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# 1,3,4-Oxadiazole Containing Silanes as Novel Hosts for Blue Phosphorescent Organic Light Emitting Diodes

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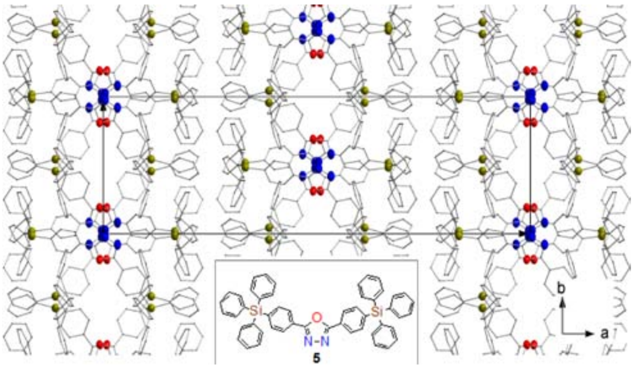
## ABSTRACT



**Five rigid oxadiazole (OXD) containing silanes, denoted 1−5, have been developed with high morphological stability. Disruption of the $\pi$-aromatic conjugation by introduction of Si atoms leads to a large band gap and high triplet energy. Among the OXDs we studied, 2,5-bis(triphenylsilylphenyl)-1,3,4-oxadiazole 5 is the best host for FIrpic, with a phosphorescent organic light emitting diode (PHOLED) turn-on voltage of 6.9 V, maximum luminance of 5124 cd/m$^2$, current efficiency of 39.9 cd/A, and external quantum efficiency of 13.1%. Special molecular stacking in the single crystal of 5 was discussed.**

Phosphorescent organic light emitting diodes (PHOLED) have attracted significant attention due to their high light-emitting efficiency.[1] In order to optimize the luminescence efficiency, the phosphorescence (PH) emitters are usually doped in a host matrix to reduce the probability of self-quenching through triplet−triplet annihilation.[2] The host matrix should have high triplet energy to prevent the reverse energy transfer from the PH emitter back to the host.[3] In a design of host for blue PHOLEDs, host molecules with long conjugation lengths are generally avoided in order to keep the triplet energy levels high. During the past decade, researchers have mainly focused on hole-transporting carbazole based

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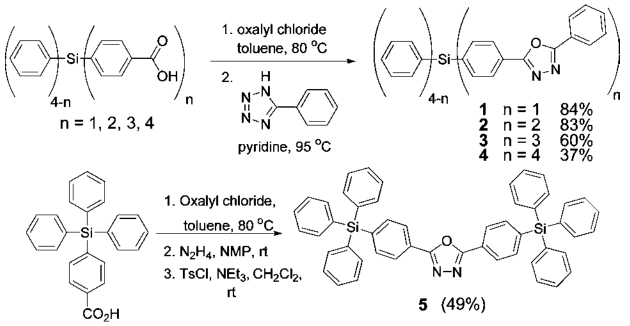
host materials.[4] A typical example is 4,4′-(bis(9-carbazoyl))-biphenyl (CBP) that has a low HOMO and large band gap. In addition, the ultrahigh singlet (~4.5 eV) and triplet (~3.5 eV) energies of tetraarylsilanes (UGHx) make them potentially useful host materials for deep blue PHOLEDs.[5]

On the other hand, examples of electron transporting (ET) host materials for PHOLED are relatively limited.[6] 1,3,4-Oxadiazoles (OXDs) form a family of electron transport molecules that have been widely used in OLED.[7] We recently reported that OXDs are appropriate ET hosts for *fac*-tris(phenylpyridine) iridium (IrPPy$_3$) and iridium(III) bis(4,6-(difluorophenyl)pyridine-*N*,*C*$^2$) picolinate (FIrpic) in PHOLEDs.[8]

Herein we report the study of OXD-silanes **1**–**5** that have high triplet energy as well as good ET properties. By using these OXDs as the host for FIrpic,[9] high efficiency blue PHOLEDs could be fabricated. When **1** and **5** were employed as the host for FIrpic in a PHOLED, current efficiencies of 36.6 and 39.9 cd/A, with an external quantum efficiency of 12.9% and 13.1%, were achieved.

The syntheses of **1**–**5** are depicted in Scheme 1. OXDs **1**–**4** were prepared from the corresponding phenylsilylbenzoic acid.[10] By adopting the Huisgen reaction,[11] the benzoic acids was converted to acylchlorides, followed by reaction with tetrazole[12] to give **1**–**4**. OXD **5** was synthesized from 4-(triphenylsilyl)benzoic acid through a reaction sequence of hydrazide formation and dehydrative ring formation.[13]

**Scheme 1.** Synthetic Pathways for **1**–**5**



Crystallographic analysis is a particularly important tool for understanding material properties.[14] Figure 1 shows the ORTEPs of **1, 2** and **5**. One can easily perceive that the diphenyloxadiazole moiety favors to have coplanar arrangement in all cases. For example, the OXD ring in the single crystal of **1** is nearly coplanar with the neighboring phenyl groups. The estimated distances of 2.544 Å for H$_4$–O$_1$, 2.536 Å for H$_{14}$–O$_1$, 2.656 Å for H$_8$–N$_2$, and 2.657 Å for H$_{10}$-N$_1$ suggest the presence of C–H–O and C–H–N intramolecular hydrogen bond interactions.[15]

On the other hand, the orientation of the Ph$_3$Si– groups is relatively flexible, dependent on the molecular packing in the lattice. A dihedral angle of 81.41° for C$_{11}$–C$_{12}$–Si$_1$–C$_{27}$ in **1** clearly suggested that one Ph–Si bond is nearly perpendicular to the diphenyloxadiazole moiety. Hyperconjugation interactions are therefore expected. Similar to that of **1**, a dihedral angle of 89.13° for C$_{21}$–C$_{20}$–Si$_1$–C$_{29}$ in **2** was observed. Different from the previous two cases, the Ph$_3$Si– groups of **5** show another conformational preference, with one Ph–Si bond almost eclipsed with the OXD moiety.

Figure 1d shows the molecular stacking of **5** in the single crystal viewed along the *b*-axis. Alternating layer structures were observed, in which the stacking of oxadiazole is formed. Electron conduction might therefore be enhanced through the OXD layer.

Differential scanning calorimetry (DSC) analysis of **1** (Table 1) shows a glass-transition temperature ($T_g$) of 57 °C which is higher than that of UGH1 (26 °C).[5] We attribute this to the lollipop shape structure of **5**, with the rigid oxadiazole group sticking out from the spherical Ph$_4$Si-surface, which restricts the molecular motion in the solid matrix. Other OXDs **2**–**4** also have high $T_g$'s of 87, 104, and 135 °C respectively, along with an increase in molecular diameter. It is noteworthy to point out that the dumbbell shape of **5** gives rise to a high $T_g$ of 98 °C. In addition, **1**–**5**

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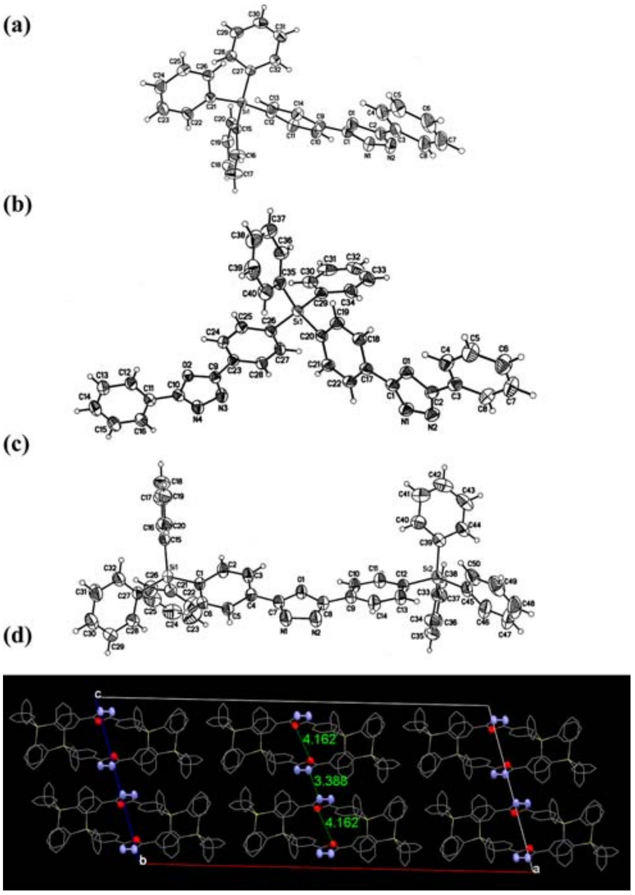

Figure 1. ORTEPs of OXDs: (a) **1**, (b) **2**, (c) **5**. (d) Crystal packing of **5** viewed along the *b*-axis, with intermolecular distances (Å) being shown.

exhibit high thermal decomposition temperatures of 356–482 °C ($T_d$, corresponding to 5% weight loss) in thermal gravimetric analysis (TGA), indicating that **1**–**5** are thermally stable.

Table 1 lists the UV–vis absorption and fluorescence spectral data of **1**–**5** in tetrahydrofuran (THF). All compounds show absorption peaking at around 290 nm that are attributed to the $\pi$–$\pi$* transitions of the OXD chromophore (Figure 2). Compared to the absorption of 2,5-diphenyloxadiazole (DPO) at 280 nm, **1**–**5** show only a small shift by 8–14 nm, indicating that the electronic perturbation arising from the $Ph_3Si$– group is weak.

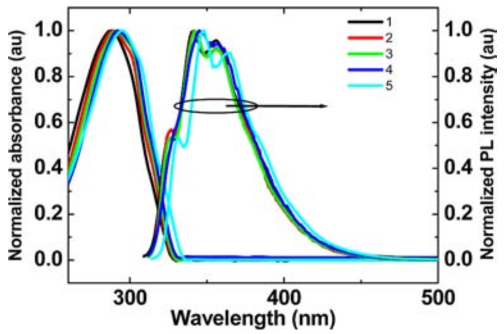

Figure 2. UV–vis absorption and PL spectra of **1**–**5** in THF.

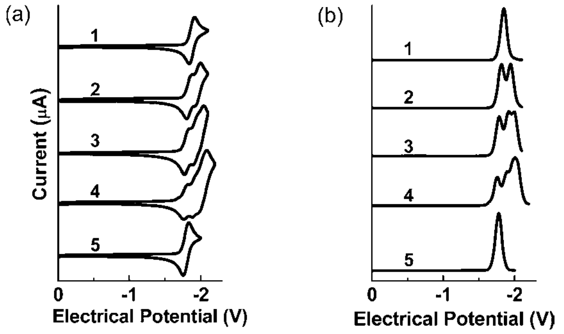

Figure 3. (a) CV and (b) DPV of **1**–**5** under $N_2$ in DMF ($Bu_4NPF_6$, 0.1 M) with a scan rate of 100 mV/s.

OXDs **1**–**5** strongly fluoresce to give emission peaking at 342–347 nm. Reasonably a small Stokes shift of 50–54 nm along with the vibronic fine pattern observed suggested that structural relaxation occurs to only small extents between the $S_1$ and $S_0$ states.

The PH spectra were collected in the THF at 77 K. The spectral data indicated that **1**–**5** have similar triplet energies of 3.00–3.06 eV, which are higher than FIrpic

Table 1. Physical Data of **1**–**5**

| compound | $T_g$ (°C) | $T_d$ (°C) | $\lambda_{abs}$[a] (nm) | $\lambda_{em,max}$[a] (nm) | $\lambda_{intersection}$ (nm) | $E_g$ (eV) | HOMO/LUMO | $E_T$[a,c] (eV) | QY[b] |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 57 | 356 | 288 | 342 | 319 | 3.89 | −6.31/ −2.42 | 3.00 | 0.77 |
| **2** | 87 | 444 | 290 | 342 | 319 | 3.89 | −6.35/ −2.46 | 3.06 | 0.77 |
| **3** | 104 | 465 | 292 | 342 | 320 | 3.88 | −6.37/ −2.49 | 3.06 | 0.78 |
| **4** | 135 | 482 | 292 | 345 | 321 | 3.87 | −6.39/ −2.52 | 3.06 | 0.75 |
| **5** | 98 | 413 | 294 | 347 | 325 | 3.82 | −6.32/ −2.50 | 3.01 | 0.83 |
| **DPO** | – | – | 280 | 332 | 312 | 3.98 | −6.24/ −2.26 | 2.92 | 0.45[17] |

[a] Measured in THF. [b] Quantum yield (QY): Quantified in THF against coumarin 1 (QY: 0.85) as standard.[16] The value obtained by this method would be within 30% accuracy. [c] $E_T$ (eV) = 1240.8/$\lambda_{ph}$ (nm).

**Table 2.** Electroluminescence Characteristics of Devices A–D

| device[a] | host | $V_{on}$[b] (V) | L max (cd/m$^2$) (V at L max, V) | $\eta_c$ (cd/A) | $\eta_p$ (lm/W) | $\eta_{ext}$ (%) |
|---|---|---|---|---|---|---|
| A | **1** | 8.1 | 5405 (12) | 36.6 | 23.0 | 12.9 |
| B | **2** | 7.2 | 4788 (12) | 27.7 | 19.8 | 9.6 |
| C | **3** | 7.0 | 2215 (11) | 10.7 | 8.4 | 3.6 |
| D | **5** | 6.9 | 5124 (11.5) | 39.9 | 31.4 | 13.1 |

[a] To evaluate the electroluminescence (EL) performance of **1**, **2**, **3**, and **5** as host for PHOLED, a device consisting of ITO(1100 Å)/NPB (500 Å)/mCP (100 Å)/host **1**, **2**, **3**, **5**-Firpic (15 wt %) (300 Å)/TAZ (400 Å)/LiF (12 Å)/Al (1000 Å) was employed. [b] The voltage of current density at 10 mA/cm$^2$.

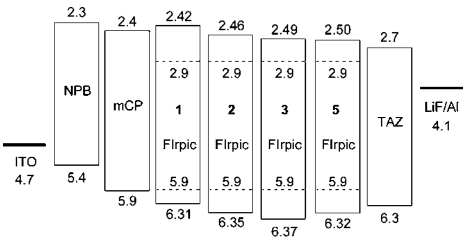

**Figure 4.** Energy levels of all organic materials used.

(2.65 eV),[3b] a blue phosphor. This result implies that **1**–**5** are potentially useful as host materials for blue-light triplet emitters.

The half-reduction potentials ($E_{1/2}^{red}$) of **1**–**5** ($10^{-3}$ M) were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The LUMO and HOMO energy levels were therefore estimated on the basis of their first $E_{1/2}^{red}$ and the corresponding optical band gaps. For **1**–**4**, the LUMO level gradually drops from −2.42 eV to −2.52 eV along with the increasing number of OXD units. The HOMO values ranging from −6.31 eV to −6.39 eV were then estimated. In Figure 3a, small split waves of **2**–**4** were observed, indicating that electronic repulsions between the reduction electrons are observable. This weak repulsive electronic coupling may originate from either through-bond or through-space interactions between the individual OXD units. The multiple waves could be clearly resolved in the DPV (Figure 3b). On the other hand, the reduction behavior of **5**, which also shows a single wave, is similar to that of **1**. Although the high triplet energy level of **1**–**5** definitely makes them the right candidates for host material, **4** is difficult to sublime due to its high molecular weight and low volatility. Therefore, only PHOLEDs of **1**, **2**, **3**, and **5** were examined.

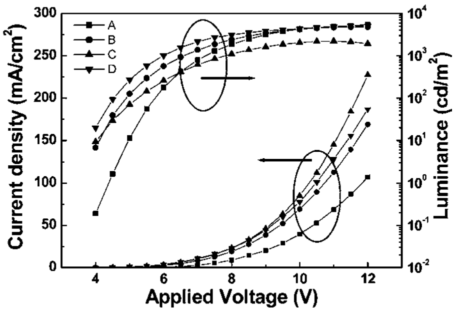

**Figure 5.** Plots of current density and luminance versus voltage of the PHOLED devices A–D.

The EL data are summarized in Table 2, and the energy level alignments are shown in Figure 4. First of all, the turn-on voltage decreases significantly from device A to C, we attribute this to the LUMO effects, in which the LUMO drops from **1** to **3**. This may help to reduce the electron injection barrier in the devices. However, for unknown reasons, the efficiency of the device drops from **1** to **3**. On the other hand, device D shows the best results (Figure 5). First, among the devices we tested, the turn-on voltage is the lowest one. In addition, the device achieves the highest current efficiency (39.9 cd/A), power efficiency (31.4 lm/W), and external quantum efficiency (13.1%). Since **5** has a LUMO level similar to that of **3**, the low turn-on voltage of device D is expected. However, the high efficiency of device D, when compared to that of device C, surprises us. We tentatively attribute this to the special OXD stacking in **5** which makes electron transport effective even in an amorphous film and therefore reduces the charge accumulation in the solid matrix.

In summary, we have developed a new application of OXD containing arylsilanes that have high triplet energy and are suitable for use as host materials for blue PHOLEDs. The high $T_g$ of the compounds is also advantageous to the device performance.

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**Supporting Information Available.** Synthesis, UV–vis, FL, NMR, CIF, EL, references. This material is available free of charge via the Internet at http://pubs.acs.org.

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