Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

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



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

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

ARTICLE INFO

Received 16 September 2014

Available online 22 October 2014

Accepted 15 October 2014

Received in revised form 14 October 2014

Article history:

Keywords: Heterocycle Ionic liquid Charge transport Chromophore Spectroscopy Electrochemistry



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 PCl₃ (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) of 3,6-dibromocarbazole; 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 BBr₃ [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 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, PCl₃, 3-anisidine, under Ar, 100–200 °C; (c) pyridine hydrochloride, under Ar, 200 °C; (d) (i) 1, K₂CO₃, DMF, under Ar, 50–60 °C; (d) (ii) KPF₆, room temperature.



Scheme 2. Synthesis of H2: (a) 3-iodoanisole, Cs₂CO₃, Cu₂O, DMF, under Ar, 120 °C; (a) [preferred alternative] 3-iodoanisole, K₃PO₄, Cul, (±)-*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, CH₂Cl₂, under air, 0 °C to room temperature; (c) BBr₃, CH₂Cl₂, under Ar, 0 °C to room temperature; (d) (i) 1, K₂CO₃, DMF, under Ar, 60 °C; (d) (ii) KPF₆, room temperature.



Scheme 3. Synthesis of H3: (a) neat, room temperature; (b) (i) Mg, chlorodiphenylphosphine, THF, under Ar, room temperature to reflux; (b) (ii) hydrogen peroxide, CH₂Cl₂, under air, 0 °C to room temperature; (d) (i) 8, K₂CO₃, DMF, under Ar, 60 °C; (d) (ii) KPF₆, room temperature.

that are observed in the synthesis of **H1** likely originate from N-alkylation or the N4-to-N1 substitution rearrangement [13] of the 1,2,4-triazole; however, low temperature and the excess of base favor the desired O-alkylation of the phenol.

We modified the hosts with an imidazolium cation because it has high-energy excited states and it is electrochemically-inert [9] (it is often used to make ionic liquids). The *m*-substitution in the "anisole" disrupts the conjugation, while a hexyloxy chain makes the hosts hydrophobic, increases their solubility in organic solvents, and minimizes interaction of the imidazolium cation with the core of the host.

The hosts were purified by chromatography and by recrystallization. They were characterized by elemental analysis and by ¹H and ³¹P NMR spectroscopy. Their ESI⁺ mass-spectra display the cation $\{M-PF_6\}^+$. The purity of the ionic hosts is not likely to be a limiting factor in solution-processed organic electronics devices that use polymers or charged metal complexes, which themselves cannot be vacuum-processed by sublimation [8].

The hosts are white solids. They are soluble in polar organic solvents and have absorption cut-off (optical gap) at short wavelength (high energy) at 330 nm (30,300 cm⁻¹) for **H1** and at 355 nm (28,200 cm⁻¹) for **H2** in dichloromethane (Fig. 1 and Table 1). Replacement of the 1,2,4-triazole with the carbazole chromophore [3,14] red-shifts the absorption spectrum from **H1** to **H2**.

In cyclic voltammetry (CV), the ionic hosts undergo oxidation and reduction processes that are irreversible at scan rates of 0.1-1 V/s in acetonitrile on glassy-carbon electrode (Fig. 2 and Table 1). The redox irreversibility in the CV experiment does not necessarily mean that the host will not function in the device.

The oxidation process is localized on the "anisole" fragment of **H1** and on the "anisole-carbazole" of **H2** [3,8]; the reduction—on the 1,2,4-triazole of **H1** [2] (it is accompanied by adsorption on the electrode) and on the phosphineoxide of **H2** [4–7]. Unlike the previously reported hole-transport ionic host that exhibits reduction at 0.77 V but no oxidation to -2.7 V against ferrocene [8], the new ionic hosts exhibit both the reduction and the oxidation and, therefore, are probably ambipolar, that is, they may support the transport of both the electrons (through the 1,2,4-triazole [2])



Fig. 1. Absorption spectra of H1 $(1.36\times10^{-4}\,M)$ and H2 $(9.98\times10^{-5}\,M)$ in dichloromethane.

 Table 1

 Absorption and redox properties.

	$\lambda_{\rm abs}/{\rm nm}~(\epsilon/10^3~{\rm M}^{-1}~{\rm cm}^{-1})^{\rm a}$	$E^{\mathrm{ox}}/V^{\mathrm{b}}$	$E^{\rm red}/V^{\rm b}$
H1	272 (25)	1.44	<(-2.5)
H2	254 (58), 278 (57), 327 (3.8), 341 (2.6)	1.28	-2.75

^a See Fig. 1. In dichloromethane at room temperature. At 250–500 nm. Errors: $\lambda_{abs}, \pm 2$ nm; $\epsilon, \pm 5\%$.

^b See Fig. 2. Irreversible processes. At scan rates of 0.1-1 V/s in acetonitrile with 0.1 M NBu₄PF₆ on glassy-carbon working electrode. Peak potentials are reported relative to the ferrocene couple at 0.1 V/s.

and the phosphineoxide [4-7]) and the holes (through the "anisole" and the carbazole [3,8]). In fact, the neutral analogs of **H2** are known to be ambipolar hosts [5-7].

The redox gap ($\Delta E_{\rm R} = E^{\rm ox} - E^{\rm red}$; >3.94 V for **H1**; 4.03 V for **H2**) and optical gap (>28,200 cm⁻¹) of the new hosts are large enough for blue-fluorescent emitters; however, these parameters may need



Fig. 2. Cyclic voltammograms of H1 and H2 on glassy-carbon electrode in acetonitrile with 0.1 M $\rm NBu_4PF_6$ at 0.1 V/s on clockwise scan. The unit on the vertical axis is 5 $\mu A.$

to be increased to make the hosts suitable for blue-phosphorescent emitters. In addition, the non-polar aliphatic *n*-hexyl bridge and *tert*-butyl group of **H1** and **H2** may inhibit ion- and charge-transport.

In order to increase the polarity and to widen the redox and optical gaps of the ionic host, we designed H3, in which the charge-transport "anisole-phosphineoxide" core [4] is connected to the ion-transport imidazolium cation by a short *n*-propyl bridge (Scheme 3). The reaction of the Grignard reagent (made from magnesium and 3-bromoanisole) with chlorodiphenylphosphine, followed by oxidation of the crude phosphine with hydrogen peroxide gave phosphineoxide 9 [15]. Deprotection of the anisole group of **9** with BBr₃ [12] gave phenol **10** [15] that was alkylated with a mixture of imidazolium salts 8 [16] to give, after the anion exchange, the ionic host H3 as a white hygroscopic solid (Scheme 3). It was characterized by elemental analysis, by ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectroscopy, and by ESI⁺ mass-spectrum, in which the cation $\{M-PF_6\}^+$ was observed. The phenol 10 and the host H3 are insoluble in dichloromethane when they are aged. The high hygroscopicity of H3 and its low solubility in organic solvents confirmed its high polarity, but made difficult its further investigation.

In conclusion, the high energy of the excited states and the potentially ambipolar charge-transport properties make the new ionic hosts suitable for blue-luminescent OLED [17] and LEC [18]. The charged organic heterocycles, similar to the ones described here, with easy-to-adjust optical and redox properties, may find use as charge- and ion-transporters in organic electronics devices with host-guest architecture [1–8,17,18]; as ligands in metal coordination chemistry [19]; and as functional ions in ionic liquids and in "soft salts" [20].

Acknowledgement

European Union (CELLO, STRP 248043).

Appendix A. Supplementary material

Experimental techniques, syntheses and characterization, and NMR spectra. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.10.034.

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