A difluorenyl-*carbo*-cyclohexadiene: prospective chromophore for two-photon absorption

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For the purpose of outlining structure-property relationships for two-photon absorption (2PA), a "σ-locked" *carbo*-cyclohexadiene with two fluorenyl substituents has been envisaged for comparison with previously studied aromatic *carbo*-benzene and non-aromatic *carbo*-quinoid congeners. A representative where the C_{10}-π-conjugated fluorenyl moieties are also connected by a C_8-π-insulating 3,6-dimethoxy-3,6-bis(trifluoromethyl)octa-1,4,7-triyn-1,8-diyl edge has thus been synthesized in four steps from known C_{8F} triyne and C_{10} triynyldial, through a [8F+10] cyclization process. In spite of a relatively strong absorbance (ε = 84 800 L.mol^{-1}.cm^{-1} at 634 nm), the non-vanishing green fluorescence (at 533 nm) of the chromophore should allow measurements of the 2PA cross section by both the TPEF and Z-scan methods.

Introduction

87 Years after Maria Göppert-Mayer's seminal dissertation [1a], third-order non-linear [illegible] photon absorption (2PA), attract a constantly renewed attention [1b,c]. Chromophores with large 2PA cross-sections (σ_{2PA}) can indeed find applications in diverse fields such as three-dimensional optical data storage [2], fluorescence microscopy [3], optical power limiting [4], photodynamic therapy [5] or microfabrication [6]. In the field of organic [illegible] dies have highlighted the high 2PA efficiency of dipolar systems of the type D-Π-A [7], and quadrupolar counterparts of the type D-Π-D or D-A-D [8], where D and A denote π-electron donating and accepting moieties, respectively, and Π a π-conjugating bridge. Aromatic macrocycles can also be

envisaged as bridging cores π: after the $C_{20}N_4$ pentacycle of porphyrines [5,9], the C_{18} monocycle of *carbo*-benzenes was recently reported to act as an efficient π core in quadrupolar 2PA chromophores [10]. Using the *Z*-scan technique, a 2PA cross section $\sigma_{2PA} = 656$ GM was indeed measured for the *carbo*-benzene **1b** upon femtosecond excitation at 800 nm (Figure 1). More recently, preliminary *Z*-scan measurements performed on the *carbo*-quinoid **2** [11] indicated that the non-aromatic C_{18} core at stake tends to provide higher 2PA than the aromatic *carbo*-benzene version ($\sigma_{2PA} = 765$ GM at 800 nm) [12].

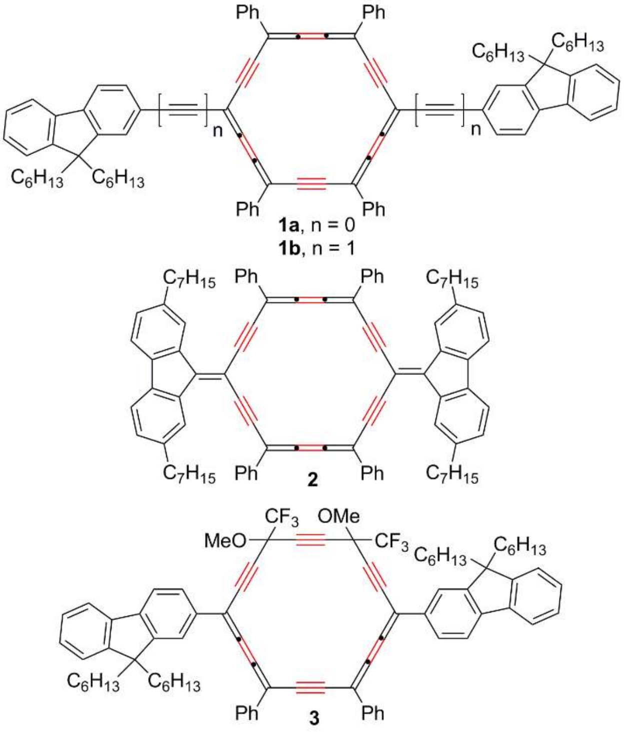


Figure 1. Previously studied *carbo*-meric 2PA chromophores.

As both the *carbo*-quinoid and *carbo*-benzene cores possess two parallel C_8 π-conjugating paths, results suggested the design of *carbo*-chromophores with a single C_8 π-conjugating path in a rigid planar environment. In order to benefit from sufficient stability and solubility [13], the 3,6-dimethoxy-3,6-bis(trifluoromethyl) octa-1,4,7-triyne moiety was selected as the rigidifying C_8 π-insulating path: the preparation of the trifluoromethylated difluorenyl-*carbo*-cyclohexadiene **3** was thus envisaged by extension of synthetic procedures previously developed for analogous targets [13].

Experimental part

Material and methods

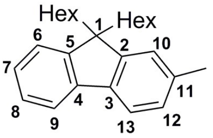
THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane and dichloromethane over P_2O_5. All other reagents were used as commercially available. In particular, commercial solutions of *n*-BuLi were 2.5 M in hexane, solutions of HCl were 2 M in diethylether. All reactions were carried out under nitrogen or argon atmosphere using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 P, 70-200 mm). Silica gel thin–layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20 %). The following analytical instruments were used. ^1H and ^{13}C NMR: Bruker DPX 300, Avance 300, Avance 400, Avance 400WB or Avance 500 spectrometers. Mass spectrometry: Quadrupolar Nermag R10-10H spectrometer. UV-vis absorption: Perkin-Elmer Win-Lab Lambda 35 spectrometer. UV-vis fluorescence: HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer. Most of the NMR spectra were recorded in $CDCl_3$ solutions. NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants *J* are in Hz.

Synthesis

3-[10-(9,9-dihexyl-9H-fluoren-3-yl)-13,16-dimethoxy-4,7-diphenyl-13,16-bis(trifluoromethyl)cyclooctadeca-1,2,3,7,8,9-hexaen-5,11,14,17-tetrayn-1-yl]-9,9-dihexyl-9*H*-fluorene 3. To a solution of HMDS (hexamethyldisilazane: 0.12 mL, 0.57 mmol) in THF (7 mL) under stirring at -78 °C was added *n*-BuLi (0.216 mL, 0.54 mmol). The mixture was stirred for 30 minutes at -78 °C before addition of a solution of **4** (27 mg, 0.09 mmol) in THF (3 mL). The reaction mixture was stirred for 30 minutes at -78 °C before dilution with THF (25 mL). This solution and a solution of **5** (90 mg, 0.09 mmol) in THF (35 mL) were then slowly syringed simultaneously into a round bottom flask filled with THF (250 mL) under stirring at -78 °C. The temperature of the resulting mixture was allowed to slowly increase up to room temperature, and the stirring was maintained overnight before treatment with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness under reduced pressure. The residue containing the poorly stable [6]pericyclynediol **6** was directly used in the subsequent reduction step without further purification (HRMS-control: HRMS (MALDI-DCTB): *m/z* calcd for $C_{86}H_{90}O_6F_6$ $[M]^+$: 1332.6642, found: 1332.6598).

To a solution of the residue in dry DCM (30 mL) under stirring at -78 °C were added $SnCl_2$ (190 mg, 1.0 mmol) and then $HCl\bullet Et_2O$ (1.0 mL, 2.0 mmol). The temperature was slowly increased up to 0 °C over 3 hours. Aqueous 1 M NaOH (2.1 mL, 2.1 mmol) was then added to the mixture. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (DCM:pentane 1:9) to give **3** (mixture of isomers) as a dark solid with 29 % yield over two steps (32 mg). R_f (DCM: pentane 1:9) ≈ 0.15. A pure fraction of one of the diastereoisomers could be separated (8 mg).

Atom numbering in the fluorenyl substituents ("Fluo") for NMR assignment:



^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J = 7.8$ Hz, 4 H, *o*-Ph), 7.86 – 7.72 (m, 8 H, *H*9,*H*10,*H*12,*H*13(Fluo)), 7.59 (t, $J = 7.9$ Hz, 4 H, *m*-Ph), 7.53 – 7.39 (m, 8 H, *p*-Ph, *H*6,*H*7,*H*8(Fluo)), 3.76 (s, 6 H, OCH_3), 2.10 – 1.95 (m, 8 H, (Fluo)$(CH_2)_2$), 1.19 – 0.54 (m, 44 H, $(CH_2)_4$-CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,

$CDCl_3$) δ 151.6, 151.5 (C_2,C_5(Fluo)), 147.3, 146.0 (C=*C*=*C*=C), 143.0, 140.1, 136.7, 135.6 (*i*-Ph, C_{11},C_3,C_4(Fluo)), 129.8, 127.2 (*C*-Ph, *C*-Fluo), 129.5, 129.0, 128.0, 127.6, 127.1, 126.7(*o-,m-,p-*Ph, C_7, C_8,C_{12}(Fluo)), 123.0, 121.7, 120.4, 120.2 (C_6,C_9, C_{10},C_{13}(Fluo)), 106.4, 103.7, 100.7, 87.3, 85.7(C-C≡C-C), 55.1 (C_1(Fluo)), 54.4 (OCH_3), 40.4 ((*C*H_2)-Fluo)), 31.4, 29.7, 23.7, 22.5 ($(CH_2)_4$), 13.9 (CH_3). Signals of *C*F_3 and *C*-CF_3 were not observed. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.73. MS (MALDI-TOF/DCTB): *m/z*: 1236.7 $[M]^+$. HRMS (MALDI-DCTB): *m/z* calcd for $C_{84}H_{82}O_2F_6$ $[M]^+$: 1236.6219, found: 1236.6313. UV-vis ($CHCl_3$): λ_{max} = 635 nm (ε = 84800 $L.mol^{-1}.cm^{-1}$). PL ($CHCl_3$): λ_{em} = 533 nm (λ_{exc} = 470).

1,10-bis(9,9-dihexyl-9*H*-fluoren-3-yl)-4,7-dimethoxy-4,7-diphenyldeca-2,5,8-triyne-1,10-dione 5. To a solution of **9** (195 mg, 0.19 mmol) in DCM (40 mL) under stirring at 0 ˚C was added solid MnO_2 (550 mg, 6 mmol), and the mixture was stirred for 1 hour at 0 ˚C, then 3 hours at room temperature. The mixture was filtered through Celite®, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:pentane 1:9) to give **5** as a light solid with 52 % yield (100 mg). M.p. 53 ˚C.

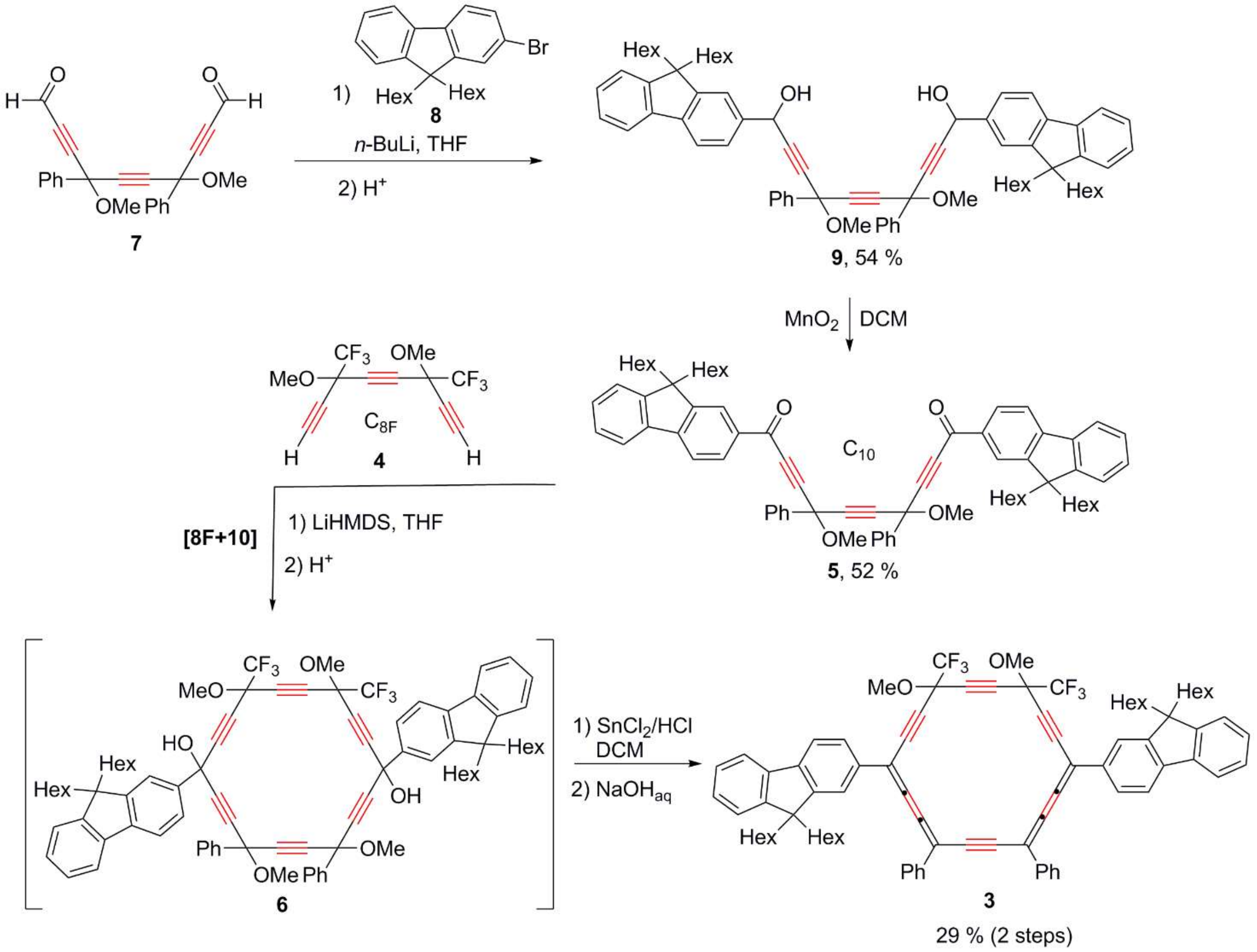
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.2 Hz, 2 H, *H*13(Fluo)), 8.12 (s, 2 H, *H*10(Fluo)), 7.96 – 7.88 (m, 4 H, *H9, H*12(Fluo)), 7.78 (d, *J* = 7.7 Hz, 4 H, *o*-Ph), 7.55 – 7.33 (m, 12 H, *m*-, *p*-Ph, *H6, H7, H*8(Fluo)), 3.77 (2s, 6 H, OCH_3), 2.01 (m, 8 H, (Fluo)($CH_2)_2$), 1.07 - 0.59 (m, 44 H, $(CH_2)_4$-CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 176.9 (C=O), 152.3, 151.3 (C_2,C_5(Fluo)), 147.7 (C_3(Fluo)), 139.4, 138.8, 135.4 (*i*-Ph, C_4,C_{11}(Fluo)), 130.5, 129.5, 128.9, 128.8, 127.2, 126.5 (*o-,m-,p*-Ph, C_7,C_8,C_{12}(Fluo)), 123.1, 123.0, 121.1, 119.7 (C_6,C_9,C_{10},C_{13}(Fluo)), 88.8, 84.5, 84.1 (-C≡C-), 72.2 (*C*-OMe), 55.3 (C_1(Fluo)), 54.1 (OCH_3), 40.2 ((*C*H_2)-Fluo)), 31.4, 29.6, 23.7, 22.5 ($(CH_2)_4$), 14.0 (CH_3). HRMS (DCI/CH_4): *m/z* calcd for $C_{74}H_{82}O_4$: 1034.6213, found: 1034.6213.

1,10-bis(9,9-dihexyl-9*H*-fluoren-3-yl)-4,7-dimethoxy-4,7-diphenyldeca-2,5,8-triyne-1,10-diol 9. To a solution of **8** (340 mg, 0.82 mmol) in THF (20 mL) under stirring at -78 °C was added *n*-BuLi (308 µl, 0.77 mmol). The mixture was stirred for 1 hour at -78 °C before addition of a solution of **7** (130 mg, 0.35 mmol) in THF (5 mL). The temperature was allowed to slowly increase up to -20 °C over 3 hours, before addition of a saturated aqueous NH_4Cl solution. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:pentane 2:8) to give **9** as a light oil with 54 % yield (195 mg). R_f (EtOAc:heptane 2:8) = 0.20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2 H- H(Fluo)), 7.75 – 7.65 (m, 4 H, *o*-Ph), 7.59 – 7.48 (m, 4 H, *m*-Ph), 7.46 – 7.30 (m, 14H, H(Fluo), *p*-Ph), 5.70 (s, 2 H, *CH*-OH), 3.60 (s, 6 H, OCH_3), 2.48 (bs, 2 H, OH), 1.96 (m, 8 H, (Fluo)$(CH_2)_2$), 1.19 – 0.62 (m, 44 H, $(CH_2)_4$-CH_3)). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.3, 151.0 (C_2,C_5(Fluo)), 141.6, 140.5, 139.9, 138.9 (*i*-Ph, C_3,C_4,C_{11}(Fluo)), 128.9, 128.5, 127.3, 126.8, 126.5, (*o-*,*m-*,*p*-Ph, C_7,C_8(Fluo)), 125.5, 122.9, 121.2, 119.9, 119.8 (C_6,C_9,C_{10},C_{12},C_{13}(Fluo)), 87.2, 84.6, 83.9 (-*C*≡*C*-), 72.0 (*C*-OMe), 65.0 (C-OH), 55.1 (C_1(Fluo)), 53.4 (OCH_3), 40.3 ((CH_2)-Fluo)), 31.5, 29.7, 23.7, 22.6 ($(CH_2)_4$), 14.0 (CH_3). MS (MALDI-TOF/DCTB): *m/z*: 1061.6 [MNa]$^{+}$. HRMS (MALDI-DCTB): *m/z* calcd for $C_{74}H_{86}O_4Na$ [MNa]$^{+}$: 1061.6424, found: 1061.6449.

Results and discussion

Among the two main synthetic procedures previously developed for the preparation of *carbo*-1,3-cyclohexadienes [13b], the strategy based on a [8F+10] macrocyclization step between the bis-trifluoromethylated C_{8F} triyne dinucleophile **4** and the C_{10} diketone dielectrophile **5** was selected for the synthesis of the [6]pericyclynediol precursor **6** (Scheme 1) [14]. The known C_{8F} triyne **4** was obtained in five steps and 37 % overall yield from tri-isopropylsilylacetylene and ethyl trifluoroacetate [13b,15]. The phenyl-substituted diketone **5** was prepared in two steps from the known dialdehyde **7** [16]. Both **4** and **5** were obtained as statistical mixtures of diastereoisomers. As previously devised for the *carbo*-benzenes **1a** and **1b**, C9-dialkylated fluorenyl substituents were used with the view to ensure sufficient solubility of the *carbo*-cyclohexadiene target **3**. The 2-bromo-9,9-dihexylfluorene **8** precursor was thus prepared from 2-bromofluorene according to a known procedure [17]. Two equivalents of the lithiated reagent of **8** were added to the dialdehyde **7**, to give the corresponding diol **9**, which was isolated with 54 % yield. After MnO_2-mediated oxidation of **9**, the C_{10} diketone product **5** was involved in a [8F+10] macrocylization step with the C_{8F} triyne **4**, in the presence of LiHMDS as base. The resulting poorly stable [6]pericyclynediol **6** was not isolated in the pure state, and was directly treated with $SnCl_2$ and HCl in DCM to give the *carbo*-cyclohexadiene **3**, which was isolated as a dark blue solid with 29 % yield over two steps. During the purification by chromatography, a fraction (8 mg) of one of the two diastereoisomers of **3** was isolated, giving unique ^{1}H and ^{19}F NMR singlet signals at 3.76 ppm and –78.73 ppm, corresponding to the two C_2- or C_s-equivalent CH_3 and CF_3 groups, respectively (Figure 2; pairs of singlet signals are observed for the mixture of diastereoisomers).



Scheme 1. Synthesis of the difluorenyl-[6]pericyclynediol **6** and reduction to the *carbo*-cyclohexadiene **3**.

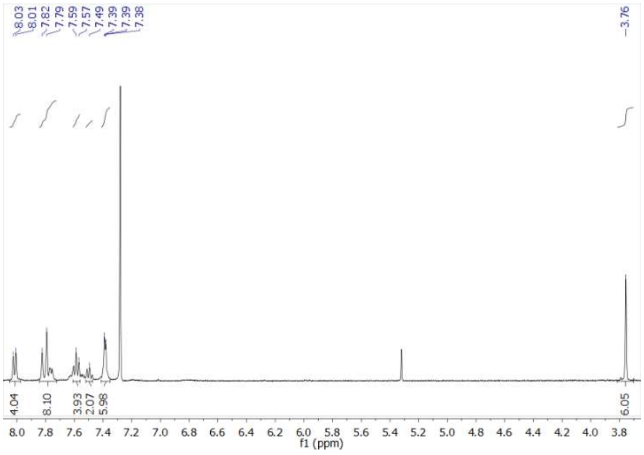


Figure 2. Aromatic and methoxy region of the ^{1}H NMR spectrum ($CDCl_3$) of one pure diastereoisomer of **3**.

In the absence of single crystals suitable for X-ray diffraction analysis, the *cis* (*meso*) or *trans* (*dl*) configuration of the isolated pure diastereoisomer of **3** could not be assigned.

The absorption properties of the blue *carbo*-chromophore **3** were studied in a chloroform solution (Figure 3). The UV-visible absorption spectrum of **3** exhibits several bands, with a maximum absorption wavelength at 634 nm, which is the highest λ_{max} value ever observed among known *carbo*-cyclohexadienes [13b]. The classical two-bands shape of the absorption spectra of *carbo*-cyclohexadienes is not observed for **3**, which presents four main bands, the one at 289 nm corresponding to the absorption of the fluorenyl moieties. The molar extinction coefficient of **3** (ε = 84 800 L.mol^{-1}.cm^{-1}) is however in the classical range for a *carbo*-cyclohexadiene, and much lower than those of related *carbo*-benzenes (ε values above 300 000 L.mol^{-1}.cm^{-1} were reported for the bis-fluorenyl-*carbo*-benzenes **1a** and **1b**)[10].

Fluorescence spectra of the fluorophore-substituted *carbo*-cyclohexadiene **3** were found to display a weak emission at λ = 533 nm upon excitation at 470 nm. This result meets previous observations of poor emission properties of *carbo*-chromophores, even those bearing fluorophore substituents, the fluorescence quenching being correlated with their high absorbance [18].

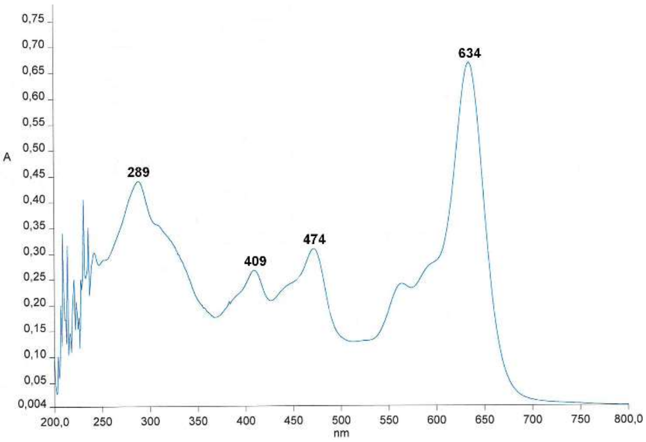


Figure 3. UV-visible absorption spectrum of **3** ($CHCl_3$).

Conclusion

The difluorenyl-*carbo*-cyclohexadiene **3** was prepared as a stable and soluble bis-trifluoromethylated *carbo*-chromophore, and completes the fluorenyl-substituted C_{18} core series of *carbo*-mers comprising the two *carbo*-benzenes **1a** and **1b**, and the *carbo*-quinoid **2**. The weak but non-zero fluorescence of **3** should allow the measurement of its 2PA cross-section by the TPEF method. Otherwise, Z-scan measurements of the 2PA cross-section could also be performed. These experiments will be carried out soon. Comparison of the values with those of **1a** and **2** (independently from the C_2 elongation effect in **2b** *vs* **2a**) should allow delineation of a qualitative structure-property relationship in a structurally homogeneous series, at least regarding the number of π-conjugating paths and aromaticity of a rigid monocyclic C_{18} core in a pseudo-quadrupolar environment.

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References

[1] a) Göppert-Mayer M. Über Elementarakte mit zwei Quantensprüngen. *Annalen der Physik*. 1931; 9: 273–294. b) He GS, Tan LS, Zheng Q,

Prasad PN. Multiphoton absorbing materials: molecular designs, characterizations, and applications. Chem. Rev. 2008; 108:1245-1330. b) Terenziani F, Katan C, Badaeva E, Tretiak S, Blanchard-Desce M. Enhanced two-photon absorption of organic chromophores: theoretical and experimental assessments. Adv. Mater. 2008; 20:4641-4678. c) Kim HM, Cho BR. Two-photon materials with large two-photon cross sections. Structure-property relationship. Chem Commun. 2009; 2:153-164.

[2] Ogawa S. Two-photon absorbing molecules as potential materials for 3D optical memory. Appl. Sci. 2014; 4:1-18.

[3] Liu H-W, Liu Y, Zhang X-B. Molecular engineering of two-photon fluorescent probes for bioimaging applications. Methods Appl. Fluores. 2017; 5:012003.

[4] Pawlicki M, Collins HA, Denning RG, Anderson HL. Two-photon absorption and the design of two-photon dyes. Angew. Chem. Int. Ed. 2009; 48:3244-3266.

[5] Ogawa K, Kobuke Y. Two-photon photodynamic therapy by water-soluble self-assembled conjugated porphyrins. BioMed Res. Int. 2013; 125658.

[6] Xing J-F, Zheng M-L, Duan X-M. Two-photon polymerization microfabrication of hydrogels: an advanced 3D printing technology for tissue engineering and drug delivery. Chem. Soc. Rev. 2015; 44:5031-5039.

[7] a) Zhang Y, Jiang M, Han G-C, Zhao K, Tang BZ, Wong KS. Solvent effect and two-photon optical properties of triphenylamine-based donor-acceptor fluorophores. J. Phys. Chem. C 2015; 119:27630-27638. b) Ricci F, Carlotti B, Keller B, Bonaccorso C, Fortuna CG, Goodson III T, Elisei F, Spalletti A. Enhancement of two-photon absorption parallels intramolecular charge-transfer efficiency in quadrupolar versus dipolar cationic chromophores. J. Phys. Chem. C 2017; 121:3987-4001.

[8] a) Hrobárik P, Hrobáriková V, Semak V, Kasák P, Rakovský E, Polyzos I, Fakis M, Persephonis P. Quadrupolar benzobisthiazole-cored arylamines as highly efficient two-photon absorbing fluorophores. Org. Lett. 2014; 16:6358-6361. b) Tran C, Berqouch N, Dhimane H, Clermont G, Blanchard-Desce M,n Ogden D, Dalko PI. Quinoline-derives two-photon sensitive quadrupolar probes. Chem. Eur. J. 2017; 23:1860-1868.

[9] a) Aratani N, Kim D, Osuka A. π-conjugation enlargement toward the creation of multi-porphyrinic systems with large two-photon absorption properties. Chem. Asian J. 2009; 4:1172-1182. b) Uoyama H, Kim KS, Kuroki K, Shin J-Y, Nagata T, Okujima T, Yamada H, Uno N, Kim D, Uno H. Highly pure synthesis, spectral assignments, and two-photon properties of cruciform porphyrin pentamers fused with benzene units. Chem. Eur. J 2010; 16:4063-4074.

[10] Baglai I, de Anda-Villa M, Barba-Barba RM, Poidevin C, Ramos-Ortíz G, Maraval V, Lepetit C, Saffon-Merceron N, Maldonado J-L, Chauvin R. Difluorenyl *carbo*-benzenes: synthesis, electronic structure, and two-photon absorption properties of hydrocarbon quadrupolar chromophores. Chem. Eur. J. 2015; 21:14186-14195.

[11] Cocq K, Maraval V, Saffon-Merceron N, Saquet A, Poidevin C, Lepetit C, Chauvin R. *Carbo*-quinoids: stability and reversible redox-proaromatic character towards *carbo*-benzenes. Angew. Chem. Int. Ed. 2015; 54:2703-2706.

[12] Cocq K, Poidevin C, Ramos-Ortíz G, Maldonado J-L, Maraval V, Chauvin R. unpublished results.

[13] a) Leroyer L, Lepetit C, Rives A, Maraval V, Saffon-Merceron N, Kandaskalov D, Kieffer D, Chauvin R. From hexaoxy-[6]pericyclynes to *carbo*-cyclohexadienes, *carbo*-benzenes, and dihydro-*carbo*-benzenes: synthesis, structure, and chromophoric and redox properties. Chem. Eur. J. 2012; 18:3226-3240. b) Rives A, Baglai I, Barthes C, Maraval V, Saffon-Merceron N, Saquet A, Vointenko Z, Volovenko Y, Chauvin R. *Carbo*-cyclohexadienes *vs carbo*-benzenes: structure and conjugative properties. Chem. Sci. 2015; 6:1139-1149. c) Lozynskyi O, Barthes C, Rives A, Maraval V, Voitenko ZV, Chauvin R. En route to dianilinyl-*carbo*-cyclohexadiene with promising electrical properties.

French-Ukr. J. Chem. 2015; 3(1):46-52. d) Barthes C, Rives A, Maraval V, Chelain E, Brigaud T, Chauvin R. First example of ring *carbo*-mer of 1,4-cyclohexadiene. French-Ukr. J. Chem. 2015; 3(1):60-65.

[14] For early references on pericyclynes see: a) Scott LT, DeCicco GJ, Hyun JL, Reinhardt G. Decamethyl[5]pericyclyne. A novel homoconjugated cyclic polyacetylene. J. Am. Chem. Soc. 1983; 105:7760-7761. b) Scott LT, DeCicco GJ, Hyun JL, Reinhardt G. Pericyclynes of order [5], [6], [7], and [8]. Simple convergent synthesis and chemical reactions of the first homoconjugated cyclic polyacetylenes. J. Am. Chem. Soc. 1985; 107:6546-6555.

[15] Maraval V, Leroyer L, Harano A, Barthes C, Saquet A, Duhayon C, Shinmyozu T, Chauvin R. 1,4-dialkynylbutatrienes : synthesis, stability, and perspectives in the chemistry of *carbo*-benzenes. Chem. Eur. J. 2011; 17:5086-5100.

[16] a) Maurette L, Tedeschi C, Sermot E, Soleilhavoup M, Hussain F, Donnadieu B, Chauvin R. Synthesis and stereochemical resolution of functional [5]pericyclynes. Tetrahedron 2004; 60:10077-10098. b) Leroyer L, Zou C, Maraval V, Chauvin R. Synthesis and stereochemical resolution of a [6]pericyclynedione: versatile access to pericyclynediol precursors of *carbo*-benzenes. C. R. Chimie 2009; 12:412-419.

[17] Chandrasekharam M, Rajkumar G, Rao CS, Suresh T, Reddy PY, Yum J-H, Nazeeruddin MK, Graetzel M. A molecularly engineered fluorine-substituted Ru-complex for efficient mesoscopic dye-sensitized solar cells. Adv. Nat. Sci.: Nanosci. Nanotechnol. 2011; 2:0350016.

[18] Baglai I, Maraval V, Voitenko Z, Volovenko Y, Chauvin R. Towards fluorescent indolyl-*carbo*-benzenes. French-Ukr. J. Chem. 2013; 1(1):48-53.