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Non-amine-based furan-containing oligoaryls as efficient hole transporting materials†

Ling-Zhi Zhang,[a] Chieh-Wei Chen,[b] Chin-Fa Lee,[ac] Chung-Chih Wu*[b] and Tien-Yau Luh*[ac]
[a] *Department of Chemistry, National Taiwan University, Taipei, Taiwan 106*
[b] *Department of Electrical Engineering, Graduate Institute of Electro-optical Engineering and Electronics Engineering, National Taiwan University, Taipei, Taiwan 106*
[c] *Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115. E-mail: tyluh@chem.sinica.edu.tw; Fax: +886-2-2651-1488; Tel: +886-2-2789-8500*

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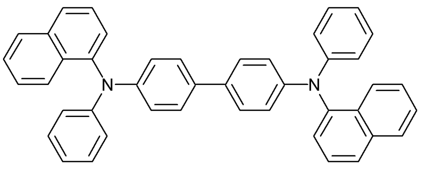
A new class of highly stable furan-based hole transporting oligomeric materials, synthesized from the corresponding propargylic dithioacetals, serve as efficient hole transporting materials in electroluminescent devices. The performance of the devices using these furan materials is comparable with or somewhat better than those employing the conventional triarylamines (*e.g.* α-NPD).

Triarylamines, such as α-NPD (4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl, **1**), have been extensively employed as the hole transporting (HT) material in OLEDs (organic light emitting devices) covering a wide range of wavelengths and generating very bright emission.[1–7] The use of oligoaryls such as thiophene derivatives in optoelectronic applications abounds,[8] whereas the corresponding furan-containing oligomers or polymers have been only sporadically explored.[9–12] It is interesting to note that furan has a similar HOMO energy level and a relatively high lying LUMO energy level in comparison with those of thiophene.[13] We felt that these properties could be used in electroluminescent applications.



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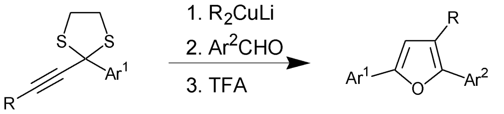
We recently reported a convenient synthesis of 2,3,5-trisubstituted furans from the corresponding propargylic dithioacetals (eqn. 1).[14] According to this protocol, a series of penta- and hexaaryls containing symmetrically two furan moieties **2a–c** were synthesized.‡ The physical properties of **2a–c** are compared with those of **1** and tris(8-oxyquinoline)aluminium (Alq_3) (Table 1). A thin film of **2a–c** on glass or a NaCl pellet was thermally stable, no decomposition being observed at 300 °C. Neither weight loss nor spectroscopic variation (NMR, IR, UV-vis, and fluorescence) was observed when the samples, under nitrogen atmosphere, were heated at 200 °C for 24 h or irradiated with a 200 W sunlamp at 150 °C for 24 h. The solid samples **2a–c** remained intact under ambient conditions for over one year. A solution of **2a–c** (*e.g.* in $CHCl_3$) was stable at room temperature in the dark, but decomposed slowly in the presence of ambient light.



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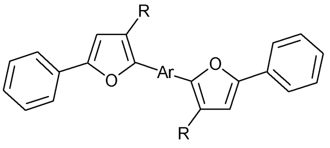
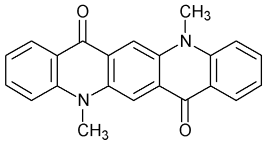


2a Ar = $-C_6H_4-$, R = Ph
2b Ar = $-C_6H_4-C_6H_4-$, R = Ph
2c Ar = $-C_6H_4-C_6H_4-$, R = Bu



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These furan-containing oligoaryls showed bright fluorescence in the blue light region with quantum yields in the range of 0.91–0.95. The emission frequencies for **2a–c** exhibited slight red shifts in the solid in comparison with those in solution.

Compounds **2a–c** showed a reversible two-electron redox wave as examined by cyclic voltammetry (Table 1). As expected, the electron donating butyl substituent may cause a reduction in the oxidation potential. The first oxidation potential for pentaaryl **2a** was somewhat lower than those for hexaaryls **2b** and **c** and the reverse was true for the second oxidation potentials. Similar redox behavior of diphenyl-α-oligopyrroles has been reported.[15]

Based on the electrochemical and photophysical data, the HOMO and LUMO energy levels of **2a–c** were estimated, and they fit very well with the frontier orbital energies for Alq_3. Typical electroluminescent results are outlined in Table 2. A

Table 1 Physical properties of **2** and related compounds

Compd.	T_g	T_c	$T_d{}^a$	λ_{max}/nm^b	λ_{em}/nm^b	$\Phi_f{}^c$	E_1/mV	E_2/mV^d	$E_{ox}{}^{1/2}$/mV^d	HOMO/eV	LUMO/eV
2a	88	98	308	245, 383 (253, 395)	439, 457 (461, 480)	0.91	596	866	548	5.35	2.45
2b	96	na^e	434	244, 374 (245, 375)	436, 459 (450, 478)	0.92	675	793	645	5.45	2.51
2c	23	73	339	240, 368 (238, 371)	424, 448 (440, 464)	0.95	612	788	550	5.35	2.34
1	102	179	382	273, 342 (345)	463 (441)	0.16	349	623	297	5.10	2.02
Alq_3				262, 388 (262, 395)	503 (520)					5.86	3.05

[a] Decomposition temperature at 5% weight loss measured by TGA under N_2 atmosphere. [b] Measured in $CHCl_3$ solution and in solid form (values for solid in parentheses). [c] Quantum yield obtained relative to Coumarin I. [d] Measured in CH_2Cl_2, all oxidation potentials are relative to ferrocene/ferrocenium half cell. [e] na: not available.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b207489c/

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Table 2 Electroluminescence data for the compounds

Device^a	λ_{EL}/nm	$V_{\mathrm{on}}{}^b$	$V_{20}{}^c$	$V_{\max}{}^d$	$B_{20}{}^e$	$B_{\max}{}^f$	$\eta_{20}{}^g$	$\eta_{\max}{}^h$	lm/W$_{20}{}^i$	lm/W$_{\max}{}^j$
1	476	4.3	8.3	11.5	7	260	0.1	0.2	0.1	0.3
2	530	2.5	8.3	12.0	770	18 600	1.2	1.3	1.5	1.6
3	540	2.5	11.5	16.0	750	16 100	1.2	1.3	1.0	1.1
4	538	2.5	9.6	12.5	1050	9000	1.7	1.8	2.1	2.2
5	532	2.5	9.0	13.0	740	16 650	1.2	1.4	1.3	1.4
6	535	2.0	6.8	11.5	870	30 400	1.4	1.5	2.1	3.6
7	537	2.0	6.8	12.0	710	30 800	1.2	1.3	1.6	2.7
8	542, 578	2.0	7.9	18.0	2050	182 800	2.8	2.8	4.1	10.1
9	542, 578	2.0	8.4		1970	180 400	2.6	2.7	3.8	9.3

^{a} Device configurations (thickness of each layer is described in the text): device 1: ITO/PEDT:PSS/**2a**/Mg:Ag/Ag; devices 2–5: ITO/PEDT:PSS/HTL/Alq$_3$/Mg:Ag/Ag (HTL for device 2: **2a**; device 3: **2b**; device 4: **2c**; device 5: **1**); devices 6–7: ITO/PEDT:PSS/HTL/Alq$_3$/LiF/Al (HTL for device 6: **2a**; device 7: **1**); devices 8–9: ITO/PEDT:PSS/HTL/Alq$_3$:**3**/Alq$_3$/LiF/Al (HTL for device 8: **2a**; device 9: **1**). ^{b} Turn-on voltage (V) at which emission starts to be detectable. ^{c} Voltage (V) taken at a current density of 20 mA cm^{-2}. ^{d} Voltage (V) at the maximum brightness. ^{e} Brightness (cd m^{-2}) taken at V_{20}. ^{f} Maximal brightness. ^{g} External quantum efficiency at 20 mA cm^{-2}. ^{h} Maximal external quantum efficiency. ^{i} Luminous efficiency at 20 mA cm^{-2}. ^{j} Maximal luminous efficiency.

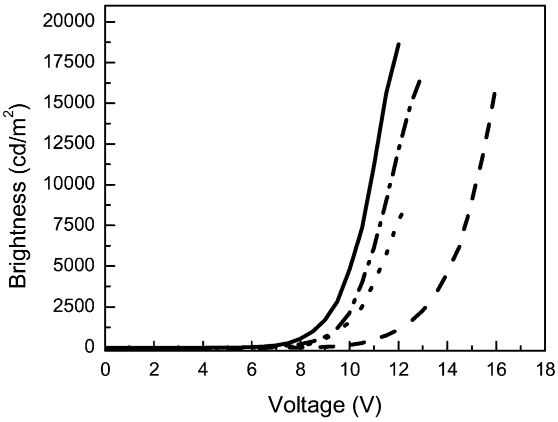

Fig. 1 A comparison of the performance of devices 2–5 with theconfiguration ITO/PEDT:PSS/HTL (40 nm)/Alq3 (60 nm)/Mg:Ag(800 nm)/Ag (150 nm), where HTL is **2a** (device 2, solid line), or **2b** (device 3, dash line), or **2c** (device 4, dotted line) or **1** (device 5, dash-dotted line).

single layer device constituted of ITO/PEDT:PSS/**2a** (120 nm)/Mg:Ag (800 nm)/Ag (150 nm) (device 1), exhibited a blue emission at 476 nm.[16] Double layered devices with the configuration ITO/PEDT:PSS/HTL (40 nm)/Alq$_3$ (60 nm)/Mg:Ag (800 nm)/Ag (150 nm) were fabricated. The HT materials used here were **2a–c** (devices 2–4) and **1** (device 5). The brightness–voltage curves are compared in Fig. 1. All of the devices exhibited typical emission of Alq$_3$ at *ca*. 535 nm having similar turn-on voltage and external quantum efficiency.

When LiF/Al was used as the cathode in the devices with the configuration ITO/PEDT:PSS/HTL (40 nm)/Alq$_3$ (60 nm)/LiF (0.5 nm)/Al (150 nm), where HTL was either **2a** (device 6) or **1** (device 7), the turn-on voltages were lowered to 2.0 V. The external quantum efficiency of device 6 was 1.5% and the maximum brightness for both devices 6 and 7 was increased to 3 × 10^4 cd m^{-2}.

When *N*,*N*-dimethylquinacridone (DMQA **3**) was employed as the dopant,[17] multilayer devices ITO/PEDT:PSS/HTL (40 nm)/Alq$_3$:**3** (20 nm)/Alq$_3$ (40 nm)/LiF (0.5 nm)/Al (150 nm), where HTL was either **2a** (device 8) or **1** (device 9), were fabricated. The optimal concentration of **3** in Alq$_3$ was found to be 0.5%, providing an external quantum efficiency of 2.8% and a maximum luminance of 182 800 cd m^{-2} at 18 V for device 8. The external quantum efficiency and the maximal luminance for device 9 were 2.7% and 180 200 cd m^{-2} at 19.5 V, respectively.

In summary, we have depicted, for the first time, a new class of highly stable furan-based hole transporting oligomeric materials for electroluminescent devices. The performance of the devices by using these furan materials appeared to be comparable with or somewhat better than those employing the conventional α-NPD **1**.

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Notes and references

‡ All new compounds gave satisfactory spectroscopic and analytical data. The details are described in the ESI.†

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