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14. ABSTRACT The recent investigations of deoxyribonucleic acid (DNA) for use in non-linear optics (NLO) are an important breakthrough. Excellent optical quality thin films of DNA were obtained by Ogata in Japan and researchers at AFRL. Recent studies suggest that DNA may prove to be a more suitable material than the polymer currently used for optical waveguide devices, due to its optical and electromagnetic properties, resistance to solvents used in device fabrication, and it is biodegradable and inexpensive. The objective was to introduce active molecules within thin films of DNA in view of obtaining highly luminescent systems by three-photon absorption (3PA) and four-photon absorption (4PA), comparing results with analog poly(methyl methacrylate) (PMMA)-based host materials, in order to advance the understanding of DNA for non-linear optics. Eight chromophores of different structures (push-pull, quadrupole, bi-chromophore) were synthesised. Most these chromophores present an absorption band around 500 nm, allowing to expect 3PA properties. Spectroscopic properties are preserved in DNA-CTMA and PMMA thin films with fluorescence properties in the NIR. Unlike in PMMA, chromophores fluorescence efficiency in DNA-CTMA seems to depend strongly on the size of the molecule. The fluorescence efficiency decreases in DNA-CTMA for large molecules, leading to a higher efficiency in PMMA, while shortest molecules with a similar charge transfer present higher response in DNA. The confirmation of these results by 3PA should be performed in the group of Dr. James Grote (US Air Force Research Laboratory). These results are promising for the design of DNA-based highly fluorescent displays by multiphotonic excitation.					
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RESEARCH REPORT

Period 2

Research project: FA8655-09-M-4001

1. Introduction

DNA is a very interesting and promising material (Fig. 1), with a high potential for application in photonics and in electronics, as it shows recent studies of N. Ogata group from Chitose Institute of Technology and J. Grote from US AF WPRL, Dayton, Ohio and coworkers¹⁻⁶.

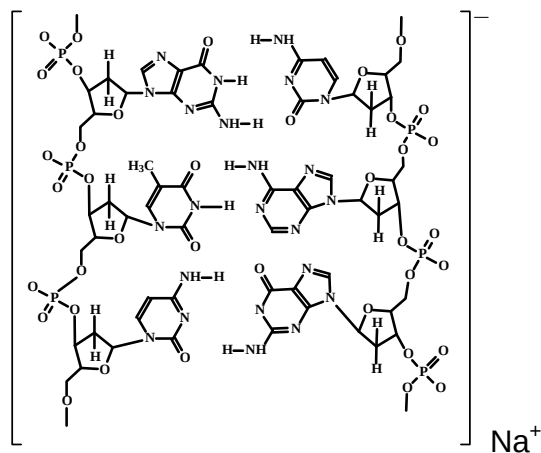


Figure 1. Chemical structure of DNA. Left side: macroscopic helicoidal structure; right site: elementary cell.

As a renewable and a biodegradable material recovered from waste of fish industry, it is expected to replace synthetic polymers, which are known to have a very long degradation time (e.g. polyethylene about 400 years). However the biopolymers, similarly to most synthetic polymers, are optically and electronically inactive materials. Therefore in order to obtain defined properties, biopolymers have to

be functionalized with active molecules, presenting well-defined properties, such as light propagation, charge mobility, luminescence... following targeted applications.

In this project we focused our work on the introduction of active molecules within thin films of DNA in view the of obtaining highly luminescent systems by three-photon absorption (3PA) or four-photon absorption (4PA) around 1500 nm, an eye-safe wavelength. Our investigation also includes the comparison with results in analog poly(methyl methacrylate) (PMMA)-based host materials. This work is performed in collaboration with Dr. James Grote group (US Air Force Research Laboratory).

The design of new fluorescent chromophores with 3PA or 4PA properties requires conjugated structures substituted at each end by donor and/or acceptor groups. In this purpose, we synthetised 8 chromophores displayed in Figure 2; these molecules are expected to feature absorption properties around 500 nm for a 3PA efficiency or around 375 nm for 4PA efficiency near 1500 nm.

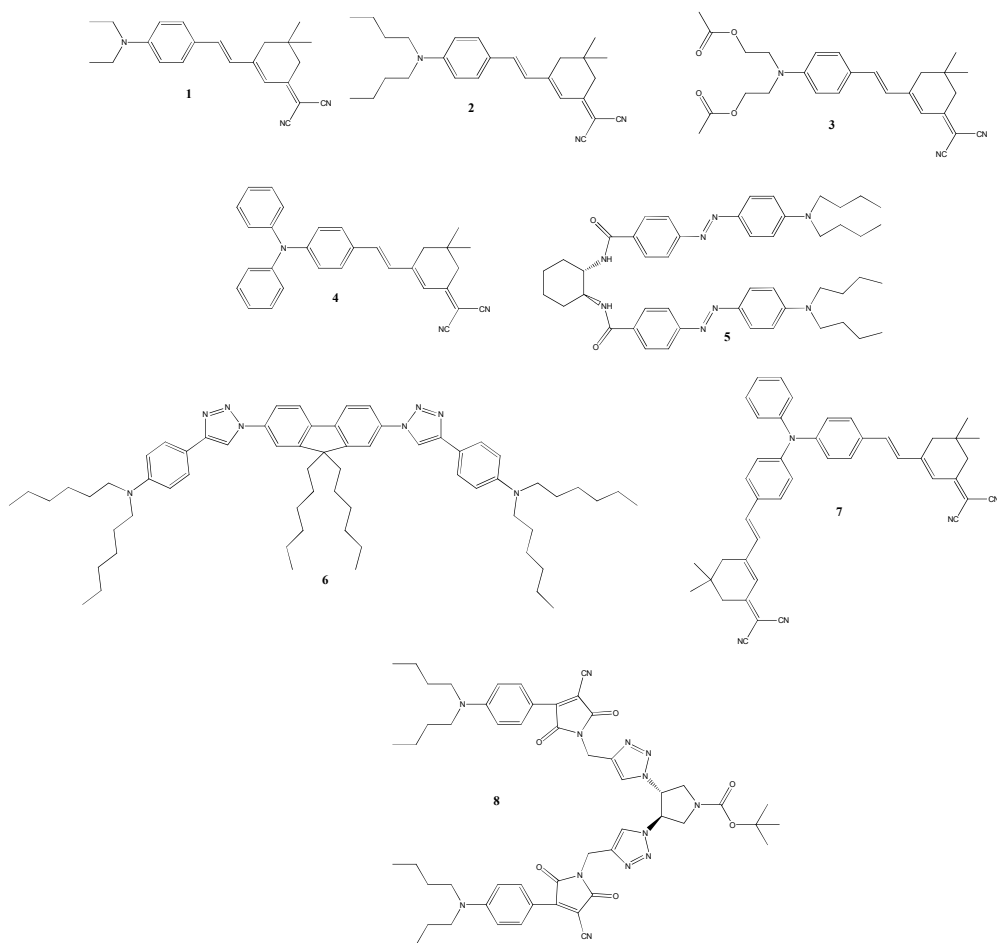


Figure 2. Chemical structures of chromophores studied for 3PA or 4PA around 1500 nm.

Chromophores **1-4** and **7** present a push-pull conjugated structure with an amine type donor and the same acceptor group for all these systems. Chromophores **5** and **8** are bi-chromophoric systems, while **6** has a quadrupolar structure.

II. Experimental section

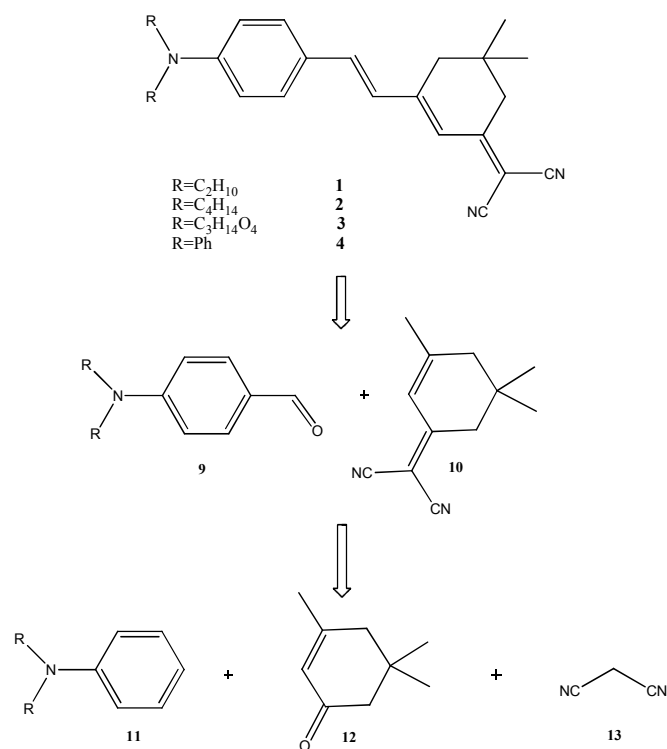
DNA (Chitose, Japan) used was extracted from Salmon sperm and was functionalized with a cationic surfactant complex hexadecyltrimethylammoniumchloride (CTMA) in order to improve its solubility in organic solvents like buthanol. This procedure improves at the same time its thermal stability and optical properties. The molecular weight of DNA used was 5×10^5 g/mol and 2×10^5 g/mol. For comparison, PMM (Aldrich, $M_w = 3.5 \times 10^5$ g/mol) was used.

The studies were performed using UV – VIS and fluorescence spectroscopic techniques on solutions and thin films, using a JASCO UV – VIS - NIR spectrophotometer (V 670) and a fluorimeter Fluorog Horiba-Jobin Yvon, respectively.

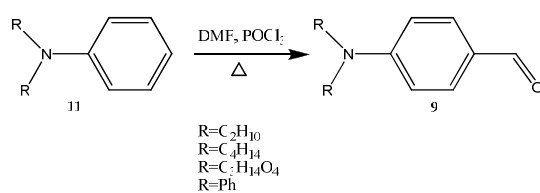
Thin films were obtained by spin coating of solutions (30 g/L) of studied compounds on glass substrates. Depending on the matrix and on the chromophore solubility, the solutions were performed in buthanol, in 1,1,2 trichloroethane or in a mixture of both solvents (7:1).

Synthesis of chromophores 1-4 :

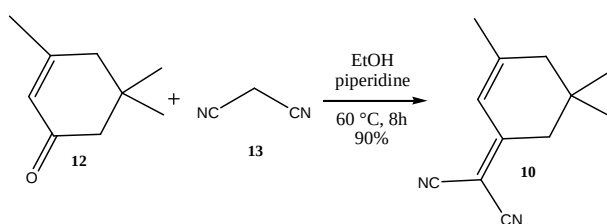
Chromophores **1**, **2**, **3** and **4** were obtained in two steps, via a convergent synthesis from commercially available molecules: appropriate disubstituted anilines **11**, isophorone **12**, and malononitrile **13**.



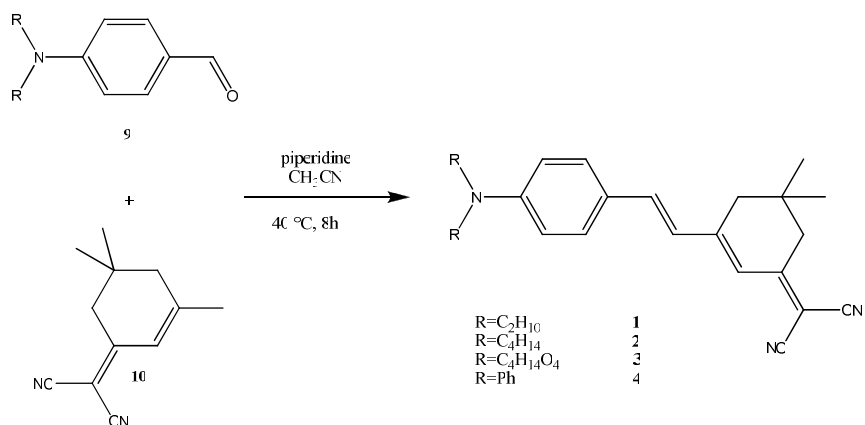
Para-amino benzaldehyde **9** was obtained by a Vilsmeier-Hack reaction under argon atmosphere using N,N-dimethyl formamide (DMF) and phosphoryl chloride with appropriate heating temperature and reaction time.



The compound **10** was obtained from commercial isophorone **12** and malonitrile **13** in dry ethanol using piperidine as catalyst. The product was purified by recrystallization from heptane, affording compound **10** in 90% yield.

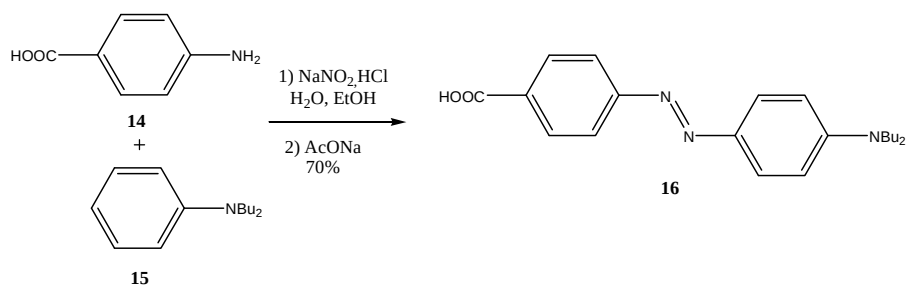


A Knoevenagel reaction between N,N-disubstituted para-amino benzaldehydes **9** and **10** gave chromophores **1-4** after purification by crystallization or column chromatography.

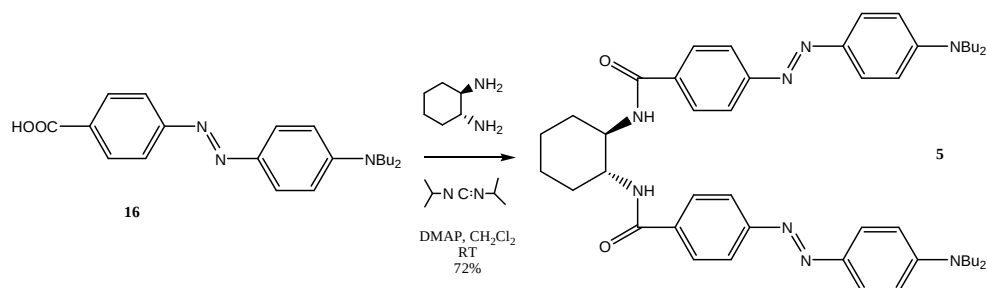


Synthesis of the chromophore 5:

The chromophore **5** was obtained in three steps from commercially available 4-aminobenzoic acid **14** and N,N-dibutyl aniline **15**. The first step is a diazotation reaction using sodium nitrite, hydrochloric acid and sodium acetate in a mixture of water and ethanol.

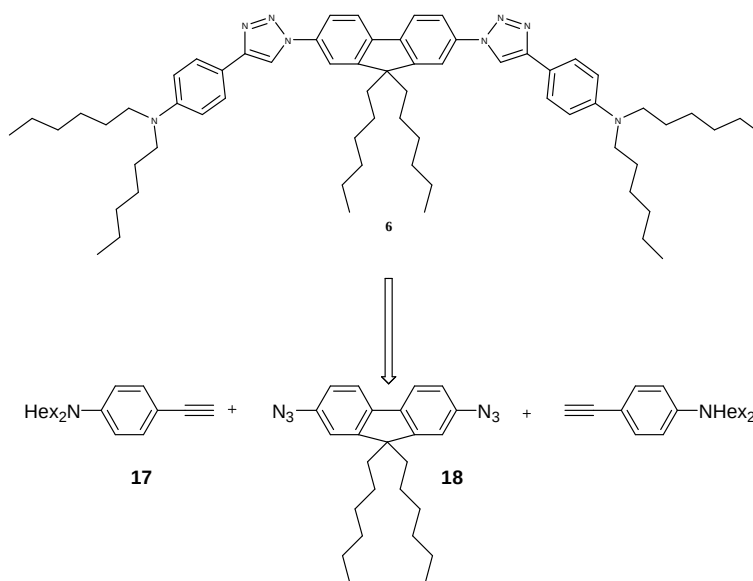


The reaction between the chromophore **16** and trans-1,2-diaminocyclohexane gave **5** in 72% yield.



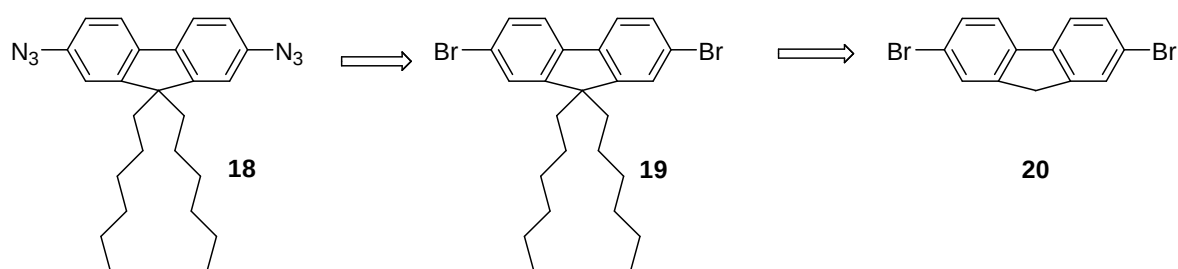
Synthesis of the chromophore **6**:

The chromophore **6** was obtained by copper (I)-catalysed dipolar [1,3]-cycloaddition between **17** and the diazido fluorene **18**.

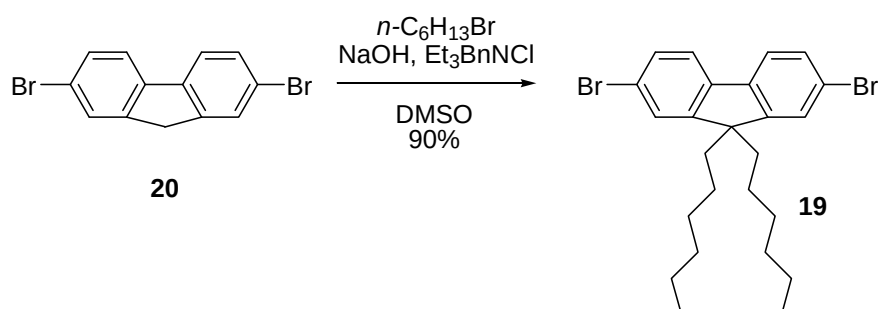


Synthesis of the diazido fluorene **18** :

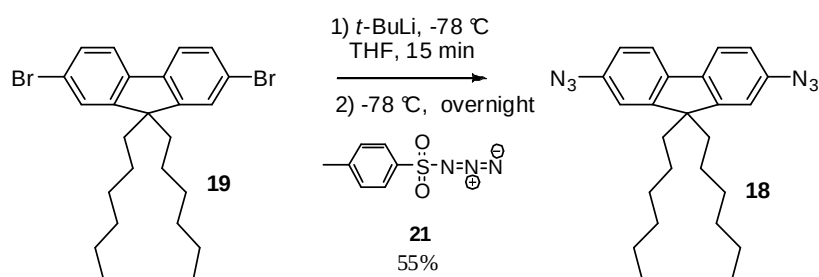
18 can be obtained in two steps from commercial 2,7-dibromofluorene **20**.



The first step consisted in the alkylation of 2,7-dibromofluorene **20** with 1-bromohexane using a phase transfer catalyst. The compound **19** was purified by crystallisation from ethanol to give compound **19** in 90% yield.

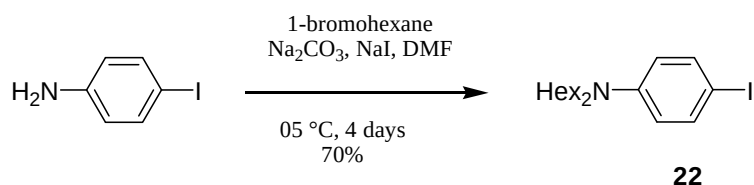


The diazido fluorene **18** was prepared according to the method described by Reek et al.⁷ A metal-halogen exchange reaction using *tert*-butyl lithium at low temperature was followed by the addition of the tosyl azide **21** to give **18** in 55% yield.

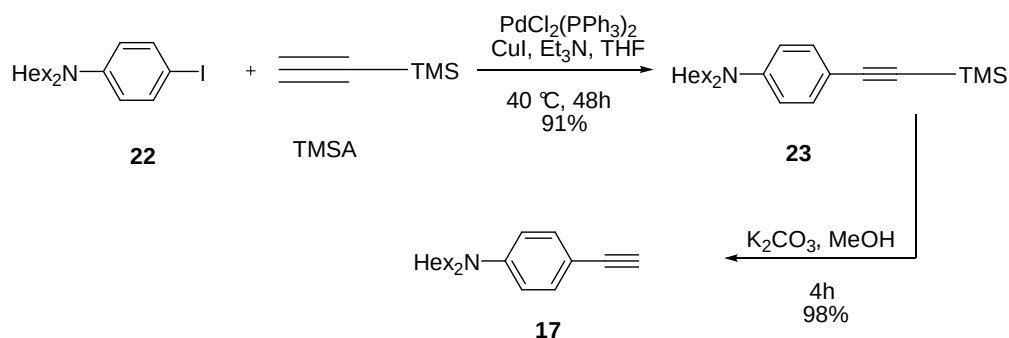


Synthesis of **17**:

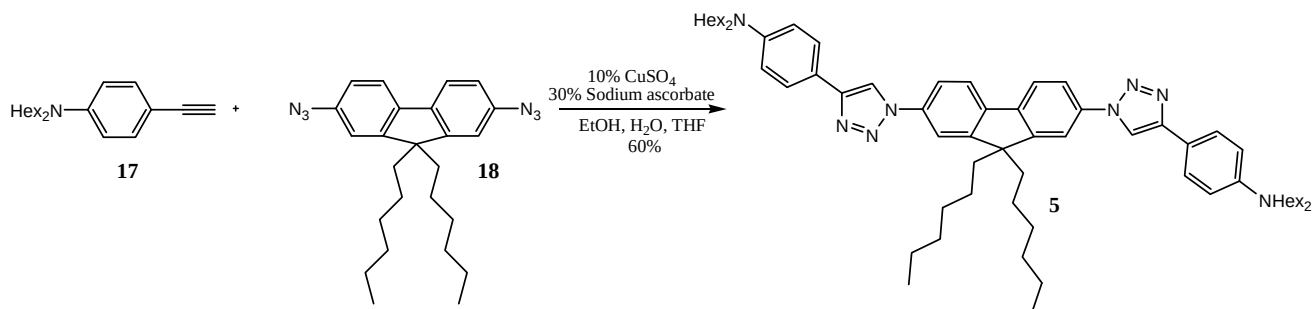
17 was obtained in three steps from the commercially available 4-iodoaniline by Sonogashira coupling. 4-iodoaniline was alkylated with 1-bromohexane giving N,N-dihexyl-4-iodo-aniline **22** in 70% yield.



The Sonogashira coupling product **23** was then deprotected to give compound **17** in 98% yield.

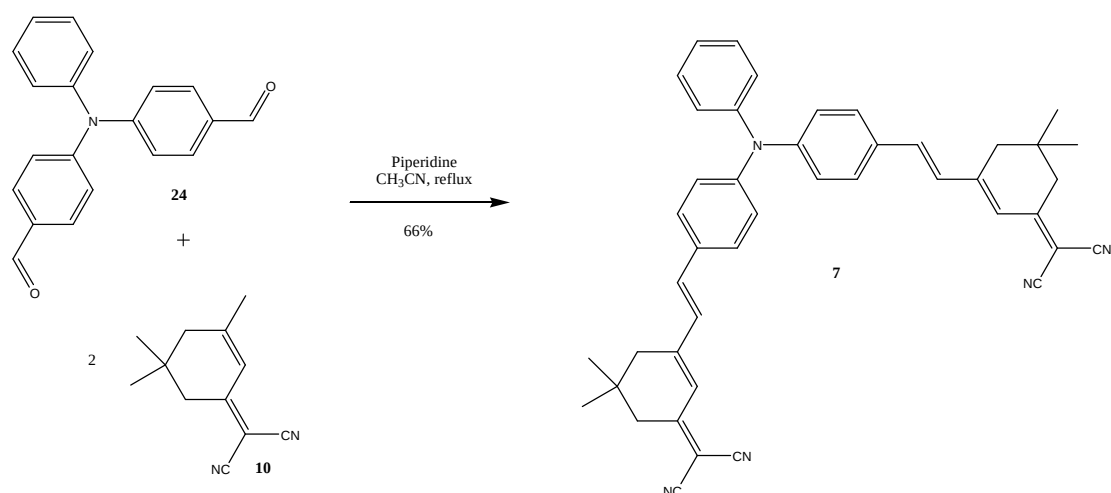


Chromophore **6** was obtained by a click reaction between **18** and **17** using sodium ascorbate and copper sulphate. The product was purified by column chromatography to afford chromophore **5** in 60% yield.

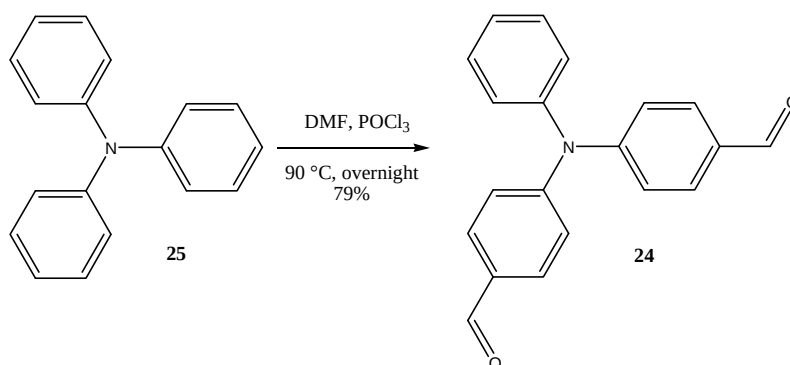


Synthesis of the chromophore 7:

The chromophore **7** was obtained by a Knoevenagel reaction between phenylamino-di-benzaldehyde **24** and the compound **10** in 66% yield.

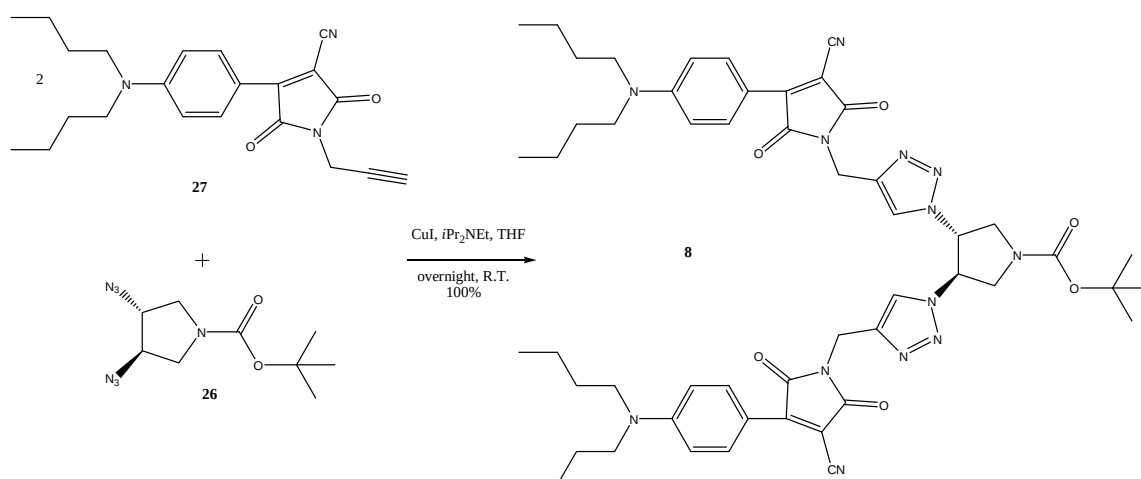


The compound **24** was obtained from tetraphenyl amine **25** by a Vilsmeier-Hack reaction under argon atmosphere using N,N-dimethyl formamide (DMF) and phosphoryl chloride (POCl_3), at 90 °C overnight. The product was purified by recrystallization from heptane, affording the compound **24** in 79% yield.



Synthesis of the chromophore **8**:

The chromophore **8** was obtained by a click reaction between the diazidopyrrolidine carboxylate **26** and **27** using copper iodide and diisopropyl ethylamine in THF. The product was purified by column chromatography to afford **8** in a quantitative yield.



III. Results and Discussion

III.1. Chromophores properties in solution.

The absorption spectra of chromophores **1-8** were recorded in different solvents. All chromophores present a broad charge transfer absorption band; the example of **1** is displayed in Figure 3. A weak solvatochromism was observed in absorption properties with solvent polarity (Fig. 3).

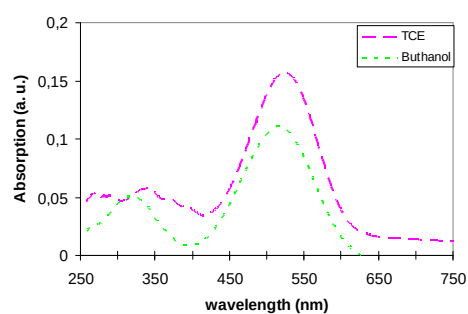


Figure 3. Absorption spectra of **1** in trichloro-ethane and butanol

All push-pull chromophores **1-4** and **7** present a maximum in absorption around 500 nm in trichloro-ethane (488 to 521 nm), allowing to expect 3PA properties at 1500 nm (Table 1).

Table 1. Spectroscopic data of molecules **1-5**, **7** and **8** in trichloro-ethane and of **6** in buthanol: linear absorption, emission and fluorescence quantum yield.

Molecule	1	2	3	4	5	6	7	8
λ_{abs} (nm)	517	521	488	489	452	307	481	529
λ_{em} (nm)	652	664	632	693	-	511	700	701
ϕ (%)	50	79	32	>90	-	58	65	1

Bichromophores **5** and **8** with maxima at 452 and 529 nm respectively are also candidates for 3PA properties, while the quadrupole **6**, which exhibits a maximum at 307 nm in buthanol, could be a candidate for 4PA properties (Fig. 4); however the weak resonance at 375 nm, which allows to assume weak 4PA properties, leads to not consider this molecule for nonlinear measurements in DNA. Nevertheless, we will compare fluorescence properties of this molecule in DNA and PMMA, in order to study, from a general point of view, the role of the molecular structure on fluorescence efficiency in DNA.

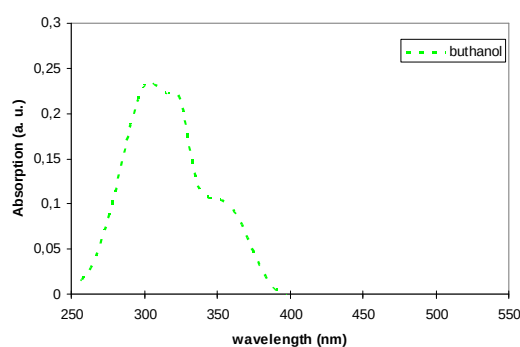


Figure 4. Absorption spectrum of **6** in buthanol.

Except the molecule **5**, all chromophores present a broad fluorescence band from 511 to 701 nm for **6** and **8** respectively, with a higher positive solvatochromism than in absorption, as illustrated for **1** in Figure 5.

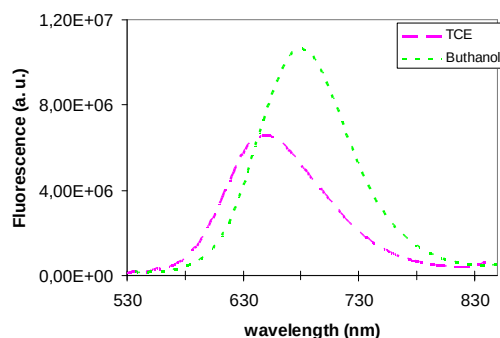


Figure 5. Fluorescence spectra of **1** in trichloro-ethane and buthanol

Fluorescence quantum yields are displayed for all chromophores in Table 1: except for **8**, values higher than 30% were obtained. This allows to expect 3P (4P) excited fluorescence properties for chromophores **1-4** and **8** (**6**). The chromophore **5**, which does not present fluorescence properties, was not used in further studies.

III. 2. Absorption and fluorescence properties of thin films

Spectroscopic properties in thin films, which were studied for several concentrations (5, 10, 15, 20%) of chromophores in matrices, are similar to those observed in solution.

Absorption spectra present a broad charge transfer band in DNA-CTMA and PMMA with an increasing intensity with the chromophore concentration (see Figures 6 and 7 respectively for chromophore **1**); this band is similar to that observed in solution. Data are summarized in Table 2 for all chromophores. Bands are generally slightly shifted between DNA-CTMA and PMMA matrices (Table 2); similarly a shift is also observed between maxima in solution and in polymers.

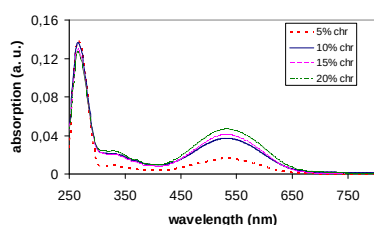


Figure 6. Absorption spectra of **1** in DNA-CTMA

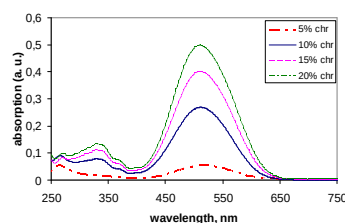


Figure 7. Absorption spectra of **1** in PMMA

Table 2. Spectroscopic data in DNA6CTMA and in PMMA: linear absorption, emission and fluorescence quantum yield for a concentration of 5%.

Molecule	1	2	3	4	6	7	8
$\lambda_{abs}^{DNA}, \lambda_{abs}^{PMMA}$ (nm)	530,521	510,525	503,500	469,495	303,318	501,516	544,546
$\lambda_{em}^{DNA}, \lambda_{em}^{PMMA}$ (nm)	684,659	681,657	652,637	652,646	442,428	627,651	645,650
ϕ^{DNA}, ϕ^{PMMA} (%)	74 , 39	39 , 25	37 , 36	13 , 89	3 , 2	24 , 75	6 , 2

In the same way, fluorescence spectra are similar to those obtained in solution, as shown in Figures 8 and 9 respectively for chromophore **1** in DNA-CTMA and PMMA for the different concentrations. An apparent red shift of the fluorescence spectra was observed at high concentration in some cases. This could be due to there-absorption phenomenon due to the small Stoke's shift. Similarly to absorption, a shift between maxima in DNA and PMMA is observed.

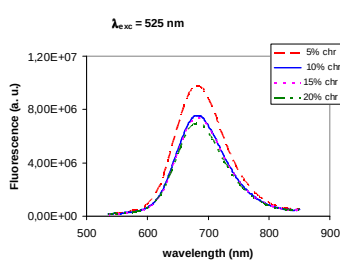


Figure 8. Fluorescence spectra of **1** in DNA-CTMA

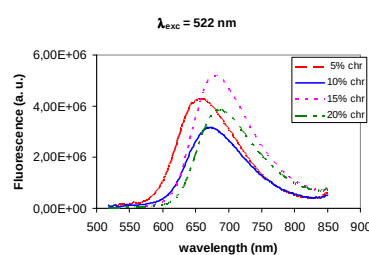


Figure 9. Fluorescence spectra of **1** in PMMA

Quantum yields of fluorescence were compared at each chromophore concentration in both matrices (Table 2). Reasonable values are obtained in both matrices, with a strong decrease in the case of **6** with respect to the solution. Variations of quantum yield values with chromophore concentration are displayed in Figures 10-16 for each matrix; except for **4** (Fig. 13), globally, the fluorescence quantum yield decreases with concentration for both matrices, due to chromophores interactions.

The comparative fluorescence efficiency in DNA-CTMA and PMMA depends strongly on the chromophore. In DNA-CTMA, the fluorescence quantum yield depends not only on the charge transfer within the chromophore, but also on the size of the molecule: the ϕ value varies from 74 to 37% for **1**, **2** and **3** ($c = 5\%$), which present exactly the same charge transfer and differ in the length of the alkyl chain on the donor group. It is worth noting that these molecules present similar quantum yields in

PMMA. This leads to a higher efficient fluorescence for **1** DNA-CTMA with respect to that in PMMA; this difference decreases strongly in **2** and **3**.

A strong value of ϕ is found for **4** and **7** in PMMA (89 and 75% respectively for a concentration of 5%); both molecules feature a similar charge transfer system. Unlike for chromophores **1-3**, weaker ϕ values were found in DNA-CTMA for **4** and **7**.

As in solution, very weak ϕ values are observed for **8** in both matrices. The molecule **6** presents also very weak ϕ values in good agreement with fluorescence efficiency observed in powder.

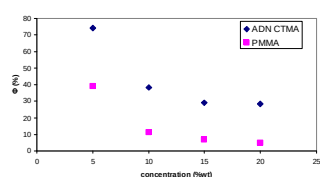


Figure 10. Fluorescence quantum yield for **1** in thin films

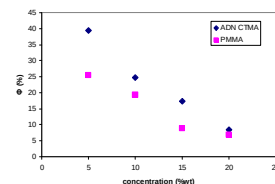


Figure 11. Fluorescence quantum yield for **2** in thin films

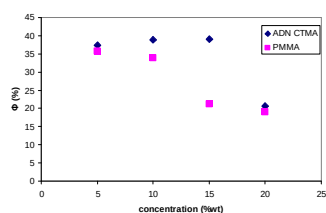


Figure 12. Fluorescence quantum yield for **3** in thin films

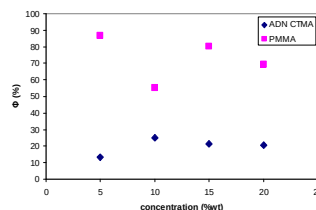


Figure 13. Fluorescence quantum yield for **4** in thin films

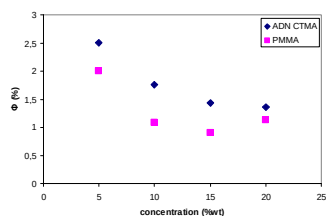


Figure 14. Fluorescence quantum yield for **6** in thin films

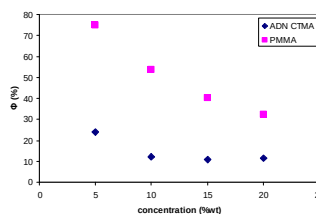


Figure 15. Fluorescence quantum yield for **7** in thin films

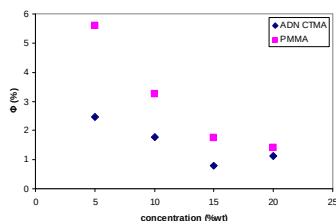


Figure 16. Fluorescence quantum yield for **8** in thin films

IV Conclusions

Eight chromophores of different structures (push-pull, quadrupole, bi-chromophore) were synthesised. Most these chromophores present an absorption band around 500 nm, allowing to expect 3PA properties. Spectroscopic properties are preserved in DNA-CTMA and PMMA thin films with fluorescence properties in the NIR.

Unlike in PMMA, chromophores fluorescence efficiency in DNA-CTMA seems to depend strongly on the size of the molecule. The fluorescence efficiency decreases in DNA-CTMA for large molecules, leading to a higher efficiency in PMMA, while shortest molecules with a similar charge transfer present higher response in DNA.

The confirmation of these results by 3PA should be performed in the group of Dr. James Grote (US Air Force Research Laboratory). These results are promising for the design of DNA based highly fluorescent displays by multiphotonic excitation.

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