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

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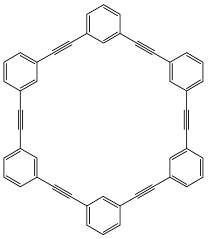
ABSTRACT

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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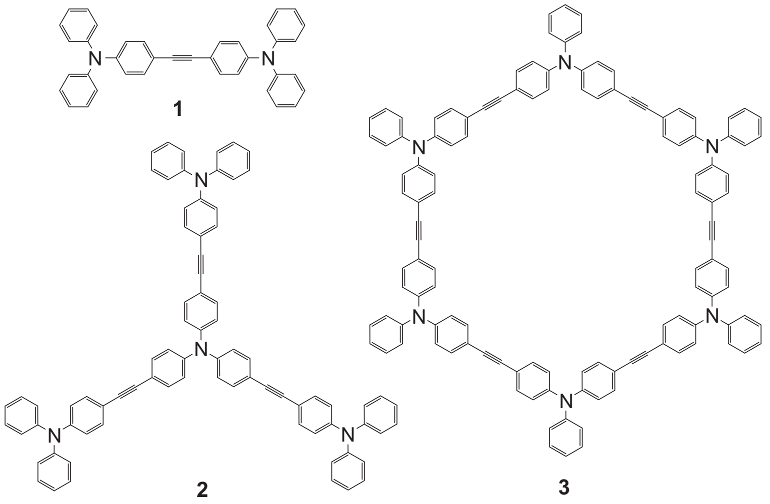
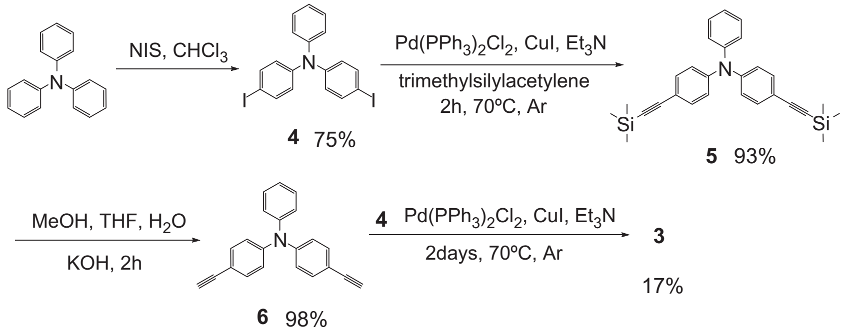


Chart 1. Structures of dimmer **1**, tetramer **2**, and hexamer **3**.



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 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.

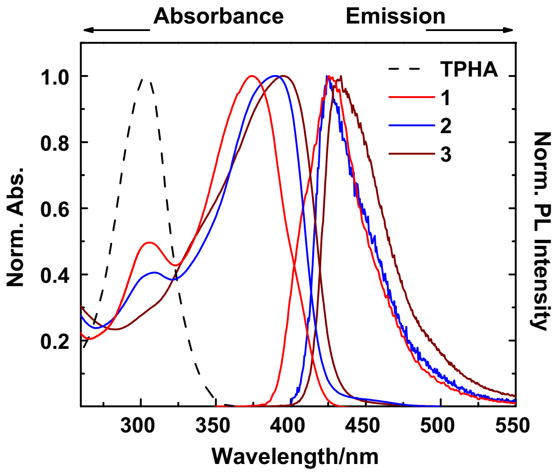


Figure 1. Absorption and emission of **1**–**3** in chloroform (5 μM), λ_{ex}: 380 nm.

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.

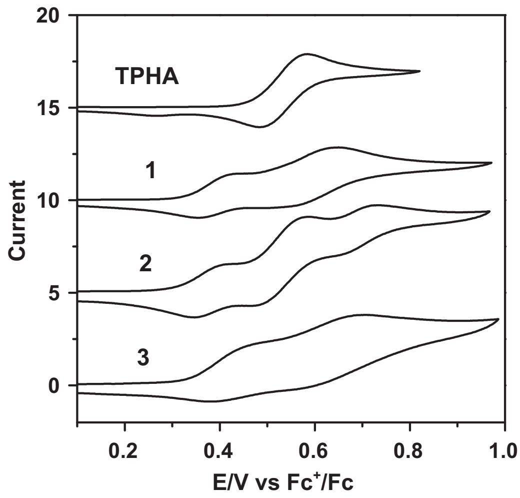


Figure 2. Cyclic voltammetry of TPHA and **1**–**3**, 1 mM solution in CH_2Cl_2 with 0.1 M Bu_4NPF_6 at a scan rate of 100 mV s^{-1}.

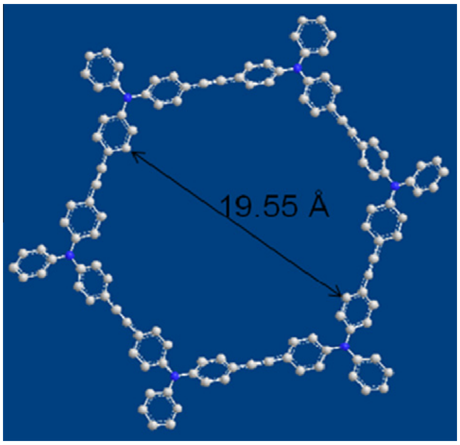


Figure 4. Simulated structure of **3**, Blue: N, Gray: C, H atoms are omitted.

Dimmer **1** displays two one-electron reversible oxidation processes with the second process 210 mV more positive that the first process (0.390 V vs Fc/Fc$^+$). Compound **2** displays a one-electron oxidation, followed by a two-electron oxidation and then another one-electron oxidation. The first oxidation processes in **1** and **2** to give the corresponding monocation at TPHA unit should be similar. While the second two-electron process in **2** forms a symmetrical trication (Fig. 3). Surprisingly, there is a significant difference in the CV curve of **3** regarding to the number of electrons transferred and the chemical reversibility, which leads to two broad oxidation processes observed, that is 0.410 V and 0.640 V. According to the CV curve, possible oxidation processes are proposed as shown in Figure 3. Although the CV shows only two oxidation curves with identical current suggesting two three-electron processes, there might be radical cation intermediates from one-electron oxidation. It has been found that the difference in peak potentials ($\Delta E^\circ = |E_1{}^\circ - E_2{}^\circ|$) is equal to 35.6 mV if there is no interaction between the redox centers.[12] Weak interaction may yield non-distinguishable processes as shown in both two processes in **3**. Meanwhile, symmetry may play a significant role for radical cation stability, where trication shows a higher symmetry than the monocation and dication in the fast oxidation process of **3**.

The structure of hexamer **3** is calculated with minimized energy as shown in Figure 4. There is no stereochemical structure found. For the individual TPHA unit, the three N–C bonds are localized in a same plane as the single TPHA molecule shows.[10] The non-bonding distance between two opposite carbons is 19.55 Å, which is comparable with the reported 1,4-diethynylphenyl derivatized PAM,[6] and thus giving us an idea of the size of the interior of the macrocycle. This large cavity provides opportunities for further modification of amphiphilic function groups at the interior of the macrocycle, achieving biocompatible materials in biotechnology.

The two-photon absorption was measured by a femtosecond laser source Z-scan method.[13] The cross-section was calculated from dependence of the nonlinear absorption of solutions on the concentration. Surprisingly, **1–3** show peak two-photon absorption cross-section at 650 nm, which is less than the double wavelength (~760 nm) of their linear absorption maxima. Similar phenomena have been observed in our and other groups' researches.[14] The possible reason is that two-photon excitation might populate the molecule to a higher energy excited singlet state with larger probability as compared to that by one-photon excitation.[15] The

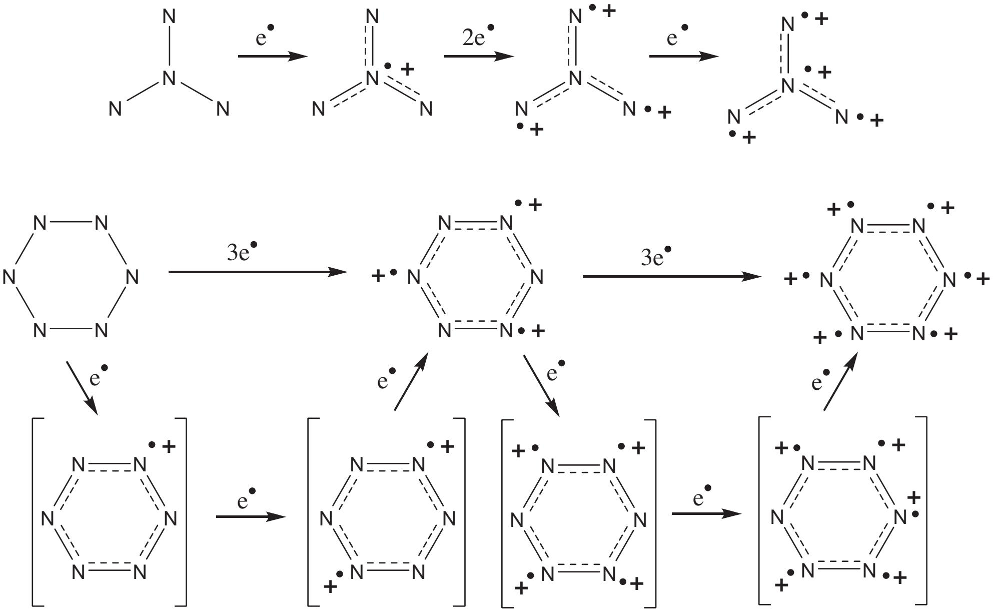


Figure 3. Oxidation process of **2** and **3**.

cross-section of dimmer **1** is 420 GM (1 GM = 1×10^{-50} cm^{4}s/photon). With the growth of molecular size, the cross-section dramatically increases to 1200 GM for tetramer **2**. However, the increase from **2** to **3** (1300 GM) is somehow saturated, which is somehow in agreement with the linear absorption. We reported dendritic hexamer with 30% enhancement relative to tetramer.[16] Compared with PAM structure, dendritic hexamer features a more branched structure, which facilitates the growth of two-photon absorption.[17] To achieve higher two-photon absorption cross-section, multifunctional groups, for example electron-donating and withdrawing groups could be introduced in future work.

In conclusion, we synthesize a triphenylamine-containing PAM by *one-step* Sonogashira reaction. Two three-electron oxidation processes have been observed in cyclic voltammetry. The two-photon absorption cross section is significantly larger than the phenylacetylene macrocycle with donor and acceptor reported with $\sim$125 GM.[7] Future studies will be focusing on the modification of exterior and interior function groups for higher cross-section and biocompatible character.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.07.003.

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