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Synthesis of Highly Luminescent *Tris*-Fluorenyl Chromophores as Intermediates of Potential Nonlinear Photonic Materials

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In our effort to enhance the cross section of simultaneous multiphoton absorption of C₆₀-based photonic nanomaterials, a novel highly luminescent *tris*-fluorenyl ring-interconnected chromophore *tris*-DPAF-C₉ was designed and synthesized using a C₃ symmetrical triaminobenzene core as the synthon. The structural moiety bears a close resemblance to that of 2-diphenylamino-9,9-dialkylfluorenyl attachment in the previously studied C₆₀(>DPAF-C_n)_x. The product *tris*-DPAF-C₉ was fully characterized by NMR, UV, IR, and MALDI-TOF MS spectroscopic methods. Based on the molecular energy calculation at MOPAC PM3 level, it suggested the presence of two possible *cis/trans* stereoisomers on the configuration of fluorenyl moieties. Consequently, a lower heat formation (ΔH_f) of 19.9 kcal/mol was found for the *tris-cis* C₉-isomer as the favorable one vs 47.9 kcal/mol for the bis-mono-*trans* C₉-isomer.

Keywords: *tris*-fluorenyl chromophore, C₃ symmetry, diphenylaminofluorene, stereoisomer, luminescent compound, photonic nanomaterials

1 Introduction

Phenomena of simultaneous multiphoton absorption (MPA) processes during the photoexcitation of organic chromophores in the NIR–IR region have attracted much attention as scientists focus on the development of unique nonlinear optical materials with enhanced photophysical properties. To achieve this goal for practical purposes, appropriate molecular design of chromophores, which exhibit a large value of multiple-photon absorption cross sections, is highly desirable (1, 2). A number of structural design strategies were successfully demonstrated for the enhancement of two-photon absorption (2PA) cross sections, including the variation of chromophore structures and arrangements such as those in a linear (3), multi-branched (4, 5), octapolar oligomeric (6–8), or dendrimeric pattern (9–11) approach.

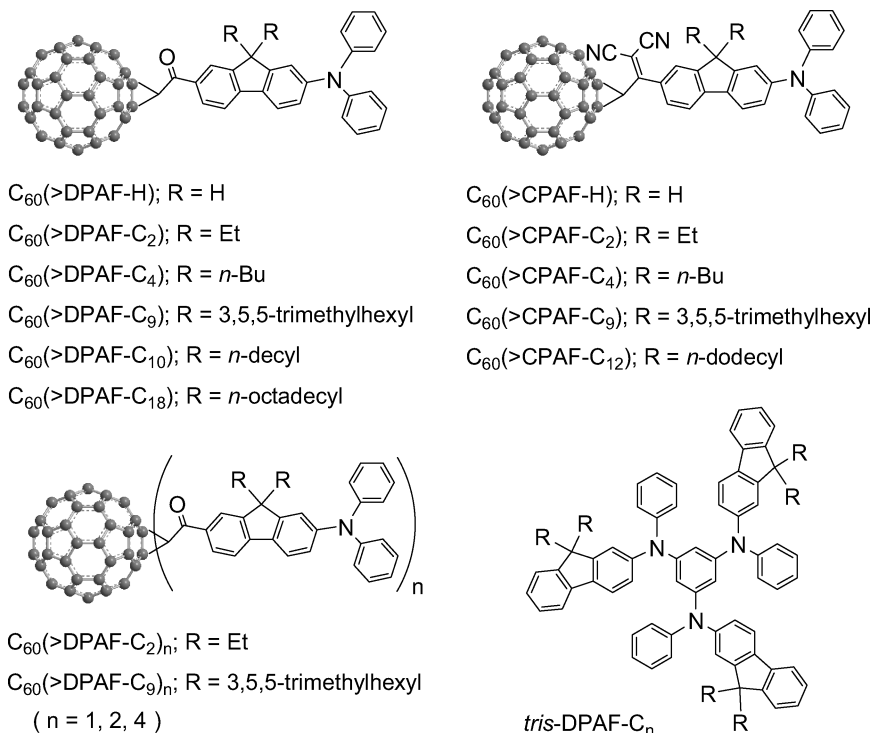
Recently, photophysical properties with highly enhanced 2PA cross sections in the NIR region were achieved by the attachment of one or multiple 1,1-diphenylamino-fluorene

moieties on a spherical C₆₀ molecule using a conjugated bridge unit (12). Accordingly, a series of donor–acceptor fullerene dyads having different alkyl chains with a variable chain length on the fluorenyl subunit, such as C₆₀(>DPAF-H) (13), C₆₀(>DPAF-C₂) (13, 14, 15), C₆₀(>DPAF-C₄) (13), C₆₀(>DPAF-C₉) (15), C₆₀(>DPAF-C₁₀) (13), and C₆₀(>DPAF-C₁₈) (14), were synthesized and well characterized by our group, as shown in Scheme 1.

Extension of this analogous of molecular design was also made to prepare and characterize several multi-adducts C₆₀(>DPAF-C₂)_n (n = 2 and 4) (15, 16) and C₆₀(>DPAF-C₉)_n (n = 2 and 4) (15, 17) with an increasing number of fluorenyl subunits attached on a center C₆₀ core moiety. Interestingly, the molecular polarity on the donor moiety can be modified by the replacement of the bridging keto unit with a highly electron-withdrawing 1,1-dicyanoethylenyl linker. That led to the structure of the fullerene dyads C₆₀(>CPAF-C_n), instead of C₆₀(>DPAF-C_n), showing highly photoactive properties at a longer wavelength range than that of C₆₀(>DPAF-C_n) (18).

High 2PA cross section values as $\sigma'_2 = 196 \times 10^{-48}$ cm⁴ sec photon⁻¹ molecule⁻¹ observed for C₆₀(>DPAF-C₂) using the laser pulse at 800 nm was slightly increased by replacing the ethyl group C₂ with a longer and bulkier alkyl chain C₉, leading to the dyad C₆₀(>DPAF-C₉)

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Scheme 1. The structure of several C_{60} -diphenylaminofluorenyl conjugated photonic.

($\sigma'_2 = 251 \times 10^{-48} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$) (19, 20). It is probably due to the decrease of aggregation morphology in solution. This dyad also showed the three-photon absorption (3PA) characteristics using laser pulses at 1460 nm with a moderate 3PA cross section value as $\sigma_3 = 2.59 \times 10^{-25} \text{ cm}^6 \text{ GW}^2$. In the case of its bisadduct $C_{60}(>DPAF-C_9)_2$, large increases of 2PA and even 3PA cross section values to $\sigma'_2 = 622 \times 10^{-48} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$ and $\sigma_3 = 6.30 \times 10^{-25} \text{ cm}^6 \text{ GW}^2$, respectively. Further increase of 2PA cross section values was observed clearly for $C_{60}(>DPAF-C_9)_n$ with the number n larger than two corresponding to the systematic increase of the degree of the starburst structure going from the monoadduct ($n = 1$), bisadduct ($n = 2$), to tetraadduct ($n = 4$). A considerable increase of 2PA cross sections for all C_{60} adducts ($n = 1, 2$, or 4) was also detected upon the concentration dilution from 1.0×10^{-2} to $1.0 \times 10^{-4} \text{ M}$ (19). These observed results, as well as the effect of the use of C_9 alkyl chain, may allow us to conclude the importance of the high dispersion ability with a minimum aggregation tendency of the $C_{60}(>DPAF-C_9)_n$ multi-adducts. However, the selective formation and the isolation of regioisomers of C_{60} multi-adducts are proven to remain as synthetic difficulties in a large scale preparation.

In the context of this concern, we propose an alternative molecular approach to construct branched chromophores using a C_3 symmetrical 1,3,5-triaminobenzene ring as the center core for the connection of three 1,1-diphenylaminofluorene arms, leading to the structure of

tris-DPAF- C_n (Scheme 2), as the intermediate building block for the preparation of new C_{60} -based photonic materials. In this paper, we report the preparation method and spectroscopic structural characterization of the novel donor molecule *tris*-DPAF- C_9 exhibiting high optical absorption intensity and the corresponding luminescent properties. We expect the effective steric separation of three diphenylaminofluorene moieties from each other, owing to the well-defined configuration around the central benzene ring, should increase the light exposure surface area of chromophores and minimize the self-quenching of its photoexcited state.

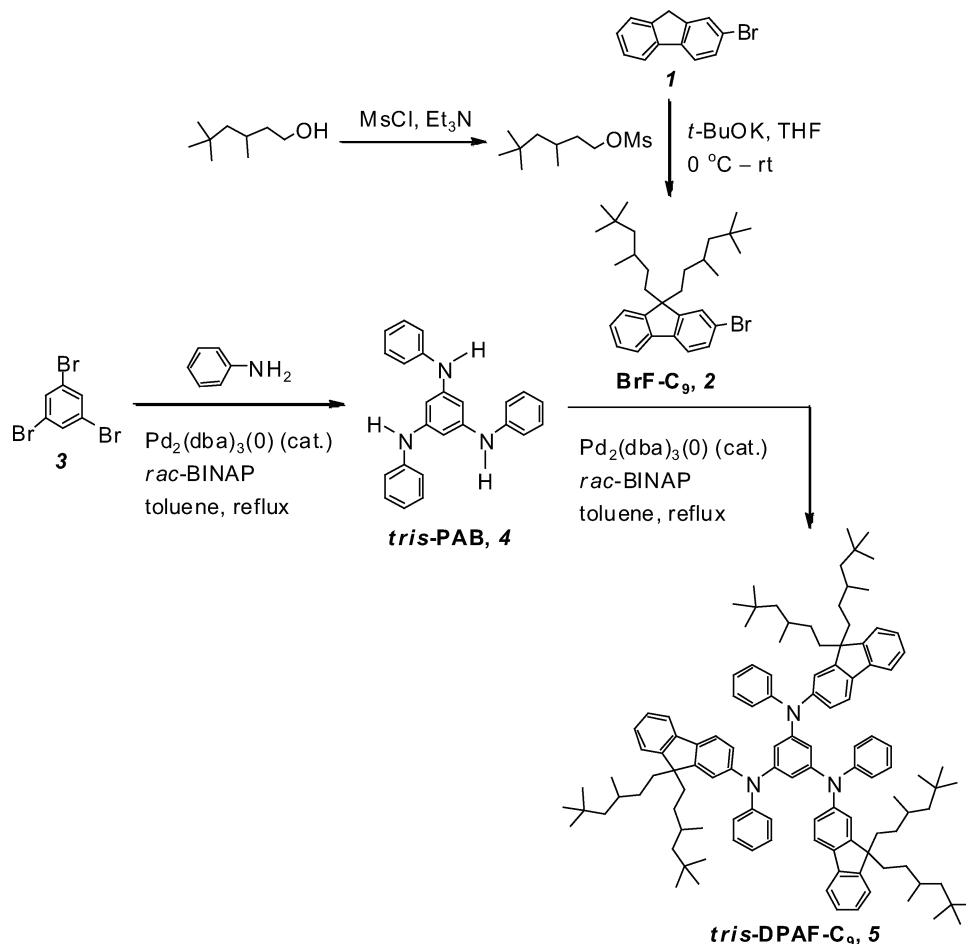
2 Experimental

2.1 Materials

Reagents of 3,5,5-trimethylhexanol, methanesulfonyl chloride, triethylamine, 2-bromofluorene, 1,3,5-tribromobenzene, *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), tris(dibenzylideneacetone)dipalladium(0), and aniline were purchased from Aldrich Chemicals. All other chemicals were purchased from Acros Ltd. The anhydrous grade solvent of THF was used for the corresponding reactions. Other solvents were used as received.

2.2 Spectroscopic Measurements

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on either a Bruker Avance Spectrospin-200 or Bruker AC-300



Scheme 2. Synthetic procedure, reagents, and conditions for the preparation of novel C₃ symmetrical chromophore *tris*-DPAF-C₉, **5**.

spectrometer. UV-Vis spectra were recorded on a Hitachi U-3410 UV spectrometer. Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. Mass spectroscopic measurements were performed by the use of positive ion matrix-assisted laser desorption ionization (MALDI-TOF) technique on a micromass M@LDI-LR mass spectrometer. The sample blended or dissolved in the matrix material was irradiated by nitrogen UV laser at 337 nm with 10 Hz pulses under high vacuum. Mass ion peaks were identified for the spectrum using the MassLynx v4.0 software.

2.3 Synthesis of 3,5,5-trimethylhexyl Methanesulfonate

To a stirred solution of 3,5,5-trimethylhexan-1-ol (5.0 g, 34.6 mmol) in anhydrous dichloroethane (75 ml) was added triethylamine (3.85 g, 38.12 mmol). This reaction mixture was cooled to 0 °C in an ice bath, followed by a dropwise addition of methane sulfonyl chloride (4.36 g, 38.12 mmol) over a period of 15 min under nitrogen. The reaction mixture was stirred overnight and quenched by the addition of water. The organic layer was washed with water (2 × 50 ml), dil. hydrochloric acid (1 × 50 ml), saturated sodium

bicarbonate (1 × 50 ml), and brine solution (1 × 50 ml). The residue was dried over sodium sulphate and concentrated on rotavapor to afford a crude light brown colored liquid. After chromatographic purification, the product 3,5,5-trimethylhexyl methanesulfonate was obtained in a yield of 95%, as a colorless liquid after vacuum distillation at 130–140 °C. Spectroscopic data: ¹H-NMR (200 MHz, CDCl₃) δ 4.29 (t, 2H, *J* = 6.2 Hz), 3.05 (s, 3H), 1.84–1.16 (m, 5H), 1.01 (d, 3H, *J* = 6.2 Hz), and 0.94 (s, 9H).

2.4 Synthesis of 2-bromo-9,9-bis(3',5',5'-trimethylhexyl)fluorene (*BrF*-C₉, **2**)

A modified literature procedure was used for this synthesis (15). To a solution of 2-bromofluorene **1** (5.0 g, 20.4 mmol) in anhydrous tetrahydrofuran (100 ml) was added potassium *t*-butoxide (5.03 g, 44.80 mmol) at 0 °C. The resulting orange brown colored reaction mixture was stirred for 30 min. To this reaction mixture, 3,5,5-trimethylhexyl methanesulfonate (9.98 g, 44.8 mmol) in anhydrous tetrahydrofuran (25 ml) was added dropwise over a period of 30 min. It was stirred for overnight and subsequently diluted with water (50 ml). The product was

extracted with ethyl acetate (150 ml), washed with water, and dried over sodium sulfate. The pale yellow crude product was purified by column chromatography using silica gel as the stationary phase and hexane–ethyl acetate (19:1) as eluent. The purified product 2-bromo-9,9-bis(3',5',5'-trimethylhexyl)fluorene **2**, BrF-C₉, was obtained as colorless liquid in 90% yield (9.1 g). Spectroscopic data of **2**: ¹H-NMR (200 MHz, CDCl₃) δ 7.72–7.30 (m, 7H), 2.12–1.90 (m, 4H), 1.33–0.43 (m, 16H), 0.78 (s, 18H, br).

2.5 Synthesis of 1,3,5-tris(*N*-phenylamino)benzene (*tris*-PAB, **4**)

A mixture of aniline (7.4 g, 79.4 mmol), 1,3,5-tribromobenzene **3** (5.0 g, 15.88 mmol), tris(dibenzylideneacetone) dipalladium(0) (0.11 g, 0.75 mol%), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 0.22 g, 2.25 mol%), and sodium *t*-butoxide (7.63 g, 79.4 mmol) in anhydrous toluene (250 ml) was heated to refluxing temperature under nitrogen for 48 hrs. The reaction mixture was cooled and then washed with water (100 ml). The organic layer was dried over magnesium sulphate. After evaporation of the solvent, a crude brown colored solid was obtained. Excess aniline was then removed by washing with methanol (3 × 50 ml) until the filtrate was virtually clear. The purified brown product 1,3,5-tris(*N*-phenylamino)benzene **4**, *tris*-PAB, was obtained in 75% yield (4.18 g). Spectroscopic data of **4**: mp 196–198 °C; ¹H NMR (200 MHz, CDCl₃) δ 7.31 (t, 6H, *J* = 7.7 Hz), 7.13 (d, 6H, *J* = 7.5 Hz), 6.97 (t, 3H, *J* = 7.3 Hz), 6.38 (s, 3H), and 5.67 (s, 3H, br, N–H); UV-Vis (CHCl₃, 1.0 × 10⁻⁵ M) λ_{max} (ε) 290 (11.5 × 10⁴ L mol⁻¹ cm⁻¹); FT-IR (KBr) ν_{max} 3402 (w), 3371 (w), 3036 (w), 1591 (s), 1495 (w), 1296 (w), 1169 (w), 754 (m), and 692 (m) cm⁻¹.

2.6 Synthesis of 1,3,5-tris(*N*-(9',9'-di(3'',5'',5''-trimethylhexyl)fluoren-2'-yl)-*N*-phenylamino)benzene (*tris*-DPAF-C₉, **5**)

A mixture of 2-bromo-9,9-bis(3,5,5-trimethyl-1-hexyl)fluorene (7.0 g, 14.22 mmol), 1,3,5-tris(*N*-phenylamino)benzene (1 g, 2.84 mmol), tris(dibenzylideneacetone) dipalladium(0) (0.02 g, 0.75 mol%), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 0.04 g, 2.25 mol%), and sodium *t*-butoxide (1.36 g, 14.22 mmol) in anhydrous toluene (75 ml) was heated to refluxing temperature under nitrogen for 48 h. The reaction mixture was cooled and then washed with water (50 ml). The organic layer was dried over magnesium sulphate. After evaporation of the solvent, it afforded a crude brown colored semi-solid. The semi-solid was purified by column chromatography using silica gel as the stationary phase and hexane–toluene (9:1) as eluent. The purified product 1,3,5-tris(*N*-(9',9'-di(3'',5'',5''-trimethylhexyl)fluoren-2'-yl)-*N*-phenylamino)benzene **5**, *tris*-DPAF-C₉, was obtained as light brown colored tarry semi-solid in 60% yield

(2.73 g). Spectroscopic data of **5**: ¹H NMR (200 MHz, CDCl₃) δ 7.64–6.83 (m, 36H), 6.60 (s, 3H, br), 1.98–1.74 (m, 12H), 1.25–0.37 (m, 48H), 0.73 (s, 54H, br); ¹³C NMR (200 MHz, CDCl₃) δ 152.2, 150.8, 149.6, 148.0, 146.8, 141.4, 136.9, 129.4, 129.3, 127.0, 126.7, 123.4, 123.0, 123.0, 120.6, 120.0, 119.5, 119.5, 55.1, 51.3, 38.5, 33.4, 33.2, 31.3, 30.3, 29.8, 29.3, and 22.9; UV-Vis (CHCl₃, 1.0 × 10⁻⁵ M) λ_{max} (ε) 322 (10.3 × 10⁴) and 351 (10.6 × 10⁴ L mol⁻¹ cm⁻¹); FT-IR (KBr) ν_{max} 3064 (w), 2953 (vs), 1579 (s), 1491 (s), 1450 (s), 1294 (m), 1250 (m), 741 (m), and 696 (w) cm⁻¹; MALDI-TOF MS calcd for C₁₁₇H₁₅₃N₃, *m/z* 1600.21; found, *m/z* 1600 (M⁺).

3 Results and Discussion

The synthesis of the C₃ symmetrical chromophore *tris*-DPAF-C₉ having both dialkylated fluorenyl and phenyl groups on each nitrogen atom of 1,3,5-triaminobenzene core center was conducted, as shown in Scheme 1. Alkylation of 2-bromofluorene **1** with mesylated 3,5,5-trimethylhexanol giving 2-bromo-9,9-bis(3',5',5'-trimethylhexyl)fluorene, BrF-C₉ **2**, was carried out by the modified literature method using potassium *t*-butoxide as a base (15). The reaction proceeded in a high yield of 90%. The synthesis of *tris*-PAB **4** was reported previously. However, we employed an alternative procedure using the palladium-catalyzed amination reaction with five equivalents of aniline in respect to the quantity of 1,3,5-tribromobenzene **3** that resulted in a good selectivity for the *tris*-product and, consequently, a higher product yield of 70%. A similar palladium catalyzed amination was also applied in the next step synthesis; *i.e.*, the reaction of *tris*-PAB **4** with five equivalents of BrF-C₉ **2** in dry toluene at the reflux temperature for a period of 48 h to afford the final product *tris*-DPAF-C₉ **5**. The crude product of **5** was subsequently purified by column chromatography (silica gel) using hexane–toluene (9:1) as eluent to give the light brownish colored semi-solid in a yield of 60%.

Structural characterization of *tris*-DPAF-C₉ **5** was performed using various spectroscopic techniques. The ¹H-NMR spectra of the precursor molecules *tris*-PAB and BrF-C₉ were used as the reference for the comparison with those of *tris*-DPAF-C₉ synthesized, as shown in Figure 1. The most critical evidence for the formation of *tris*-DPAF-C₉ was observed in the region of δ 5.0–7.0, where the broad N–H proton signal assigned for *tris*-PAB at δ 5.67 (peak a) completely disappeared. It was accompanied with a singlet aromatic proton peak at δ 6.38 (peak b), corresponding to the center benzene ring proton of *tris*-PAB, with a slightly broadened and downfield shift to δ 6.60 (peak b') in the spectrum of *tris*-DPAF-C₉. A considerably increased number of peaks in both the aromatic and aliphatic regions of *tris*-DPAF-C₉ provided the evidence of an additional fluorenyl and C₉-alkyl groups onto *tris*-PAB moiety, respectively.

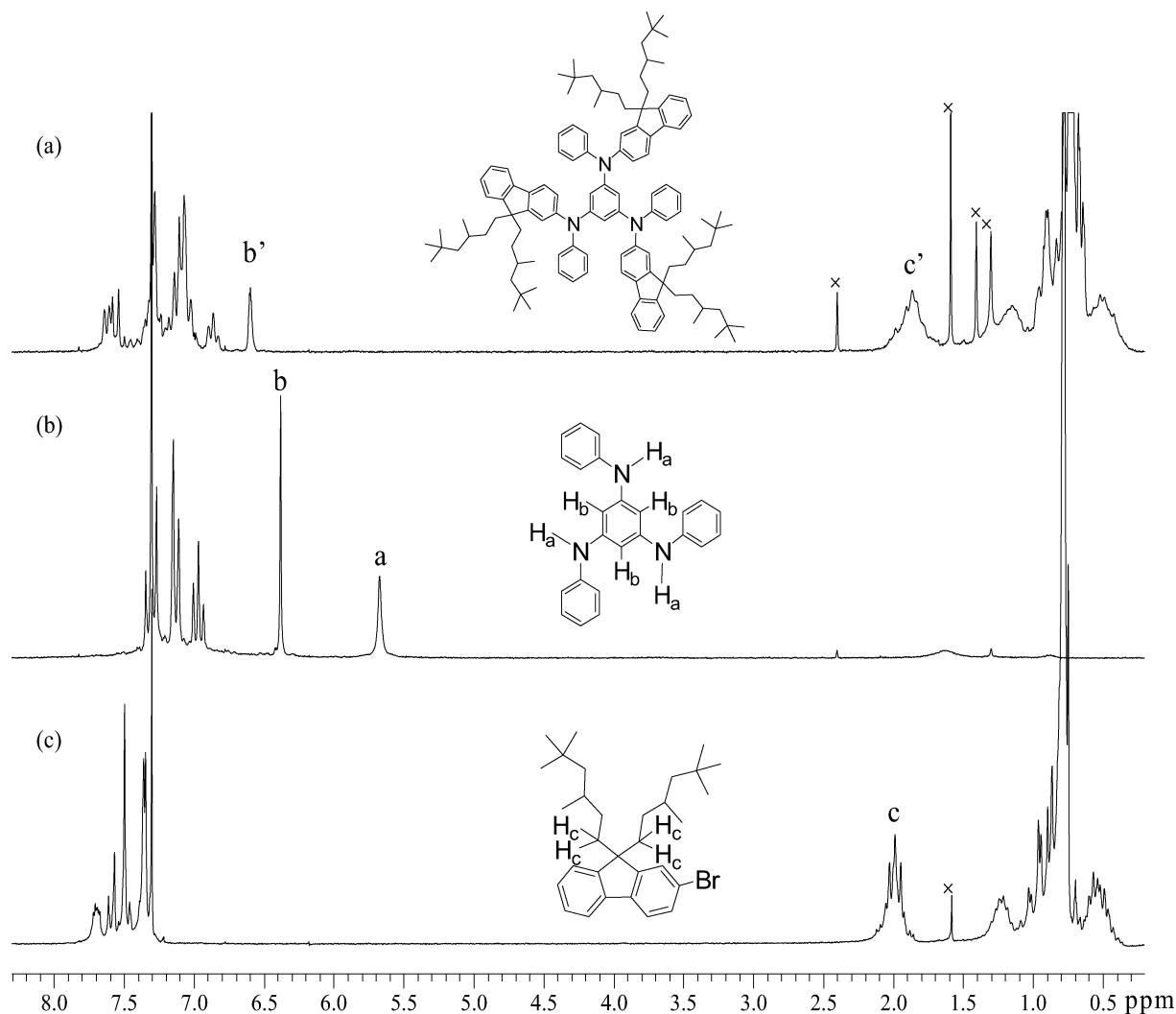
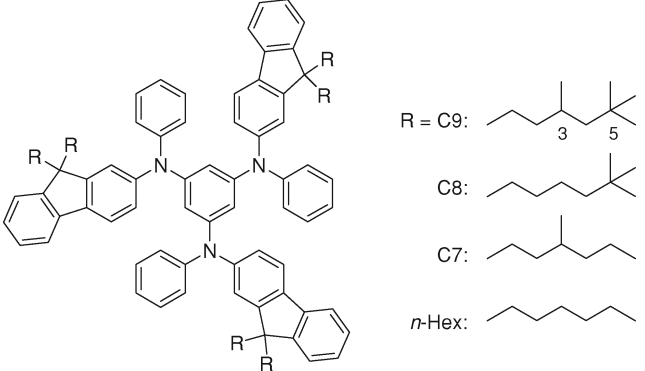


Fig. 1. $^1\text{H-NMR}$ spectra of (a) *tris*-DPAF- C_9 **5**, (b) *tris*-PAB **4**, and (c) BrF- C_9 **2**.

In the aromatic region of δ 7.0–8.0 in the spectrum of *tris*-DPAF- C_9 , the coupling pattern was rather complex as compared to those of the precursor *tris*-PAB or BrF- C_9 . This phenomenon, as well as the broadening of the center benzene ring's proton peak, may be explained by the highly crowded structure of *tris*-DPAF- C_9 or by the presence of unisolable *cis/trans* isomers. In the latter case, it is reasonable to expect two possible stereoisomers as, namely, bis-mono-*trans* and *tris-cis* analogues (*vide infra*), in spite of only one chromatographic spot being detected for this fraction of the compound on TLC (silica gel, toluene–hexane, 5:95). A similar tendency of both complex and broadening pattern for *tris*-DPAF- C_9 was also observed in the aliphatic region of the spectrum. Moreover, the methylene protons adjacent to fluorenyl ring of BrF- C_9 around δ 2.0 (peaks c) was found to shift slightly upfield to δ 1.8 (peak c') due to the shielding effect of neighboring benzene rings. This observation clearly suggests that the 3D structure of *tris*-DPAF- C_9 may not be a planar configuration

with the fluorenyl and/or the phenyl rings being possibly twisted relative to the center core position, forming a pair of *cis/trans* stereo-conformers or isolable isomers. In order to estimate the C–C bond rotational barrier energy of *tris*-DPAF- C_9 between possible stereo-conformers, we conducted the variable temperature NMR measurement in the range of 300–335K in CDCl_3 . However, we did not observe any clear difference except small peak broadening. This result suggests that the rotational barrier energy is enough high to afford the isolable isomers at least in room temperature.

The molecular energy calculation at MOPAC PM3 level showed a lower heat of formation (ΔH_f) of 19.9 kcal/mol for the *tris-cis* C_9 -isomer vs 47.9 kcal/mol for the bis-mono-*trans* C_9 -isomer (Table 1). The calculation data envisage the strong alkyl-alkyl chain-interactions among adjacent 9,9-dialkylfluorenyl rings that provides the stabilization force resulting in the observation of the *tris-cis* isomer as the potential major product regardless of the steric hindrance

Table 1. Calculated heat of formation for *tris-DPAF-C_a* with a variation of the alkylchain


R	ΔH_f (kcal/mol)		$\Delta\Delta H_f$ (kcal/mol) cis-trans
	cis	trans	
H	283.5	283.3	0.2
Me	263.5	263.1	0.4
n-Hex	120.6	131.3	-12.8
C9	19.9	47.9	-28.0
C8	45.1	64.4	-19.3
C7	89.1	105.0	-15.9

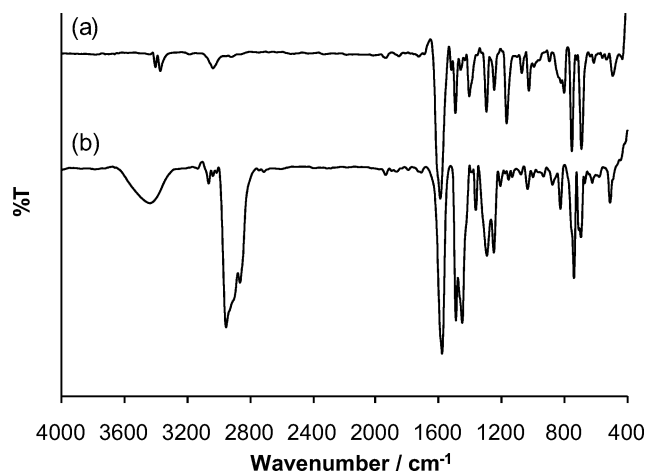
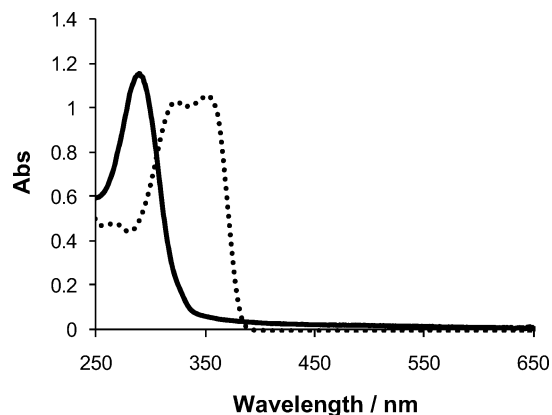
C9: 3,5,5-trimethylhexyl group (3-Me-4' Bu).

C8: 5,5-dimethylhexyl group (4' Bu).

C7: 3-methylhexyl group (3-Me).

of bulky 9,9'-dialkylphenylfluorenylamino groups located at the central benzene ring.

From the IR spectra of *tris-DPAF-C₉* **5** and *tris-PAB* **4**, the introduction of dialkylated fluorenyl moiety on *tris-PAB* **4** was clearly confirmed by the appearance of the strong aliphatic C–H stretching vibration band at 2953 cm^{-1} (Fig. 2). While some other peaks in both spectra around 3050 (aromatic C–H), 1585 (C=C), 750, and 690 cm^{-1} , respectively, closely resembling each other, the

**Fig. 2.** Infrared spectra of (a) *tris-PAB* **4** and (b) *tris-DPAF-C₉* **5** collected on a KBr pellet.**Fig. 3.** UV-Vis spectra of *tris-PAB* **4** (solid line) and *tris-DPAF-C₉* **5** (dotted line) in CHCl_3 at a concentration of 1.0×10^{-5} M.

small and sharp N–H stretching peaks at 3402 and 3371 cm^{-1} detected for *tris-PAB* disappeared in the spectrum of *tris-DPAF-C₉*. The broad N–H peak is generally observed for the primary amine-like aniline. However, such sharp N–H peaks can be seen in the IR spectrum of diphenylamine, which has the similar structure as *tris-PAB*, due to the rigidity of the molecule. The broad O–H band in the spectrum of *tris-DPAF-C₉* is attributed to the residual water owing to the solvent and water molecules encapsulated or uptaken by flexible C_9 -substituents in the shape of armed-chains as evident by its semi-solid form of the material collected.

The UV-Vis spectra of *tris-PAB* **4** and *tris-DPAF-C₉* **5** in chloroform were shown in Figure 3. The chemical modification with the fluorenyl moiety led to a large bathochromic shift from the absorption of *tris-PAB* centered at 290 nm (λ_{max} , $\epsilon = 11.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) to that of *tris-DPAF-C₉* at 322 and 351 nm ($\epsilon = 10.3$ and $10.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively). The shift corresponds to the partially extended π -conjugation among three fluorenyl moieties interconnected by a benzene ring consistent with the structure of **5** synthesized.

4 Conclusions

A novel highly luminescent *tris*-fluorenyl ring-interconnected chromophore *tris-DPAF-C₉* was designed and synthesized using a C_3 symmetrical triaminobenzene core as the synthon. The structural moiety bears a close resemblance to that of 2-diphenylamino-9,9'-dialkylfluorenyl attachment in the starburst nonlinear photonic materials $\text{C}_{60}(>\text{DPAF-C}_n)_x$, demonstrated in our recent reports. The synthesized chromophore *tris-DPAF-C₉* was well characterized via various spectroscopic techniques including the analyses of ^1H and ^{13}C -NMR, IR, and UV-Vis spectra. Interestingly, the 3D structural configuration of *tris-DPAF-C₉* implies the presence of two possible

stereoisomers as, namely, bis-mono-*trans* and tris-*cis* analogues. The molecular energy calculation data envisage the strong alkyl-alkyl chain-interactions among adjacent 9,9-dialkylfluorenyl rings that provides the stabilization force resulting in the observation of the tris-*cis* isomer as the potential major product regardless of the steric hindrance of bulky 9,9'-dialkylphenylfluorenylamino groups located at the central benzene ring.

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