A New Class of High-Performance Red-Fluorescent Dyes for Organic Electroluminescent Devices, [7-Diethylamino-3-(2-thienyl)chromen-2-ylidene]-2,2-dicyanovinylamine and {10-(2-Thienyl)-2,3,6,7-tetrahydro-1H,5H-chromeno[8,7,6-ij]quinolizin-11-ylidene}-2,2-dicyanovinylamine

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A new and better generation of red-fluorescent dyes based on a chromene-2-ylidene moiety, [7-diethylamino-3-(2-thienyl)-chromen-2-ylidene]-2,2-dicyanovinylamine (ACY) and {10-(2-thienyl)-2,3,6,7-tetrahydro-1H,5H-chromeno[8,7,6-ij]quinolizin-11-ylidene}-2,2-dicyanovinylamine (CQY), has been designed and synthesized, and has been proven to function as excellent red-emitting dopants in high-performance red-emitting organic electroluminescent devices.

Luminescent dyes have been receiving a great deal of attention in view of both academic interest and application for organic electroluminescent (EL) devices. Doping of a luminescent material in a host matrix is an effective method for attaining high brightness and desirable emission color in organic EL devices.[1] Among blue-, green-, and red-emitting materials that are required for full-color display, few materials that emit red light of high brightness and narrow emission bandwidth are known. It is a subject of current interest and importance to develop high-performance red-emitting materials that function either as the recombination center for holes and electrons or as dopants dispersed in a host matrix. We report here the synthesis of a new and better generation of red-fluorescent dyes and the fabrication of high-performance red-emitting organic EL devices using these dyes as dopants.

Hitherto reported red-emitting materials include chelates[2] and organic dyes.[3] Europium complexes exhibit emission with narrow bandwidths at around 610 nm; however, the luminance of organic EL devices using europium complexes as red emitters has been reported to be very low, being in the range from 30 to 460 cd m^{-2} at driving voltages from 9 to 26 V.[2a,2b] Organic EL devices using ruthenium complexes exhibit luminances from 1000 to 2000 cd m^{-2}.[2c,2d] Red-emissive dyes, e.g., 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM1) and 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-8-yl)vinyl]-4H-pyran (DCM2), have been used most extensively as luminescent dopants for red-emitting organic EL devices.[3a–3e] The devices using such DCM dyes exhibit relatively high luminances from several hundreds to 4,000 cd m^{-2};[3d,3e] however, the full width at the half maximum (FWHM) of their emission bands is wide, being ca. 100 nm. In addition, the synthetic procedure of the DCM dyes requires several steps. Organic EL devices using other red-emissive dyes as dopants, e.g., tetraphenylchlorin and 6,13-diphenylpentacene, have been reported to exhibit luminances of 100 and 1,000 cd m^{-2}, respectively.[3f,3g] In addition to the above fluorescence emitters, triplet phosphors such as platinum and iridium complexes have also been receiving attention as emissive dopants.[4]

In this work, we have focussed our attention to the design and synthesis of a new class of red-fluorescent dyes based on a chromene-2-ylidene moiety, [7-diethylamino-3-(2-thienyl)chromen-2-ylidene]-2,2-dicyanovinylamine (ACY) and {10-(2-thienyl)-2,3,6,7-tetrahydro-1H,5H-chromeno[8,7,6-ij]quinolizin-11-ylidene}-2,2-dicyanovinylamine (CQY). The incorporation of diethylamino and dicyanovinyl moieties as the electron-donating and electron-accepting groups is intended to provide intramolecular charge-transfer character, and hence, to bring about significant red shift of the emission bands relative to those of coumarin dyes. These dyes exhibit red emission with both high brightness and narrow FWHM, functioning as highly efficient red-emissive dopants for use in organic EL devices.
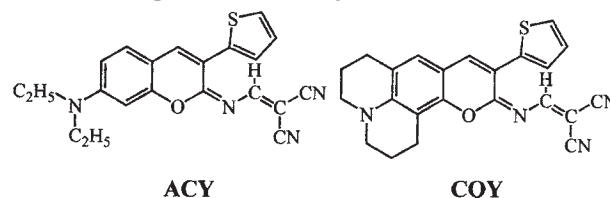
ACY was synthesized by the reaction of 2-thienylacetonitrile (TAN) with 4-(diethylamino)salicylaldehyde (DMSA) to give 7-diethylamino-3-(2-thienyl)iminocoumarin, followed by the reaction with ethoxymethylenemalonitrile. The synthetic procedure of ACY is shown in Scheme 1.
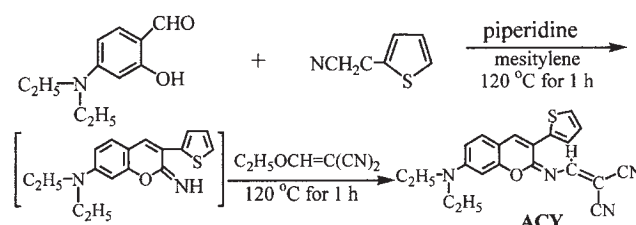
Scheme 1. Synthesis of ACY.

The reaction mixture of TAN and DMSA was heated in mesitylene at 120 °C for 1 h in the presence of piperidine, and the resulting dark green-colored solution was cooled to room temperature. To this solution was added ethoxymethylenemalonitrile, and the reaction solution was again heated at 120 °C for further 1 h. When the resulting solution was cooled, the product precipitated from the solution. The precipitate was purified by silica-gel column chromatography, followed by vacuum sublimation to yield dark blue metallic luster powders of ACY. Likewise, CQY was synthesized starting from 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinolizin-9-carboxaldehyde and purified by the same procedure. The new compounds, ACY and CQY, were identified by various spectroscopic methods, mass spectrometry, and elemental analysis.[5]

Figure 1 shows the electronic absorption and fluorescent spectra of ACY and CQY in dilute THF solution $(1.0 \times 10^{-5} \text{ mol dm}^{-3})$. ACY and CQY show two bands peaking at 357 $(\varepsilon = 4.94 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1})$ and 550 nm $(\varepsilon = 5.69 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1})$, and 365 $(\varepsilon = 3.08 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1})$ and 572 nm $(\varepsilon = 4.57 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1})$, respectively. They exhibit intense red fluorescence peaking at 615 and 632 nm in dilute solution with high quantum efficiencies of 0.81 and 0.93 for ACY and CQY, respectively. The absorption and fluorescence bands undergo red shift with increasing polarity of solvents. Bright red fluorescence is observed when these dyes are dispersed at small concentrations in a host matrix such as tris(8-quinolinolato)aluminum (Alq_3) film. The photoluminescence (PL) spectra of ACY and CQY (1 mol%)-doped Alq_3 films (ca. 100 nm thick) show fluorescence emission bands with a peak at ca. 645 and 655 nm originating from ACY and CQY, respectively, by irradiation with 380 nm monochromatic light which is absorbed by both Alq_3 and the dyes. No fluorescence emission attributable to Alq_3 was observed. This result indicates that efficient singlet excitation energy transfer takes place from the host Alq_3 to the guest ACY or CQY.
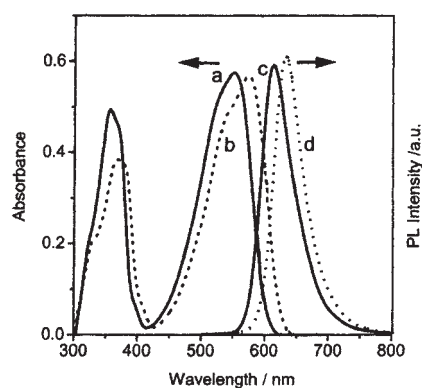

Figure 1. The electronic absorption and fluorescence spectra of ACY (a and c, solid lines) and CQY (b and d, dotted lines) in THF solution $(1.0 \times 10^{-5} \text{ mol dm}^{-3})$.

Double-layer organic EL devices using 4,4′,4″-tris[3methyl-phenyl(phenyl)amino]triphenylamine (m-MTDATA)[6] as a hole-transport layer and ACY or CQY-doped Alq_3 as an electron-transporting emitting layer were fabricated by sequential vacuum deposition of the organic materials onto an indium-tin-oxide (ITO)-coated glass substrate (sheet resistance 50 $\Omega/\square$) at 8×10^{-6} torr, followed by vacuum deposition of an alloy of magnesium and silver (Mg : Ag = 10 : 1) (4 mm^2) onto the organic layer.

The fabricated devices, ITO/m-MTDATA(50 nm)/ACY(1 - mol%)-doped Alq_3(50 nm)/MgAg (Device A) and ITO/m-MTDATA(50 nm)/CQY(2.2 mol%)-doped Alq_3 (50 nm)/MgAg (Device B), exhibited bright red light originating from ACY and CQY, respectively. The red emission was uniform over the entire active area of the devices. The EL spectra of both devices were in good agreement with the PL spectra of ACY and CQY dispersed in the Alq_3 film, respectively. Neither green emission resulting from Alq_3 nor yellow emission resulting from the exciplex[7] formed at the interface between the hole-transporting m-MTDATA and electron-transporting Alq_3 layers was observed. It is indicated that efficient excitation energy transfer takes place

from the host Alq_3 to the dopant ACY or CQY and that the exciplex formation at the interface between m-MTDATA and Alq_3 is effectively prevented by doping.

It is noteworthy that the devices using ACY or CQY as the red-emissive dopant exhibit the EL spectra with a FWHM of 68 and 60 nm, respectively, which are significantly narrower than those of the reported devices using DCM dyes as dopants. Device A using ACY as the dopant exhibited very high performance with a turn-on voltage of 5 V, a maximum luminance of 6,400 cd m^{-2} at 15 V, a luminous efficiency of 1.3 lm W^{-1}, and an external quantum efficiency of 0.8% at a luminance of 300 cd m^{-2}. To the best our knowledge, the performance of this device, in particular, the maximum luminance and luminous efficiency are of the highest level among hitherto reported fluorescence-based red-emitting organic EL devices. Although the performance of Device B, which exhibited a maximum luminance of 1,000 cd m^{-2} at 15 V, a luminous efficiency of 0.28 lm W^{-1}, and an external quantum efficiency of 0.12% at a luminance of 300 cd m^{-2}, was lower than that of Device A, it is expected that the selection of host materials whose fluorescence bands better overlap with the absorption band of CQY will improve the performance. The CIE coordinates for Device A and Device B using ACY and CQY as the dopant were (0.68, 0.32) and (0.70, 0.30), respectively.

In summary, a new and better generation of red-fluorescent dyes based on a chromene-2-ylidene moiety have been synthesized and characterized. They exhibit bright red fluorescence with high quantum efficiencies and narrow bandwidths, and in particular ACY has proved to function as an excellent red-emitting dopant for high-performance red-emitting organic EL devices. The present molecular design based on the chromene-2-ylidene moiety will enable the synthesis of a variety of dyes containing various functional groups, paving the way for the exploitation of further new red dyes for organic EL devices.

References and Notes

1 C. W. Tang, S. A. Vanslyke, and C. H. Chen, *J. Appl. Phys.*, **65**, 3610 (1989).
2 a) J. Kido, H. Hayase, K. Hongawa, K. Nagai, and K. Okuyama, *Appl. Phys. Lett.*, **65**, 2124 (1994). b) G. E. Jabbour, J. F. Wang, B. Kippelen, and N. Peyghambarian, *Jpn. J. Appl. Phys.*, **38**, L1553 (1999). c) H. Rudmann and M. F. Rubner, *J. Appl. Phys.*, **90**, 4338 (2001). d) F. Gao and A. J. Bard, *J. Am. Chem. Soc.*, **122**, 7426 (2000).
3 a) C. H. Chen, C. W. Tang, J. Shi, and K. P. Klubeck, *Macromol. Symp.*, **125**, 1 (1997). b) V. Bulivić, A. Shoustikov, M. A. Baldo, E. Bose, V. G. Kozlov, M. E. Thompson, and S. R. Forrest, *Chem. Phys. Lett.*, **287**, 455 (1998). c) C. H. Chen, C. W. Tang, J. Shi, and K. P. Klubeck, *Thin Solid Films*, **363**, 327 (2000). d) Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, and T. Usuki, *Appl. Phys. Lett.*, **75**, 1682 (2000). e) X. H. Zhang, B. J. Chen, X. Q. Lin, O. Y. Wong, C. S. Lee, H. L. Hwong, S. T. Lee, and S. K. Wu, *Chem. Mater.*, **13**, 1565 (2001). f) Y. Sakakibara, S. Okutsu, T. Enokita, and T. Tani, *Appl. Phys. Lett.*, **74**, 2587 (1999). g) L. C. Picciolo, H. Murata, and Z. H. Kafafi, *Appl. Phys. Lett.*, **78**, 2378 (2001).
4 a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature*, **395**, 151 (1998). b) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, and M. E. Thompson, *J. Am. Chem. Soc.*, **123**, 4304 (2001).
5 ACY: MS: m/z 374 (M$^+$) mp 252.8 °C. Anal. Calcd for $C_{21}H_{18}N_4OS$: C, 67.36; H, 4.85; N, 14.96; S, 8.56. Found: C, 67.22; H, 4.84; N, 14.77; S, 8.58. ^{1}H NMR (750 MHz, CDCl$_3$) δ: 8.65 (1H, s), 8.00 (1H, s), 7.74 (1H, d, $J = 7.45$), 7.40 (1H, d, $J = 1.65$), 7.39 (1H, d, $J = 1.65$), 7.10 (1H, t, $J = 4.94$), 6.75 (1H, d, $J = 8.92$), 6.56 (1H, s), 3.51 (4H, q, $J = 7.14$), 1.30 (6H, t, $J = 7.14$). CQY: MS: m/z 398 (M$^+$). mp 254.6 °C. Anal. Calcd for $C_{23}H_{18}N_4OS$: C, 69.32; H, 4.82; N, 13.59; S, 8.05. Found: C, 69.32; H, 4.55; N, 14.06; S, 7.82. ^{1}H NMR (750 MHz, CDCl$_3$) δ: 8.52 (1H, s), 7.93 (1H, s), 7.72 (1H, d, $J = 3.71$), 7.37 (1H, d, $J = 5.08$), 7.08 (1H, dd, $J = 3.71, 5.08$), 6.92 (1H, s), 3.38 (4H, m), 2.85 (4H, m), 2.05 (4H, m).
6 Y. Shirota, T. Kobata, and T. Noda, *Chem. Lett.*, **1989**, 1145.
7 K. Itano, H. Ogawa, and Y. Shirota, *Appl. Phys. Lett.*, **72**, 636 (1998).