts of interests

There are no conflicts to declare.

Acknowledgments

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1,1,4,4-Tetracyanobutadienes (TCBDs) derived from ynamides and bearing diverse fluorene-based chromophores or other tricyclic aromatic hydrocarbons were prepared. The conceived sulfonamido-TCBDs showed remarkable photophysical properties covering a large range of wavelengths from the visible region to the near-IR. They displayed an environment-sensitive emission that was observed in nonpolar solvents and in the solid state but was very weak in dichloromethane. Quantum yields in cyclohexane reached values up to 7.8%.

