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Ortho-Substituent Effect on Fluorescence and Electroluminescence of Arylamino-Substituted Coumarin and Stilbene

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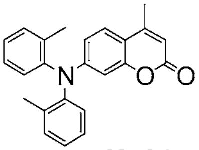
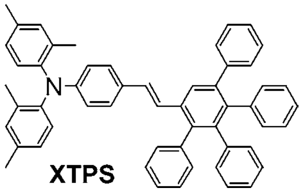
ABSTRACT



MeC1



XTPS

Newly synthesized arylamino-substituted coumarins and stilbenes show enhanced fluorescence emission (bluer and brighter) both in solution and in solid film. Pure blue efficient electroluminescence with 2.7% and 4.1% of external quantum efficiency can be achieved with MeC1 and XTPS, respectively.

Many fluorescent organic compounds exhibit high fluorescent quantum yields (Φ_f) in solution but suffer from "concentration quenching", showing little or no fluorescence at highly concentrated solution or in the solid state.[1] The "concentration quenching" causes emission band broadening and a *bathochromic* shift. From a structural point of view, incorporation of bulky as well as nonplanar molecular moieties should prevent orderly molecular packing, and may alleviate the fluorescence quenching resulting from molecular interactions.[2] Structural moieties, such as bulky *tert*-butyl, isopropyl, and tetraphenylsilyl,[3] or sterically crowded tetra- or pentaphenylphenyl polycycle,[4] provide satisfactory effects on inhibiting molecular aggregation in the solid state. Molecules with a starburst or dendrimer shape show the effect as well.[5] Nonplanar triarylamine structural moieties have been studied in depth,[6] and have been found to be

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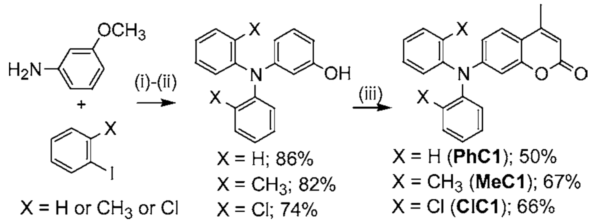
effective in generating molecular glass materials. However, besides preventing molecules from crystallization, none of these structural moieties or shapes per se have a direct control on the photophysical properties of the fluorophores. In this Letter, we take one step further to show a molecular strategy, namely the ortho-substitutent effect of arylamine, which can effectively enhance fluorescence in the solid state while preserving the intrinsic Φ_f in solution with a concomitant *hypsochromic* emission shift. The structural strategy is successfully applied to two kinds of fluorophores, coumarin and stilbene. In addition, bright and efficient blue electroluminescence (EL) observed for nondoping organic light-emitting diodes (OLEDs) fabricated from structure-tailored coumarin and stilbene derivatives further strengthens the validity of the approach.

Coumarin 1 (7-diethylamino-4-methylcoumarin, **C1**) is an appropriate fluorophore to serve as the molecular platform to illustrate the strategy owing to its near unit blue fluorescence efficiency in solution, but weak fluorescence in the solid state.[7] Accordingly, diaryl appended **C1** derivatives (denoted by **PhC1**, **MeC1**, and **ClC1**) are synthesized (Scheme 1). Although Pd-catalyzed aromatic amination reactions[8] are commonly employed in the synthesis of triarylamines,[9] they failed to give 3-bisarylamino anisole, but only a monosubstituted compound isolated even after a prolonged reaction time or by the addition of an excess of chelating or nonchelating phosphine ligands. The aryl groups were thus introduced to the amino group via the Ullmann reaction[10] starting with 3-methoxyaniline followed by the treatment of BBr_3 to give the corresponding phenols, which were further condensed with ethyl acetoacetate under a Pechmann condition to yield the aryl-substituted coumarins. Low reaction yields were observed if Lewis acids such as zinc chloride were used as catalysts for the condensation.

Scheme 1[a]



[a] Reagents and conditions: (i) 1,2-dichlorobenzene, copper bronze, 18-crown-6, K_2CO_3, reflux, 4 days, 85% (X = H), 77% (X = CH_3), 30% (X = Cl); (ii) BBr_3, CH_2Cl_2, −78 °C → rt, 8 h; (iii) acetoacetate, 70% H_2SO_4(aq).

PhC1 displays relatively low fluorescence yield (Φ_f = 48%) and a large bathochromic shift relative to **C1** in emission wavelength, indicating there is partial conjugation between the chromen-2-one and the diphenylamino group. The solid-state fluorescence intensity of **PhC1** was improved relatively (Figure 1), although fluorescence quantum yield in the solid state awaited for measurement. Nevertheless, the fluorescence emission maximum (λ_{max}^{em}) of the solid film appeared at 474 nm corresponding to the greenish blue hue. The color purity is thus not appropriate for the application in OLED, strictly requiring good blue-color purity. In the cases of **MeC1** and **ClC1**, the ortho substituents (i.e., methyl and chloro groups) of phenyl groups augment the non-planarity of the triarylamino center to prevent crystallization, as well as reduce the extent of conjugation between the chromen-2-one and the diarylamino group.

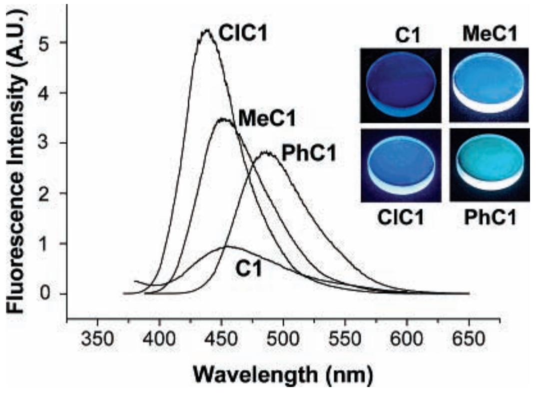


Figure 1. Left: Fluorescence emission spectra of Coumarin 1 (**C1**), **ClC1**, **MeC1**, and **PhC1** as solid films on quartz. Right: Color photographs of the same solid films under UV irradiation (365 nm) qualitatively revealing relative fluorescence intensity and varied blue hue.

The structural features are reflected in the photospectroscopic and electrochemical data. The fluorescence quantum yields of **MeC1** and **ClC1** are 77% and 86%, respectively, and emission wavelengths are much shorter than that of **PhC1** (Table 1, Figure 1), either in solutions or in solid films. The gradually increasing oxidation potentials, implying wider energy gaps between HOMO and LUMO, are observed at 0.56, 0.64, and 0.88 V in the order of **PhC1**, **MeC1**, and **ClC1** (Table 1) consistent with blue-shifted wavelengths in absorption and fluorescence spectra. The LUMO energy level of the compounds remained mostly the same due to the very similar reduction potential. This is understandable because of the reduction site, assuming the carbonyl of chromenone has the same chemical structure in three molecules. Besides the energy gap law, the rather pronounced fluorescence

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Table 1. Spectral, Thermal, and Electrochemical Data of Coumarin and Stilbene Compounds

	Φ_f (%)[a]	λ_{max}^{abs} (nm)[b]	λ_{max}^{em} (nm)		T_g (°C)	T_m (°C)	T_d (°C)	E^{oxd} (V)[g]
			solution[b]	solid				
C1	99	365	416	456[c]	*e*	71	*f*	*f*
PhC1	48	367	464	474[c]	42	171	253	0.56
MeC1	77	362	443	451[c]	56	160	257	0.64
ClC1	86	347	411	435[c]	61	185	285	0.88
ATPS	36	382	502	492[d]	110	210	348	0.21
TTPS	56	380	474	471[d]	114	235	354	0.32
XTPS	54	370	462	465[d]	120	*e*	370	0.36

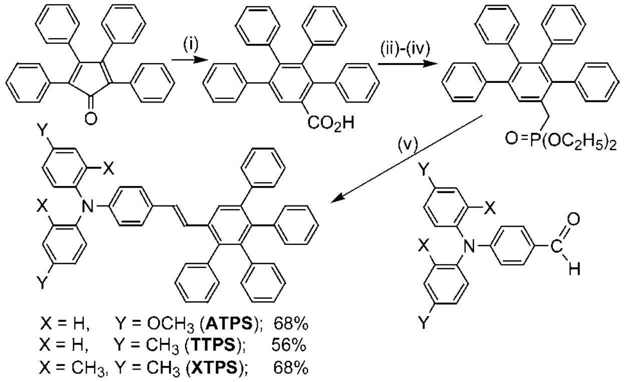
[a] Coumarin 1 ($\Phi_f = 99\%$ in ethyl acetate)[7] was used as the standard for the fluorescence quantum yield determination. [b] Samples were dissolved in ethyl acetate when spectra were recorded. [c] Solid films were prepared by thermal deposition under vacuum. [d] Solid films were prepared by spin-casting from solution and then vacuum dried. [e] Not detectable. [f] Not measured. [g] Sample was dissolved in deoxygened dichloromethane with tetrabutylammonium hexfluorophosphate (**PhC1**, **MeC1**, and **ClC1**) or perchlorate (**ATPS**, **TTPS**, and **XTPS**) as the electrolyte. A platinum working electrode and a saturated Ag/AgNO$_3$ reference electrode were used. Ferrocene was used for potential calibration (all reported potentials are referenced to ferrocene/ferrocenium).

enhancements for **MeC1** and **ClC1** in solutions compared to **PhC1** could be attributed to the increase of the potential energy of nonradiative twisted intramolecular charge transfer (TICT) by tuning the electronic properties of aryl amino groups.[11]

Three coumarin derivatives reported here sharing the same triarylamino structural features do exhibit improved amorphous properties relative to **C1**. The crystallinic **C1** shows a melting temperature (T_m) around 71 °C. In contrast, T_m of **PhC1** is detected at 171 °C by DSC (differential scanning calorimetry) examination in the first heating scan, and neither a melting nor a crystallization signal, rather a steplike endothermic signal corresponding to the glass transition temperature (T_g), is observed at 42 °C in the second and subsequent heating scans. Similar to **PhC1**, T_g values are detected for **MeC1** and **ClC1** at 56 and 61 °C, respectively. The results indicate that **PhC1**, **MeC1**, and **ClC1** possess suppressed intermolecular interactions in the solid state. The thermal properties mirror the solid-state fluorescence studies of these derivatives: the crystallinic **C1** showing the largest red-shift difference between solutions and solid states (Table 1), owing to the severe molecular interactions, and **ClC1** exhibiting the bluest and brightest solid-state fluorescence emission (Figure 1).

To explore the generality of the "ortho-substituent effect" shown for **C1**, a new type of stilbene, **ATPS**, **TTPS**, and **XTPS**, is synthesized (Scheme 2). The Horner–Wadsworth–Emmons reaction was used for the formation of the C=C double bond to connect triarylamine and tetraphenylbenzene. The required diethyl tetraphenylphenylphosphonate was elaborately prepared in a stepwise manner by the Diels–Alder cycloaddition of propiolic acid and tetraphenylcyclopentadienone, followed by functional group transformations to yield the corresponding phosphonate ester.

Scheme 2[a]



[a] Reagents and conditions: (i) propiolic acid, bromobenzene, 160 °C, 12 h, 81%; (ii) LiAlH$_4$/THF, 0 →80 °C, 7 h, 97%; (iii) CCl$_4$/PPh$_3$, toluene, 120 °C, 6 h, 60%; (iv) P(OC$_2$H$_5$)$_3$, 160 °C, 4 h, 90%; (v) NaH/THF.

The combination of sterically crowded tetraphenylphenyl moieties and the ortho-substituted arylamine in molecular structures should provide us with noncrystallinic stilbene derivatives with strong fluorescence emission, as well as good blue-color purity. In fact, **XTPS** is the only fluorophore in this report showing T_g in the absence of T_m on DSC thermograms. Their thermal, spectral, and electrochemical data are summarized in Table 1 for comparisons. As we expected, the **XTPS** bearing the ortho-substituted arylamino moiety displays the best fluorescence properties: relatively high Φ_f (54%) and a good blue-color hue either in solution (λ_{max}^{em} 462 nm) or in the solid state (λ_{max}^{em} 465 nm). **TTPS** exhibits a comparable fluorescence quantum yield with **XTPS**,[12] but its emission wavelengths (λ_{max}^{em} 474 nm in solution and 471 nm in solid film) are somewhat deviated from the blue hue. Similar to **PhCl**, **MeC1**, and **ClC1**, increasing oxidation potentials are parallel to the blue-shifting wavelength of absorption and emission spectra (Table 1) in the order **ATPS**, **TTPS**, and **XTPS**. Here, we see the ortho-substituent effect on both blue-shifting fluorescence and inhibiting crystallization of molecules.

Good OLEDs primarily require materials with efficient emission in the solid state and are ideal for the demonstration of ortho-substituent effect on blue fluorophores. Accordingly, two nondoping OLEDs, in the configuration of ITO/NPB (40 nm)/**MeC1** (30 nm)/TPBI (40 nm)/Mg$_9$:Ag$_1$ and ITO/**XTPS** (60 nm)/TPBI (40 nm)/Mg$_9$:Ag$_1$ are fabricated.[13] Both devices show one blue EL band centered at 458 and 462 nm, respectively (Figure 2). These wavelengths are rather close to those of PL observed for each blue fluorophore in the solid state (Table 1), indicative of the fluorophore origin of the EL.

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(12) Nearly the same Φ_f values of **XTPS** and **TTPS** are not unexpected. Arylamino-substituted stilbene fluorophores bearing sterically hindered ortho substituents have a higher chance of going through trans-cis isomerization at the photoexcited state and hence exhibit weaker fluorescence intensity than those without an ortho substituent. Yang, J.-S.; Chiou, S.-Y.; Liau, K.-L. *J. Am. Chem. Soc.* **2002**, *124*, 2518.

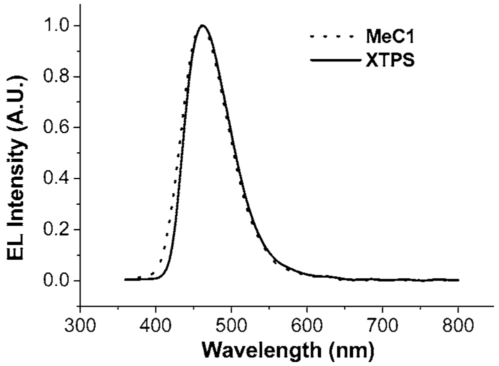

Figure 2. Electroluminescence spectra of OLEDs containing **MeC1** (dotted line) and **XTPS** (solid line).

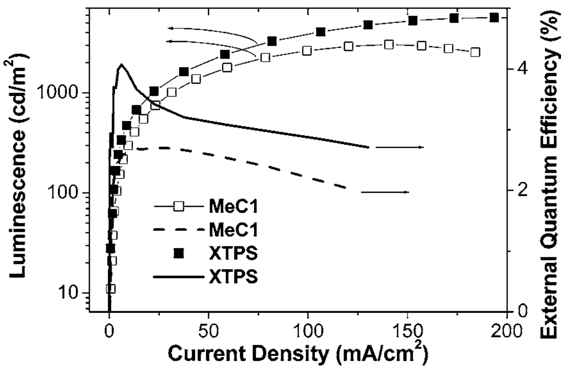

Figure 3. Electroluminescence intensity and external quantum efficiency of OLEDs containing **MeC1** (dashed line and open symbol) and **XTPS** (solid line and solid symbol).

The **MeC1**-based device shows the maximum luminance around 3000 cd/m^2 and 2.7% external quantum efficiency (equivalent to 3.2 cd/A or 1.1 lm/W) (Figure 3). The **XTPS**-based device outperforms the **MeC1**-based one, displaying luminance as high as 5650 cd/cm^2, and maximum external quantum efficiency of 4.1% (equivalent to 5.5 cd/A or 2.9 lm/W)[14] at a low current density of 6 mA/cm^2 and a driving voltage of 6 V.

Nevertheless, at a current density of 20 mA/cm^2 or lower, intense blue EL values as strong as 640 cd/m^2 (**MeC1**-based device) and 940 cd/m^2 (**XTPS**-based device) are observed for each device (Figure 3), which are practical for display application. To our knowledge, either of these blue emissions is one of the brightest among known blue OLEDs at a comparable range of low current density.[13,15]

In summary, we have successfully demonstrated that the ortho-substituted arylamino donor is an effectively structural tailor for blue-shifting fluorescence wavelength and for enhancing the fluorescent intensity of blue fluorophores either in solution or in the solid state (herein illustrated by two classes of compounds: Coumarin 1 and stilbene). Efficient and bright blue OLEDs, fabricated with **XTPS** or **MeC1** blue light-emitting materials, also justify our structural approach.

Acknowledgment. We thank the National Science Council, the Academia Sinica, and the Ministry of Education of Taiwan for financial support. The assistance from Prof. Yu-Tai Tao in the fabrication and measurement of the OLED devices is also acknowledged.

Supporting Information Available: Structural characterization of new coumarin and stilbene compounds; EL characterizations of **MeC1** and **XTPS**-based OLEDs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) TPBI here denotes 2,2′,2″-(1,3,5-phenylene)tris(1-phenyl-1*H*-benzimidazole) and NPB is 1,4-bis(1-naphylphenylamino)biphenyl. ITO is an indium−tin oxide-coated glass. The fabrication and characterization of the devices follow a similar procedure to that reported by Chan et al.: Chan, L.-H.; Lee, R.-H.; Hsieh, C.-F.; Yeh, H.-C.; Chen, C.-T. *J. Am. Chem. Soc.* **2002**, *124*, 6469.

(14) At first glance, the very high 4.1% external quantum efficiency of the **XTPS**-based device seems unreasonable, considering the moderate Φ_f (54%) of **XTPS**. However, recent reports indicate that the light out-coupling factor (η_{coupling}) of OLEDs needs reevaluation. Underestimation of η_{coupling} is possibly as high as 2-fold in previous estimations. (a) Chen, H. Y.; Lam, W. Y.; Luo, J. D.; Ho, Y. L.; Tang, B. Z.; Zhu, D. B. *Appl. Phys. Lett.* **2002**, *81*, 574. (b) Patel, N. K.; Cina, S.; Burroughes, J. H. *IEEE J. Sel. Top. Quantum Electron.* **2002**, *8*, 346.

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