Fine tuning of the photophysical and electroluminescent properties of DCM-type dyes by changing the structure of the electron-donating group†

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Using 2*H*-indene-1,3-dione as an electron-withdrawing group and aromatic amines of different structures as electron-donating groups, four new DCM-type dyes, IN-1, IN-2, IN-3, and IN-4, were designed and synthesized for application in organic light-emitting diodes (OLEDs) as red light-emitting materials. IN-2 exhibits a red shift in fluorescence but a blue shift in absorption with respect to IN-1. Similarly, IN-4 exhibits a red shift in fluorescence but a blue shift in absorption with respect to IN-3. These unique photophysical properties were utilized to optimize the electroluminescence color purity and efficiency of these red emitters in OLEDs. In EL devices with the configuration of ITO/NPB (60 nm)/Alq₃ (or Gaq₃) : red dopant (2.0 wt%) (7 nm)/BCP (12 nm)/Alq₃ (45 nm)/LiF (0.3 nm)/Al (300 nm), IN-3 in Alq₃ and IN-1 in Gaq₃ show CIE coordinates of (0.64, 0.36) and (0.65, 0.34), and current efficiencies of 3.24 cd A⁻¹ and 3.02 cd A⁻¹, respectively, much better than the other guest/host combinations. This can be ascribed to the good spectrum overlap either between IN-3 and Alq₃ or between IN-1 and Gaq₃, indicating that the absorption spectrum has the same importance as the fluorescence spectrum in the improvement of color purity of red emitters.

1. Introduction

Among the blue-, green-, and red-emitting materials required for full color organic light-emitting diodes (OLEDs), redemitting materials remain one of the greatest challenges in terms of both color purity and efficiency for dynamic research.¹⁻⁴ To realize red light emission, two strategies are commonly applied in material design, *i.e.* utilizing either elongated conjugation structures or intramolecular charge transfer characters.⁵ Thus, most organic red emitters can be classified into two categories, polycyclic aromatic hydrocarbon (PAH) and electron donor- π bridge-electron acceptor (D-n-A) systems. Compared with PAH, D-n-A systems have a remarkable advantage: the ease in fine tuning of their photophysical and electrochemical properties including absorption band, emission color, emission efficiency, as well as redox potentials. This advantage was fully taken over the past decade to develop lots of promising red emitters, such as 4-dicyanomethylene-4H-pyran based dyes (the so called DCM-type dyes), of which 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) still represents one of the most efficient red-emitting materials for OLED applications and has received extensive studies.^{2,4,6-13} Considering its emission color purity, however, DCJTB is far

from ideal. At low doping levels in tris(8-hydroxyquinolinato) aluminium (Alq₃), a well known host material for emitters of different colors, part of the DCJTB emission falls in the region below 600 nm. Although the emission of DCJTB undergoes a red shift upon increasing the doping level, the luminance and efficiency are greatly compromised due to the concentration quenching effect. One solution to this problem is to shift the emission bands of DCM-type dyes to longer wavelengths by structure modification, nevertheless the absorption bands of the resultant dyes generally shift to longer wavelengths also,¹⁴⁻¹⁶ which impairs the spectrum overlap between the emission of Alq₃ and the absorption of DCM-type dyes, and thus decreases the energy transfer efficiency between host and guest. Recently, we designed and synthesized a new congener of DCJTB, DCQTB (2-(2-tert-butyl-6-((E)-2-(2,6,6-trimethyl-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1-ij]quinolin-8-yl)vinyl)-4Hpyran-4-ylidene)malononitrile, Fig. 1), which emits at longer wavelengths but absorbs at shorter wavelengths with respect to DCJTB.¹⁷ This desirable property was obtained by only changing the connecting mode of the nitrogen atom with the N-phenyl ring in the aniline moiety. In DCJTB the nitrogen atom is locked by two six-membered rings, while one sixmembered ring is replaced by a five-membered ring in DCQTB. Thus, it is necessary to investigate further the role of the D structure in DCM-type dyes. While the D structure is receiving increasing attention, the A moiety in DCM-type dyes was little changed for property optimization. Using 2H-indene-1,3-dione to serve as A and 1-phenylpiperidine or 4-phenylmorpholine as D, Kim and co-workers¹⁸ once prepared two new DCM-type dyes, IAP-1 (2-(2-(4-(piperidin-1yl)styryl)-6-methyl-4H-pyran-4-ylidene)-2H-indene-1,3-dione) and IAP-2 (2-(2-(4-morpholinostyryl)-6-methyl-4H-pyran-4ylidene)-2H-indene-1,3-dione). Though it was claimed that

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Fig. 1 Chemical structures of IN-1, IN-2, IN-3, IN-4, DCJTB, DCQTB, and the other materials used in the preparation of EL devices.

IAP-1 had improved color purity compared with DCJTB, the Commission Internationale de l'Eclairage (CIE) coordinates of IAP-1 were x = 0.61, y = 0.38, far from the saturated red emission. With the above-mentioned efforts in mind, four new pyran-containing D– π –A structures (Fig. 1), IN-1, IN-2, IN-3, and IN-4, were prepared to examine the effects of D and A structures on their photoluminescence (PL) and electroluminescence (EL) properties. In solutions, the fluorescence maxima of these four dyes are all located at longer wavelengths than DCJTB, while the absorption maxima cover a wide range with that of DCJTB just in the middle of them. These features make it possible to optimize the color purity of red OLEDs without impairing the energy transfer efficiency between host and guest. As expected, the four dves exhibit promising electroluminescence behaviors, and these behaviors correlate very well with their photophysical properties in solutions.

2. Results and discussion

2.1. Synthesis

Scheme 1 shows the synthetic routes for IN-1, IN-2, IN-3, and IN-4. As an example, IN-2 was prepared as follows. Conventional *N*-alkylation of 1 (Scheme 1) with 1 equiv. of 1-bromo-3-methyl-2-butene gave 2. After annulation in concentrated H_2SO_4 , 2 was transformed into 3. Then, 4 was prepared from 3 by Vilsmeier reaction using DMF/POCl₃ as condensing agent. Finally, the target molecule IN-2 was obtained by the condensation between 4 and 15. IN-1, IN-3, and IN-4 were synthesized in a similar way. As shown in Scheme 1, all reactions have high collection yields (over 70%), which means that the four new DCM-type dyes can be synthesized easily and cost-effectively.

2.2. Photophysical properties

Table 1 shows the absorption and fluorescence maxima of the four new DCM-type dyes in solutions with varied polarity, along with their relative fluorescence quantum yields in THF. For comparison, the corresponding data for DCJTB are also included (see ESI[†] for their absorption and fluorescence spectra).

Compared with DCJTB, both the absorption and fluorescence spectra of IN-1 undergo bathochromic shifts. Considering the fact that the oxidation peak potential of IN-1 is less positive than that of DCJTB (Table 2), the electron-withdrawing ability of the 2H-indene-1,3-dione moiety is not likely to be stronger than that of the dicyanomethylene group. As a result, the red shift is more probably due to the larger conjugation system of IN-1 (see ESI[†] Fig. 4S). To better understand the role of the electron-donating moiety in tuning the photophysical properties, the four new DCM-type dves can be classified into two groups based on their structures, i.e. IN-1 vs. IN-2, and IN-3 vs. IN-4. Very similar to the case of DCJTB vs. DCQTB,¹⁷ substitution of one five-membered locking ring for a six-membered locking ring gives rise to a red shift in the fluorescence but a blue shift in the absorption of IN-2 relative to IN-1. As a result, IN-2 exhibits a bigger Stokes shift than IN-1. The same phenomena can be found in a spectral comparison between IN-3 and IN-4 (λ^{ab}_{max} of IN-4 < λ^{ab}_{max} of IN-3; however, λ^{em}_{max} of IN-4 > λ^{em}_{max} of IN-3) as the result of the structure variation of the aromatic amine moiety.

Fig. 2 shows the plots of the Stokes shifts of DCJTB, IN-1, IN-2, IN-3, and IN-4 as a function of the solvent polarity parameter $f(\varepsilon, n)$, which is defined as eqn (1) where ε is the static dielectric constant and n is the optical refractive index of the solvent.¹⁹ From the slopes, the dipole moment differences ($\Delta\mu$) between the fluorescent singlet excited state (μ_e) and the ground state (μ_g) were calculated (Table 2), based on the Lippert and Mataga theory (eqn (2)).²⁰ In eqn (2), a_0 represents the radius of the Onsager cavity, which was deduced from their energetically optimized ground state geometries obtained with the B3LYP/6-31G(d) basis set (see below). In terms of the energetically optimized ground state geometries, μ_g can also be achieved, thus, μ_e can be estimated as well (Table 2).

$$f(\varepsilon, n) = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$$
(1)

$$v_{\rm a} - v_{\rm f} = 2(\mu_{\rm e} - \mu_{\rm g})^2 \cdot f(\varepsilon, n) / (hca_0^3) + {\rm const}$$
 (2)



Scheme 1 Synthetic routes of IN-1, IN-2, IN-3 and IN-4.

The dipole moment of a $D-\pi$ -A molecule directly depends on the extent of charge separation and the distance across which charge transfer occurs.²¹ The latter factor is similar in both IN-1 and IN-2, assuming that the center of the positive charge lies on the nitrogen atom of the aromatic amine moiety and the center of the negative charge lies on the

Table 1 Absorption and emission properties of IN-1, IN-2, IN-3, IN-4, and DCJTB in solvents of varied polarity

	DCJTB		IN-1		IN-2		IN-3		IN-4	
Solvent	λ^{ab}_{max}/nm^a	$\lambda^{\rm em}_{\rm max}/{\rm nm}^{b}$	λ^{ab}_{max}/nm^a	$\lambda^{\rm em}_{\rm max}/{\rm nm}^b$	λ^{ab}_{max}/nm^a	$\lambda^{\rm em}_{\rm max}/{\rm nm}^{b}$	λ^{ab}_{max}/nm^a	$\lambda^{\rm em}_{\rm max}/{\rm nm}^{b}$	λ^{ab}_{max}/nm^a	$\lambda^{\rm em}_{\rm max}/{\rm nm}^{t}$
Cyclohexane	476.5	530.4	495.2	555.6	461.4	566.0	482.8	542.2	468.5	578.6
Tetrachloromethane	484.5	548.4	504.6	574.2	465.6	584.0	489.8	555.4	474.5	591.8
Chloroform	508.5	607.4	542.0	643.0	493.2	653.0	520.2	616.2	483.5	654.2
Ethyl acetate	493.0	617.0	529.0	656.2	489.2	665.0	506.0	623.4	474.0	656.4
Tetrahydrofuran	498.5	618.0	534.0	660.8	493.4	668.6	510.0	628.0	477.8	661.0
Acetonitrile	503.5	653.8	535.0	717.2	487.6	721.4	509.8	667.6	474.8	718.4
Methanol	510.0	655.0	552.2	718.6	493.6	722.4	521.6	677.0	482.8	722.6
Dimethylformamide	515.5	661.0	547.0	720.8	496.2	723.8	521.4	669.8	482.4	721.2
Dimethylsulfoxide	521.5	668.8	557.4	726.8	499.0	729.2	524.8	680.4	488.2	724.0
$\Phi_{\mathrm{f}}^{\ c}$	1.00		0.85		0.36		1.06		0.50	

Table 2The dipole moments and energy levels of DCJTB, IN-1,IN-2, IN-3, and IN-4

	$\Delta \mu / \mathbf{D}^a$	$\mu_{\rm g}/{ m D}^b$	$\mu_{\rm e}/{\rm D}^c$	$a_0/\text{\AA}^d$	$E_{\rm p}^{\rm ox}/{\rm eV}^e$
DCJTB	13.1	5.9	19.0	6.10	1.08
IN-1	16.3	3.8	20.1	6.05	0.94
IN-2	17.1	3.7	20.8	6.23	1.03
IN-3	16.4	3.5	19.9	6.08	1.01
IN-4	16.9	2.8	19.7	6.61	1.38

^{*a*} Difference between the dipole moments (in Debye) of the excited state and the ground state, obtained from Fig. 2 and eqn (2). ^{*b*} Dipole moment of the ground state obtained from quantum-chemical calculation. ^{*c*} Dipole moment of the excited state obtained from $\Delta\mu$ and $\mu_{\rm g}$. ^{*d*} Onsager cavity obtained from quantum-chemical calculation. ^{*e*} The oxidation peak potential *vs.* SCE.



Fig. 2 Plots of the Stokes shifts of DCJTB, IN-1, IN-2, IN-3, and IN-4 as a function of the solvent polarity parameter $f(\varepsilon, n)$.

2*H*-indene-1,3-dione moiety. Thus, the larger μ_e implies that the structure variation of IN-2 from IN-1 facilitates the intramolecular charge transfer in the excited states. Moreover, the bigger Stokes shift and $\Delta \mu$ of IN-2 suggest that the excited state equilibrium nuclear geometry distorts from the ground state equilibrium nuclear geometry more greatly in IN-2 than in IN-1, as shown in Fig. 3. In this situation, the absorption of IN-2, *i.e.*, the transition from the lowest vibrational level in the



Fig. 3 Pictorial illustration of the potential energy curves of the ground state (GS) and singlet excited state (ES) of IN-1 and IN-2. The vertical arrows denote the absorption and emission transitions.

ground state to the singlet excited state, is observed at higher energy, but the fluorescence of IN-2, *i.e.*, the jump from the lowest vibrational level of the singlet excited state to the ground state, is at lower energy. The greater distortion extent of the excited state with respect to the ground state also increases the vibrational overlap and favors non-radiative decay,²² which is in line with the fact that the fluorescence quantum yield of IN-2 is lower than that of IN-1 (Table 1). Recently, Ishitani et al. observed that the intramolecular interactions between ligands in Re(I) complexes red shifted absorption but blue shifted emission, and a similar explanation was applied to these discrepant phenomena.²³ The red shift in fluorescence and blue shift in absorption of IN-4 with respect to IN-3 can be understood similarly. The possible structureproperty relationships underlying these interesting findings are discussed below.

It is worthwhile to note that (1) all the four new DCM-type dyes emit at longer wavelengths than DCJTB, and (2) their absorption maxima fall in a wide range with that of DCJTB just located between them (Table 1). The former feature may help the improvement of the color purity of EL devices based on these new red emitters, while the latter one may facilitate the choice of adequate host material to get better spectral overlap and thus energy transfer efficiency between host and guest.

2.3. Redox properties

The redox behaviors of these DCM derivatives were determined by cyclic voltammetry $(CV)^{24}$ in dry chloroform, and the oxidation peak potentials are shown in Table 2 (see ESI† for their cyclic voltammograms). While IN-1, IN-2, and IN-3 have similar oxidation peak potentials, the oxidation peak potential of IN-4 shifts to the positive direction remarkably, implying its stronger resistance to oxidation. The sharp contrast of IN-4 with respect to its three congeners may be the result of its distorted structure and therefore impaired conjugation extent (see below).

2.4. Quantum-chemical calculation of electronic structure

In an effort to understand at the molecular level the nature behind the different photophysical properties of these new DCM-type dyes, density functional theory (DFT) was used to calculate their electronic structures. Fig. 4 shows their optimized ground-state geometries obtained with the B3LYP/ 6-31G(d) basis set, while the main dihedral angles, by which the structures can be defined, are tabulated in Table 3. Moreover, the sum of bond angles (θ) about the N atom in the aromatic amine moiety is also included in Table 3. One would expect a larger orbital overlap between the amine nitrogen and the *N*-phenyl when the θ value is closer to 360° .²⁵ Thus, the replacement of one six-membered locking ring by a five-membered one decreases the electronic communication between the amine nitrogen and the N-phenyl in IN-2, reflected by the smaller θ (354.1° in IN-2 vs. 360° in IN-1) and larger dihedral angels ($|C53-N17-C2-C3| = 14.1^{\circ}$ and $|C13-N17-C2-C1| = -12.0^{\circ}$ in IN-2 vs. |C62-N15-C2-C3| = 6.9° and $|C12-N15-C2-C1| = 6.9^{\circ}$ in IN-1). The decreased orbital overlap between the amine nitrogen and the N-phenyl



Fig. 4 Optimized ground-state geometries of IN-1, IN-2, IN-3, and IN-4 obtained with the B3LYP/6-31G(d) basis set.

Table 3 Structure parameters for IN-1, IN-2, IN-3, and IN-4 calculated using the DFT/B3LYP/6-31G(d) method

	IN-1	IN-2	IN-3	IN-4
$ heta^a l^\circ \ lpha^b l^\circ$	360.0 $ 62-15-2-3 = 6.9$ $ 12-15-2-1 = 6.9$ $ 4-5-16-18 = -0.2$ $ 16-18-20-21 = -180.0$ $ 21.40, 41.42 = 0.0$	354.1 $ 53-17-2-3 = 14.1$ $ 13-17-2-1 = -12.0$ $ 4-5-26-28 = -0.8$ $ 26-28-30-31 = 179.5$ $ 21-50-50-51 = -0.1$	357.5 $ 12-74-2-1 = -2.6$ $ 63-74-2-75 = 18.8$ $ 3-4-23-25 = -0.8$ $ 23-25-27-28 = 179.2$ $ 28-25-27-28 = 179.2$	$\begin{array}{l} 357.9\\ 11-73-2-1 = 33.3\\ 62-73-2-74 = 54.4\\ 3-4-22-24 = -27.8\\ 22-24-26-27 = 177.8\\ 27-24-26-27 = 177.8\\ 27-24-26-27 = 0.1\\ \end{array}$
^a The sum	121-40-41-43 = 0.0 of bond angles about the N ator	51-50-59-61 = -0.1 n. ^b Some dihedral angels asso	26-47-48-50 = 0.2	2/-40-47-49 = 0.1 ne text. The numbers within the two

vertical lines denote the atoms involved in the corresponding dihedral angles (see Fig. 4).

will weaken the electron-donating ability of the corresponding aromatic amine, as a result, IN-2 exhibits a somewhat smaller dipole moment in the ground state ($\mu_g = 3.7 \text{ D}$) with respect to that of IN-1 (μ_g = 3.8 D). Upon excitation, IN-2 experiences a larger dipole moment change and thus exhibits a greater excited state dipole moment ($\mu_e = 20.8$ D) than IN-1 ($\mu_e =$ 20.1 D), suggesting that the aromatic amine moiety of IN-2 may adopt a more planar conformation in the excited state than in the ground state, while that of IN-1 may deviate from the original planarity to adapt the varied electron density distribution in the excited state. In the case of IN-3 and IN-4, the presence of an extra phenyl structure (naphthalene group) in IN-4 introduces a remarkable steric hindrance, and accordingly, distorts the ground state structure greatly, which is evidenced by the larger dihedral angle of |C3-C4-C22-C24| (-27.8°) in IN-4 than that of |C3-C4-C23-C25| (-0.8°) in IN-3. Thus, the charge transfer is restricted in IN-4 due to the weakened conjugation between the aromatic amine and the other part of the molecule, though the θ angles are very similar in both IN-3 and IN-4. The smaller ground state dipole moment of IN-4 (μ_g = 2.8 D) than that of IN-3 (μ_g = 3.5 D) agrees with the distorted conjugation system of IN-4. In the excited state, the difference between the dipole moments of IN-4 and IN-3 becomes smaller, implying the steric hindrance caused by the naphthalene group is alleviated to some extent, probably due to the shift of the electron density from the aromatic amine moiety to the electron-withdrawing moiety upon excitation.

Fig. 4S (ESI[†]) shows the plots of the molecular orbitals in the ground states of IN-1, IN-2, IN-3, IN-4, and DCJTB. In these molecules, the HOMOs are mainly localized within the electron-donating fraction. In contrast, the LUMOs are mainly localized within the electron-withdrawing fraction, indicative of the great extent of intramolecular charge transfer upon excitation.

2.5. Electroluminescent properties

Generally, the EL color and efficiency of the DCM-type dyes depend remarkably on their doping level in host materials. Thus, EL devices, having the configuration of ITO/NPB (60 nm)/Alq3 : IN-1 (x wt%) (7 nm)/BCP (12 nm)/Alq3 (45 nm)/ LiF (0.3 nm)/Al (300 nm), were first fabricated and examined (Fig. 5). In these devices, NPB serves as the hole-transporting material, BCP as the hole-blocking material, and Alq₃ as both the host material and electron-transporting material. At the doping concentration of 0.5 wt%, the EL emission from Alq₃, which is located at around 520 nm, is obvious (Fig. 5b), indicating the inefficient energy transfer from Alq₃ to IN-1. With the increase of the doping level, EL emissions shifted to longer wavelengths gradually, however, the luminance efficiency decreased simultaneously (Fig. 5a and Table 4). The spectrum shift is due to the polarization $effect^{26,27}$ and the efficiency decrease is the result of concentration quenching. Considering the trade-off between efficiency and color purity, the EL property comparison of our four new DCM-type dyes were all based on the devices at 2 wt% doping concentration.



Fig. 5 Electroluminescence characteristics of IN-1 doped in Alq_3 at different concentrations. (a) Luminance vs. current density; (b) EL spectra at the applied voltage of 9 V.

Table 4 EL characteristics of IN-1, IN-2, IN-3, IN-4, along with those of DCJTB cited from references for comparison

	$L_{\rm max}/{\rm cd}~{\rm m}^{-2-f}$	(J, V) at $L_{\text{max}}/$ mA cm ⁻² , V ^g	(η_c, L) at 20 mA cm ⁻² /cd A ⁻¹ , cd m ^{-2h}	EL peak/nm	CIE $(x, y)^i$	Reference	
$[N-1 (0.5)^a]$	12270	(357.7.13)	(3.86, 770.7)	632	(0.52, 0.42)	This work	
IN-1 $(1.0)^a$	7900	(373, 15)	(3.65, 718)	644	(0.62, 0.37)	This work	
IN-1 $(2.0)^a$	5654	(376.6, 14)	(2.22, 471)	652	(0.63, 0.36)	This work	
IN-1 $(3.5)^a$	4892	(388.3, 12)	(1.24, 260)	660	(0.65, 0.34)	This work	
$IN-1(2.0)^{b}$	7842	(404.4, 15.5)	(3.02, 630.6)	652	(0.65, 0.34)	This work	
$(N-2(2.0)^a)$	6100	(305.8, 15)	(2.47, 508.2)	668	(0.66, 0.33)	This work	
$(N-3(2.0)^a)$	8387	(393, 16.5)	(3.24, 642.6)	628	(0.64, 0.36)	This work	
$(10.4)^{a}$	4472	(499, 15)	(1.47, 288)	654	(0.62, 0.37)	This work	
DCJTB ^c	_	_	$(1.89, 378)^{i}$	620	(0.63, 0.37)	8	
$DCJTB^{d}$	15000	_	$(-, 1200)^{i}$	628	(0.62, 0.38)	10	
DCJTB ^e	_	_	$(4.44, 966)^{i}$	630	(0.65, 0.35)	7	

^{*a*} ITO/NPB (60 nm)/Alq₃ : dopant (x wt%) (7 nm)/BCP (12 nm)/Alq₃ (45 nm)/LiF (0.3 nm)/Al (300 nm), x is shown in the bracket following the compound name. ^{*b*} ITO/NPB (60 nm)/Gaq₃ : dopant (x wt%) (7 nm)/BCP (12 nm)/Alq₃ (45 nm)/LiF (0.3 nm)/Al (300 nm). ^{*c*} ITO/CFx/NPB/Alq₃ : DCJTB (1%)/Alq₃/LiF/Al. ^{*f*} ITO/NPB/Alq₃ : QAD (0.5%) : DCJTB (1%)/Alq₃/LiF/Al. ^{*f*} ITO/CFx/NPB/Alq₃ : rubrene (60%) : DCJTB (2%)/Alq₃/LiF/Al. ^{*f*} Maximum luminance. ^{*g*} Current density (*J*) and voltage (*V*) at L_{max} . ^{*h*} Current efficiency (η_c) and luminance (*L*) at 20 mA cm⁻². ^{*i*} CIE coordinates. ^{*j*} Maximum current efficiency (η_c) and luminance (*L*) at 20 mA cm⁻².

At this doping level, the device based on IN-1 : Alq₃ still showed residual Alq₃ emission, suggesting poor spectral overlap between host and guest. When Gaq₃ was used as the host material instead of Alq₃, whose emission spectrum has a red shift over that of Alq₃,²⁶ significant improvements in both color purity and current efficiency were achieved. At the driving voltage of 9 V, the CIE coordinates of IN-1 (2 wt%) : Gaq₃ and IN-1 (2 wt%) : Alq₃ are (0.65, 0.34) and (0.63, 0.36), respectively. The current efficiency of IN-1 doped in Gaq₃ (2 wt%) is 3.02 cd A^{-1} , about 40% higher than that doped in Alq₃ at the same doping concentration. The improved performance can be attributed to the better spectral overlap between IN-1 and Gaq₃. Another way to strengthen the spectrum overlap of the dopant with Alq₃ is to use red emitters with blue shifted absorption compared with that in IN-1. IN-2 has a blue shifted absorption spectrum compared with that of IN-1 in solution, this character is expected to be still valid in the doped film. On the other hand, IN-2 emits at longer wavelengths than IN-1. Thus, the combination of IN-2 with Alq₃ might give promising EL properties. As expected, the device based on IN-2 (2 wt%) : Alg₃ indeed exhibited improved color purity (CIE coordinates of 0.66, 0.33 vs. 0.63, 0.36, Table 4) and even enhanced current efficiency $(2.47 \text{ cd } \text{A}^{-1} \text{ vs. } 2.22 \text{ cd } \text{A}^{-1} \text{ at } 20 \text{ mA cm}^{-2}$, Table 4 and Fig. 6a) compared with those of the device based on IN-1 (2 wt%): Alq₃, though the fluorescence quantum yield of IN-2 in THF is only about half that of IN-1 (Table 1). Among the four new DCM-type dyes, IN-3 showed the highest current efficiency (Table 4 and Fig. 6c). Considering the facts that its absorption maximum (510 nm in THF) is just between those of IN-1 (534 nm) and IN-2 (493.4 nm), and its fluorescence quantum yield in THF is the highest (Table 1), its EL behavior is not difficult to understand. In contrast, IN-4 behaves the worst in both color purity and current efficiency. The CIE coordinates of the IN-4 (2 wt%) : Alq₃ based device are (0.62,0.37), much inferior to its three congeners. The over-blueshifted absorption spectrum of IN-4 ($\lambda^{ab}_{max} = 477.8$ nm) may impair the spectrum overlap with Alq₃ emission, and thus be responsible for its poor EL color. Additionally, this point combined with its low fluorescence quantum yield results in the decreased current efficiency.

Table 4 also includes the data from the red OLEDs based on DCJTB and assistant dopants. Though the device structure was not fully optimized, IN-3 in Alq₃ and IN-1 in Gaq₃ show comparable electroluminescent behaviors to the tertiary emitting systems of DCJTB–rubrene or quinacridone–Alq₃,^{7,10,25} showing the importance of the fine tuning of the photophysical properties of DCM-type dyes.



Fig. 6 Electroluminescence characteristics of IN-1, IN-2, IN-3, and IN-4 dopants. (a) Luminance vs. current density; (b) luminance vs. voltage; (c) current efficiency vs. current density; (d) EL spectra at the applied voltage of 9 V.

3. Experimental

General information

¹H NMR spectra were recorded on a Varian Gemini-300 (300 MHz) or Bruker-400 (400 MHz) spectrometer. Mass spectra (MS) were measured on a Finnigan GC-MS 4021 C spectrophotometer. Elemental analyses were carried out on a Carlo Erba 1106 using the Flash EA 1112 method. Absorption and fluorescence spectra were run on a Shimadzu UV-1601PC UV-Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The redox potentials were measured by cyclic voltammetry on an EG&G Instruments Potentiostat/Galvanostat (Model 283) with a scanning rate of 100 mV s^{-1} , in which a three-electrode single-compartment electrochemical cell was used with two platinum wires as working and counter electrodes, and a saturated calomel electrode (SCE) as reference. A 0.1 M solution of Bu₄NClO₄ in CHCl₃ was used as the electrolyte and was flushed with N₂ prior to the measurements to avoid oxygen contamination. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was purchased from Aldrich. 4-(2H-Indene-1,3-dione)-2-tert-butyl-6-(julolidyl-9-enyl)-4H-pyran (IN-1), (2-(2-tert-butyl-6-((E)-2-(2,6,6trimethyl-2,4,5,6-tetrahydro-1*H*-pyrrolo[3,2,1-*ij*]quinolin-8-yl) vinyl)-4H-pyran-4-ylidene)-2H-indene-1,3-dione (IN-2), 2-(2tert-butyl-6-((E)-2-(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylquinolin-6-yl)vinyl)-4H-pyran-4-ylidene)-2H-indene-1,3-dione (IN-3), and 2-(2-tert-butyl-6-((E)-2-(1,2,3,4-tetrahydro-4,4dimethyl-1-phenylbenzo[h]quinolin-6-yl)vinyl)-4H-pyran-4ylidene)-2H-indene-1,3-dione (IN-4) were synthesized through

procedures as shown in Scheme 1 (see below for the details). N,N'-Bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), tris(8-hydroxyquinolinato)aluminium (Alq₃), and tris(8-hydroxyquinolinato)gallium (Gaq₃) were prepared *via* published methods. All these materials were subjected to train sublimation before device fabrication.

Synthesis of IN-2

To a refluxed suspended solution of 2.8 g of (0.07 mol, 60 wt)sodium hydride in 100 ml of 1,2-dimethoxyethane (monoglyme), was added under a dry nitrogen atmosphere a solution of 6.66 g (0.05 mol) of 2-methylindoline (1 in Scheme 1) in 50 ml of monoglyme, followed, after 45 min, by a solution of 7.45 g (0.05 mol) of 1-bromo-3-methyl-2-butene in 50 ml of monoglyme. The reaction mixture was refluxed for 6 h. Most of the solvent was then removed under reduced pressure and the pasty residue was cooled in an ice-water bath. Diethyl ether (150 ml) and cold water (100 ml) were added, and the formed two layers were separated. The water layer was extracted with two 100 ml portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The solvent was evaporated to leave 10.74 g of oily residue (crude 2-methyl-1-(3-methylbut-2-enyl) indoline, 2, in Scheme 1). The oily residue was dissolved slowly in 50 ml of cold concentrated sulfuric acid (0 °C), and then was poured into ice water. After being neutralized by saturated NH4OH solution, the resulting slurry was extracted with four 150 ml portions of ether. The extracts were combined and dried over anhydrous sodium sulfate. Removal of ether left an oily residue, which, after crystallization from 5 ml of 95% ethanol,

gave 8.66 g (86% yield based on 1) of 2,6,6-trimethyl-2,4,5,6tetrahydro-1*H*-pyrrolo[3,2,1-*ij*]quinoline (3 in Scheme 1). Then 2,6,6-trimethyl-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1*ij*]quinoline-8-carbaldehyde (4 in Scheme 1) was prepared from 3 via the Vilsmeier reaction using 3.0 equiv of POCl₃/ DMF as condensation agent (75% yield based on 3). Finally, the synthesis was completed by condensation of 4 with 2-(2tert-butyl-6-methyl-4H-pyran-4-ylidene)-2H-indene-1,3-dione (15) to give the target molecule IN-2 in 80% yield (based on 4). The intermediate 15 was synthesized using the approach reported by us recently.²⁸ The chemical structure of IN-2 was characterized as follows. ¹H NMR (CD₃COCD₃, 300 MHz): δ (ppm) = 8.40–8.32 (m, 2 H), 7.79–7.73 (d, J = 15.99 Hz, 1 H), 7.70-7.67 (m, 2 H), 7.58 (s, 1 H), 7.53 (s, 1 H), 7.46 (s, 1 H), 7.34 (s, 1 H), 6.96–6.90 (d, J = 15.87 Hz, 1 H), 3.68–3.63 (m, 1 H), 3.36-3.28 (m, 1 H), 3.17-3.09 (m, 1 H), 2.96-2.85 (m, 1 H), 2.63–2.54 (m, 1 H), 2.0–1.7 (m, 2 H), 1.5–1.4 (m, 18 H); MS m/z 505 (M⁺); Anal. Calc. for C₃₄H₃₅NO₃ C, 80.76; H, 6.98; N, 2.77; Found. C, 80.81; H, 6.94; N, 2.73%.

IN-1, IN-3, and IN-4 were prepared similarly (Scheme 1), and their structure characterization data are as follows.

IN-1: $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 8.41–8.40 (1 H, J = 1.7 Hz, d), 8.32–8.33 (1 H, J = 1.7 Hz, d), 7.60–7.73 (4 H, m), 7.4–7.5 (1 H, J = 15.8 Hz, d), 7.18 (2 H, s), 6.9–6.8 (1 H, J = 15.8 Hz, d), 3.3–3.2 (4 H, J = 5.6 Hz, t), 2.76–2.73 (4 H, J = 5.5 Hz, t), 1.98–1.84 (4 H, m), 1.44 (9 H, s); MS *m*/*z* 477 (M⁺); Found. C, 80.53; H, 6.52; N, 2.90. Calc. for C₃₂H₃₁NO₃ C, 80.47; H, 6.54; N, 2.93%.

IN-3: $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 8.42 (2 H, s), 7.72–7.76 (2 H, m), 7.56–7.61 (2 H, m), 7.45–7.46 (1 H, J = 2 Hz, d), 7.40–7.44 (2 H, J = 7.6 Hz, t), 7.33–7.37 (1 H, J = 15.9 Hz, d), 7.25–7.28 (2 H, m), 7.19–7.24 (1 H, J = 7.4 Hz, t), 7.13–7.15 (1 H, $J_1 = 8.6$ Hz, $J_2 = 2$ Hz, m), 6.65–6.69 (1 H, J = 15.9 Hz, d), 6.62–6.64 (1 H, J = 8.6 Hz, d), 3.68–3.71 (2 H, J = 6 Hz, t), 1.89–1.92 (2 H, J = 6 Hz, t), 1.43 (6 H, s), 1.44 (9 H, s); MS *m*/*z* 541 (M⁺); Found. C, 82.10; H, 6.46; N, 2.62. Calc. for C₃₇H₃₅NO₃, C, 82.04; H, 6.51; N, 2.59%.

IN-4: $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 8.55–8.56 (1 H, *J* = 1.7 Hz, d), 8.48–8.49 (1H, *J* = 1.7 Hz, d), 8.25–8.29 (1 H, *J* = 15.7 Hz, d), 8.04–8.07 (1 H, *J* = 8.4 Hz, d), 7.92 (1 H, s), 7.76–7.8 (1 H, *J* = 8.4 Hz, d), 7.76–7.80 (2 H, m), 7.61–7.63 (2 H, m), 7.43–7.45 (1 H, m), 7.24–7.27 (1 H, m), 7.17–7.21 (2 H, *J* = 7.5 Hz, m), 6.97–7.01 (1 H, *J* = 15.7 Hz, d), 6.91–6.94 (1 H, *J* = 7.34 Hz, t), 6.83–6.85 (2 H, *J* = 7.6 Hz, d), 3.87–3.90 (2 H, m), 1.80–1.84 (2 H, m), 1.50 (9 H, s), 1.48 (6 H, s); MS *m*/*z* 591 (M⁺); Found. C, 83.17; H, 6.35; N, 2.42. Calc. for C₄₁H₃₇NO₃, C, 83.22; H, 6.30; N, 2.37%.

Preparation and testing of electroluminescent (EL) devices

OLED devices were fabricated by thermal vacuum deposition. The substrate was indium tin oxide (ITO)-coated glass with a sheet resistance of about 50 ohms per square. The pretreatment of ITO conducting glass included a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. All organic layers were successively deposited onto the ITO conducting glass substrate by thermal evaporation at high vacuum (5 \times 10⁻⁶ Torr), and the thickness of each layer was determined by a quartz thickness monitor. The deposition rates for the organic layers and the cathode were 0.1 and 6 nm s⁻¹, respectively. The emissive area of the device was 2 mm \times 2.5 mm. The EL devices fabricated in this work have a configuration of ITO/NPB (60 nm)/Alq₃ (or Gaq₃) : red dopant (*x* wt%, 7 nm)/BCP (12 nm)/Alq₃ (45 nm)/LiF (0.3 nm)/Al (300 nm), in which NPB was used as the hole-transporting layer, doped Alq₃ (or doped Gaq₃) as the emissive layer, BCP as the hole-blocking layer, and undoped Alq₃ as the electron-transporting layer. The emissive layer was prepared by co-evaporating the red dopant and Alq₃ (or Gaq₃) simultaneously from two sources at calibrated rates to achieve the desired mass ratio. The EL spectra and brightness–current density–voltage characteristics of the devices were measured with a PR650 Spectra Scan in air at room temperature.

Theoretical methods

All calculations were done on the Gaussian03 program package²⁹ by using density functional theory (DFT). Becke's three-parameter functional³⁰ combined with Lee, Yang, and Parr's correlation functional³¹ (B3LYP), along with the 6-31G(d) basis set, was used. Geometry optimizations attempt to locate the minima on the potential energy surface to predict equilibrium structures of a given molecule. Before performing optimization of ground-state geometries by B3LYP/6-31G*, the molecular structures were initially optimized in semiempirical PM3^{32,33} calculations as recommended in the Gaussian03 program package. Single-point energy calculations of the electronic properties of the DCM-type dyes at their optimized ground-state geometries were carried out by utilizing DFT at the B3LYP/6-31G(d) level. All the geometries and electronic properties were calculated by assuming the target molecules to be isolated molecules.

4. Conclusions

Using 2H-indene-1,3-dione as an electron-withdrawing group and aromatic amines of different structures as electrondonating groups, four new DCM-type dyes, IN-1, IN-2, IN-3, and IN-4, were designed and synthesized for application in red OLEDs. Due to the large dipole moment difference which occurs in the transition from the ground state to the excited state, IN-2 exhibits a red shift in fluorescence but a blue shift in absorption with respect to IN-1. Similar phenomena are also found in spectral comparisons between IN-3 and IN-4. These findings indicate the important role of the structure of the aromatic amine in the photophysical properties of DCM-type dyes. In EL devices with the configuration of ITO/NPB (60 nm)/Alq₃ (or Gaq₃) : red dopant (2.0 wt%) (7 nm)/BCP (12 nm)/Alq₃ (45 nm)/LiF (0.3 nm)/Al (300 nm), IN-3 in Alq₃ and IN-1 in Gaq₃ show comparable properties to the DCJTB-assistant dopant (rubreen or quinacridone)-Alq₃ tertiary system. This can be ascribed to the good spectral overlap either between IN-3 and Alq₃ or between IN-1 and Gaq₃, indicating that the absorption spectrum has the same importance as the fluorescence spectrum in the improvement of color purity of red emitters. Following the guidelines provided in this work, it may be possible to achieve new DCM-type red light-emitting materials, even better than DCJTB in the applications of OLEDs.

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