

Synthesis, spectroscopy, and electrochemistry of ionic hosts for organic electronics



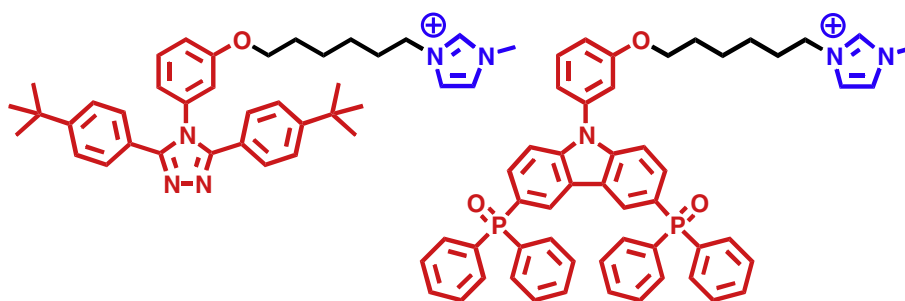
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HIGHLIGHTS

- New charge- and ion-transport ionic hosts.
- The hosts are imidazolium-cation-modified heterocycle chromophores.
- The hosts exhibit high-energy optical gap and a wide redox gap.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on charge- and ion-transport ionic hosts made from an imidazolium-cation-modified aryl-1,2,4-triazole, phosphineoxide-carbazole, and phosphineoxide. The hosts are white solids that have short-wavelength absorption cut-off at <355 nm (high-energy optical gap of >28,200 cm⁻¹) and that exhibit oxidation at <1.44 V and reduction at >(-2.75) V against ferrocene with a wide redox gap of >3.9 V.

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Introduction

Host (matrix) materials are used in organic light-emitting diodes (OLED) to facilitate the transport of charges (holes and electrons) and to dilute the emitter in order to prevent its aggregation and concentration quenching of its luminescence [1–8]. The host, often a neutral polar organic heterocycle or a neutral/charged metal complex [1–7], must have suitable redox potentials and

sufficiently high energy of excited states to avoid dissipative energy- and charge-transfer processes between the host and the emitter. Ionic liquids are used in organic electronics to facilitate the transport of ions [9]. Recently, we successfully applied an ionic charge-transport carbazole host in blue light-emitting electrochemical cells (LEC) to transport both the holes and the ions in the device [8].

Here, we describe new charge- and ion-transport ionic hosts made from an imidazolium-cation-modified aryl-1,2,4-triazole (H1), phosphineoxide-carbazole (H2), and phosphineoxide (H3) (Schemes 1–3).

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Results and discussion

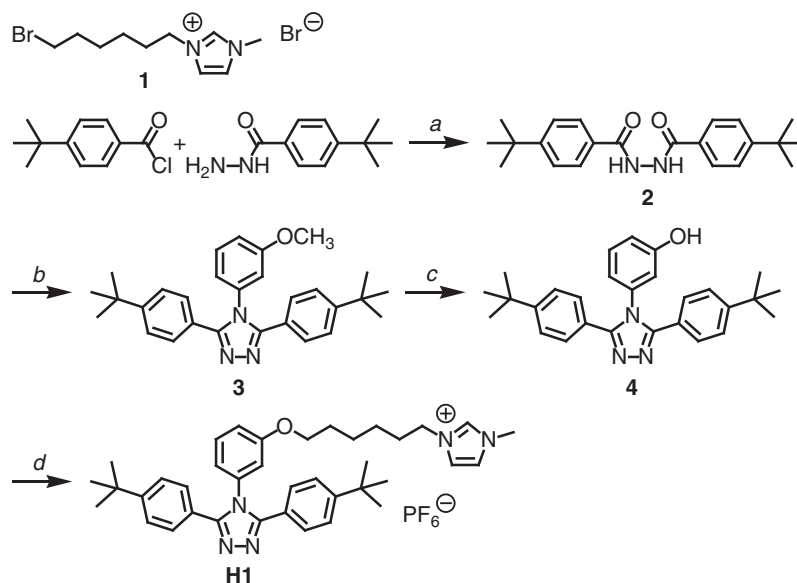
The multi-step syntheses of the hosts **H1**–**H3** are summarized in Schemes 1–3.

The aryl-1,2,4-triazole **3** was prepared by cyclization of the hydrazide **2** with 3-anisidine and PCl_3 (Scheme 1) [2]. The *tert*-butyl groups improve solubility of **3**. The aryl-carbazole **5** was obtained by a copper-catalyzed C–N coupling of 3,6-dibromocarbazole with 3-iodoanisole (Scheme 2) [10,11]. The side-reactions in the synthesis of **5** are de-bromination and oligomerization (self C–N coupling); however, low temperature favors the desired C–N coupling. Lithiation of **5** with *n*-butyllithium, quenching with chlorodiphenylphosphine, and oxidation of the crude phosphine to phosphineoxide with

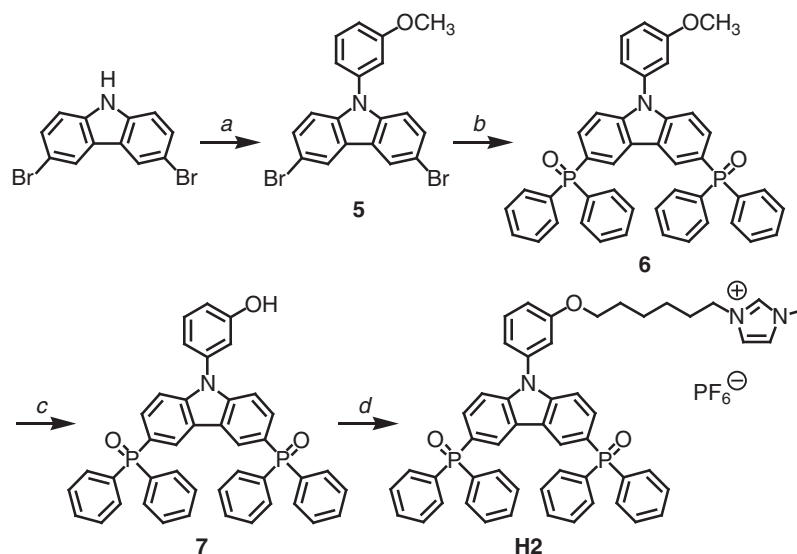
hydrogen peroxide gave **6** (Scheme 2). We note that neutral polar heterocycles **3** and **6** themselves may be used as hosts in organic electronics [2,5–7].

The anisole group of **3** and **6** was converted to a phenol by deprotection with pyridine hydrochloride [8] or with BBr_3 [12] (Schemes 1 and 2). The phenols **4** and **7** are soluble in dichloromethane when they are freshly prepared, but become insoluble when they are dried and aged. The insolubility likely arises from the formation of a network of hydrogen bonds between the hydroxyl group of the phenol and the imine bonds between the hydroxyl group of the phenol and the imine nitrogen of the 1,2,4-triazole in **4** or the oxygen of the phosphineoxide in **7**.

The phenols **4** and **7** were alkylated with imidazolium salt **1** [8] to give new ionic hosts **H1** and **H2** as hexafluorophosphate salts after the anion exchange (Schemes 1 and 2). The side-products



Scheme 1. Synthesis of **H1**: (a) THF/pyridine, under Ar, room temperature; (b) 1,2-dichlorobenzene, PCl_3 , 3-anisidine, under Ar, 100–200 °C; (c) pyridine hydrochloride, under Ar, 200 °C; (d) (i) **1**, K_2CO_3 , DMF, under Ar, 50–60 °C; (d) (ii) KPF_6 , room temperature.



Scheme 2. Synthesis of **H2**: (a) 3-iodoanisole, Cs_2CO_3 , Cu_2O , DMF, under Ar, 120 °C; (a) [preferred alternative] 3-iodoanisole, K_3PO_4 , CuI , (\pm)-*trans*-1,2-diaminocyclohexane, 1,4-dioxane, under Ar, 110 °C; (b) (i) *n*-butyllithium, chlorodiphenylphosphine, THF, under Ar, –78 °C to room temperature; (b) (ii) hydrogen peroxide, CH_2Cl_2 , under air, 0 °C to room temperature; (c) BBr_3 , CH_2Cl_2 , under Ar, 0 °C to room temperature; (d) (i) **1**, K_2CO_3 , DMF, under Ar, 60 °C; (d) (ii) KPF_6 , room temperature.

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