

**Engineering & Applied Sciences****Aryl Substituted Tetraazaphenanthrenes as Electron Transport Material for EL-Devices****Naoki Matsumoto<sup>1</sup>, Hideo Une<sup>2</sup>, Hideki Gorohmaru<sup>2</sup>, Thies Thiemann<sup>3</sup>, Shuntaro Mataka<sup>3\*</sup>, Akihiro Seno-o<sup>4</sup>, Kazunori Ueno<sup>4</sup>**<sup>1</sup> Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan<sup>2</sup> Graduate School of Engineering, Kyushu University, 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816-8580, Japan<sup>3</sup> Institute of Advanced Material Study, Kyushu University, 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816-8580, Japan<sup>4</sup> Electrophotography Research Center, Canon Inc., 30-2 Shimomaruko 3-Chome, Ohta-ku, Tokyo 146-8501, Japan**Abstract**

Aryl substituted tetraazaphenanthrenes (9) were synthesized as electron transport material for electroluminescent-devices (EL-devices). Their synthesis and their physical properties are discussed. The results of an experimental EL-device using tetraphenyltetraazaphenanthrene (9a) as an electron transport material are presented.

**Introduction**

With the fast growing array of electronic equipment, a demand for novel types of displays has arisen over the last few years. These range from small, flat panel displays, useful for mobile telephones and for the 'back-rest' movie and entertainment screens recently installed in certain aircraft, to large full-color displays for new generations of televisions, video players and perhaps even cinema viewing screens. The characteristics required of such displays are manifold, but difficult to achieve: long life-time, high brightness, high resolution, fast response time, low operating voltage. Anybody who has worked with flat panel displays realizes that a wide viewing angle is of great importance.

Against this background, the discovery of electroluminescence in non-crystalline organic material (in both 'low-weight' and polymeric material) was propitious. While light-emitting diodes (LEDs) based on inorganic solids have been known for some time, it was shown in the 1960s that single crystals of anthracene sandwiched between two electrodes exhibit electroluminescence (Helfrich 1965, Pope 1963). The underlying principle of this is the injection of electrons into the semiconducting material from one electrode and a concomitant creation of migrating 'positive' holes at the other electrode. The capture of the electron by the hole (recombination) is associated with the emission of radiative energy, produced by the so-called excited electron-hole state (exciton). Over 25 years later, Tang and Van Slyke demonstrated that organic polymers could be used in making LEDs (Tang 1987). These devices consisted of a hole-transporting layer of an aromatic diamine and an emissive layer of (8)-hydroxyquinoline aluminum (Alq<sub>3</sub>). Although the quantum efficiency of the devices was on

the order of 0.05% and the driving voltage was  $> 10$  V, the potential advantages associated with organic materials versus inorganic materials in the variability of compounds that can be used and the processability of these materials to form uniform, thin layered coatings, made the use of organic compounds in LEDs an attractive alternative. Another 15 years have passed since then. The research effort devoted to organic luminescent material has been tremendous. (For a review of organic materials in modern display technology, see Ziemelis 1999, Friend 1999). Last year, a number of products were announced which feature electroluminescent displays based on organic materials (Philipps, Pioneer). Today, the research in this area is an interplay of chemistry (designing of new organic compounds), physics and engineering. In order to achieve a balanced injection and transport of electrons and holes into the emissive layer, additional organic layers have been introduced into the device structure, providing for the crucial separation of the emissive layer from the electrodes. Thus, much higher quantum efficiencies and much lower driving voltages have been achieved. The research, however, is far from over. The development of improved full-color LEDs is one of the major targets in the next few years.

For the fabrication of high-performance LEDs, hole and electron-transporting material, as well as light emitting material, are required. The aim of our work is the synthesis of electron-transporting material. Important for this type of material is a strong electron acceptor characteristic and the ability to form amorphous films. Pyrazino-annelated benzenes are known to accept an electron relatively easily. Thus, 1,4,5,8,9,12-hexaazatriphenylene (HAT) (see also: Nasielski-Hinkens 1981) has been studied extensively in our laboratory. Previously, it had been reported to be a strong electron acceptor. Albeit it crystallizes easily and has a high melting point. Hexaphenyl-HAT is also expected to be a good electron-acceptor. Moreover, due to the phenyl groups, hexaphenyl-HAT crystallizes less easily, thus a better result was expected for the formation of an amorphous film incorporating this material. Its preparation was carried out via hexaaminobenzene (2) as the key intermediate, using a known procedure. The synthesis of hexaaminobenzene (2) had been described via reduction of 1,3,5-triamino-2,4,6-trinitrobenzene (1) (Rogers 1986). As this compound is explosive, a new route had been devised, which takes the advantage of the reducibility of nitrobenzothiadiazoles, e.g. (6) and (7), to the corresponding polyaminobenzenes (Mataka 1989). In a method similar to this route, it was also possible to prepare 1,4,5,8-tetraazaphenanthrene. In the following text, the synthesis and the physical properties of some substituted 1,4,5,8-tetraazaphenanthrenes (9) are described, with attention to the fact that substituents are needed to tailor the electronic properties and to facilitate the formation of amorphous films with this material at a later stage.

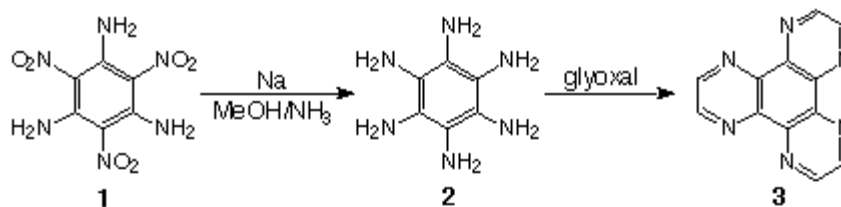
## Experimental Procedure

A mixture of 1,2,3,4-tetraaminobenzene bishydrochloride (8) (211 mg, 1.0 mmol) and 1,2-bis-(4-chlorophenyl)-1,2-diketone (560 mg, 2.0 mmol) in ethanol (10 mL) and acetic acid (3 mL) was heated under reflux for 15 hours under an argon atmosphere. Thereafter the cooled reaction mixture was poured into water (xx mL) and the formed precipitate was filtered off. The precipitate was dried and purified by column chromatography (silica gel, eluant  $\text{CHCl}_3$ ) and recrystallised from ethanol to give 2,3,6,7-tetrakis-(4-chlorophenyl)-1,4,5,8-tetraazaphenanthrene (9e) (150 mg, 24%) as yellow needles; mp  $> 300^\circ\text{C}$ ; IR ( $\text{KBr}/\text{cm}^{-1}$ )  $\nu$  1594, 1492, 1365, 1250, 1097, 1014;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 - 7.41 (m, 8H), 7.58 - 7.67 (m, 8H), 8.36 (s, 2H).

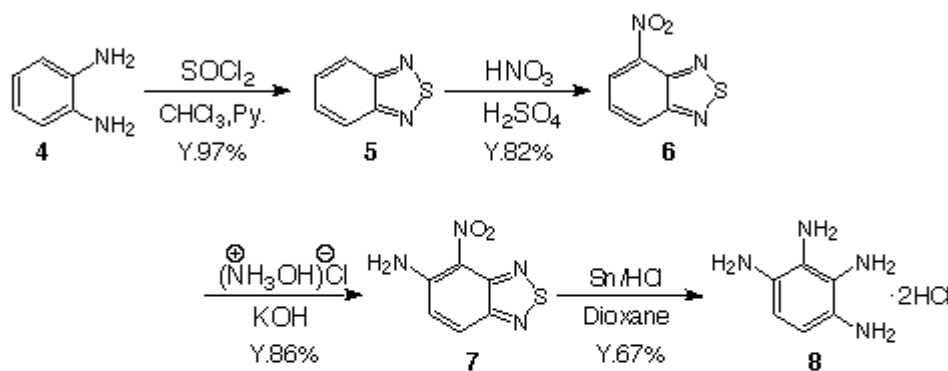
## Synthesis of 2,3,6,7-tetraaryl substituted 1,4,5,8-tetraazaphenanthrenes (9)

The key intermediate in the synthesis of the substituted tetraazaphenanthrenes is the

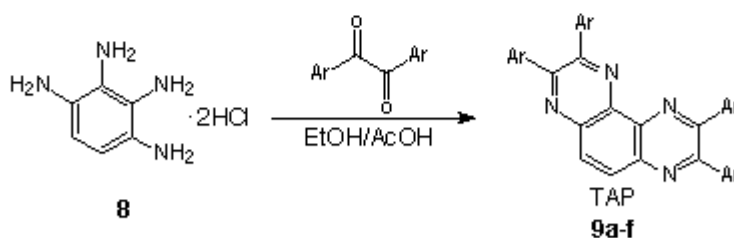
1,2,3,4,-tetraaminobenzene bishydrochloride (8). Starting from o-phenylenediamine (4), which is reacted with thionyl chloride in the presence of pyridine to give 2,1,3-benzothiadiazole (5), 5-amino-4-nitro-2,1,3-benzothiadiazole (7) can be prepared in four steps as shown in Scheme 2. (7) can be reduced with ease to (8) with tin-hydrochloric acid in dioxane.



Scheme 1



Scheme 2



- Ar = **9a**: Ph- (Y.42%)  
 = **9b**: 4-Me-C<sub>6</sub>H<sub>4</sub>- (Y.15%)  
 = **9c**: 4-MeO-C<sub>6</sub>H<sub>4</sub>- (Y.5%)  
 = **9d**: 3,4,5-tri-MeO-C<sub>6</sub>H<sub>2</sub>- (Y.3%)  
 = **9e**: 4-Cl-C<sub>6</sub>H<sub>4</sub>- (Y.24%)  
 = **9f**: 2,6-di-F-C<sub>6</sub>H<sub>3</sub>- (Y.15%)

Scheme 3

(8) was reacted with a number of substituted 1,2-diaryl-1,2-diketones (benzils). The reaction has not been optimized as of yet. Nevertheless, it can be noted that unsubstituted benzil gave the best yield. Furthermore, electron-acceptor substituted benzils gave better yields than the corresponding electron-donor substituted substances. This is not surprising as the carbonyl 'reactivity' of the former is higher than that of the latter. While the melting point of most

compounds could be reduced relatively to the parent compound, especially in the case of the methoxy-substituted tetraazaphenanthrenes (9c) and (9d), the fluoro-substituted tetraazaphenanthrene (9f) showed a remarkably high melting point. The crystallizability of the compounds was investigated by multiple TG/DTA scans. The tetrakis (trimethoxyphenyl) tetraaza-phenanthrene (9d) clearly showed amorphous behaviour upon cooling (after melting the sample). Tetraphenyltetraazaphenanthrene (9a) formed an amorphous thin layer after vacuum deposition (see experimental EL-device, below).

## Physical properties

### *UV data*

All the tetraazaphenanthrenes synthesized are colored materials. For the most part, they are yellow. The UV data of the TAP derivatives are listed in Table 1. Substituting tetraphenylazaphenanthrenes with electron withdrawing moieties such as with fluoro, or chloro groups induces a hypochromic shift in the wavelength of the absorption maximum, when compared with molecules having one or more electron donors on the phenyl groups (e.g., methoxy-(9c), or trimethoxy-(9d)). Nevertheless, all substituted tetraphenylazaphenanthrenes experience a bathochromic shift in relation to the unsubstituted tetraphenylazaphenanthrene. This is in reasonable agreement with the expected data.

**Table 1.** UV data of TAP derivatives

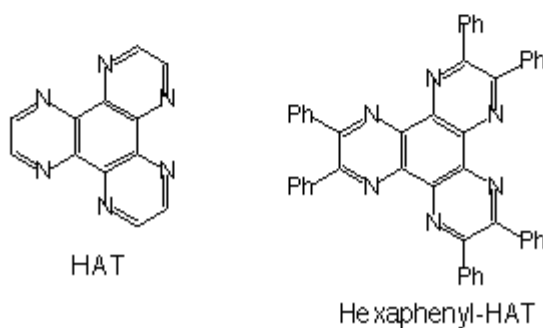
compound	Ar	Absorption	
		$\lambda$ max (nm)	log $\epsilon$
<b>9a</b>	Ar = Ph-	344.5	4.51
<b>9b</b>	Ar = 4-Me-C <sub>6</sub> H <sub>4</sub> -	357.5	4.65
<b>9c</b>	Ar = 4-MeO-C <sub>6</sub> H <sub>4</sub> -	377.5	4.67
<b>9d</b>	Ar = 3,4,5-MeO-C <sub>6</sub> H <sub>2</sub> -	381.5	4.48
<b>9e</b>	Ar = 4-Cl-C <sub>6</sub> H <sub>4</sub> -	352.0	4.71
<b>9f</b>	Ar = 2,6-F-C <sub>6</sub> H <sub>3</sub> -	360.5	4.63

c = 1.0x10<sup>-5</sup>M in CH<sub>2</sub>Cl<sub>2</sub>

**Table 2.** Half-wave reduction potential of TAP derivatives

compound	Ar	E <sub>1/2</sub> <sup>red</sup> (V vs. Ag/AgCl)
<b>9a</b>	Ar = Ph-	-1.87
<b>9b</b>	Ar = 4-Me-C <sub>6</sub> H <sub>4</sub> -	-1.91
<b>9c</b>	Ar = 4-MeO-C <sub>6</sub> H <sub>4</sub> -	-1.96
<b>9d</b>	Ar = 3,4,5-tri-MeO-C <sub>6</sub> H <sub>2</sub> -	-1.87
<b>9e</b>	Ar = 4-Cl-C <sub>6</sub> H <sub>4</sub> -	-1.78
<b>9f</b>	Ar = 2,6-di-F-C <sub>6</sub> H <sub>3</sub> -	-1.69

c = 5.0x10<sup>-4</sup>M in CH<sub>2</sub>Cl<sub>2</sub>/0.1M Bu<sub>4</sub>NPF<sub>6</sub>, V = 500mVs<sup>-1</sup>

**Figure 1**

### CV data

Cyclic voltammetry (CV) of the TAP derivatives was carried out in dichloromethane using a glassy carbon electrode as the working electrode. The results can be found in Table 2. The potentials are given versus Ag/AgCl as reference electrode. The CV data holds no surprises insofar as the substances substituted with electron-withdrawing groups (i.e., relatively electron poor tetraazaphenanthrenes) are reduced at comparatively lower half potentials than the corresponding electron-donor substituted tetraazaphenanthrenes (i.e., relatively electron-rich tetraazaphenanthrenes). Thus, the gradation di-*o*-F-Ph < *p*-Cl-Ph < Ph < *p*-Me-Ph < *p*-MeO-Ph would be expected from the electron-donor capability of the substituents and is in accordance with the Hammett parameters (where it is known that *o*-fluoro substituents are usually not well reflected). The only TAP derivative that does not seem to fit is the

trimethoxy derivative (9d), which reduces at a half wave potential comparable to that of the unsubstituted tetraphenyltetraazaphenanthrene (9a). The reason for this may be due to steric overfreighting within the perimeter of the phenyl groups. Thus, the methoxy groups may effect a deviation from planarity of the phenyl groups with concurrent loss of some *p-p* interaction with the tetraazaphenanthrene core unit.

An EL-device [ITO/0.1%FL-03(Spin-coated; Canon hole transport material)/Alq<sub>3</sub> (600 Å; luminescent layer)/tetraphenyltetraazaphenanthrene (9a) (50 Å or 200 Å; electron transport layer)/Al-electrode 1500 Å] was built and tested. It was noted that at higher driving voltages the use of tetraphenyltetraazaphenanthrene was beneficial as compared to using no added layer of electron transport carrier or to using hexaphenyl-HAT in the electron transport layer.

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