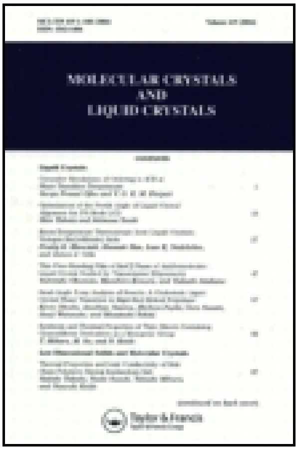

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Polymethine Dyes as Novel Efficient Infrared Electroluminescence Materials

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We examined the electroluminescence (EL) characteristics of four polymethine dyes to evaluate both their advantages and limitations as infrared (IR) EL materials. The IR EL intensity showed a marked dependence on the IR dye, and an IR EL quantum efficiency of 3.6×10^{-2}*% photons/electron was measured for the most efficient IR EL dye, 2-[2-[2-chloro-3-[2-(1-dodecyl-1,2-dihydro-benzo[***c,d***]-indol-2-ylidene)-ethylidene]-1-cyclohexen-1-yl]-ethenyl]-1-dodecyl-benzo[c,d]indolium chloride (SO447). We discuss the IR EL characteristics of these dyes in terms of photoluminescence efficiency, competitive visible/near-IR EL and dimer EL, and trapping efficiency.*

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Keywords: electroluminescence; optical communication; optical devices; organic infrared light-emitting materials; polymethine dyes

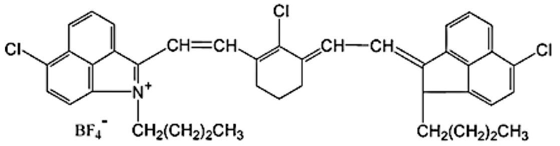
1. INTRODUCTION

The development of organic infrared (IR) light-emitting materials is important since they can provide a novel IR light source for use in future optical communication [1]. Current optical communication networks use IR light at around 1.3 and 1.5 μm for signal transmission and processing because silica optical fiber exhibits its minimum transmission loss in these wavelength regions. Novel transmission media such as polymer optical fiber or silicon photonic crystal circuits are also compatible with IR lights longer than 1 μm for signal transmission over limited distances.

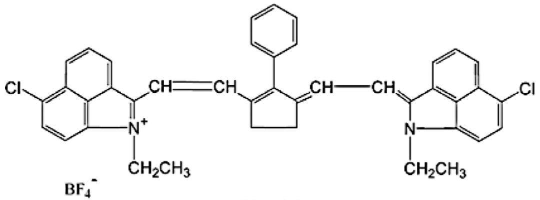
The organic IR light-emitting materials reported to date are divided mainly into organic ionic dyes [2–4] and organic rare-earth complexes [5–7]. There is an essential limitation to the luminescence efficiency of organic rare-earth complexes that consist of a central trivalent rare-earth ion such as Er^{3+} [5], Nd^{3+} [6], or Pr^{3+} [7], and organic ligands, since their IR luminescence originates from the parity-forbidden radiative 4f-4f transitions of the central trivalent rare earth ions. In contrast, organic ionic dyes such as polymethine dyes are species where the IR luminescence originates from the allowed S_1-S_0 transitions of their organic components and thus are free from the luminescence efficiency limitation. However, very few ionic dyes have been reported with EL at a wavelength longer than 1.2 μm in solid film. Thus, the search for additional ionic dyes exhibiting IR EL is an important challenge with a view to fabricating practical organic IR light sources. Here, we examine the EL characteristics of four polymethine dyes to evaluate both their advantages and limitations as IR EL materials.

2. EXPERIMENTAL

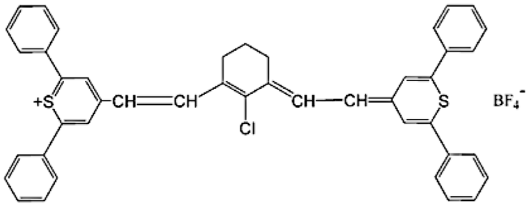
Single-layer light-emitting diodes (LEDs) were prepared on an indium-tin-oxide (ITO) coated glass substrate (20 Ω/□) by spin coating a 200 nm-thick poly(N-vinylcarbazole) (PVK) film from a 1,2-dichloroethane solution containing an IR dye and 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD) (30 wt%), and then vacuum evaporating an Al electrode as a cathode. The molecular structures of the four IR dyes studied in this work are shown in Figure 1. We investigated two



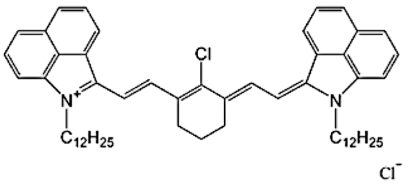
IR1050



IR1051



IR1061



S0447

FIGURE 1 Molecular structures of the IR dyes.

cyanine dyes, 1-butyl-2-[2-[3-[(1-butyl-6-chlorobenz[*c,d*]-indol-2(1H)-ylidene)ethylidene]-2-chloro-5-methyl-1-cyclohexen-1-yl]ethenyl]-6-chlorobenz[*c,d*]-indolium tetrafluoroborate (IR1050) and 2-[2-[2-chloro-3-[2-(1-dodecyl-1,2-dihydro-benzo[*c,d*]-indol-2-ylidene)-ethylidene]-1-cyclohexen-1-yl]-ethenyl]-1-dodecyl-benzo[*c,d*]indolium chloride (SO447) and one thiopyrilium dye, 4-[2-[2-chloro-3-[(2,6-diphenyl-4H-thiopyran-4-ylidene)ethylidene]-1-cyclohexen-1-yl]ethenyl]-2,6-diphenyl-thiopyrilium tetrafluoroborate (IR1061). We used the fourth dye, 6-chloro-2-[2-[3-[(6-chloro-1-ethylbenz[*c,d*]-indol-2(1H)-ylidene)-ethylidene]-2-phenyl-1-cyclopenten-1-yl]ethenyl]-1-ethylbenz[*c,d*]-indolium tetrafluoroborate (IR1051), as a reference material since its

EL characteristics have already been studied [4]. The IR dye concentration was 1 wt% except in the experiments on the dye concentration dependence of the EL characteristics. All the IR dyes (Sigma-Aldrich and FEW chemicals), PBD (Dojindo Laboratories) and PVK (Aldrich) were obtained commercially and used without further purification. We measured the EL characteristics using previously reported experimental setups [8].

3. RESULTS

Figures 2(a) and (b), respectively, show the IR EL spectra and the EL intensity as a function of electric field strength of the four IR dyes. The EL starts to be detected at an electric-field strength of around 1 MV/cm regardless of the dye. The EL spectra of the IR dyes located at around 1100 nm agree closely with the photoluminescence (PL) spectra of the same dyes [3]. The IR EL spectra of IR1050 and IR1051 exhibit an additional emission band on the shorter wavelength side of the main IR EL band, as indicated in Figure 2(a). This emission band can be ascribed to EL originating from dimers [2,4], which are also characterized by absorption and weak fluorescence bands located on the blue side of the monomer band. IR EL materials unaccompanied by dimers are better as regards achieving high-efficiency IR EL since the dimer EL competes with the main IR EL.

Figure 3 plots the IR EL intensities of the four IR dyes as a function of current density. In these experiments the dye concentration was fixed at 1 wt%. The dimer EL intensity increases with the current density for IR1050 and IR1051 whereas the IR EL spectrum shape for IR1061 and S0447 is independent of the current density without any accompanying dimer EL. The IR EL intensity is the largest for SO447 and is about eight times larger than that of the other three IR dyes. The IR EL efficiency for S0447 reaches $1.7 \times 10^{-2}\%$ photons/electron. This value is comparable to the visible EL of Rhodamine B ($1.0 \times 10^{-2}\%$ photons/electron) [9] and Rhodamine 6 G ($1.9 \times 10^{-2}\%$ photons/electron) [9] and the near-IR EL of LDS821 ($1.5 \times 10^{-2}\%$ photons/electron) [8] in LEDs having the same material composition and device structure (a single organic functional layer and an Al cathode). The IR EL efficiency for SO447 is increased to $3.6 \times 10^{-2}\%$ photons/electron at its optimized concentration of 0.6 wt% (PBD concentration: 30 wt%). As previously detected in IR1051 [4], all the IR dyes exhibit visible/near-IR EL and the visible/near-IR EL intensity also depends strongly on the doped dye. As with the IR EL, the visible/near-IR EL intensity is the largest for SO447 and is about six and thirty-one times larger than those for IR1050 and IR1061, respectively. The visible/near-IR EL is another dominant process that

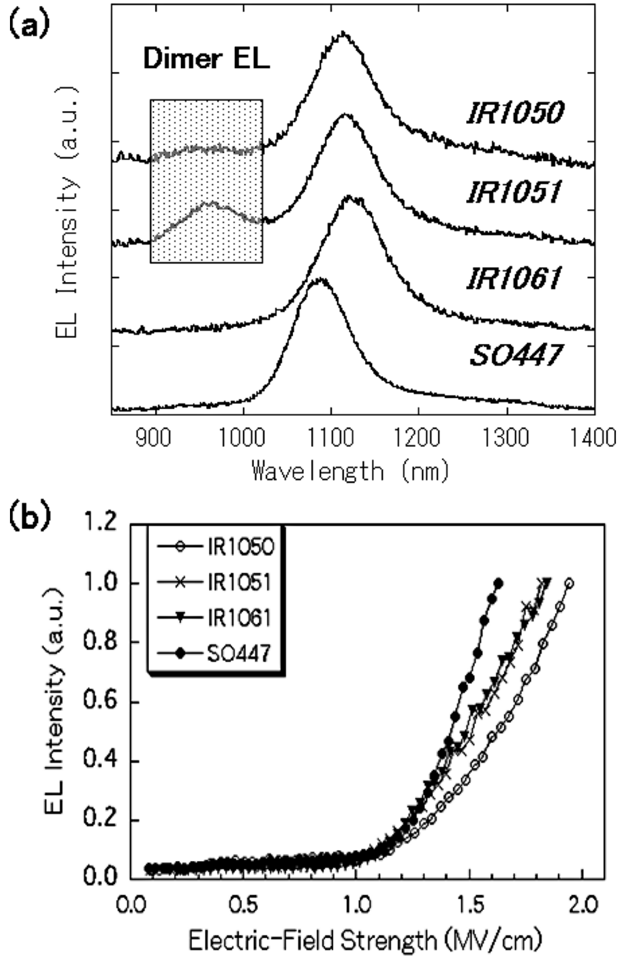


FIGURE 2 The IR EL spectra (a) and the EL intensity as a function of electric-field strength curves (b) of the IR dyes. The spectrum baselines in (a) are shifted for clarity.

competes with the main IR EL process since it has a larger intensity than the IR EL.

4. DISCUSSION

Here we discuss the marked doped dye dependence of the EL characteristics observed in this study. The EL efficiency η is given by $\eta = \varphi\xi\psi$ where φ, ξ, and ψ are the charge carrier trapping efficiency of the

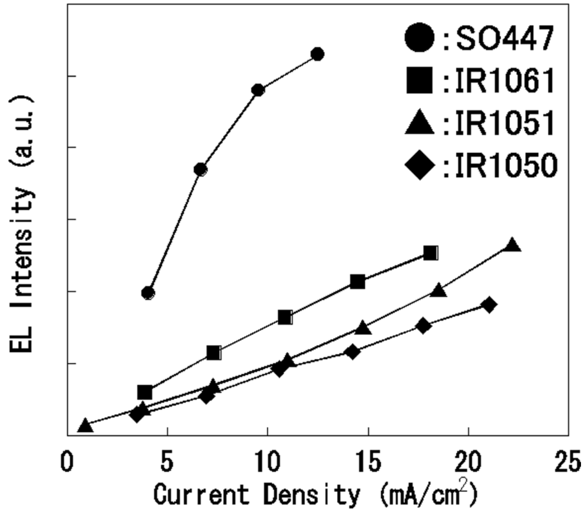


FIGURE 3 IR EL intensity as a function of current density. The EL intensity was taken to be the maximum intensity of the main IR EL since its spectral shape is approximately independent of the doped dye (see Fig. 2(a)).

doped dye, the probability of singlet excited state formation by the electron-hole recombination, and the radiative decay efficiency of the singlet excited state, respectively. Since we can reasonably assume ξ to be independent for the doped dyes used in this study and ψ to be given by the PL efficiency ϕ, we can discuss the observed doped dye dependence of the IR EL efficiency in terms of ϕ and φ, namely, $\eta \propto \varphi\phi$. The ϕ values of the doped dyes in 1,2-dichloromethane solution are listed in Table 1. Table 1 and Figure 3 clearly indicate that the PL efficiency ϕ is a major factor in determining the observed marked dye dependence. However, the observed ratio is different for the PL efficiency (1:4.3:12.5 for IR1050:IR1061:SO447) and for the IR EL

TABLE 1 The Characteristics of Processes Related to the Main IR EL

	PL efficiency	Dimer EL	Relative vis/ near-IR EL intensity	m at high V[a]
IR1050	0.004 ± 0.001^5	Observed	5.1	2.8
IR1061	0.017 ± 0.005^5	Not observed	1	3.0
SO447	0.05 ± 0.01	Not observed	31	4.3

[a] Voltages after EL emission.

(1:1.8:8.1 for IR1050:IR1061:SO447). This discrepancy is evidence of the fact that the dimer and visible/near-IR EL are additional factors that influence the observed dye dependence since they compete with the IR EL in the deactivation process of the excited singlet states generated by the electron-hole recombination. This situation is clearly seen in IR1050 and 1061, where the IR EL intensity becomes larger as the visible/near-IR EL intensity becomes smaller. This balancing behavior is the result of mutual competition between the three types of EL process, namely the IR, visible/near-IR and dimer EL, in the

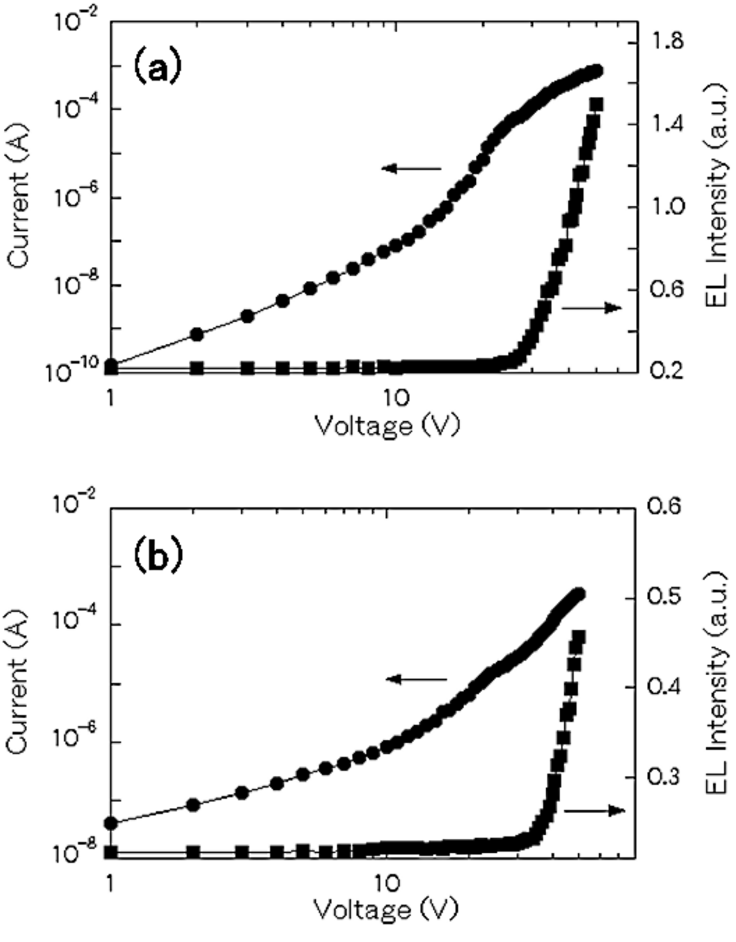


FIGURE 4 Double logarithmic plots of the current-voltage-EL intensity curves for IR1061 (a) and SO447 (b).

radiative deactivation processes of the excited states generated with a comparable efficiency by the electron-hole recombination. In contrast, SO447 has the largest IR and visible/near-IR EL intensity, indicating that the excited states are the most efficiently generated in this dye during the operation.

This is explained by analyses of the current-voltage-EL intensity (I-V-EL) curves of these LEDs. In spite of their marked dependence on the doped dye, the I-V-EL curves can be fitted by the power law ($I \propto V^{m+1}$), namely the space-charge-limited current (SCLC) model [10]. Figure 4(a) and (b) show double logarithmic plots of the I-V-EL curves for IR1061 and SO447, respectively. In the LEDs examined in this study, the current was dominated by holes, whereas the EL intensity reflects the supply of electrons. We therefore primarily see holes in the I-V curves. The low voltage current is determined by the accumulated space charges at hole traps and the doped dyes. At high voltages, electrons start to be injected into the organic layer leading to EL emission by recombination with the trapped holes. This recombination, in turn, neutralizes the space charges in the organic layer, which results in an increase in the m value caused by the increase in the hole current. Therefore, the m value after the EL emission is directly related to the EL efficiency since it is a qualitative measure of the magnitude of the effectiveness of the space-charge neutralization, which is determined by the φ value of the doped dyes. In practice, this has been experimentally demonstrated in the visible EL from various visible light-emitting materials [11]. The m values after the EL emission obtained by the fitting are listed in Table 1. Of the IR dyes studied here, the m value is the largest for SO447, and thus this dye has the largest φ value. This, together with the fact that it has the largest PL efficiency and exhibits no dimer EL, reveals why SO447 is the most efficient IR EL dye.

5. CONCLUSION

We investigated the EL characteristics of four IR polymethine dyes, IR1050, IR1051, IR1061 and SO447, and we obtained a measured IR EL quantum efficiency of $3.6 \times 10^{-2}\%$ photons/electron for SO447 by optimizing its concentration. We discussed the marked dye dependence of the IR EL characteristics in terms of PL efficiency, competitive visible/near-IR EL and dimer EL, and the trapping efficiency, which is qualitatively obtained by analyzing the I-V-EL curves on the basis of the SCLC model. SO447 is promising with a view to fabricating active and/or passive optical devices since its EL wavelength is compatible with various optical media such as silicon photonic crystals

[12], polymer optical fibers and polymer waveguides. If we use an IR dye with a larger PL intensity and a lower visible/near-IR and dimer EL intensity, and optimize the device structure we will further improve the IR EL efficiency of polymethine dyes.

REFERENCES

[1] Suzuki, H. (2004). *J. Photochem. Photobiol. A: Chemistry*, *166*, 155.
[2] Casalboni, M., De Matteis, F., Merlo, V., Prosposito, P., Russo, R., & Schutzmann, S. (2003). *Appl. Phys. Lett.*, *83*, 416.
[3] Casalboni, M., De Matteis, F., Prosposito, P., Quatela, A., & Sarcinelli, F. (2003). *Chem. Phys. Lett.*, *373*, 372.
[4] Suzuki, H. (2002). *Appl. Phys. Lett.*, *80*, 3256.
[5] Gillin, W. P. & Curry, R. J. (1999). *Appl. Phys. Lett.*, *75*, 1380.
[6] Kawamura, Y., Wada, Y., Hasegawa, Y., Iwamuro, M., Kitamura, T., & Yanagida, S. (1999). *Appl. Phys. Lett.*, *74*, 3245.
[7] Hong, Z., Liang, C., Li, R., Zang, F., Fan, D., Li, W., Hung, L. S., & Lee, S. T. (2001). *Appl. Phys. Lett.*, *79*, 1942.
[8] Suzuki, H. (2000). *Appl. Phys. Lett.*, *76*, 1543.
[9] Suzuki, H. (2001). *Thin Solid Films*, *393*, 352.
[10] Pope, M. & Swenberg, C. E. (1982). *Electronic Processes in Organic Crystals*, Oxford: New York, USA.
[11] Suzuki, H. & Hoshino, S. (1996). *J. Appl. Phys.*, *79*, 8816.
[12] Notomi, M., Suzuki, H., & Tamamura, T. (2001). *Appl. Phys. Lett.*, *78*, 1325.