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Triphenylamine derivatized phenylacetylene macrocycle with large two-photon absorption cross-section

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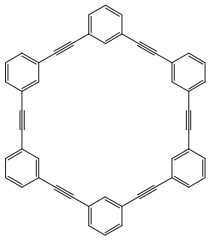
ABSTRACT

A phenylacetylene macrocycle (PAM) derivative containing triphenylamine as the framework was synthesized in *one-step* Sonogashira coupling. The photophysical and electrochemical properties were investigated in details. This hexamer shows significant enhancement in two-photon absorption cross-section relative to reported PAM derivatives.

Phenylacetylene macrocycles (PAMs) have been extensively studied,[1] since the first synthesis of unsubstituted PAM in 1970s.[2] The conformationally rigid and shape persistent molecules with nanoscale dimensions have attracted much interests because of their potentials in molecular crystals,[3] conducting tubular liquid crystals,[4] and molecular turnstiles.[5] Due to the large cavity, PAMs with multipolar structures have been developed to bind organic substrates and catalyze chemical reactions functioning as natural cyclodextrins.[6] Meanwhile, multipolar PAMs with large two-photon absorption cross-section have been investigated for potential application in imaging.[7] Their electronic and optical properties can be fine-tuned by modifying the size and shape of the macrocycles and the characteristics of side functional groups.



PAM

Triphenylamine (TPHA) has attracted considerable attention in light emitting diode,[8] and nonlinear optics because of its unique structure.[9] Crystallography and quantum mechanical calculation have confirmed that the three N–C bonds are in one common plane and continuous π conjugation extends through the lone electron of nitrogen atom,[10] which makes it a good chromophore for luminescent devices as well as particularly for two-photon absorption application. This leads us hereby present a macrocycle (hexamer **3**, in Chart 1) as a connection of triphenylamine and PAM moieties, exploring the structure–property relationship. We report the syntheses, electrochemical and optical properties of **3**, while dimmer **1** and tetramer **2** are demonstrated for comparison. Through a femtosecond Z-scan technique, we have observed significant improvement for two-photo absorption cross-section from dimmer, tetramer to hexamer.

The bifunctional monomer 4-ethynyl-*N*-(4-ethynylphenyl)-*N*-phenylbenzenamine (**6**) was synthesized by Sonogashira coupling from 4-iodo-*N*-(4-iodophenyl)-*N*-phenylbenzenamine (**4**) and trimethylsilyl acetylene followed by the removal of trimethylsilyl group in a basic solution with a high yield. Hexamer **3** was obtained in 17% yield by coupling from **4** and **6**. The target compound was prepared by *one-step* synthesis and further purification was realized by flash chromatography and precipitation from CH_2Cl_2 and methanol. To avoid cross-coupling polymerization of **4** and **6**,

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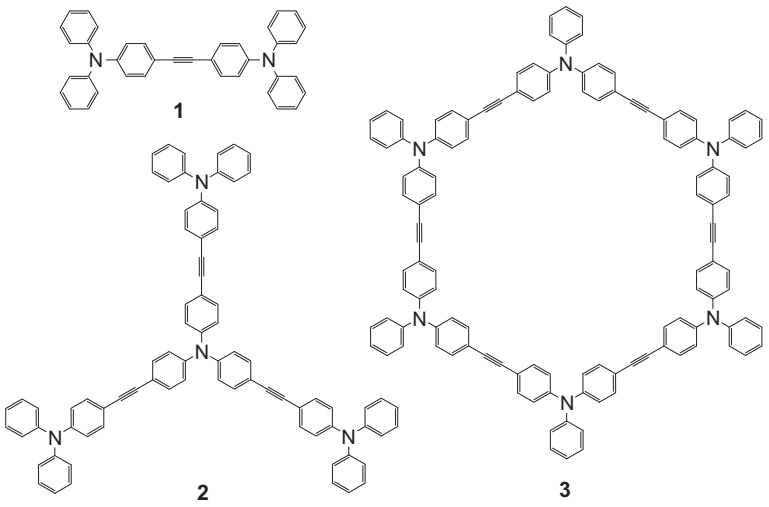
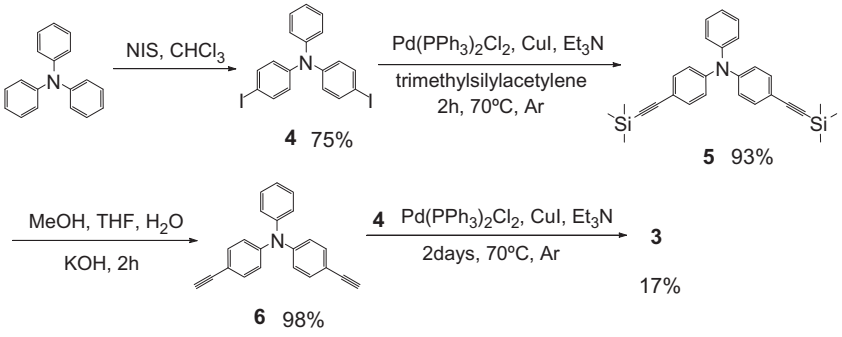


Chart 1. Structures of dimmer **1**, tetramer **2**, and hexamer **3**.



Scheme 1. Synthesis of **3**.

a dilute concentration is required with the addition of catalysts well controlled. Compared with reported methods via a trimmer halide and corresponding trimmer acetylene, this method affords an overall moderate yield with straight forward and convenient work up.[6,7] The synthesis route is summarized in Scheme 1 (details in Supplementary data).

Figure 1 shows the normalized absorption and emission of **1**, **2**, and **3**. The absorption spectrum of TPHA is shown for reference. Compound **1**–**3** all show maxima at ~380 nm attributable to the

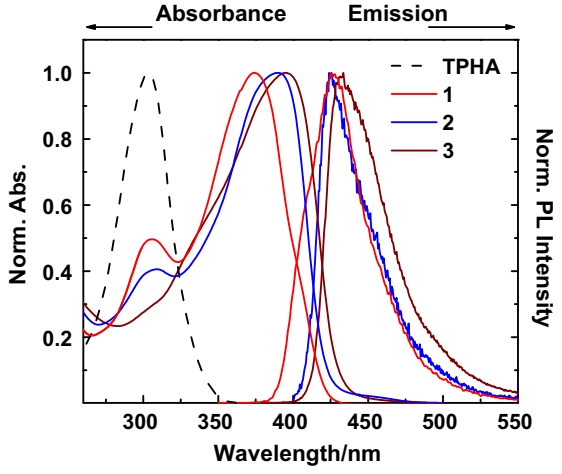


Figure 1. Absorption and emission of **1**–**3** in chloroform (5 μM), λ_{ex}: 380 nm.

π–π^* transition, while a shoulder at 300 nm in **1** and **2** corresponds to the triphenylamine unit in agreement of the absorption of TPHA. The ratio of the absorbance at 300 nm to the maximum one decreases from **1** to **2** and finally diminishes in **3** indicating that the electron delocalization completely through the TPHA and ethynyl segment in **3**. Meanwhile, the maximum absorption red-shifts from **1** to **3** suggest the finding of extended conjugation length, corresponding to the π–π^* transition of the molecular backbone. As shown in emission spectra, compound **1**–**3** emit blue light maximized at ~430 nm. Their quantum yields (Φ) have been measured with quinoline sulphate in 0.1 M H_2SO_4 as the reference. Compounds **1**, **2**, and **3** show comparable quantum yields, with Φ of 45%, 60%, and 58%, respectively. It indicates no significant aggregation, in agreement with the UV absorption spectra. While there is no appreciable variation in their fluorescence maxima going from **1** to **3**, indicating that there is no significant change in conjugation effect in extending the conjugated molecular framework from dimmer to hexamer, although the slight onset emission redshift may be attributed to the more extended conjugation.

Figure 2 shows the electrochemical behavior of TPHA and **1**–**3** examined by cyclic voltammetry (CV) and square wave voltammetry (SWV). TPHA displays a one-electron oxidation process at 0.535 V versus Fc/Fc^+, where the anodic (i_p^{ox}) to cathodic (i_p^{red}) peak current ratio (i_p^{ox}/i_p^{red}) is >1 at a scan rate of 100 mV s^{-1}. This indicates chemical instability of the oxidized compound, that is the radical cation of **1** (an EC mechanism, where E signifies an electron transfer and C represents a chemical step).[11] As the scan rate increases to approximately 1 V s^{-1}, the i_p^{ox}/i_p^{red} value approaches unity, due to the chemical step being outrun.