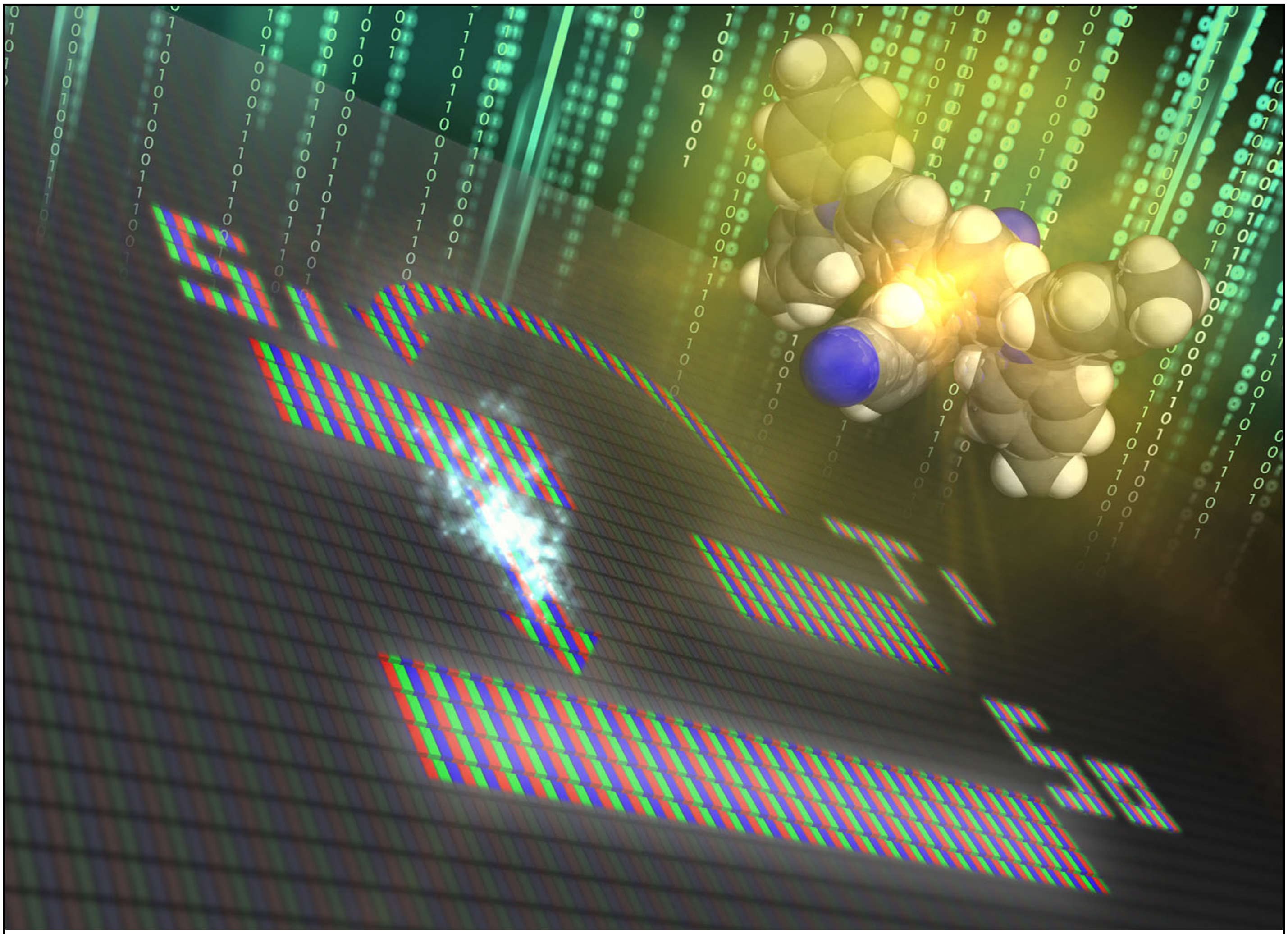

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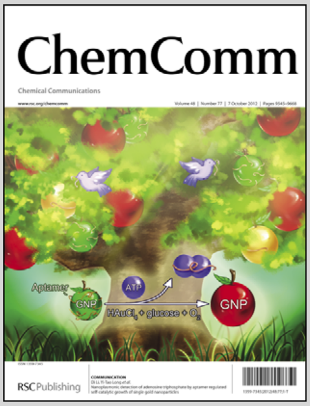

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Cite this: *Chem. Commun.*, 2012, **48**, 9580–9582

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COMMUNICATION

Electroluminescence based on thermally activated delayed fluorescence generated by a spirobifluorene donor–acceptor structure†

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Received 28th February 2012, Accepted 16th April 2012
DOI: 10.1039/c2cc31468a

An organic light emitting diode based on thermally activated delayed fluorescence (TADF) has been produced using a spirobifluorene derivative (Spiro-CN) having the donor–acceptor moieties as an emitter.

Organic light emitting diodes (OLEDs) have attracted significant attention because of their promising applications in flat-panel displays[1] and in general lighting applications.[2] Their characteristic organic semiconducting material features will realize flexibility over a large-area, low cost of fabrication and high-performance optical and electrical properties. In particular, advances in the molecular design of modern optoelectronics have contributed significantly toward the commercialization of highly efficient OLEDs.

Phosphorescent materials such as Ir(III) complexes[3] and Pt(II) complexes[4] are possible solutions for highly efficient OLEDs because of their highly intrinsic exciton generation efficiency. On the other hand, fluorescence materials have an intrinsic limitation with regard to electroluminescence efficiency because of their low exciton generation efficiency. However, a recent study revealed that highly efficient OLEDs are potentially feasible by using delayed fluorescence materials that enhance the exciton generation efficiency because of the upconversion of a triplet exciton into a singlet excited state.[5–7] Until now, two mechanisms have been identified for delayed fluorescence. One is a triplet–triplet annihilation: TTA (P-type delayed fluorescence),[8] and the other is thermally activated delayed fluorescence: TADF (E-type delayed fluorescence),[9] which thermally converts triplet excitons into singlet excited states. Among them, the TADF process is more promising because the additional singlet exciton generation efficiency (75%) is potentially higher than that of TTA (37.5%). Although fluorescent materials have been widely studied, TADF materials remain quite rare and this behaviour has been observed in some dyes,[10] fullerenes[11] and metal complexes.[12]

In this communication, we report the observation of TADF based on a spirobifluorene derivative and its application in OLEDs. Spirobifluorene derivatives have become promising candidates for OLEDs since these compounds exhibit a high glass transition temperature,[13] excellent thermal stability and color stability.[14] Although a large number of spirobifluorene derivatives have been reported as emitters[15] as well as host materials,[16] no TADF property has been reported for them.

In our recent study, we found that a fluorescent molecule containing a sufficiently separated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) shows efficient thermally activated delayed fluorescence.[17] In the case of this molecule, spatially separated HOMO and LUMO orbitals lead to efficient TADF due to the small energy gap (ΔE_{ST}) between the lowest excited singlet (S_1) state and the lowest excited triplet (T_1) state. This finding prompted us to expand our methodology to spirobifluorene derivatives. Here, we focus on a spirobifluorene derivative with electron donating and electron accepting units in the same molecular structure. Fig. 1 shows the molecular structure of 2′,7′-bis(di-*p*-tolylamino)-9,9′-spirobifluorene-2,7-dicarbonitrile (Spiro-CN) containing two di-*p*-tolylamino electron donating units and two cyano electron accepting units. Details of the synthetic scheme are given in the ESI.† Calculations to determine the HOMO and LUMO of Spiro-CN were carried out with the Gaussian 09 package[18] at the B3LYP/6-31G(d) level. Since the donor and acceptor units are orthogonally connected *via* the spirobifluorene moiety, the HOMO and LUMO are located on the donor and acceptor units, respectively.

The photoluminescence (PL) spectra and transient PL characteristics of a 6 wt% Spiro-CN:1,3-bis(carbazole-9-yl) benzene (mCP) co-deposited film were measured as shown in Fig. 2. Spiro-CN showed yellow emission with a PL quantum efficiency of Φ_{PL} = 27%. The transient PL characteristics of 6 wt% Spiro-CN:m-CP co-deposited film showed prompt and delayed PL spectra at 300 K. A prompt component with a transient decay time of 24 ns and a

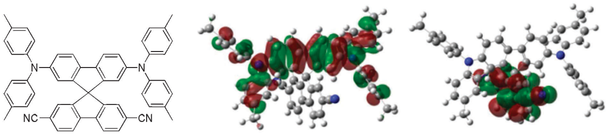

Fig. 1 Molecular structure of Spiro-CN and its HOMO and LUMO calculated at the B3LYP/6-31G(d) level.

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† Electronic supplementary information (ESI) available: Synthesis scheme for Spiro-CN, experimental details, additional photophysical data and complete ref. 18. See DOI: 10.1039/c2cc31468a

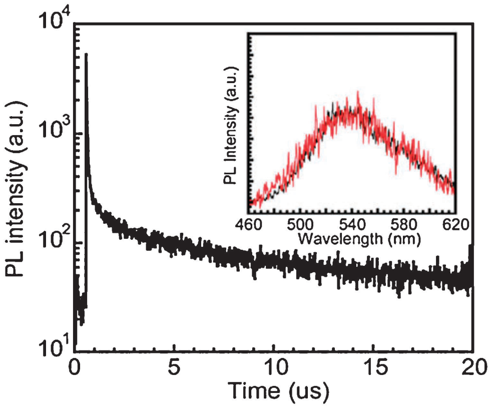

Fig. 2 Transient PL of a 6 wt% Spiro-CN:mCP co-deposited film. The inset shows PL spectra of a 6 wt% Spiro-CN:mCP co-deposited film: prompt component (fluorescence, red line), delayed component (delayed fluorescence, black line).

delayed component of 14 μs were clearly observed. Since both spectra are nearly coincident, the delayed component can be attributed to the TADF process. In order to further clarify the origin of the delayed component, we measured the transient PL characteristics of Spiro-CN in a toluene solution with and without oxygen. As shown in Fig. S1 (ESI†), the emission decay of the nitrogen-purged solution showed both prompt and delayed components. In contrast, the delayed component disappeared in a non-degassed solution. This oxygen sensitive behaviour of the emission decay provides a good indication that the delayed component is caused by the TADF that occurs *via* a triplet excited state. Similar triplet quenching behaviour was also observed in a 6 wt% Spiro-CN:α-NPD co-deposited film as shown in Fig S2 (ESI†). Furthermore, the PL efficiency (5.4%) of a 6 wt% Spiro-CN:α-NPD co-deposited film was found to be significantly smaller than that of a 6 wt% Spiro-CN:mCP co-deposited film.

To investigate the TADF property, a temperature dependent luminescence measurement was obtained. The overall Φ_{PL}, prompt fluorescence efficiency (Φ_{prompt}) and delayed fluorescence efficiency (Φ_{delayed}) are shown in Fig. 3(a), the prompt components showed almost no temperature dependence (for the determination method of Φ_{prompt} and Φ_{delayed}, see ESI†). On the other hand, an increase in the delayed fluorescence intensity with an increase in temperature was clearly observed. These results indicate the presence of thermal activation energy during delayed fluorescence.

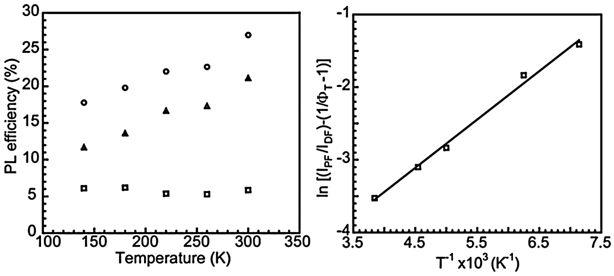

Fig. 3 (a) Temperature dependence of the total photoluminescence (Φ_{PL}): open circles, prompt fluorescence (Φ_{prompt}): open squares and delayed fluorescence (Φ_{delayed}): open triangles. (b) Log plot of the intensity ratio of prompt fluorescence to delayed fluorescence *vs.* $1/T$.

Based on these results, the thermal activation energy was estimated using a Berberan-Santos plot and the energy difference (ΔE_{ST}) between the lowest excited singlet (S_1) state and the lowest excited triplet (T_1) state can, in principle, be obtained from the temperature dependence of the emission intensity ratio ($I_{\mathrm{prompt}}/I_{\mathrm{delayed}} = \Phi_{\mathrm{prompt}}/\Phi_{\mathrm{delayed}}$) from the following equation,[11]

$$\ln\left[\frac{I_{\mathrm{prompt}}}{I_{\mathrm{delayed}}} - \left(\frac{1}{\Phi_{\mathrm{T}}} - 1\right)\right] = \ln\left(\frac{k_{\mathrm{p}} + k_{\mathrm{nr}}}{k_{\mathrm{RISC}}}\right) + \frac{\Delta E_{\mathrm{ST}}}{RT} \qquad (1)$$

where Φ_{T} is the triplet formation efficiency, k_{p} is the phosphorescence rate constant, k_{nr} is the non-radiative rate constant from T_1, k_{RISC} is the $T_1 \rightarrow S_1$ reverse intersystem crossing rate constant and R is the gas constant. The Berberan-Santos plot gave a straight line as shown in Fig. 3(b) and from the slope we obtained $\Delta E_{\mathrm{ST}} = 5.5$ kJ mol^{-1} (57 meV). Thus, Spiro-CN shows an efficient TADF ($\Phi_{\mathrm{delayed}} \ggg \Phi_{\mathrm{prompt}}$) at room temperature and a far smaller ΔE_{ST} compared with those of common TADF compounds such as C_{70} (~25 kJ mol^{-1})[11] and tin(IV) fluoride–porphyrin (~39 kJ mol^{-1}).[7] Furthermore, the triplet formation efficiency (Φ_{T}) was estimated to be 78% (for the determination method of Φ_{T}, see Fig. S3, ESI†).

To study the electroluminescence properties of Spiro-CN, a multilayer device with a configuration of glass/ITO/α-NPD (60 nm)/6 wt% Spiro-CN:mCP (20 nm)/Bphen (40 nm)/MgAg (100 nm)/Ag (20 nm) was fabricated, where 4,4-bis[*N*-(1-naphthyl)-*N*-phenylamino]]biphenyl (α-NPD) was used as a hole-transport layer and 4,7-diphenyl-1,10-phenanthroline (Bphen) as an electron-transport layer. This device gives yellow electroluminescence with maximum current and power efficiencies of 13.5 cd A^{-1} and 13.0 lm W^{-1} and a maximum external quantum efficiency of 4.4% (Fig. 4(a)), which are the highest values reported to date for a device containing spirobifluorene as an emitter. Furthermore, a high luminance of 12 000 cd m^{-2} was observed at 15 V, as shown in Fig. 4(b).

It is noteworthy that the external quantum efficiency observed at low current density (<1 mA cm^{-2}) in the Spiro-CN based device is about 3 times higher than the theoretical maximum of about 1.4% for common fluorescent-type molecular materials with a PL efficiency of 27%. As mentioned above, a recent study proposed that two possible mechanisms for such an unusual increase in external quantum efficiency are the TTA and the TADF. For a discussion of the mechanism we examined the

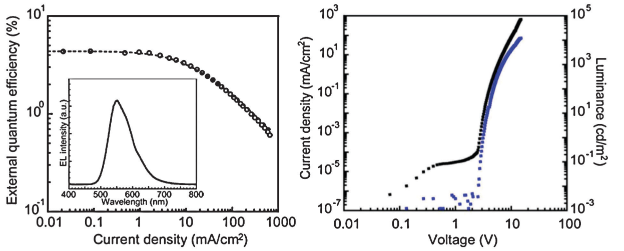

Fig. 4 (a) External quantum efficiency *versus* current density for glass/ITO/α-NPD (60 nm)/6 wt% Spiro-CN:mCP (20 nm)/Bphen (40 nm)/MgAg (100 nm)/Ag (20 nm). The inset shows an electroluminescence spectrum. (b) Current density (black closed squares)–luminance (blue closed squares)–voltage characteristics for glass/ITO/α-NPD (60 nm)/6 wt% Spiro-CN:mCP (20 nm)/Bphen (40 nm)/MgAg (100 nm)/Ag (20 nm).

current density dependence of the luminance. For the TTA, the luminance is known to increase more than linearly with an increase in current density.[19] On the other hand, we observed a linear increase in the luminance with an increase in current density, as shown in Fig. S4 (ESI†), suggesting that the high external quantum efficiency is not due to the TTA.

Next, we estimated the theoretical maxima of the internal and external electroluminescence efficiency for the TADF. Under electrical excitation, triplet excitons formed directly by carrier recombination and they were up-converted to the S_1 level leading to the total internal electroluminescence efficiency. The theoretical maxima of internal electroluminescence efficiency ($\Phi_{EL(int)}$) and external electroluminescence efficiency ($\Phi_{EL(ext)}$) are given by the following equations,

$$\Phi_{EL(int)} = \eta_r(S_1)\eta_f + \eta_r(S_1)\eta_{TADF} + \eta_r(T_1)\eta_{TADF} \quad (2)$$

$$\Phi_{EL(ext)} = \Phi_{EL(int)}\eta_{out} \quad (3)$$

where $\eta_r(S_1)$ is the branching ratio of singlet exciton formation (0.25), $\eta_r(T_1)$ is the branching ratio of a triplet exciton (0.75), η_f is the fluorescence efficiency ($\sim$0.05), η_{TADF} is the TADF efficiency ($\sim$0.22) and η_{out} is the light out-coupling efficiency ($\sim$0.20). Therefore, $\Phi_{EL(int)}$ is estimated to be 23% and the theoretical maximum of the external quantum efficiency is, therefore, $\Phi_{EL(ext)} = 4.6\%$ assuming a light out-coupling efficiency of 20%. The experimental external quantum efficiency maximum of 4.4% agrees well with the theoretical external quantum efficiency maximum. Therefore, we conclude that the unusual increase in the external quantum efficiency observed in this study can be attributed to the TADF.

In summary, efficient thermally activated delayed fluorescence as well as efficient electroluminescence based on a spirobifluorene derivative are reported. The Spiro-CN based device shows an unusual increase in the external quantum efficiency. Although the external quantum efficiency of the present system is almost comparable to that of efficient yellow fluorescent materials,[20] the external quantum efficiency of the present system is still lower than that of yellow phosphorescent materials.[21] However, it is expected that external quantum efficiency can be enhanced by developing spiro-based TADF materials with high PL efficiency by suppression of nonradiative transition. Furthermore, it is also expected that emission color of spiro-based TADF materials can be controlled from blue to red by controlling the π-conjugation of the electron donor and acceptor units, respectively. We believe that these findings are of fundamental interest for the development of highly efficient OLEDs based on fluorescent materials.

This research is granted by the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)," initiated by the Council for Science and Technology Policy (CSTP).

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