

Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Synthesis and spectral characterization of bisanaphthylmethyl and trinaphthylmethyl cations

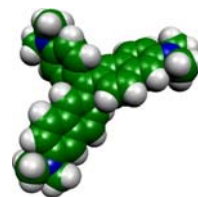
Lionel Sanguinet^a, Robert J. Twieg^{a*}, Jarrod C. Williams^a
Greg Wiggers^b, Guilin Mao^b, Kenneth D. Singer^b, Rolfe G. Petschek^b

^a*Kent State University, Department of Chemistry, Kent, Ohio, USA, 44242*

^b*Case Western Reserve University, Department of Physics, Cleveland, Ohio, USA 44106*

Triarylmethane dyes containing one, two or three naphthalene moieties have been prepared. Their synthesis and spectral characterization are reported here.

Leave this area blank for abstract info.





Pergamon

TETRAHEDRON
LETTERS

Synthesis and spectral characterization of bisnaphthylmethyl and trinaphthylmethyl cations

Lionel Sanguinet^a, Robert J. Twieg^{a*}Greg Wiggers^b, Guilin Mao^b, Kenneth D. Singer^b, Rolfe G. Petschek^b^aKent State University, Department of Chemistry, Kent, Ohio, USA 44242^bCase Western Reserve University, Department of Physics, Cleveland, Ohio, USA 44106

Abstract— Cationic triarylmethane dyes containing one, two or three naphthalene moieties have been prepared. Their synthesis and preliminary spectral, nonlinear optical and theoretical characterization are reported here. The major electronic and steric hindrance effects of the 1,4-linked naphthalene have been examined by comparison of the UV-Vis absorption of the 1,4-linked and 2,6-linked series. © 2006 Elsevier Science. All rights reserved

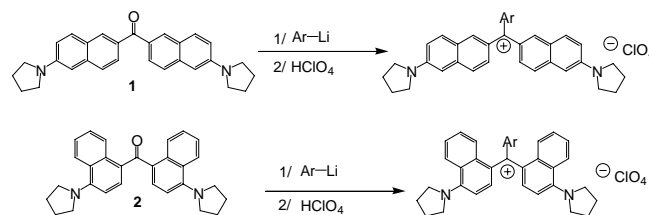
Triarylmethane cations (TAMCs) such as Crystal Violet have been the subject of numerous investigations of their physical and photophysical chemistry.^{1,2} The applications for these dyes range from biochemistry³ to optical data storage⁴. We are interested here in their properties as nonlinear optical (NLO) chromophores and especially their multipolar properties.⁵ In order to increase the first hyperpolarizability of Crystal Violet, researchers have modified TAMC structures by incorporation of different heterocycles,⁶ as well as stilbene⁷ and phenylethynyl groups.⁸ At the same time, there have been attempts to shift the main absorption band to the near infrared. TAMCs with multiple naphthyl groups have been described but often not isolated and fully characterized.^{9,10,11} An objective of this study has been the synthesis of some bisnaphthyl and trinaphthylmethane cations and the comparison of their UV/Vis spectra with those of some well-known TAMCs.

Synthesis

TAMC synthesis can be accomplished by two main methods. The first route involves the reaction between a bis-dialkylaminoketone and an arene or heterocycle in the presence of POCl₃.¹² The second synthetic pathway involves the use of the bis-dialkylaminoketone and an organolithium reagent to form the corresponding carbinol, followed by ionization after treatment with an inorganic

acid such as perchloric acid. The experience of most investigators indicates that the latter route is more useful and can be extended to the synthesis of many TAMCs.¹³ In any case, for either route, we must prepare the requisite naphthyl derivatives related to Michler's ketone, bis(6-pyrrolidinonaphthalen-2-yl) methanone (**1**) and bis(4-pyrrolidinonaphthalen-1-yl) methanone (**2**) in Scheme 1.

Scheme 1: Synthetic pathway for the preparation of the bisnaphthylmethyl



and trinaphthylmethyl cations.

The synthesis of such diarylketones has been described and usually requires a multistep synthesis.¹⁴ We have successfully employed a one step method developed by Olah *et al.*¹⁵ based on the reaction between an aryllithium reagent and N-carboethoxypiperidine. The synthesis of ketone **1** starts from 6-bromo-2-naphthol which is transformed into 6-bromo-2-naphthalamine by a Bucherer reaction, alkylation with 1,4-diodobutane to provide 6-

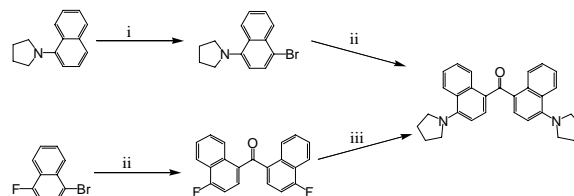
* Corresponding author. Tel.: +1-330-2791; fax: +1-330-672-3816; e-mail: rtwieg@lci.kent.edu.

bromo-2-pyrrolidinonaphthalene and, finally, conversion to an organolithium reagent and reaction with N-carboethoxypiperidine to form the ketone **1** in good yield (56%) and useful overall yield (22%).

The preparation of ketone **2** proved to be more problematic. The first challenge was the preparation of 4-bromo-1-naphthylamine. Direct reaction of 1-naphthylamine with elemental bromine resulted in a complex mixture of mono-, di- and polybromination products¹⁶. Amongst the bromination reagents examined 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one proved to be the most effective to produce the desired 4-bromopyrrolidinonaphthalene.¹⁷ In contrast to the case of ketone **1**, the organolithium derivative of 4-bromopyrrolidinonaphthalene afforded ketone **2** in poor yield (<10%). This difference in reactivity between the 1,4- and 2,6-naphthyl isomers can be explained by the greater peri steric demands in the 1,4-isomer. To circumvent this problem we modified our strategy and used instead 1-bromo-4-fluoronaphthalene to give bis(4-fluoronaphthalen-1-yl) methanone. The pyrrolidine donors were next introduced by aromatic nucleophilic substitution. The two approaches examined for preparation of ketone **2** are described in Scheme 2.

The preparation of the bisnaphthyl and trinaphthylmethyl cations has been performed by reaction between the ketones **1** and **2** with an organolithium reagent and then treatment of the reaction mixture with perchloric acid (Scheme 1). We have used organolithium reagents obtained by bromine-metal exchange from 4-bromopyrrolidinobenzene, 4-bromopyrrolidinonaphthalene,

6-bromo-2-pyrrolidinonaphthalene, or by acid/base reaction from phenylacetylene and 1-(4-ethynylphenyl)-pyrrolidine. It is important to note that even if the carbinol can be prepared, in some cases the isolation of the cationic salt is not possible, as in the cases when Ar is either a phenyl, an ethynylphenyl or a 1-(4-ethynylphenyl)-pyrrolidine. In successful cases the carbocation was isolated in a yield between 42 and 80 %.



Scheme 2: Two synthetic strategies for the preparation of bis(4-pyrrolidinonaphthalen-1-yl)methanone i/ 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one, CH_2Cl_2 , -10°C , ii/ *n*-BuLi, THF, -78°C , N-carboethoxypiperidine, iii/ pyrrolidine, DMSO, reflux.

Spectral Characterization

It is known that the modification of a donor group in a charge transfer chromophore can have a large influence on the UV-Visible spectrum. Thus, within a series of triarylmethyl cations, the substitution of the dimethylamino group by most dialkylamino or cycloaliphatic amine groups causes a red shift of the main absorption band due to increased electron donation.¹⁸

Table 1. Spectroscopic properties of TMAC chromophores in ethanol solution (ca 1.10^{-5}M). λ_{max} is given in nm, ϵ in $1.10^4 \cdot \text{cm}^{-1}$, and $\Delta\lambda$ represents the full width in nm at half maximum.

Compound					
λ_{max} (ϵ)	630 ($8.96 \cdot 10^4$)	594 ($1.87 \cdot 10^5$)	587 ($6.98 \cdot 10^4$) 633 ($6.96 \cdot 10^4$)	662 ($4.10 \cdot 10^4$)	701 ($3.88 \cdot 10^4$)
$\Delta\lambda$	49	77	119	131	137
Compound					
λ_{max} (ϵ)	702 ($5.21 \cdot 10^4$)	701 ($2.9 \cdot 10^4$)	697 ($8.47 \cdot 10^4$)	668 ($6.81 \cdot 10^4$)	790 ($9.83 \cdot 10^4$)
$\Delta\lambda$	148	162	148	124	141

The substitution of 4-pyrrolidinophen-1-yl by 4-pyrrolidinonaphthalen-1-yl also produces a bathochromic shift as charge transfer through the naphthalene is more facile than in benzene due to the difference in resonance energy. At the same time, the annulated ring in the 1,4-substituted naphthalene will be a steric obstacle to planarity of the cation contributing to a hypsochromic effect. These two effects are in opposition. Comparison of the UV-Vis spectra of the molecules with one, two and three 1,4-linked (transverse) naphthalene moieties (**bPN14**, **bN14P** and **tN14** respectively) indicates that the electronic contribution is dominant, as increased bathochromic shifts are observed with each 1,4-naphthalene addition. To better understand this behavior, we performed a series of *ab initio* geometry optimizations and molecular orbital calculations (RHF and MCSCF) with GAMESS¹⁹. The geometry of the molecules was optimized using RHF theory with an effective core potential and the Stevens/Basch/Krauss/Jasien/Cundari (SBKJC) basis. For **bPN14** (2 phenyls, 1 transverse naphthalene) and **bN14P** (1 phenyl, 2 transverse naphthalenes) we find that the unsubstituted phenyl(s) become more planar (a 29° twist for phenyls in **bPN14** and a 26° twist for the phenyl in **bN14P**, as compared to *ca* 33° for the phenyls in **tP**), whereas the 1,4-naphthyl substituents are rotated 45°-50°. MCSCF calculations show that the first excited states of these molecules are well approximated by the transfer of one electron from the HOMO to the LUMO of the RHF ground state. The HOMO in each of these molecules is on the naphthyl substituents, while the LUMO is mainly concentrated on the central carbon and also spreads to the phenyl(s) (Figure 2). Thus, raising the energy of the HOMO through 1,4 naphthyl substitution is offset by the decreased conjugation, but the increased conjugation of the phenyl(s) lowers the LUMO slightly, leading to overall moderate red shifts.

The substitution of a pyrrolidine group (in **tP**) by a hydrogen (in Pyrrolidine Green, **PG**) results in a red shift of about 36 nm. Akiyama et al²⁰ explain this by the observation that all highly symmetrical molecules have a degeneracy of their HOMO and the substitution of one pyrrolidine group by one hydrogen breaks this degeneracy and decreases the transition energy. More specifically, calculations show that while the H-substituted ring in **PG** has a torsion angle of *ca* 45°, the unsubstituted phenyls become more conjugated (torsion angle of 29°). MCSCF calculations show that the HOMO is spread over the unsubstituted phenyls and the LUMO has moderate representation there as well. It results that the increased conjugation of these phenyls decreases amount of energy needed to transfer an electron to the LUMO.

The variations in the absorption bands of the TAMCs can also be explained by the calculations. The UV-Vis spectra of the TAMCs are composed mainly of two bands (x and y) which calculations show are HOMO to LUMO and HOMO-1 to LUMO transitions respectively. In **PG**, the large twist angle of the H-substituted phenyl leads to the large bathochromic shift of the y-band, This separation of x and y-bands is not seen in **bN14P** (and possibly **bPN14** and others as well), where the phenyl along the y axis is much

more conjugated. This is supported by MCSCF calculations which suggest that the x and y bands of **bN14P** are only separated by 18nm.

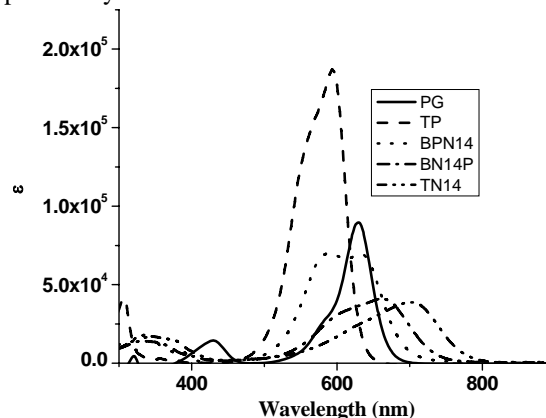
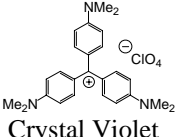
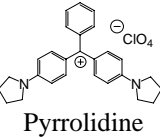
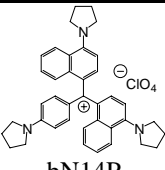


Figure 1. Molar extinction coefficients of the transverse naphthyl series in ethanol solution (*ca* 10⁻⁵M, ϵ is in l.mol⁻¹.cm⁻¹ and λ in nm).

Just as the enhancement of the donor group may induce a bathochromic shift, the extension of the conjugated pathway may act in the same direction. The substitution of a phenyl by a 2,6-linked naphthalene (longitudinal naphthalene) moiety extends the conjugated bridge, but does not introduce the steric effect characteristic of the transverse naphthalene. Calculations show that the twist of the longitudinal naphthalenes in all of the compounds studied does not deviate much ($\pm 5^\circ$) from the 33° twist of the phenyls in **tP**. Nevertheless, the electronic effect in this kind of 2,6-linkage is smaller than seen previously. There are red shifts with the addition of longitudinal naphthalene moieties, *ca* 100 nm between **tP** (3 phenyls) and **bPN26** (two phenyls, one longitudinal naphthalene) and *ca* 200 nm between **tP** and **tN26** (three longitudinal naphthalenes). In contrast to the transverse naphthalene substitutions, where each additional substitution produces a greater red shift, this is not the case for the longitudinal systems, as compound **bN26P** possesses a band at shorter wavelength than **bPN26**. The reason for this is not completely understood. In general, the smaller steric effect in the 2,6-naphthyls suggests that the degeneracy of the HOMO and HOMO-1 is less important in this system. We believe the results for the 2,6-naphthyls are a consequence of the LUMO in these molecules being less concentrated on the central carbon and more spread out onto the naphthyl rings. This conjugation, of course, lowers the energy of the LUMO and hence the excitation energy of the molecules. Thus the redshifts in the 2,6-naphthyls are primarily related to a decrease in the energy of the LUMO.

A common effect of the extension of the aromatic core in the naphthalene derivatives is a broader absorption band than in the triphenylmethyl cation series that typically have a width (at half height) between 50 and 80 nm. On the other hand, in the TAMCs where at least one naphthalene moiety is incorporated, this value increases to a range between 119 and 141 nm. This expansion of the bandwidth results in absorption tailing into the near infrared, especially in the case for **tN26**.

Table 2. Absolute value of the rotational invariants of the hyperpolarizability (10^{-30} esu) obtained from TCSPC-45°-HRS.

	 Crystal Violet	 Pyrrolidine Green	 bN14P
$ \beta_{1ss} $	393 ± 30	226 ± 19	655 ± 35
$ \beta_{1mm} $	255 ± 21	337 ± 32	429 ± 26
$ \beta_{2mm} $	200 ± 17	275 ± 27	360 ± 23

To understand the influence of these structural modifications on the NLO properties, we have undertaken a series of measurements of the first hyperpolarizability of these new TAMCs by the Time-Correlated Single Photon Counting 45° hyper-Rayleigh scattering (TCSPC-45°-HRS) technique. The TCSPC method distinguishes HRS from two-photon fluorescence in the time-domain, resulting in improvement of the accuracy of measurements of Kleinman-disallowed components. This measurement permits the figure of merit of this kind of compound for chiral axial nonlinear optical media.²¹ The measurements of these second order non-linear optical properties are more sensitive to the nature, symmetry and overlap between the various orbitals. The results obtained for the compound **bN14P** and two other classical TAMCs are summarized in Table 2. We see that **bN14P** possesses better nonlinear properties than Crystal Violet in both the dipolar and the Kleinman disallowed parts, due to a large charge transfer from the ground to first excited state. This indicates the potential of these new bisnaphthyl and trinaphthylmethyl cations for NLO applications.

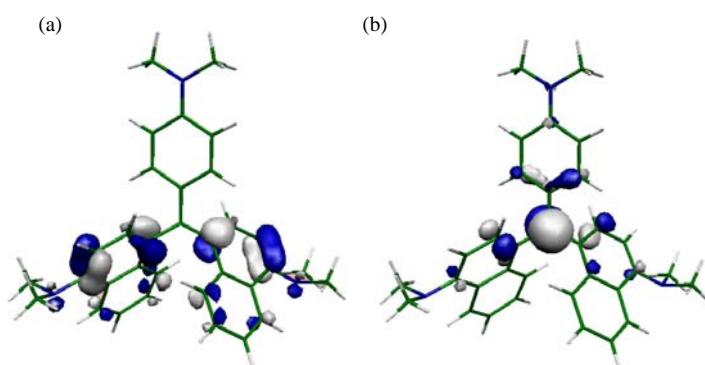


Figure 2. Singly occupied orbitals in the first excited state of BN14P (a) lower lying (RHF HOMO) SOMO (b) higher lying (RHF LUMO) SOMO. Note the large charge transfer in the y (symmetry axis) direction, which produces a large NLO response. Graphics were made using Molekel²² software.

Acknowledgments

This work was financially supported by NSF grant DMR-0308701.

Supplementary Material

Synthetic methods and spectroscopic data for the compounds discussed here are provided along with a brief description of the light scattering experiments.

References

- Rao, Y.; Guo X.; Tao, Y.; Wang, H.; *J. Phys. Chem. A* **2004**, *108*, 7977-7982.
- Duxbury, D. F.; *Chem. Rev.* **1993**, *93*, 381-433.
- Cho, B. P.; Yang T., Blamkenship, L. R.; Moody, J. D.; Churchwell, M.; Beland, F. A., Culp, S. J.; *Chem. Res. Toxicol.* **2003**, *16*, 285-294.
- Abe, M.; Sato, T.; Oba, H.; Umehara, M.; Ueda, Y.; Yamamuro, T.; US Patent 4 758 499, 1988.
- Zyss, J.; Ledoux, I.; *Chem. Rev.* **1994**, *94*, 77-105.
- Malpert, J.H.; Grinevich, O.; Strehmel B., Jarikov, V.; Mejiritski, A.; Neckers, D.C.; *Tetrahedron*, **2001**, *57*, 967-974.
- Arbez-Gindre, C.; Secrettas, C.G.; Fiorini, C.; Schimdt, C.; Nunzi, J.M. *Tetrahedron. Lett.*, **1999**, *40*, 7413-7416.
- Akiyama, S.; Nakatsuji, S.; Nakashima, K.; Watanabe, M.; *J. Chem. Soc. Chem. Commun.* **1987**, 710-711.
- Olah, G.A.; Liao, Q.; Casanova, J.; Bau, R.; Rasul, G.; Prakash, G.K.; *J. Chem. Soc., Perkin Trans 2*, **1998**, 2239-2242.
- G. Hallas, D. R. Waring, *J. Chem. Soc. B.*, **1970**, 979.
- G. Hallas, K. N. Paskins, D. R. Waring, *J. Chem. Soc. Perkin Trans 2*, **1972**, 2281.
- Pazenok, S. V.; Trushanina, L. I.; Chaika, E. A.; Yagupol'skii, L. M.; *Zh. Org. Khim.* **1991**, *27*(5), 1121-1123.
- Noack, A.; Schroder, A.; Hartmann, H. *Dyes and Pigments*, **2002**, *57*, 131-147.
- Olah, G.A.; Ohannesian, L.; Arvanaghi, M.; *Chem. Rev.* **1987**, *87*, 672.
- G.K. Surya Prakash, C. York, Q. Liao, K. Kotian, G.A. Olah, *Heterocycles*, **1995**, *40*, 79.
- Zhao, J.; Jia, X.; Zhai, H. *Tetrahedron. Lett.*, **1999**, *44*, 9371-9373.
- Guinot, S.G.R.; Hepworth, J.D.; Wainwright, M.; *J. Chem. Soc., Perkin Trans. 2*, **1998**, 297-303.
- Clayton, S.E.; Guinot, S.G.R.; Hepworth, J.D.; Wainwright, M. *J. Chem. Soc., Perkin Trans. 2*, **2000**, *2*, 263-269.
- Schmidt, M.W., Baldrige, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M. Montgomery, J.A., *J. Comput. Chem.*, **1993**, *14*, 1347-63.
- Akiyama, S.; Nakatsuji S.; Nakashima, K. Watanabe, M.; *J. Chem. Soc., Perkin Trans 1*, **1988**, 3155-3161.
- Ostroverkhov, V.; Petschek, R.G.; Singer, K.D.; Twieg, R.J.; *Chem. Phys. Lett.* **2001**, *340*, 109-115.
- Portmann, S., Lüthi, H.P., *CHIMIA*, **2000**, *54*, 766-770.



Pergamon

TETRAHEDRON
LETTERS

Synthesis and spectral characterization of bisnaphthylmethyl and trinaphthylmethyl cations

Lionel Sanguinet^a, Robert J. Twieg^{a*}

Greg Wiggers^b, Guilin Mao^b, Kenneth D. Singer^b, Rolfe G. Petschek^b

^aKent State University, Department of Chemistry, Kent, Ohio, USA 44242

^bCase Western Reserve University, Department of Physics, Cleveland, Ohio, USA 44106

Supplementary Material

1. Synthesis:

Instrumentation. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Varian Mercury-400 (400 MHz), Inova-500 (500 MHz), or an Inova-600 (600 MHz) NMR spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent (CDCl₃ δ 7.25). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane.

Materials. Commercial reagents were purchased from Sigma Aldrich, Acros or Lancaster, and used as received with the exception of tetrahydrofuran, which was distilled from sodium at 760 Torr.

Bis(4'-fluoronaphthyl)ketone

To a solution of 1-bromo-4-fluoronaphthalene (1.00 g, 4.5 mmol) in anhydrous THF cooled at -80°C, was added 1.8 ml (4.5 mmol) of n-BuLi (2.5M in Hexane) under argon. The reaction was stirred for a half hour, and then N-carboethoxypiperidine (0.350 g, 2.2 mmol) was added. The temperature was allowed to increase to room temperature and the stirring was maintained overnight. The reaction was quenched by addition of water (10 ml) and the reaction mixture was extracted with dichloromethane. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The compound was purified by flash chromatography (0.300 g, 43%).

¹H NMR (400 MHz, CDCl₃): 8.62-8.60 (m, 2H); 8.26-8.24 (m, 2H); 7.71-7.66 (m, 4H); 7.65 (dd, J=10Hz, J'=8Hz, 2H); 7.13 (dd, J=10Hz, J'=8Hz, 2H)

¹³C NMR (100 MHz, CDCl₃) δ: 197.5, 162.4, 159.8, 133.2(q), 131.4(d), 129.0, 127.0, 126.2, 125.5(d), 124.1(d), 123.6 (d)

Bis(4'-pyrrolidinonaphthyl)ketone

Method A

In a 100ml round-bottom flask with magnetic stirbar, bis(4'-fluoronaphthyl)ketone (0.5 g, 1.57 mmol) was mixed with pyrrolidine (6 ml, 5.2 g, 73.2 mmol) and K₂CO₃ (6 g, 43 mmol) in 10 ml of DMSO. The reaction mixture was heated at reflux overnight. After cooling to room temperature, the reaction mixture was poured into water (200ml), the product was filtered off and purified by flash chromatography (0.43 g, 65%).

Method B

To a solution of 4-pyrrolidino-1-bromonaphthalene (2.57 g, 9.3 mmol) in dry THF (30 ml) cooled to -80°C, under argon, a solution of n-butyllithium (3.7 ml, 9.25 mmol) in hexane (2.5M) was added. After a half hour at this temperature, N-carboethoxypiperidine (0.73 g, 9.3 mmol) was added dropwise. The temperature was allowed to increase to room temperature and stirring was maintained overnight. The reaction mixture was quenched by addition of 10 ml of

* Corresponding author. Tel.: +1-330-2791; fax: +1-330-672-3816; e-mail: rtwieg@lci.kent.edu.

water and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The product was purified by flash chromatography (0.2g, 10%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.71 (d, $J=8\text{Hz}$, 2H), 8.24 (d, $J=8\text{Hz}$, 2H), 7.51-7.47 (m, 4H), 7.42 (t, $J=8\text{Hz}$, 2H), 6.8 (d, $J=8\text{Hz}$, 2H), 3.51 (m, 8H), 2.02 (m, 8H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 197.8, 151.2, 133.9, 132.5, 129.2, 127.1, 126.8, 126.6, 125.3, 124.0, 107.5, 52.7, 25.5

1-Pyrrolidinonaphthalene

In a 100ml round-bottom flask with magnetic stir bar was placed 1-naphthalamine, (3.0 g, 21 mmol), 1,4-diiodobutane (6.37 g, 21 mmol), K_2CO_3 (6 g, 43.5 mmol) and 20 ml of DMAc. The mixture was stirred and heated at 80°C overnight. After cooling to room temperature, the reaction mixture was poured into 300 ml of water and extracted with hexane. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The product was used with any further purification (4.1 g, 20.8 mmol, 99 %).

$^1\text{H NMR}$ (100 MHz, CDCl_3) δ : 8.33-8.31 (m, 1H), 7.92-7.89 (m, 1H), 7.48-7.52 (m, 3H), 7.46 (t, $J=8\text{Hz}$, 1H), 7.07 (d, $J=8\text{Hz}$, 1H), 3.45 (m, 4H), 2.10 (m, 4H)

4-Bromo-1-pyrrolidinonaphthalene

A solution of 1-pyrrolidinonaphthalene (5.57 g, 28.3 mmol) in dichloromethane (50 ml) cooled to -10°C was treated with small portions of 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one¹ (11.6 g, 28.3 mmol) such that temperature was maintained below 0°C . The solution was stirred at room temperature for 4 hours. The solvent was removed and the product was purified by flash chromatography (5.64 g, 20.4 mmol, 72%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.19 (d, $J=8\text{Hz}$, 1H), 8.18 (d, $J=8\text{Hz}$, 1H), 7.60 (d, $J=8\text{Hz}$, 1H), 7.53 (t, $J=8\text{Hz}$, 1H), 7.43 (t, $J=8\text{Hz}$, 1H), 6.79 (d, $J=8\text{Hz}$, 1H), 3.31 (m, 4H), 1.99 (m, 4H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 148.0, 132.8, 129.8, 129.4, 127.4, 126.9, 125.2, 125.0, 114.3, 112.0, 52.9, 24.8.

5-Bromo-2-naphthalamine

In a 100ml pressure vessel (steel bomb) with a magnetic stir bar was placed 5-bromo-2-naphthol (17.84 g, 8 mmol) dispersed in ammonium hydroxide (60 ml) and ammonium sulfite monohydrate (18.2 g, 13 mmol). The bomb was heated at 180°C for 24 hours. After cooling to room temperature the reaction mixture was poured into 300 ml of water, extracted with ethyl acetate, washed with aqueous of NaOH (2M) and then dried over magnesium sulfate. The drying agent was removed by filtration and the solvent was removed under vacuum. The product was recrystallized from ethanol/water (~50/50) to give 7.27g (32.7mmol, 41%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.83 (s, 1H), 7.56 (d, $J=8.4\text{Hz}$, 1H), 7.47-7.43 (m, 2H), 6.96-6.90 (m, 2H), 3.87 (b, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 144.7, 133.5, 129.8, 129.1, 128.5, 127.6, 127.3, 119.3, 115.8, 108.5

6-Pyrrolidino-2-bromonaphthalene

In a 100ml round-bottom flask with magnetic stir bar was placed 6-bromo-2-naphthalamine, (2.0 g, 9.0 mmol), 1,4-diiodobutane (2.79 g, 9.0 mmol) K_2CO_3 (5.0 g, 36 mmol) and 10 ml of DMF. The mixture was stirred and heated at 80°C for 24 hours. After cooling to room temperature the reaction mixture was poured into 300 ml of water. The product was filtered off by suction and was sufficiently pure for further use, 2.31g (8.3 mmol, 93 %).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.80 (d, $J=1.6\text{Hz}$, 1H), 7.58 (d, $J=9\text{Hz}$, 1H), 7.48 (d, $J=8.7\text{Hz}$, 1H), 7.38 (dd, $J=8.7\text{Hz}$, $J'=1.6\text{Hz}$, 1H), 6.99 (dd, $J=9\text{Hz}$, $J'=2.4\text{Hz}$, 1H), 6.69 (d, $J=2.4\text{Hz}$, 1H), 3.38 (m, 4H), 2.05 (m, 4H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 146.2, 133.9, 129.6, 129.4, 128.1, 127.6, 116.7, 114.2, 104.6, 47.9, 25.6

Bis(6-pyrrolidinonaphthal-2-yl) ketone

To a solution of 6-pyrrolidino-2-bromonaphthalene (2 g, 7.24 mmol) in dry THF (30 ml) cooled at -80°C , was added under argon 2.5 M nBuLi in hexane (3 ml). After reaction at this temperature for one half hour, N-carboethoxypiperidine (0.568 g, 3.62 mmol) was added dropwise. The temperature was allowed to increase to room temperature and stirring was maintained during 48 hours. The reaction mixture was quenched by addition of 10 ml of water. The yellow precipitated was filtered off to produce 850 mg of the desired compound (56%, 0.71 mmol).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.19 (s, 2H), 7.89 (dd, $J=9\text{Hz}$, $J'=1.5\text{Hz}$, 2H), 7.75 (d, $J=9\text{Hz}$, 2H), 7.68 (d, $J=9\text{Hz}$, 2H), 7.02 (dd, $J=9\text{Hz}$, $J'=1.5\text{Hz}$, 2H), 6.78 (d, $J=1.5\text{Hz}$, 2H), 3.45 (m, 4H), 2.07 (m, 4H)

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 196.5, 147.6, 137.5, 132.4, 131.3, 130.8, 127.1, 125.7, 124.8, 116.3, 104.4, 47.9, 25.7

Preparation of the triarylmethyl cations: general procedure

In a 100 ml flask, a solution of arylhalide (2.65 mmol) in anhydrous THF (20 ml) was stirred and cooled at -80°C under nitrogen. A solution of n-butyllithium (1ml, 2.5 mmol) in hexane (2.5M) was slowly added to solution and the solution was stirred during 30 min. Then a suspension of the corresponding ketone (0.48mmol) in 10ml anhydrous THF was added. After one hour, the cooling bath was removed and stirring was continued 4 hours (except for the trinaphthyl case

where the stirring was maintained overnight). The reaction mixture was quenched by addition of 10 ml of water and extracted with dichloromethane. The solvent was removed under vacuum. The residue was dissolved in toluene (50 ml) and concentrated perchloric acid (0.1ml) was added. The solution color changes and a precipitate appears which was filtered off, washed with ether and chromatographed.

PG:

¹H NMR (400 MHz, DMSO) δ: 7.77(*t*, J=8.Hz, 1H), 7.63 (*t*, J=8.Hz, 2H), 7.36-7.31 (*m*, 6H), 6.95 (*d*, J=9Hz, 4H), 3.62 (*m*, 8H), 2.05 (*m*, 8H).

¹³C NMR (400 MHz, DMSO) δ: 175.5, 154.2, 140.6, 139.9, 134.7, 133.3, 129.1, 127.0, 115.2, 49.27, 25.2

TP

¹H NMR (400 MHz, DMSO) δ: 7.27(*d*, J=8.8Hz, 6H), 6.85 (*d*, J=8.8Hz, 6H), 3.52 (*m*, 12H), 2.04 (*m*, 12H).

¹³C NMR (100 MHz, DMSO) δ: 176.5; 153.1; 139.6; 126.2; 113.6; 48.6; 25.3.

BPN26:

¹H NMR (400 MHz, DMSO) δ: 7.91 (*d*, J=8.4Hz, 1H), 7.90 (*s*, 1H), 7.35 (*d*, J=9Hz, 4H), 7.23 (*d*, J=8.4Hz, 1H), 7.16 (*d*, J=8.4Hz, 1H), 6.92 (*d*, J=9Hz, 4H), 6.90 (*s*, 1H), 3.58 (*m*, 8H), 3.47 (*m*, 4H), 2.05 (*m*, 12H).

¹³C NMR (100 MHz, DMSO) δ: 176.9; 153.7; 149.1; 140.4; 138.6; 132.4; 131.9; 131.8; 129.4; 128.7; 127.0; 125.3; 117.6; 114.4; 104.6; 48.9; 48.1; 25.5; 25.3.

BPN14

¹H NMR (400 MHz, DMSO) δ: 8.33 (*d*, J=8Hz, 1H), 7.41-7.19 (*m*, 8H), 6.95 (*d*, J=8Hz, 1H), 6.81 (*d*, J=8.8Hz, 4H), 3.84 (*m*, 4H), 3.52 (*m*, 8H), 2.09-2.01 (*m*, 12H).

¹³C NMR (100 MHz, DMSO) δ: 173.6; 153.9; 153.1; 140.6; 139.3; 137.8; 128.4; 127.8; 127.1; 126.9; 126.8; 125.3; 124.7; 114.0; 109.0; 53.5; 48.7; 25.9; 25.3.

BN14P

¹H NMR (400 MHz, DMSO) δ: 8.31 (*d*, J=8Hz, 2H), 7.49 (*d*, J=8Hz, 2H), 7.38 (*t*, J=8Hz, 2H), 7.32-7.28 (*m*, 4 H), 7.23 (*d*, J=9Hz, 2H), 6.90 (*d*, J=9Hz, 2H), 6.72 (*d*, J=9Hz, 2H), 3.85 (*m*, 8H), 3.49 (*m*, 4H), 2.05-1.99 (*m*, 12H)

¹³C NMR (100 MHz, DMSO) δ: 169.6, 154.3, 152.7, 140.6, 138.7, 137.6, 129.1, 128.7, 128.7, 127.0, 126.7, 125.5, 125.0, 113.9, 109.9, 53.6, 48.6, 25.9, 25.3

BN26P

¹H NMR (400 MHz, DMSO) δ: 8.00 (*d*, J=9Hz, 2H), 7.94 (*d*, J=2Hz, 2H), 7.81 (*d*, J=9Hz, 2H), 7.56 (*d*, J=9Hz, 2H), 7.34 (*dd*, J=9Hz, J'=2Hz, 2H), 7.23 (*dd*, J=9Hz, J'=2Hz, 2H), 6.98 (*d*, J=2Hz, 2H), 3.8 (*m*, 4H), 3.56 (*m*, 8H), 2.15-2.10 (*m*, 12H).

¹³C NMR (100 MHz, DMSO) δ: 177.7, 154.8, 149.6, 141.9, 140.0, 138.9, 132.9, 132.1, 129.4, 128.7, 128.5, 126.3, 125.5, 117.7, 116.1, 104.9, 49.7, 48.2, 25.4, 25.2

BN26N14

¹H NMR (400 MHz, DMSO) δ: 8.32 (*d*, J=8.Hz, 1H), 7.85-7.82 (*m*, 4H), 7.65 (*d*, J=8Hz, 2H), 7.59 (*d*, J=8Hz, 1H), 7.45 (*d*, J=8Hz, 2H), 7.30 (*t*, J=8Hz, 1H), 7.23 (*d*, J=8Hz, 2H), 7.14-7.09 (*m*, 3H), 6.86 (*s*, 2H), 4.12 (*m*, 4H), 3.45 (*m*, 8H), 2.08-2.02 (*m*, 12H).

¹³C NMR (100 MHz, DMSO) δ: 169.5; 157.7; 148.9; 146.0; 138.8; 138.1; 137.8; 133.9; 132.1; 131.5; 130.3; 129.7; 128.9; 127.8; 126.6; 126.4; 125.8; 125.7; 117.4; 113.9; 104.8; 54.8; 48.1; 25.8; 25.5.

BN14N26

¹H NMR (400 MHz, DMSO) δ: 8.32 (*d*, J=8.4Hz, 2H), 7.81 (*s*, 1H), 7.76 (*d*, J=8.8Hz, 1H), 7.46-7.36 (*m*, 6H), 7.26 (*t*, J=8Hz, 2H), 7.18 (*d*, J=8.8Hz, 1H), 7.06 (*d*, J=8.8Hz, 1H), 6.97 (*d*, J=8.8Hz, 2H), 6.81 (*s*, 1H), 3.92 (*m*, 8H), 3.43 (*m*, 4H), 2.06-2.00 (*m*, 12H).

¹³C NMR (100 MHz, DMSO) δ: 167.2; 155.2; 148.8; 141.7; 137.9; 137.6; 136.7; 134.8; 132.0; 129.8; 129.1; 127.3; 127.2; 126.6; 125.7; 125.5; 117.2; 111.3; 104.9; 54.0; 48.1; 25.8; 25.5

TN26

$^1\text{H NMR}$ (400 MHz, DMSO) δ : 8.01-7.99 (m, 3H), 7.76 (d, J=8.8Hz, 2H), 7.56 (d, J=8.8Hz, 1H), 7.54 (d, J=8.8Hz, 1H), 7.47 (s, 1H), 7.37 (d, J=8.8Hz, 2H), 7.33 (d, J=8.8Hz, 1H), 7.19 (d, J=8.8Hz, 2H), 6.99-6.95 (m, 3H), 6.73 (s, 1H), 3.56 (m, 8H), 3.48 (m, 4H), 2.07 (m, 8H), 2.00 (m, 4H).

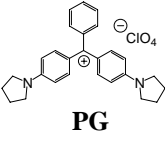
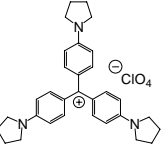
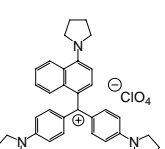
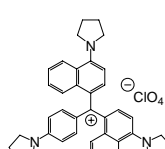
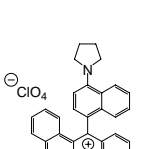
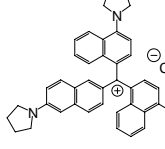
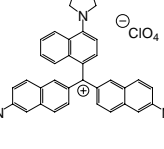
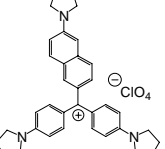
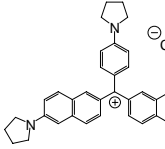
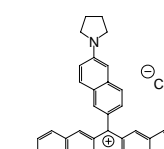
$^{13}\text{C NMR}$ (100 MHz, DMSO) δ : 179.9, 150.7, 142.6, 139.7, 134.2, 133.0, 126.7, 126.1, 118.0, 105.6, 48.5, 25.4

TN14

$^1\text{H NMR}$ (400 MHz, DMSO) δ : 8.30 (d, J=8.4Hz, 3H), 7.50 (d, J=8.4Hz, 3H), 7.38-7.31 (m, 6H), 7.20 (d, J=8.4Hz, 3H), 6.88 (d, J=8.4Hz, 3H), 3.83 (m, 12H), 2.09 (m, 12H).

$^{13}\text{C NMR}$ (100 MHz, DMSO) δ : 166.6; 152.9; 140.1; 137.8; 129.5; 127.1; 127.2; 125.3; 124.7; 110.2; 53.5; 25.9.

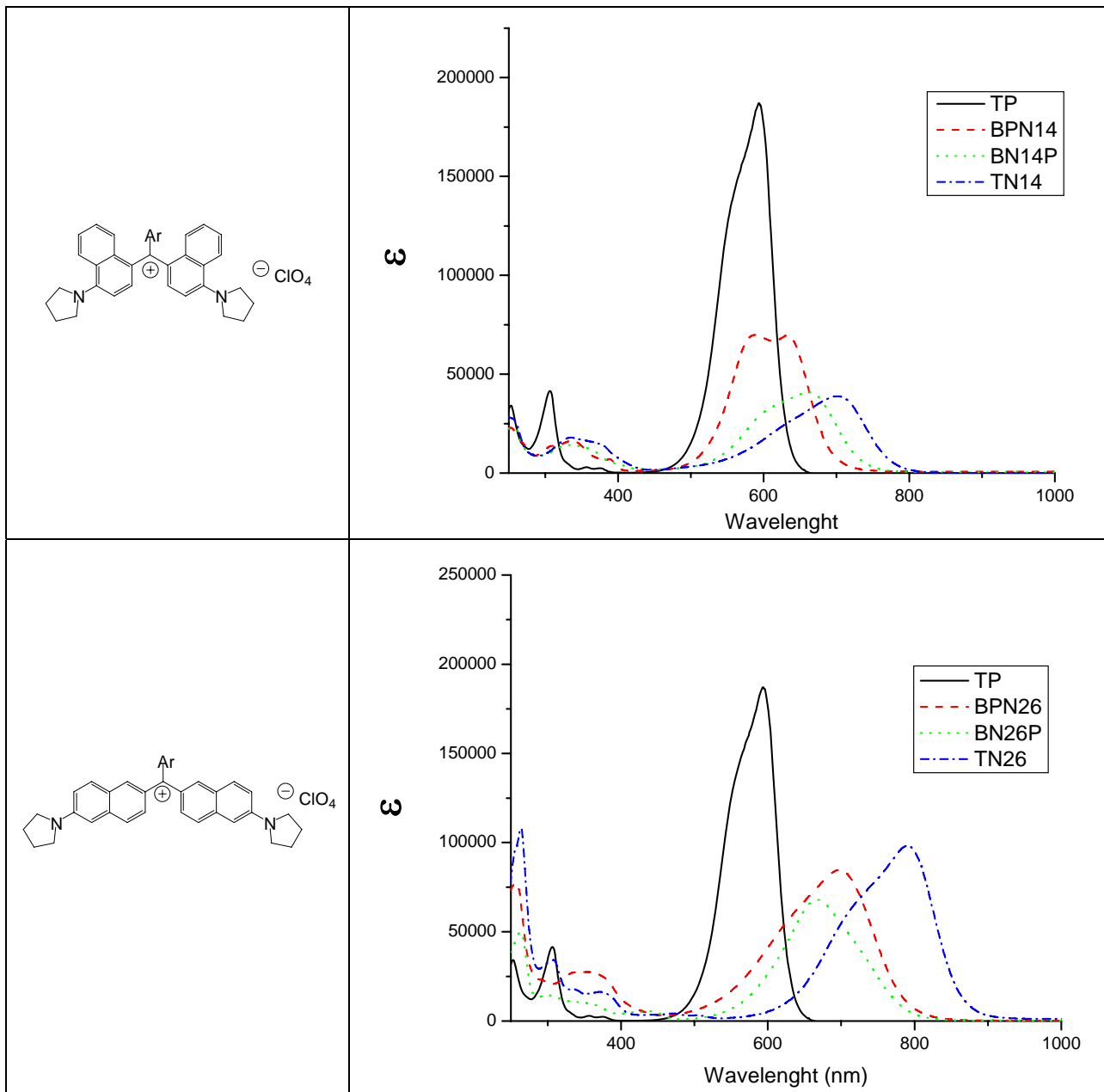
Table. This table contains structure and spectral data for compounds discussed in the synthesis section and also in the UV-Vis spectra section. The spectroscopic properties of the TAMC chromophores were obtained in ethanol solution (ca 1.10^{-5}M). The λ_{max} is given in nm, ϵ in $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $\Delta\lambda$ represents the full width at half maximum in nm.

Compound	 PG	 tP	 bPN14	 bN14P	 tN14
λ_{max} (ϵ)	630 ($8.96 \cdot 10^4$)	594 ($1.87 \cdot 10^5$)	587 ($6.98 \cdot 10^4$) 633 ($6.96 \cdot 10^4$)	662 ($4.10 \cdot 10^4$)	701 ($3.88 \cdot 10^4$)
$\Delta\lambda$	49	77	119	131	137
Compound	 bN14N26	 bN26N14	 bPN26	 bN26P	 tN26
λ_{max} (ϵ)	702 ($5.21 \cdot 10^4$)	701 ($2.9 \cdot 10^4$)	697 ($8.47 \cdot 10^4$)	668 ($6.81 \cdot 10^4$)	790 ($9.83 \cdot 10^4$)
$\Delta\lambda$	148	162	148	124	141

2. Spectral characterization

UV-Visible

The UV-Visible absorption spectra were recorded on a Hewlett Packard model 8453 spectrophotometer in absolute ethanol solution with a concentration around $10^{-5} \text{ mol.l}^{-1}$. The spectra are summarized below.



HRS spectroscopy: Time-Correlated Single Photon Counting (TCSPC)

The setup is based on a Kerr mode-locked Ti:Sapphire laser operating at 780nm wavelength. The TCSPC setup consists of super-fast multi-time-channel chip, TimeHarp200, a supersensitive photon detector PMA185, and an Avalanche photodetector. A reverse start-stop scheme to trigger the signal acquisition was used where the arrival of a single photon signal initiated the START of the time counting, and the arrival of the delayed laser pulse detection at the STOP input completes the time measurement. The time is resolved into 4096 channels, and the signal pulses are histogrammed according to the time delay between the laser pulse and the signal. In order to provide sufficient time for the fluorescence signal to decay before the next mode-locked pulse, an extra-long cavity laser design was used to provide an interpulse spacing exceeding 20 ns. Relative time offsets were compensated using transmission cable delays.

Experimental setup

The description of TCSPC-45°-HRS experiment setup is shown in Fig.1. The incident fundamental light is elliptically polarized by a linear polarizer and followed by an 800nm quarter-wave plate that can be rotated by the stepper motor from 0° to 360°. The output light is also elliptically polarized by a linear polarizer and followed by a 400nm quarter-wave plate.

To extract the information of all the rotational invariants, previous theoretical calculations show that the optimized configurations for the output polarizer angle (α_0) and the output quarter-wave plate angle (γ_0) are two independent runs: $\alpha_0 = -30.4^\circ$, $\gamma_0 = -30.4^\circ$ and $\alpha_0 = 57.8^\circ$, $\gamma_0 = -75.3^\circ$.² Our fast Fourier transform data processing procedure³ was used to extract the six rotational invariants, and the system was calibrated using para-nitroaniline (pNA).

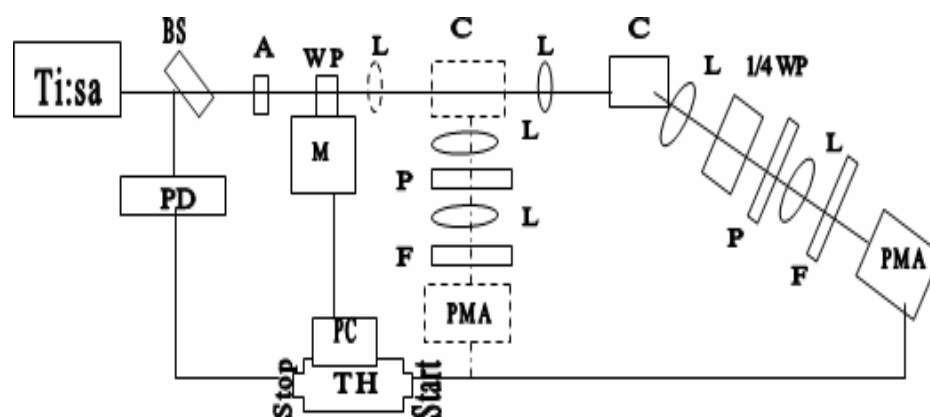


Fig.1. TCSPC-45°-HRS setup scheme. The dashed path is only for the 90°-HRS setup, used to determine β_{1ss} . BS: beam splitter; A: Analyzer; WP: quarter-wave plate for TCSPC-45°-HRS and half-wave plate for 90°-HRS; L: Lens; C: Cell; 1/4WP: quarter-wave plate; P: polarizer; F: filter for 400nm light; PD: Avalanche photo detector; M: stepper motor; PMA: PMA185; TH: TimeHarp200

¹ The preparation of the 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one can be found here: G.J. Fox; G. Hallas; J.D. Hepworth, K.N. Paskins, *Organic Syntheses*, **1976**, (55), 20-23

² S.F. Hubbard, R.G. Petschek, K.D. Singer, N. D'Sidocky, C. Hudson, L.C. Chien, and P.A. Cahill, *J. Opt. Soc. Am. B* **1998**, *15*, 289.

³ V. Ostroverkhov, R.G. Petschek, K.D. Singer, L. Sukhomlinova, R.J. Twieg, S.-X. Wang, and L.C. Chien, *J. Opt. Soc. Am. B*, **2000**, *17*, 1531.