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## Tetracyanoethylene substituted triphenylamine analogues

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## ABSTRACT

A set of tetracyanoethylene (TCNE) substituted triphenylamine analogues (**4–6**) exhibiting strong intramolecular charge transfer (ICT) were designed and synthesized by the [2+2] cycloaddition–retroelectrocyclization reaction of **3** (tris-(4-phenylethynyl-phenyl)-amine) with TCNE. The reaction was found to be temperature dependent. The blue shift in the  $\pi \rightarrow \pi^*$  transition and intramolecular charge transfer (ICT) in amines **4–6** were found to be directly proportional to the number of TCNE units. The computational study shows good agreement with the experimental results and reveals that as the number of TCNE units in amine increases, HOMO–LUMO gap increases.

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Triphenylamine is a strong donor and its functionalized derivatives have been explored for various optoelectronic applications.<sup>1</sup> Triphenylamine derivatives have received substantial interest in photoconductors due to their excellent hole transporting properties.<sup>2</sup> The photonic properties of the triphenylamines can be tuned by the peripheral modification.<sup>3</sup> Incorporation of strong acceptors at the periphery of the triphenylamine results in strong intramolecular charge transfer (ICT).<sup>4–7</sup> Diederich and co-workers have explored tetracyanoethylene (TCNE) as a strong electron acceptor, which undergoes [2+2] cycloaddition–retroelectrocyclization reaction with electron rich alkynes.<sup>8–13</sup> Wang and co-workers have attached cyano acceptors on the periphery of one of the phenyl units of triphenylamine and studied its intramolecular charge transfer (ICT) properties.<sup>14</sup> Michinobu et al. have explored tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) substituted triphenylamine as a photosensitizer in dye-sensitized solar cells (DSSCs).<sup>15</sup> Our group is interested in the design and synthesis of donor–acceptor materials for optoelectronic applications.<sup>16</sup> We were interested to incorporate the TCNE acceptor at the periphery of the phenyl units of the triphenylamine and to explore its photophysical properties. Therefore we designed and synthesized tris-(4-phenylethynyl-phenyl)-amine **3**, and their TCNE derivatives **4–6** and studied their photophysical, electrochemical, and computational properties.

The tris-(4-phenylethynyl-phenyl)-amine **3**, and their tetracyano ethylene (TCNE) derivatives **4–6** were synthesized by the

Pd-catalyzed Sonogashira cross-coupling, and [2+2] cycloaddition–retroelectrocyclization reactions, respectively (Scheme 1).

The intermediate **2** was synthesized by the iodination reaction of triphenylamine **1**.<sup>17</sup> The Pd-catalyzed Sonogashira cross-coupling reaction of **2** (tris-(4-iodo-phenyl)-amine) with ethynyl-benzene resulted in **3** in ~70% yield.<sup>18</sup> The [2+2] cycloaddition–retroelectrocyclization reaction of tris-(4-phenylethynyl-phenyl)-amine **3** with TCNE was found to be temperature dependent.

The reaction of TCNE with **3** at room temperature resulted in a mono substituted product, whereas the microwave assisted reaction with varying temperatures resulted in di and tri TCNE substituted products.

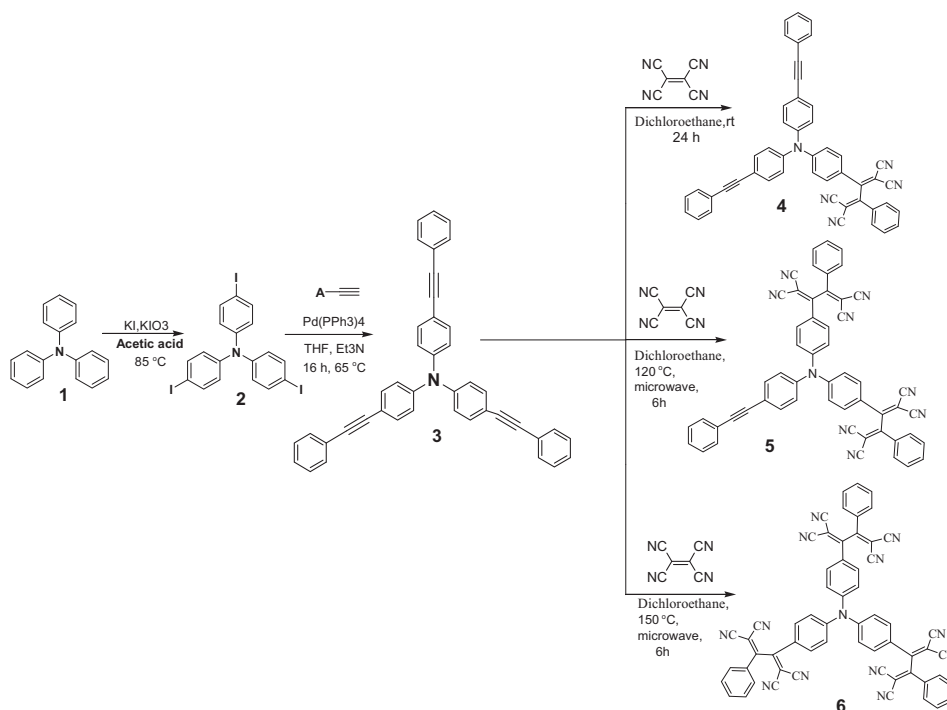
The [2+2] cycloaddition–retroelectrocyclization reaction of amine **3** with excess TCNE at room temperature for 24 h resulted in an exclusive mono TCNE substituted amine **4** in 54 % yield. The reaction of tris-(4-phenylethynyl-phenyl)-amine **3** with TCNE, under microwave condition at 120 °C for 6 h resulted in amine **5**, whereas increasing the reaction temperature to 150 °C under microwave for 6 h resulted in amine **6** (Scheme 1).

The amines **3–6** were purified by column chromatography and characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR, and HRMS techniques.

The single crystal of amine **3** was obtained via slow evaporation of dichloromethane solution at room temperature, which shows a monoclinic P21/n space group. The crystal structure of **3** is shown in Figure 1. The dihedral angles between the triphenylamine core, and the substituted phenyl rings were found to be 28.82°, 24.61°, and 52.55°. Important bond lengths and bond angles are listed in the Table S2 (see ESI for details).

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Scheme 1. Synthesis of amines 3–6.

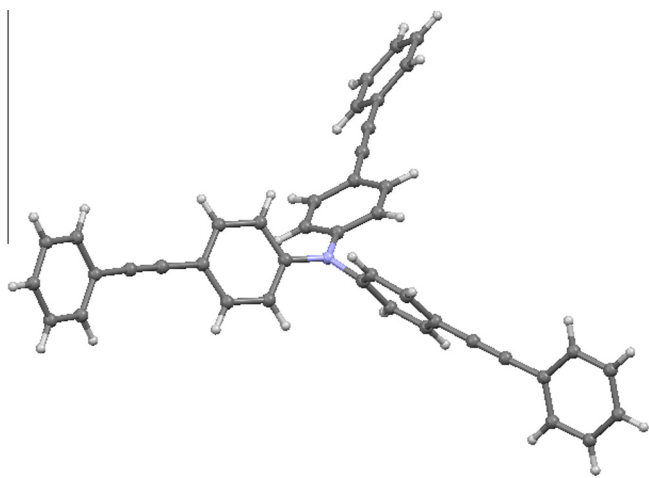
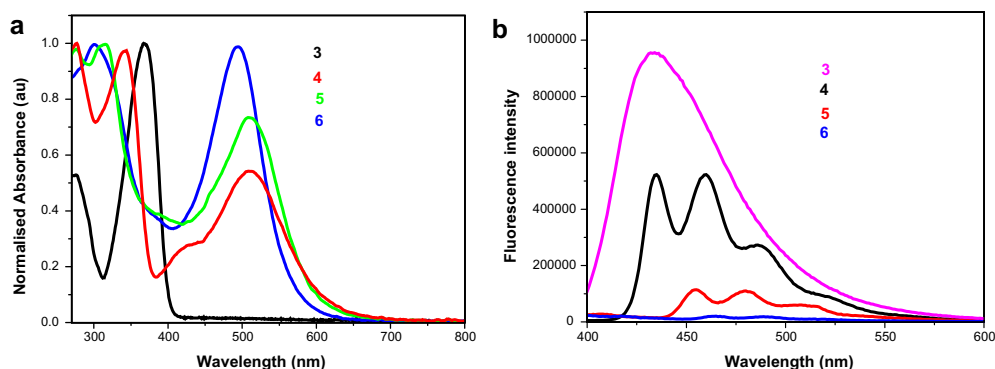


Figure 1. Single crystal X-ray structure of amine 3.

The electronic absorption, and fluorescence spectra of the tris-(4-phenylethynyl-phenyl)-amine **3**, and their TCNE derivatives **4–6** were recorded in dichloromethane at room temperature (Fig. 2), and their photophysical data are listed in Table 1. Tris-(4-phenylethynyl-phenyl)-amine **3** shows  $\pi \rightarrow \pi^*$  transition at 367 nm, whereas amines **4–6** show blue shifted  $\pi \rightarrow \pi^*$  transition at 342 nm, 313 nm and 299 nm, respectively. The donor–acceptor amines **4**, **5**, and **6** exhibit low energy charge transfer bands at 510 nm, 507 nm, and 494 nm, respectively.<sup>14,19,20</sup> These results show good agreement with the DFT calculation, which shows that increasing the number of TCNE groups in **4–6** results in a higher HOMO–LUMO gap. The HOMO–LUMO gap in amine **4–6** is directly proportional to number of TCNE groups. Tris-(4-phenylethynyl-phenyl)-amine **3** shows high fluorescence at 434 nm, whereas their TCNE derivatives **4–6** show quenching of fluorescence, reflecting strong donor–acceptor interaction. Figure S15 displays the colors of the amines **3–6** in dichloromethane.

The electrochemical behavior of the amines **3–6** was investigated by the cyclic voltammetric (CV) analysis in dry dichloromethane (DCM) solution at room temperature using tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte. The elec-

Figure 2. (a) Normalized electronic absorption spectra of the amines **3–6** in CH<sub>2</sub>Cl<sub>2</sub> (1.0 × 10<sup>−4</sup> M) and (b) fluorescence spectra of the amines **3–6**.

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