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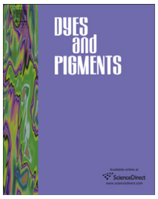

Photophysical properties of acid-responsive triphenylamine derivatives bearing pyridine fragments: Towards white light emission

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ABSTRACT

The synthesis, thermal, electrochemical, and optical properties of a series of triphenylamine derivatives bearing pyridine fragments and their trifluoroacetate salts are described. A dramatic increase in the intramolecular charge transfer is observed upon protonation, as evidenced by a significant reduction in the HOMO-LUMO gap and a red shift of both the absorption and the emission band. White photoluminescence was obtained in solution by the controlled protonation of blue emitting pyridine derivatives, which resulted in the yellow-orange emissive acidified form. In the solid state the emission color of doped polystyrene thin films could be tuned from steel blue to lawn green when the ratio of the protonated form was increased. These compounds have potential applications in the fabrication of multicolor OLEDs based on only one material.

1. Introduction

In the past decade there has been great interest in the development of white light emitting systems [1,2]. The recent commercialization of White Organic Light Emitting Diodes (WOLEDs), first reported by Kido [3,4], has been the subject of numerous studies. When compared to their inorganic counterparts, all-organic light emitting molecules have advantages such as lower cost, easy fine tuning of the solution processability, low toxicity, and sufficient flexibility for device fabrication [2,5–7]. White light can be obtained by mixing three primary color emitters (red, green, and blue). Mixing two complementary color emitters in appropriate proportions can also generate white light. White emission was defined by the Commission Internationale d'Eclairage standard colorimetric system (CIE 1931) and it corresponds to color coordinates close to the Plankian locus around the equi-energy white point ($x = 0.33$, $y = 0.33$) [2,8].

White light is generally obtained by the combination of independent chromophores, but a new strategy has recently been proposed that involves the use of two different forms of the same chromophore in equilibrium. The two forms should exhibit complementary emitting colors and can consist of monomer/excimer [9–11], neutral/(de)protonated species [12–17], Lewis base/adduct [16] or free/complexed ligand [18].

Nitrogen-based π-deficient heterocycles such as pyridine [19–21], pyrimidine [22–25], pyrazine [26,27], quinazoline [12,28] or benzimidazole [19,29] can be used as the electron-withdrawing unit in push-pull luminophores. Protonation [12,22,26,27,30–33], complexation [18,34–36] or alkylation [33,36,37] of such heterocycles enhances their electron-withdrawing character by engaging nitrogen electron lone pairs, thus increasing the intramolecular charge transfer (ICT). This process can lead to emission quenching,

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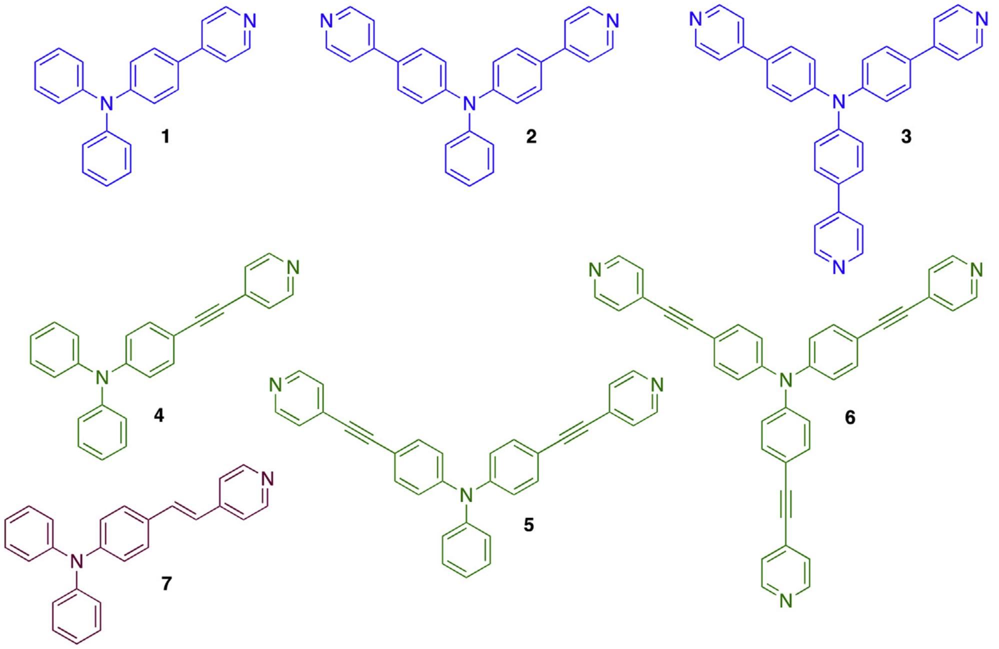
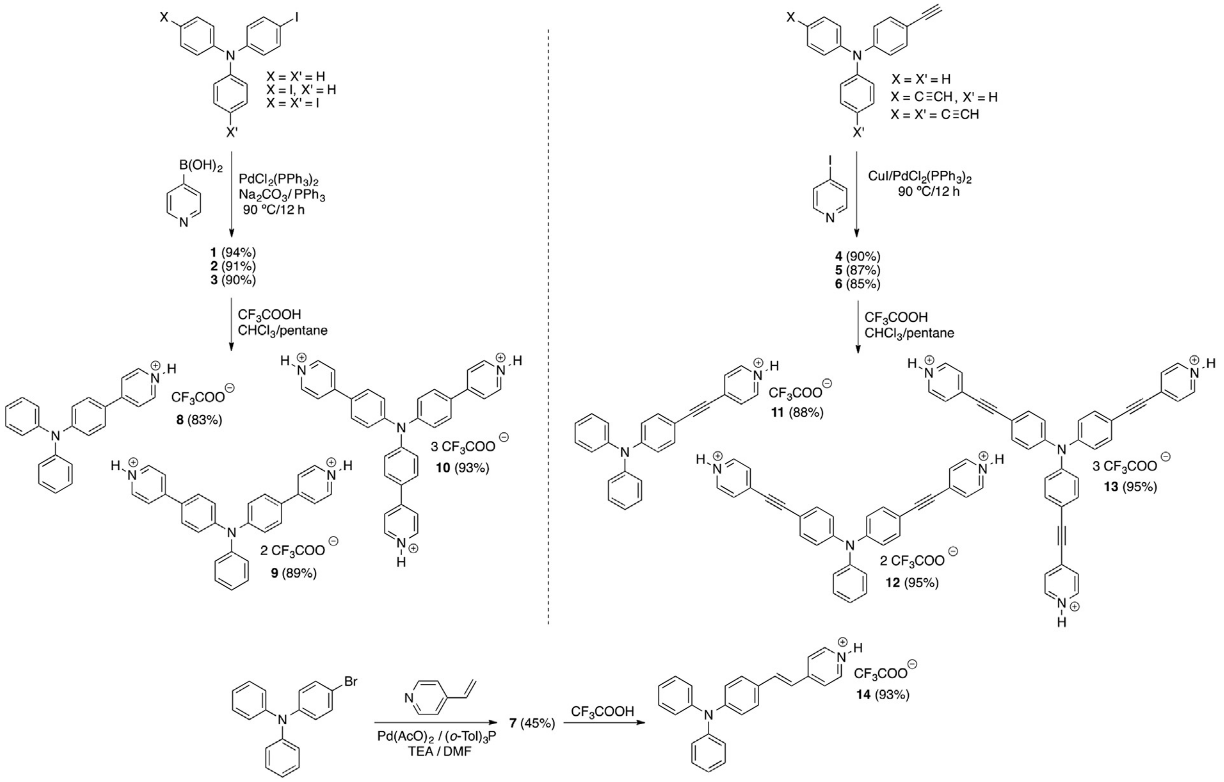


Chart 1. Structure of studied chromophores.

but in some cases red shifted emission is observed [12,22,30–33]. Recently, we described white light emission, both in solution and in thin films, from mixtures of neutral and protonated forms of methoxy-substituted pyrimidine derivatives [38,39].

The triphenylamine (TPA) fragment can be used as a moderate electron-donating unit in push-pull luminophores. Such compounds have been used for their sensing activities *versus* metal cations [40–42], cyanide [43–45], water [46] or nitro aromatic explosives [47–50]. The TPA moiety has been extensively used in the design of two photon excited fluorophores [51–55], mainly for bioimaging applications [56–59]. Moreover, TPA derivatives are known to exhibit aggregation-induced emission properties [46,60,61] and some of these systems have been used in a range of electroluminescent devices [62–64].



Scheme 1. Synthesis of compounds **1**–**14**.