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A New Family of Red Dopants Based on Chromene-Containing Compounds for Organic Electroluminescent Devices

X. H. Zhang,[†,‡] B. J. Chen,[†] X. Q. Lin,[†] O. Y. Wong,[†] C. S. Lee,*[,†] H. L. Kwong,[§]
S. T. Lee,[†] and S. K. Wu[‡]

Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Material Science, City University of Hong Kong, Hong Kong, SAR, China, Institute of Photographic Chemistry, The Chinese Academy of Science, Beijing 100101, China, and Department of Biology and Chemistry, City University of Hong Kong, Hong Kong, SAR, China

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4-Dicyanomethylene-chromene moiety has been introduced as a π-electron acceptor in red fluorescent dye molecules for organic light-emitting devices (OLEDs). On the basis of this moiety, a new family of red dopants with saturated emission, higher fluorescent quantum yield, and convenient synthetic procedures have been designed and synthesized. Their photoluminescent and electroluminescent properties have been examined and compared. On the basis of the results, useful guidelines for the molecular design of saturated red-emission fluorescent dopants for OLED applications are presented.

Introduction

Organic light-emitting devices (OLEDs) have received considerable attention because of their potential applications in flat-panel displays.[1,2] For full-color applications, it is necessary to have a set of red, green, and blue emitters with sufficiently high luminous efficiency and proper chromaticity. After 1 decade of intensive research, organic materials for green and blue OLEDs with high luminance, high efficiency, saturated emission, and practical lifetimes have been developed.[3,4] However, the corresponding development of organic materials for red electroluminescence (EL) lags significantly behind that for the other two primary colors. Presently, most high-performance red OLEDs are made by doping a red dye into a suitable host.[5,6] The dopants reported include pyran-containing compounds,[7−9] porphyrin compounds,[10−13] and europium chelate complexes.[14−16] While saturated red emissions have been obtained from the porphyrin compounds and europium chelate complexes, the luminescent efficiency of most of them is unacceptably low. The most promising red dopant in the porphyrin compounds and europium chelate complexes for OLEDs is platinum octaethylporphyrin (PtOEP), the phosphorescent quantum yield of which is about 0.45. Although the devices with PtOEP doped into tris(8-quinolinolato) aluminum (Alq_3) show higher efficiencies at a low injection current, the efficiency and chromaticity of the devices at a higher injection current densities are not practicable.[17] The pyran-containing compounds, such as DCM,[7] DCM2,[8] DCJT, and DCJTB,[18] have been widely studied and are regarded as important red dopants for OLED applications. However, their performance as red emitters is still significantly inferior to that of the prototypical green and blue emitters. In particular, color saturation is far from ideal. This problem of color purity is partly due to the fact that the PL peaks of these compounds are in the range of 590−615 nm. A significant portion of their

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* To whom correspondence should be addressed. Fax: 852-27887830. E-mail: apcslee@cityu.edu.hk.

[†] COSDAF and Department of Physics and Material Science, City University of Hong Kong.

[‡] The Chinese Academy of Science.

[§] Department of Biology and Chemistry, City University of Hong Kong.

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emission spectra is in fact below 600 nm, and thus they cannot emit a saturated red color. Inefficient energy transfer from the typical host materials, such as Alq_3, also contributes to the unsaturated emission.[21] The latter cause may be remedied by using a second dopant material as a bridge to assist energy transfer from the host[21] or by using another host material with an emission energy closer to the absorption peaks of the red dopants.[5] On the other hand, the emission peaks of the dopants have to be shifted further to the long wavelength region, so that the emission below 600 nm can be substantially reduced. In addition, synthetic procedures for some of these compounds are rather complicated and would significantly increase the production cost for red OLEDs. There still remains much room for improvement on the materials for red OLEDs.

The pyran-containing red dopants are typically intramolecule charge transfer compounds, which typically consists of two parts, an electron donor part and an electron acceptor part. All the pyran-containing red dopants mentioned contain a 4-dicyanomethylene-4H-pyran as the electron acceptor. In this study, we introduce a 4-dicyanomethylene-chromene moiety as a π-electron acceptor in red dopant molecules for OLEDs. On the basis of this moiety, we have designed and synthesized a new family of red dopants and studied their photoluminescence (PL) in solutions and electroluminescence (EL) as dopants.

Experimental Section

Materials Synthesis. Synthetic schemes for the red dopants (hereafter referred to as RED1, RED2, and RED3) are shown in Figure 2. Compound 3 was synthesized according to the literature procedure.[19] Procedures for reactions (2) and (3) can be found respectively in refs 20 and 18. RED1, RED2, and RED3 were characterized spectroscopically and by elemental analysis.

RED1. mp 252−253 °C. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 8.1 (d, 1H), 7.7−7.3 (m, 4H), 7.0 (s, 2H), 6.73 (s, 1H), 6.5 (d, 1H), 3.3 (t, 4H), 2.7 (t, 4H), 1.9 (t, 4H). MS: m/z 392 ($M^+ + 1$). Anal. Calcd for $C_{26}H_{21}N_3O$: C, 79.86; H, 5.41; N, 10.74. Found: C, 79.75; H, 5.44; N, 10.76.

RED2. mp 267−268 °C. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 8.7 (d, 1H), 7.64−7.2 (m, 5H), 6.6 (s, 1H), 6.4 (d, 1H), 3.66 (s, 3H), 3.1 (t, 2H), 3.0 (t, 2H), 1.57 (t, 4H), 1.26 (s, 6H), 1.15 (s, 6H). MS: m/z 479 ($M^+ + 1$). Anal. Calcd for $C_{31}H_{31}N_3O_2$: C, 77.89; H, 6.54; N, 8.79. Found: C, 77.85; H, 6.57; N, 8.81.

RED3. mp 272−273 °C. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 8.9 (d, 1H), 7.7−6.6 (m, 20H). MS: m/z 464 ($M^+ +1$). Anal. Calcd for $C_{32}H_{21}N_3O$: C, 83.01; H, 4.57; N, 9.07. Found: C, 82.98; H, 4.58; N, 9.07.

Photoluminescence and Energy Levels Measurement. The absorption and fluorescence spectra of the red dopants were measured from a 1×10^{-5} M solution of 1,2-dichloroethane. The fluorescence quantum yields of these compounds were determined by comparing to a Rhodamine B calibration standard with a fluorescence quantum yield, ϕ_f, of 0.67. The energy levels of the organic materials were measured by using ultraviolet photoelectron spectroscopy and UV−visible optical absorption spectroscopy. All the absorption and fluorescence spectra were recorded using a Perkin-Elmer Lambda 2S UV−vis spectrophotometer and a Perkin-Elmer LS50 fluorescence spectrophotometer, respectively.

Preparation of EL Devices and Testing. EL devices fabricated in this work have a configuration of indium tin oxide (ITO)/TPD (80 nm)/Alq_3:red dopant (60 nm)/Alq_3 (20 nm)/Mg:Ag (200 nm). *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (TPD) was used as a hole-transporting layer, Alq_3 doped with one of the red dopants was the emissive layer, and the undoped Alq_3 was used an electron-transporting layer. ITO-coated glasses with a sheet resistance of 50 Ω/square were used as the substrate and anode. All organic layers were successively deposited onto the surface of ITO glass at a pressure of 5×10^{-5} mbar. A metallic cathode, Mg:Ag (10:1), with a thickness of 0.2 μm, was deposited on top of the Alq_3 layer at 1.5×10^{-6} mbar. The rates of deposition for the organic layers and metallic cathode were 0.2 and 0.5 nm/s, respectively. The emissive area of the devices was 3 × 3 mm. The EL spectrum and the brightness of the devices were measured with a PR650 Spectra Scan at room temperature and atmospheric conditions.

Results and Discussions

Design and Synthesis of Molecules. The structures of the new red dopants, RED1, RED2, and RED3, and of the widely reported red dopants, DCM2 and DCJTB, are shown in Figure 1. DCM2 is the most extensively studied red dopant in OLEDs and DCJTB is the most promising material among this group of red dopants.[18] As DCM2 and DCJTB are state-of-the-art red dopants, it is of interest to compare their molecular structures with those of the red dopants synthesized in the present work. In the design of the intramolecule charge-transfer compounds as a red OLED dopant, the following considerations are essential:[5]

1. The dopant molecules should contain a strong electron acceptor and a strong electron donor and a suitably long conjugation system so that the proper red chromaticity and saturated red emission can be achieved.
2. Molecular structure of the dopant should be rigid so that it can have a high fluorescent quantum efficiency.
3. The dopant molecule should have a sterically hindered structure so as to decrease the concentration quenching of the dye.
4. The synthesis of the dopant should be simple so that production cost can be minimized.

It can be seen from Figure 1 that the difference between the red dopants synthesized in this work and the typical red dopants, DCM2 and DCJTB, is in their electron-accepting group. The new family of red dopants has a 4-dicyanomethylene-chromene as the electron acceptor, instead of a 4-dicyanomethylene-4H-pyran in DCM2 and DCJTB. Because of this difference, the new dopants are expected to have the following characteristics:

1. Basically, the electron-accepting and -donating abilities of the electron acceptors and the electron donors in both the new and typical red dopants molecules are similar. However, because of the longer conjugation in the new dopants, it is expected that the new dopants

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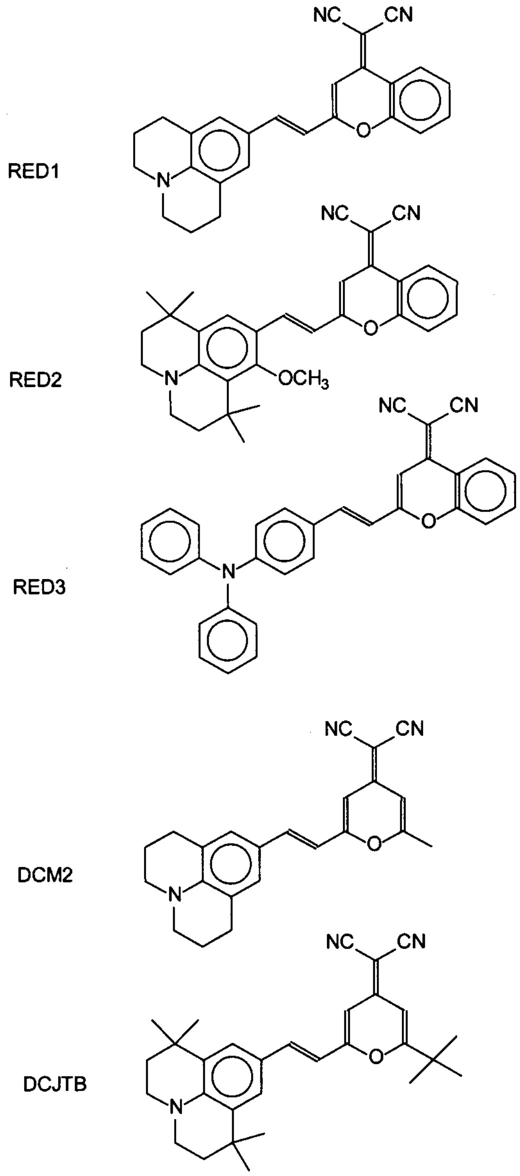

Figure 1. Chemical structures of the new family of red dopants and DCM2 and DCJTB.

should emit with a longer wavelength than DCM2 and DCJTB. Thus, a better red chromaticity should be obtained in the new dopants.

2. As the rigidity of the molecular structure of the new dopants is similar to that of the DCM2 and DCJTB, it is expected that the high fluorescent quantum efficiency could be maintained.

3. As mentioned above, the new red dopants have a chromene, instead of pyran, moiety as the electron acceptors. The chromene moiety has a benzyl group, which is beneficial for further chemical modifications of the new dopants. Therefore, steric hindrance can be much more easily added to the red dopants than to the pyran group of DCM2 and DCJTB.

4. The synthetic procedures of the new dopants are simpler than those of DCM2 and DCJTB. Comparing their synthetic scheme (Figure 2) with those of DCM2 and DCJTB,[18] it can be seen that all of these dopants are synthesized by condensation of the electron acceptors with an active methyl group (compound 4) and the electron donors with an aldehyde group (compound 5) (reaction (3)). Therefore, the key intermediates of the new red dopants, DCM2, and DCJTB are 4-dicyanomethylene-2-methylchromene (compound 4), 4-dicyanomethylene-2-methyl-6-methyl-4H-pyran, and 4-dicyanomethylene-2-(*tert*-butyl)-6-methyl-4H-pyran, respectively. The key intermediate of the new red dopants has an unsymmetrical structure, while that of DCM2 is symmetric. Unlike the synthesis of DCM2, therefore, the formation of nonfluorescent and difficult-to-remove bis-condensed byproduct can be avoided in the synthesis of the new red dopants.[18] On the other hand, the key intermediate of the new red dopants (compound 4) can be more easily synthesized compared to that of DCJTB.[18] In short, synthesis of the new red dopants is more convenient.

Photoluminescence Characteristics and Energy Levels. Table 1 shows the photoluminescence (PL) data of the present red dopants and DCJTB and DCM2 in solution. As expected, the emission peaks of the new dopants are of longer wavelengths and can thus deliver an inherently better red chromaticity compared to DCM2 and DCJTB. However, the fluorescent quantum yields of the new red dopants are lower than those of DCM2 and DCJTB. Nevertheless, the fluorescent quantum yields of the present red dopants are already comparable to the highest values reported for those saturated red dopants used in OLEDs[10−16](DCM2 and DCJTB are not among the group of saturated red dopants[12]).

From the molecular structures, it can be seen that all the new red dopants have the same electron acceptor but different electron donors. As the electron-donating abilities of the donors in RED1 and RED2 are similar, their emission peaks and fluorescent quantum efficiencies are similar. However, as the electron-donating ability of RED3 is weaker than those of RED1 and RED2, RED3 has a shorter emission peak wavelength and the highest fluorescent quantum yield, which is close to that of DCM2 and DCJTB.

It can also be found in Table 1 that the band gaps of the present red dopants are smaller than those of DCM2. In addition, the HOMO and LUMO of the RED series are between those of Alq_3 (Alq_3:Ea $= 2.85$; $I_p = 5.62$).[21] Therefore, Alq_3 can be used as the host material for the RED series in OLEDs.

Electroluminescent Performances. The EL emission spectra of the devices with RED1, RED2, and RED3 at doping concentrations of 1 wt % (RED1(1), RED2(1), and RED3(1)) and 3 wt % (RED3(3)) are shown in Figure 3. It can be seen that the devices RED1(1), RED2(1), and RED3(3) can emit saturated red light with emissive peaks at about 630−660 nm. The device RED3(1) has an orange emission with a peak at about 615 nm.

Figure 4 shows their Commission Internationale d'Éclairage (CIE) chromaticity coordinates and the current characteristics of the devices. It can be found that the CIE coordinates of the devices are nearly unchanged with increasing current density. This characteristic offers better device operation compared to the saturated red OLEDs with PtOEP-doped Alq_3 for which the color purity decreases with increasing driving voltage.[17]

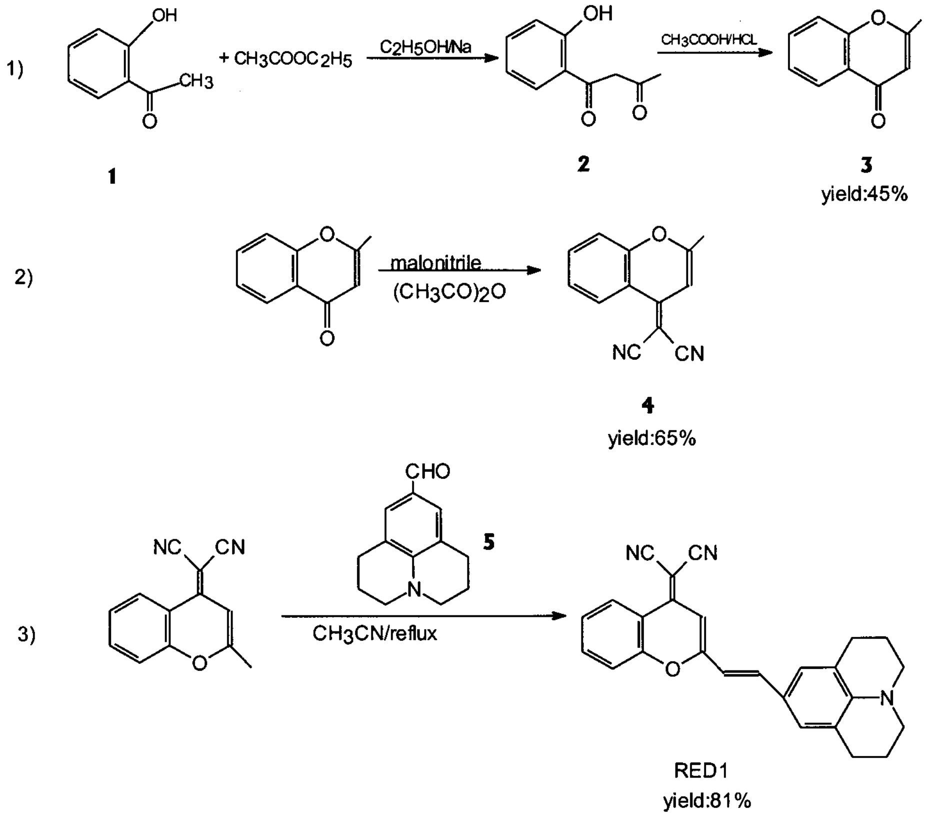

Figure 2. Synthetic schemes of the new dopants.

Table 1. Comparison of Photoluminescence Data in Dilute Solution and Energy Levels of the New Dopants with These of DCM2 and DCJTB

dyes	absorption λ_{max} (nm)	emission λ_{max} (nm)	quantum yield (%)	I_p[a] (eV)	E_a[b] (eV)	E_g[c] (eV)
RED1	553	641	18	5.2	3.27	1.93
RED2	562	645	15	5.2	3.28	1.92
RED3	505	623	54	5.4	3.25	2.15
DCM2[d]	—	600	above 70	5.26	3.11	2.15
DCJTB[e]	512	615	78	—	—	—

[a] Ionization potential. [b] Electron affinity. [c] Energy gap. [d] Reference 5. [e] Reference 18.

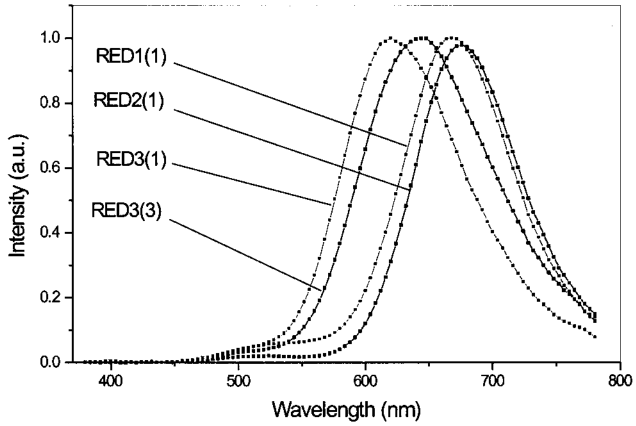

Figure 3. EL emission spectra of the fabricated devices.

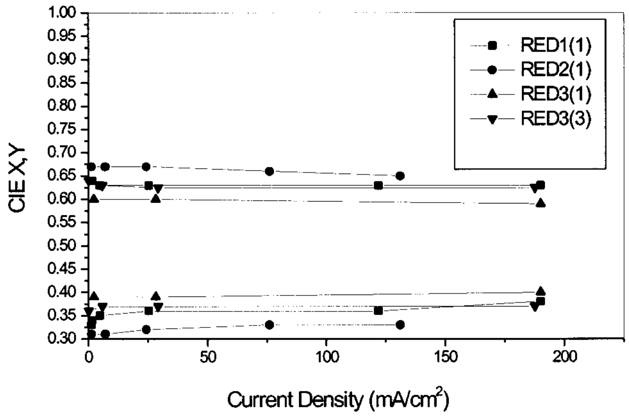

Figure 4. CIE chromaticity coordinates—current density characteristics of the fabricated devices.

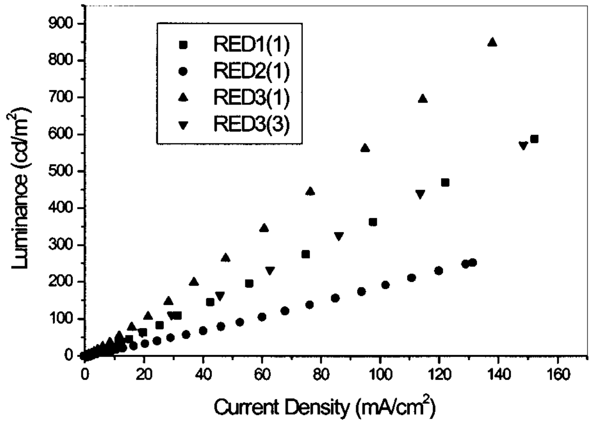

Figure 5. Luminance—current density characteristics of the present devices.

Figure 5 shows the luminance—current density characteristics of the four devices. The RED3(1) device has the highest current efficiency and the RED2(1) device has the lowest efficiency at high current density. This can be understood by considering their fluorescent quantum yield and the energy transfer between the Alq$_3$ host and these red dopants. The absorption peak of

Table 2. EL Characteristics of Red OLEDs, Including Maximum Reported Luminance under dc Bias (L_{max}), Current (I) and Voltage at L_{max}, Power Efficiency (η_{max}), and CIE Coordinates

material/ method	L_{max} (cd/m^2)	I,V (L_{max}) (mA/cm^2, V)	η_{max} (lm/w)	CIE (x, y)	ref
RED1(1)	1010	280, 20	0.071	0.63, 0.35	this work
RED2(1)	250	130, 25	0.042	0.66, 0.33	this work
RED3(1)	2130	390, 19	0.139	0.60, 0.39	this work
RED3(3)	850	230, 23	0.059	0.63, 0.37	this work
DCM(10)[a]	150	–, 10	–	0.62, 0.36	22
DCM2(10)[a]	1400	2200, 19	0.011	0.64, 0.36	8
DCJTB(1)[a]	–	–, –	0.65[b]	0.62, 0.37	26
TPC (1.7)[a]	100	–, –	0.061	0.67, 0.29	23
TPP (3)[a]	60	45, 35	0.012	0.68, 0.32	24
Eu(DMB)$_3$(phen) in PBD	460	300, 16	0.030	0.68, 0.32	16
Eu(TTA)$_3$(phen)	30	100, 16	0.006	0.68, 0.32	25

[a] Alq$_3$ as the host material and the dopant concentration at 10%, 10%, 1%, 1.7%, and 3%, respectively. [b] Efficiency at 20 mA/cm^2.

RED3 is 505 nm (Table 1), which is the closest to the emission peak of Alq$_3$ (about 520 nm). Thus, a more efficient energy transfer in the RED3–Alq$_3$ system is expected. In addition, RED3 also has the highest fluorescent quantum yield among the three dopants. As a result, it delivers the highest efficiency at high current density among the RED series. On the other hand, RED2 has the lowest quantum yield and an absorption peak wavelength (562 nm) farthest away from the emission peak of Alq$_3$. It showed, therefore, the lowest efficiency at high current density.

Table 2 summarizes the EL characteristics of the present devices as well as those from a number of reported OLEDs, which have emission in the same spectral region and a similar cell configuration as the present devices. It can be seen that although the efficiency of present devices is not as good as those made from DCJTB, the chromaticity of the device RED1(1) and RED2(1) is better than those made from DCJTB. In addition, the present devices do show comparable, or sometimes better, performances compared to the other saturated red dopants. Furthermore, the present dopants have several advantages over the pyran-containing red dopants. These include the following: (1) more saturated red emissions; (2) more convenient synthesis for the dopant; (3) and the fact that substitutional groups can be readily added onto the benzene ring of the chromene group and thus offer more opportunities for further improvement of the present dopants.

Conclusions

We introduced a 4-dicyanomethylene-chromene moiety as a π-electron acceptor in the red dopant molecules for OLEDs. On the basis of this moiety, we created a new family of red dopants (RED series) with saturated emission, higher fluorescent quantum yield, and convenient synthesis. The present study presents useful new guidelines for the molecular design of saturated red-emissive fluorescent dopants for OLEDs.

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