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Vapor-Phase Processable Novel Nonplanar Donor−Acceptor Quaterayls for Blue OLEDs[#]

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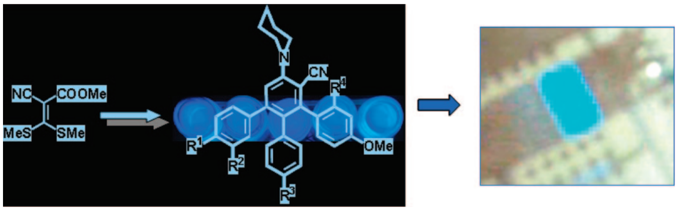
ABSTRACT



A novel series of thermally stable blue light emitting quaterayls with a piperidine donor and a nitrile acceptor was prepared from a ketene-*S*,*S*-acetal under mild conditions without using an organometal catalyst. The performance of a blue quaterayl 6e was investigated by fabricating a multilayer OLED with a configuration of ITO/PEDOT:PSS (40 nm)/quaterayl (60 nm)/BCP (6 nm)/Alq_3 (20 nm)/LiF (0.5 nm)/Al (200 nm), which exhibited blue emission with a low turn on voltage of 4 V at a brightness of 0.22 cd/m^2.

Small organic light emitting diode (OLED) displays such as displays of mobile phones, mp3 players, and car radios are on the verge of establishing themselves in the market with great potential to expand in the near future. For full-color flat-panel displays, three primary colors, red, green, and blue, with equal performance are required.[1] Several green and red light emitting organic molecules are commercially available; however, substances suitable for long-term use as blue light emitters are still far from the standards of color purity and thermal stability.[2]

For blue OLEDs, several tailor-made multiple π-conjugated molecular architectures such as spiro- (**I**, spirofluorenes),[3] ladder- (**II**, biphenalenes, phenylenes),[4] and polyfluorene[5] dendritic systems (**III**) have been synthesized (Figure 1). Among them, fluorene-based oligomers and polymers are the most promising family of blue light emitters, but they are prone to oxidation (keto defect or

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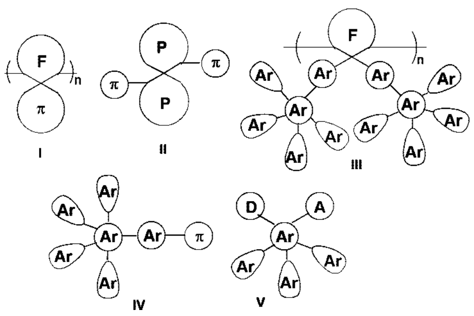

Figure 1. Various π-conjugated frameworks for blue light emitting materials (**I**−**III**), small molecule polyphenylphenyl dendron (**IV**), and new donor−acceptor quateraryl (**V**). F, fluorenyl; P, phenalenyl; Ar, aryl; D, donor; A, acceptor.

green-emission defect)[6] resulting in an additional undesirable low-energy broadband in the EL spectrum, which not only reduces emission efficiency but also destroys the blue color purity.[6] The blue light emitting materials generally have a low affinity for the electrons from the cathode in OLEDs due to the large band gap energy. Recently Komatsu and co-workers[7] elucidated electronic properties of fluorene having a radical cation and dication through computational and experimental studies, which provided insights for low electrical conductivity observed for poly(2,7-fluorene)s. Therefore, new chemical entities that may overcome the drawbacks of existing blue light emitters are urgently required for preparing B-OLEDs.

Recently, a great deal of attention has been focused on synthesizing small molecule polyphenylphenyl dendrons (**IV**) for preparing B-OLEDs.[8] Studies have also shown that the presence of strong electron-donating *N*,*N*-dialkylamine functionalities in π-conjugated materials enhances the device efficiency by elevating the HOMO energy levels of the molecules for ease of hole injection/transporting in the film,[8] and the presence of the cyano group influences photophysical and electroluminescent properties by lowering the energy of the LUMO, thus exhibiting a relatively low threshold voltage and high quantum efficiency in LED devices.[9] Considering these aspects, we designed quateraryls (**V**) functionalized with amine donor and nitrile acceptor moieties and examined their optical properties. In this letter, we report a new series of thermally stable donor−acceptor nonplanar quateraryls and their potential use in preparing multilayer blue OLED devices.

Benzene rings functionalized with polyaryl groups have been synthesized either by the coupling of biaryltriflate compounds with Grignard reagents in the presence of a palladium catalyst in moderate to good yields[10] or by the iterative coupling of aryl boronic acid with aromatic halides[11] separately. However, it has been observed that iterative coupling on functionally crowded aryl trihalides to prepare triarylated-benzene compounds places constraints on the choice of reagents/catalysts.[12] Our aim to prepare blue light emitting compounds with donor−acceptor groups was achieved by preparing a key intermediate α-oxo-ketene-*S*,*S*-acetal[13] **1** from easily accessible precursors methyl cyanoacetate, carbon disulfide, and methyl iodide, following the Tominaga protocol.[14] Substrate **1**, on Michael addition−cyclization reaction with various substituted acetophenones **2a**−**e** under alkaline conditions, furnished 6-aryl-2*H*-pyran-2-ones **3a**−**e** in excellent yields (Scheme 1). In order to prepare compounds with *N*,*N*-dialkylamino functionality, a good leaving methylsulfanyl group of lactones **3a**−**e** was replaced with an amine (piperidine) to furnish 6-aryl-2-oxo-4-piperidin-1-yl-2*H*-pyran-3-carbonitriles (**4a**−**e**) in good yields. These compounds **4a**−**e** were reacted with functionalized deoxybenzoins **5** to yield 5′-(piperidin-1-yl)-[1,1′;2′,1″;3′,1‴]quaterphenyl-4′-carbonitriles (**6a**−**e**) in excellent yields (Scheme 1).

A plausible mechanism, depicted in Scheme 2, suggests that the reaction is initiated by the Michael addition of an anion, generated from a molecule of deoxybenzoin **5**, to the 2*H*-pyran-2-one **4** followed by intramolecular cyclization to form a bicyclic intermediate. This bicyclic intermediate on decarboxylation, protonation, and dehydration furnished quateraryl **6** in excellent yield.

To examine the solid state molecular organization, the crystallizations of these quateraryls in various solvent systems were attempted. All the quateraryls except **6c** were amorphous substances. The X-ray structural analysis of compound **6c** (Figure 2) revealed that the aryl rings are arranged

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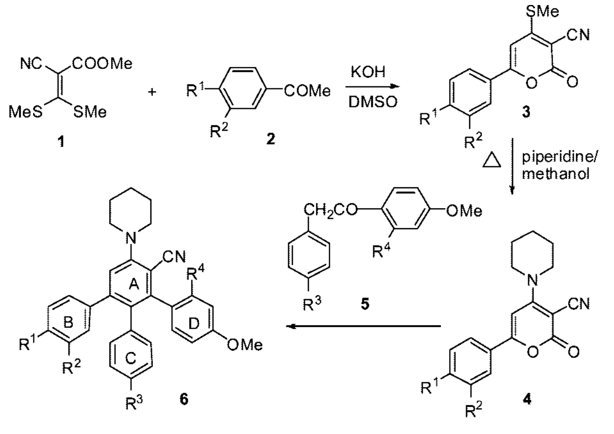
Scheme 1. Synthesis of Quaterarylys



entry	R^1	R^2	R^3	R^4	yield[a] (%)
6a	OMe	H	OMe	H	90
6b	Br	H	OMe	H	89
6c	Me	H	OMe	H	91
6d	-OCH$_2$O-		OMe	H	85
6e	H	H	H	OH	94

[a] Yields calculated with respect to compound **4**

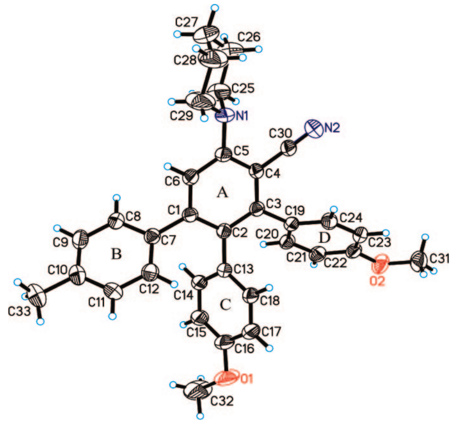


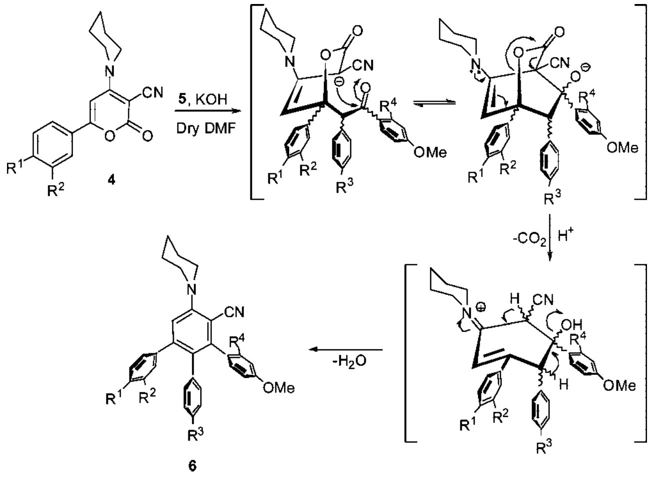
Figure 2. ORTEP diagram of **6c** with a thermal ellipsoid plot (50% probablity).

cofacially in a half-circular array around the central benzene ring. The mean plane angles for the twist of the peripheral phenyl rings B, C, and D from the plane of the central benzene ring A are 47.9°, 64.1°, and 54.5°, respectively, with an average twist of 55.49°, giving each molecule a propeller conformation. The crystal packing showed weak C−H···π interactions, but no π−π interaction was observed, which supports developing nonplanar molecular blocks.

Figure 3 shows the normalized UV−vis and PL spectra of quaterarylys (**6a**−**e**). Table 1 shows the $\lambda_{\max}$ of their UV and fluorescence spectral data along with the extinction coefficient, Stokes shift and the fluorescent quantum yield of quaterarylys **6a**−**e** in tetrahydrofuran solution. The different fluorophoric groups at the *para*-position of the peripheral B-phenyl ring of the quaterarylys (**6a**−**d**) did not make any remarkable difference in the longest absorption maximum (345−351 nm). A strong red shift (>50 nm) was observed when a hydroxy group was attached at position 2 of the peripheral D-phenyl ring (**6e**, 406 nm). The increase in the wavelength and intensity of aborption of **6e** may be due to the presence of an auxochrome (OH) directly in conjugation with the π-system of the chromophore.

The thermal properties of quaterarylys were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compound **6e** exhibited good thermal stability, showing less than 5% decomposition up to 300 °C under nitrogen and losing about 50% weight at about 360 °C. In the DSC, **6e** showed a melting temperature (T_m) of 215.91 °C in the first heating scan at the rate of 5 °C/min. Rapid cooling at the rate of 25 °C/min to room temperature and subsequent slow heating scans detected a

Scheme 2. Plausible Reaction Mechanism



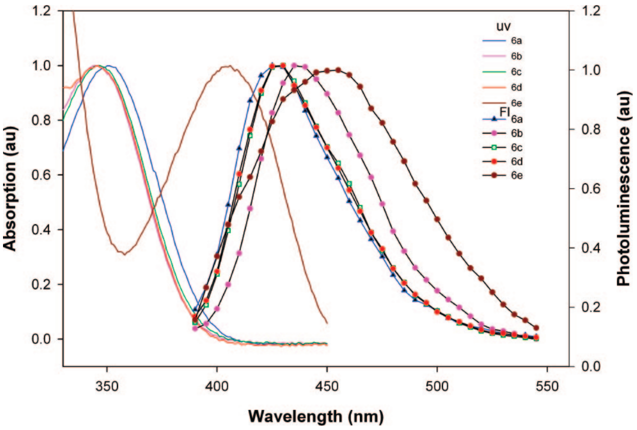


Figure 3. Normalized absorbance and fluorescence spectra of quaterarylys **6a**−**e** in THF (~10^{-5} M).

Table 1. Photophysical Properties of Quateraryls **6a−e**

compd	$\lambda_{\mathrm{max;abs}}$ (nm)^a	ϵ ($\times 10^4$ M^{-1} cm^{-1})^b	$\lambda_{\mathrm{max;em}}$ (nm)^c	$\Delta\bar{\nu}$ (cm^{-1})^d	T_m (°C)^e	Φ^f
6a	351	2.80	424	4900	171	0.48
6b	345	2.85	433	5900	194	0.38
6c	347	2.97	429	5500	157	0.43
6d	346	2.61	425	5400	173	0.45
6e	406	1.39	447	2300	216	0.51

^{a} Longest wavelength absorption maximum. ^{b} Molar extinction coefficients. ^{c} Fluorescence emission maximum. ^{d} Stokes shift. ^{e} Melting temperatures by DSC. ^{f} Fluorescence quantum yield relative to harmine in 0.1 M H_2SO_4 as a standard ($\Phi = 0.45$).

signal of >200 °C corresponding to the glass transition temperature (T_g). The high T_g is likely to be good for long lifespan device operations. Compounds **6a−e** produced efficient blue fluorescence and exhibited good fluorescent quantum yields[15] (Φ, 0.38−0.51).

Multilayer devices were fabricated to investigate the performance of a blue light emitting material (**6e**) with the device configuration of ITO/PEDOT:PSS (40 nm)/quateraryl **6e** (60nm)/BCP (6 nm)/Alq_3 (20 nm)/LiF (0.5 nm)/Al (200 nm). The patterned ITO glass plate was cleaned in 6:1:1 RCA-I solution, rinsed in DI water a number of times, and then dried. The ITO surface was treated in ozone for 15 min. Immediately, the first layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated on the patterned ITO to form a hole injection layer. The PEDOT-PSS was vaccuum-dried at 120 °C for 1 h. All other organic layers and metal layers were sublimed in high vacuum ($\sim 1-5 \times 10^{-6}$ mbar). Then the devices were sealed with a covering glass plate using UV epoxy. The ILV characteristics of the sealed devices were obtained using the Keithley source-measure unit. EL spectra were recorded with an Ocean Optics USB2000 miniature fiber optic spectrometer.

The current density−voltage and luminance−voltage characteristics for a device of **6e** are plotted in Figure 4, and the EL spectra of **6e** are shown as an insert. The turn on voltage (at a brightness of 0.22 cd/m^2) of **6e** is 4 V. The EL spectrum of **6e** shows a sharp peak emission at 489 nm, with the CIE coordinates of (0.2358, 0.3670), corresponding to bluish emission. To the best of our knowledge, this is the first report on donor−acceptor quateraryls utilized as emissive layers in an OLED device.

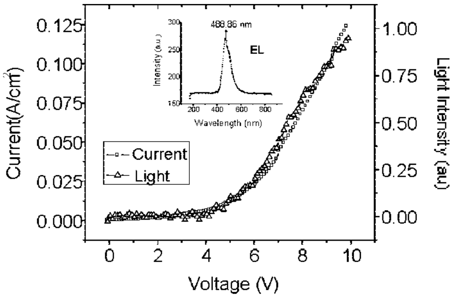


Figure 4. ILV characteristics of device of **6e** (insert shows the EL spectrum)

In summary, we have prepared new nonplanar small molecule quateraryls with donor−acceptor groups from ketene-*S*,*S*-acetals in excellent yields through carbanion-induced ring transformation of 2*H*-pyran-2-ones as key steps. These molecules exhibited blue fluorescence, high quantum yields and good thermal stability with a glass transition temperature >200 °C, which indicates that these new quateraryl scaffolds with donor−acceptor functionalities are good candidates for developing blue organic light emitting diodes (B-OLEDs).

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Supporting Information Available: Complete experimental details, characterization data, UV−vis and fluorescence spectra, DSC, TGA, X-ray data (CIF, **6e**) for the compounds **6a−e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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