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Intramolecular Cyclization

A Convenient Strategy to Realize Efficient BT.2020 Blue Multi-Resonance Emitter for Organic Light-Emitting Diodes

Cao, Chen; Tan, Ji-Hua; Zhu, Ze-Lin; Lin, Jiu-Dong; Tan, Hong-Ji; Chen, Huan; Yuan, Yi; Tse, Man-Kit; Chen, Wen-Cheng; Lee, Chun-Sing

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Research Article

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Intramolecular Cyclization: A Convenient Strategy to Realize Efficient BT.2020 Blue Multi-Resonance Emitter for Organic Light-Emitting Diodes

Chen Cao⁰⁰⁰⁰⁻⁰⁰⁰²⁻¹⁷⁶³⁻¹⁹¹²,^[a] Ji-Hua Tan⁰⁰⁰⁰⁻⁰⁰⁰²⁻⁸³⁵⁶⁻⁴⁴⁵⁵,^[a] Dr. Ze-Lin Zhu,^[a] Jiu-Dong Lin⁰⁰⁰⁰⁻⁰⁰⁰²⁻⁸⁹¹⁵⁻⁹⁰⁴⁷,^[c] Hong-Ji Tan,^[a] Huan Chen⁰⁰⁰⁰⁻⁰⁰⁰²⁻⁰⁷⁹²⁻³³⁹⁹,^[a] Dr. Yi Yuan⁰⁰⁰⁰⁻⁰⁰⁰²⁻⁴⁵⁴²⁻³⁷⁰⁷,^{*[b]} Dr. Man-Kit Tse,^[a] Dr. Wen-Cheng Chen,^[a] and Prof. Chun-Sing Lee^{0000-0001-6557-453X}^{*[a]}

[a] <orgDiv/>Center of Super-Diamond and Advanced Films (COSDAF) and Department of Chemistry, <orgName/>City University of Hong Kong <city/>Hong Kong SAR, <postCode/>999077 (<country/>P. R. China) E-mail: apcslee@cityu.edu.hk

[b] <orgDiv/>School of Chemistry and Chemical Engineering <orgName/>University of South China <city/>Hengyang <postCode/>421001 (<country/>P. R. China) E-mail: yyuanac@126.com

[c] <orgName/>WISPO Advanced Materials (Suzhou) Co., Ltd. <street/>No. Building 12, 200 Xingpu Rd, SIP, <city/>Suzhou (<country/>P. R. China)

A multi-resonance emitter using intramolecular cyclization endows BT.2020-compliant deep blue emission with an ultranarrow full width at half maximum (FWHM) of 16^{nm} and CIE coordinates of (0.153, 0.042) in toluene, thus achieving a high external quantum efficiency of 25.6% in a hyper-fluorescent organic light-emitting diode.

Rationally tuning the emission position and narrowing the full width at half-maximum (FWHM) of an emitter is of great importance for many applications. By synergistically improving rigidity, strengthening the resonant strength, inhibiting molecular bending and rocking, and destabilizing the HOMO energy level, a deep-blue emitter (CZ2CO) with a peak

wavelength of 440^{nm} and an ultranarrow spectral FWHM of 16^{nm} (0.10^{eV}) was developed via intramolecular cyclization in a carbonyl/N resonant core (QAO). The dominant ν_{0-0} transition character of CZ2CO gives a Commission Internationale de l'Éclairage coordinates (CIE) of (0.144, 0.042), nicely complying with the BT.2020 standard. Moreover, a hyper-fluorescent device based on CZ2CO shows a high maximum external quantum efficiency (EQE_{max}) of 25.6[%] and maintains an EQE of 22.4[%] at a practical brightness of 1000^{cd/m^{M-2}}.

Aromatic Diketone

Blue Thermally Activated Delayed Fluorescence

Intramolecular Cyclization

Multi-Resonance Emitter

Organic Light-Emitting Diodes

Introduction

Multiple resonance thermally activated delayed fluorescence (MR-TADF) emitters exhibiting narrowband emission and 100[%] exciton utilization in the device are appealing to the research and industrial communities as these features enable organic light-emitting diodes (OLEDs) to access a wider color gamut and get rid of color filters in displays.^[1-7] The demand for ultrahigh-definition displays drives researchers to pursue red, green, and blue (RGB) emitters with color index meeting the standard of Broadcast Service Television 2020 (BT.2020). To date, the development of blue MR-TADF emitter is lagging behind red and green hues.^[8-10]

To meet the BT.2020 blue standard, an emitter's emission should have a Commission Internationale de l'Éclairage coordinate y value (CIEy) of 0.046, which corresponds to an emission profile with a peak (λ_{em}) at $\approx 440^{nm}$ and a full width at half-maximum (FWHM) of $\approx 15^{nm}$.^[11] Considering emission peak, the renowned parental compounds of both boron/nitrogen (B/N) and carbonyl/N (C<C=>O/N) resonance systems are near the BT.2020 criteria (the λ_{em} /FWHM of B/N and C<C=>O/N parental compounds are 462/33^{nm}

(DABNA-1) and 466/33 nm (QAO) in toluene).^[12,13] Therefore, fine tuning of the emission position and judicious modification to significantly reduce the FWHM are needed, and the latter will be more challenging. The strategies in Scheme 1 can theoretically reduce emission FWHM: 1) increasing molecular rigidity to suppress structural deformation between the S₁ and the S₀ states (reducing Δq);^[14,15] 2) strengthening the resonant effect to raise the frequency of stretching vibration and narrow the potential energy surface curve (larger energy difference between ν level);^[16] 3) inhibiting bending and rocking to reduce the minor vibrations (blue lines) between different stretching vibration energy levels;^[17,18] 4) restricting line-broadening effects from the surrounding.^[17,19-21] The first three factors are controlled by the molecular structure, and the last one is mainly determined by the environment but can still be affected by the molecular structure. By improving rigidity and strengthening the resonant effect, Hatakeyama et al. extend the aromatic resonating system of DABNA-1 and developed ν -DABNA with $\lambda_{em}/FWHM=468/14$ nm in toluene.^[18] Further replacing two N atoms of ν -DABNA with two O atoms (lower orbital energy, omitting peripheral phenyl ring to restraint π area and reduce rocking), Yasuda et al. obtained BOBO-Z with blue-shifted emission ($\lambda_{em}/FWHM=441/15$ nm in toluene) complied with BT.2020 standard through synergistically improving rigidity, and inhibiting bending and rocking.^[8] So far, molecular optimizing in a B/N resonant system (Figure S1 in Supporting Information) has revealed the potential of MR-TADF in achieving BT.2020 standard blue emission. However, the harsh reaction conditions (involving lithiation reagents and superacid) and low yield (typically $\approx 20\%$) in synthesizing DABNA-derivatives are still hurdles for large-scale production.

Alternatively, the C=C=O/N resonant derivatives (QAO) can be obtained via Friedel-Crafts reactions in mild conditions with higher yields up to 96.8%.^[12] Previous efforts in modifying QAO with the above-mentioned strategy similar to B/N counterparts gave QA-2 with $\lambda_{em}/FWHM=440/24$ nm in toluene, which is near the BT.2020 standard (Figure S2).

Tactics like peripheral decoration often lead to emission profile broadening and red-shifting.^[12,15,22-27] Novel and effective strategies to realize BT.2020 standard blue emission in C<C=>O/N resonant derivatives are needed to provide easy access to state-of-the-art deep blue emitters.

In this work, we unveil a simple strategy for simultaneously blue-shifting and narrowing FWHM in the QAO resonant core by simply fusing up the bay area of QAO. The simple modification indeed regulates the FWHM by synergistically improving rigidity, increasing the resonant strength, and inhibiting bending and rocking.^[19,28,29] As a result, a new emitter, 2,5,9-tri-*tert*-butylbenzo[8,1]indolizino[2,3,4,5,6-*defg*]acridine-7,11-dione (CZ2CO), presents deep blue emission with an ultranarrow FWHM meeting the BT.2020 standard (440/16^{nm} equal to CIE coordinates of (0.153, 0.042) in toluene). When used as a terminal emitter, a hyper-fluorescence OLED based on CZ2CO shows a maximum external quantum efficiency (EQE_{max}) of 25.6% and maintains an EQE of 22.4% at 1000^{cd/m²}. This evidences the molecular design concept and enriches the molecular platform for ultimate narrowband deep-blue emission.

Results and Discussion

For comparison we also synthesized 3,6-di-*tert*-butyl-8*H*-indolo[3,2,1-*de*]acridin-8-one (CZCO) by omitting a carbonyl group from CZ2CO.^[24] CZ2CO and CZCO were each synthesized with a three-step route, including Ullman coupling, hydrolysis reaction and Friedel-Crafts acylation (Scheme^{S1}). The experimental details and ¹H- and ¹³C^{NMR} and Mass spectra of related compounds were given in the synthesis section and Figures^{S3--S7} in the Supporting Information.

The UV/Vis absorption spectra of CZCO and CZ2CO present sharp absorption bands at 410 and 434^{nm}, respectively (10^M in toluene, Figure^{S8}), which are attributed to short-range charge transfer transitions of MR-compounds.^[22] Compared to their parental

QAO-core, CZCO and CZ2CO show blue-shifted emissions ($\lambda_{em}=430$ and 440 nm, respectively). Notably, small Stokes shifts ($\Delta\nu$)/FWHMs of CZCO ($20/32$ nm) and CZ2CO ($6/16$ nm) indicate small Δq s between the S_0 and the S_1 states in these molecules. This ultimate narrowband feature contributes to BT.2020-compliant CIE coordinates of (0.156, 0.035) and (0.153, 0.042), respectively. CZCO shows blue-shifted and broadened emission compared to CZ2CO primarily because of only one $C=C=O$ group, resulting in less charge transfer (blue-shifting), rigidity, and resonant strength (broadening). Compared to compound QAO, the confinement in CZ2CO results in one more five-membered aromatic ring, which undoubtedly improves molecular rigidity and inhibits bending and rocking (a twisting angle of 42.4° between two planes of QAO while the degree for CZ2CO would be zero, Figure S9). Nevertheless, the five-membered ring strengthens the electron-donating feature of the N atom in the carbazole-like area and weakens that in the upper *tert*-butyl phenyl group. In other words, the N atom becomes more polarized in CZ2CO, thus strengthening its resonant effect. This is evidenced by natural bond orbital (NBO) analyses (Figure 1 and Table S1-2)^[30] with enhanced *p*-orbital components in C1-N and C2-N (from $sp^{1.99}$ in QAO to $sp^{2.08}$ in CZ2CO) and a reduction in C3-N (from $sp^{2.01}$ in QAO to $sp^{1.85}$ in CZ2CO). Further NBO analysis reveals a reduced contribution of *p*-electron pair of N atom to the molecular π -orbital (electron population decrease from 1.297 in QAO to 1.259 in CZ2CO), giving a less electron-donating feature and thus destabilize the highest occupied molecular orbital (HOMO). As a result, energy gap of CZ2CO is widened and gives a blue-shifted emission compared to QAO. This is further supported by the theoretical calculation, which shows a deeper HOMO energy level (-6.42 vs. -6.55 eV) (Figure 1 and Figure S11) and less lowest unoccupied molecular orbitals (LUMO) involvement in the carbazole-like area from QAO to CZ2CO.^[13,31]

The time-dependent density functional theory (TD-DFT) calculations were then carried out in toluene at the PBE0/6-31G (d,p) level to analyze the reorganization energies

(E_{reo}) of QAO, CZCO and CZ2CO as shown in Figure². The E_{reo} value of CZ2CO turns out to be only about half of those of QAO and CZCO (0.131 vs. 0.260 eV and 0.277 eV), which is the combined result of the above-mentioned factors and proves the molecular design concept. The small E_{reo} value contributes to the smallest Stokes shift and narrowest band emission in CZ2CO.^[32-36] Vibrationally resolved fluorescence spectra are calculated to determine the main vibration of the $S_1 \rightarrow S_0$ (first singlet excited state to ground state) transition. As shown in Figure²b-d and Table^{S3}, CZCO shows the most blue-shifted emission while CZ2CO exhibits the smallest FWHM with 358 cm^{-1} (6 nm), which is consistent with the experimental trends. Again, intramolecular cyclization brings about improving rigidity, strengthening the resonant strength, and inhibiting bending and rocking in CZ2CO and endows it with a single strong dipole, resulting in a dominant ν_{0-0} transition. For QAO and CZCO, each has several strong dipoles contributing to their emissions, which results in broader FWHMs compared to CZ2CO.

We then study the TADF properties of the two compounds. To estimate energy difference between the first singlet (S_1) and triplet (T_1) excited state (ΔE_{ST}), low temperature emission spectra of CZCO and CZ2CO were recorded in toluene at 77 K (Figure^{S12} and Table¹). S_1/T_1 energy levels of CZCO and CZ2CO were estimated to be 2.88/2.55 and 2.82/2.45 eV, giving ΔE_{ST} of 0.33 and 0.37 eV for CZCO and CZ2CO, respectively. Accordingly, delay emission lifetime of CZ2CO is observed to be slightly longer than that of CZCO (431.8 vs 392.8 μs , measured with 3 wt% doped in 1,3-di(9H-carbazol-9-yl)benzene, mCP matrices) (Figure^{S13}). Figure^{S14} depicts the orbital energy alignment for CZCO and mCP, the exciplex-like host-guest interaction could be the origin of TADF.^[25] The emitters' triplet spin density distribution shows in Figure^{S15}. Photoluminescence quantum yields (Φ_{PLS}) of CZCO and CZ2CO doped in mCP films were determined to be 75 and 84%, respectively. The more rigid structure of CZ2CO is believed to suppress non-radiative decay and enhance its Φ_{PL} . We also study the decay of these emitters in two

common solvents, dichloromethane and toluene. We find that those two emitters show faster decay in toluene than in dichloromethane (Figure^{S16}).

The HOMO/LUMO energy levels of the emitters were determined with the cyclic voltammetry (CV) method, as shown in Figure^{S17}. One quasi-reversible oxidation wave with the oxidative onset potential of 1.34 V for CZCO and 1.4 V for CZ2CO was observed. The HOMO levels of CZCO and CZ2CO were determined to be -5.73 and -5.78 eV, referring to a HOMO level of -4.8 eV for ferrocene. By adding the optical absorption onset energy to the HOMO energy levels, the LUMO energy levels of CZCO and CZ2CO are determined to be respectively -2.83 and -3.02 eV.

To evaluate the electroluminescent (EL) performance of the two emitters, two types of devices were fabricated: device type I: ITO/(4,4'-(cyclohexane-1,1-diyl)bis(*N,N*-di-*p*-tolylaniline)) TAPC (45 nm)/(tris(4-(9*H*-carbazol-9-yl)phenyl)amine) TCTA (5 nm)/mCP (5 nm)/mCP:3 wt% emitters (20 nm)/(dibenzo[*b,d*]furan-2,8-diylbis(diphenylphosphine oxide)) PPF (5 nm)/(1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene) TPBi (35 nm)/LiF (1 nm)/Al (100 nm) and type II: ITO/TAPC (45 nm)/TCTA (5 nm)/mCP (5 nm)/PPF: 15 wt% (5-(2,12-di-*tert*-butyl-5,9-dioxo-13b-boranaphtho[3,2,1-*de*]anthracen-7-yl)-10,10-diphenyl-5,10-dihydrodibenzo[*b,e*][1,4]azasiline) TDBA-PAS :3 wt% emitters (20 nm)/PPF (7 nm)/(4,7-Diphenyl-1,10-phenanthroline) Bphen (40 nm)/LiF (1 nm)/Al (100 nm). For type I devices, the maximum current efficiencies (CE_{max}) are 8.6 and 9.4 $cd^M A^{-1}$, power efficiencies (PE_{max}) are 7.1 and 5.9 $lm^M W^{-1}$, and EQE_{max} are 15.6 and 13.0 % for the devices based on CZCO and CZ2CO (Figure^{S18}), respectively. All the devices emit deep-blue EL peaking at 432 and 445 nm with FWHM of 35 and 23 nm (0.22 and 0.14 eV) for CZCO and CZ2CO, respectively. The long delay emission lifetime ($\approx 400 \mu s$) is believed to undermine the emitters' performances in type I devices. The broadening of

FWHM in EL should be related to the interaction of the emitters with the surrounding environment.

Considering their rather short prompt emission lifetimes (Table¹, ≈ 3 ns), CZCO and CZ2CO were employed as terminal emitters in hyper-fluorescent OLEDs (type II). TDBA-PAS with an anti-concentration quenching feature was selected as an assistant dopant, and the related excited state energies were shown in Figure¹⁹.^[37] The spectral overlap between sensitizer's PL spectra and emitter's absorption was shown in Figure²⁰. It shows TDBA-PAS would be a suitable sensitizer. The CE_{\max} of 13.6 and 16.4 $\text{cd} \cdot \text{A}^{-1}$, PE_{\max} of 7.9 and 5.1 $\text{lm} \cdot \text{W}^{-1}$, and EQE_{\max} of 26.9 and 25.6% (Figure³ and Table²) are obtained for the devices with CZCO and CZ2CO, respectively. These devices performances stand on the cutting edge of similar color gamut (Table⁴). Benefiting from the short prompt lifetimes of the new emitters and the fast reversible intersystem crossing rate of TDBA-PAS, efficiency roll-off was greatly suppressed in the type II devices (EQE maintained above 24% @ 1000 $\text{cd} \cdot \text{m}^{-2}$). The transient EL data (Figure²¹) reveal that the TADF assistant dopant is effective in shortening emission from long-lived excitons in type I devices. As shown in Figure⁴, deep-blue emissions were observed from the devices, with peaks at 432 and 445 nm and FWHMs of 44 and 26 nm (0.28 and 0.16 eV) for CZCO and CZ2CO, respectively. The red-shifting and broadening of emission compared to the PL is due to the effects of the environmental factors and the emission contribution from the assistant TADF dopant.^[10,38]

Conclusion

A deep-blue emitter (CZ2CO) with an ultranarrow emission $\lambda_{\text{em}}/\text{FWHM}$ of 440/16 nm was developed via intramolecular cyclization in a carbonyl/N resonant core. Theoretical calculations reveal that the cyclization of CZ2CO results in synergistically improving rigidity, strengthening the resonant strength, inhibiting bending and rocking, and

destabilizing of HOMO energy level, which endows the emitter with narrowed, blue-shifted emission with a dominant ν_{0-0} transition character. The hyper-fluorescent OLED based on CZ2CO shows high EQE_{max} at 25.6% and 22.4% at 1000 cd m^{-2} , which represent the highest efficiency for OLEDs based on C \rightleftharpoons O/N multi-resonance emitters close to the BT.2020 standard. We believe the design strategy reported in this study is inspiring and attractive for future narrowband deep blue emitters.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request

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Figure[^]1 a)[^]Chemical structures and fluorescence spectra with corresponding CIE coordinates of CZCO and CZ2CO, b)[^]Calculated HOMO and LUMO energy levels and distributions of CZ2CO, CZCO and QAO (omitting *t*-Bu groups for clearance) and comparison of hybrids status (sp^x) of C-C-N bonds in QAO and CZ2CO based on NBO analysis.

Figure[^]2 a)[^]Potential energy surfaces in the ground and the excited states. The transition and reorganization energies were calculated using TD-DFT at the PBE0/6-31G(d,p) level in toluene. b), c) and d)[^]Calculated vibrationally resolved fluorescence spectra with dipole strengths of different vibrational modes for QAO, CZCO and CZ2CO, respectively.

Figure[^]3 Type II device performance: a)[^]EL spectra at 9[^]V, b)[^]*J-V-L* characteristic curves, c) Plots of CE-luminance-PE and Luminance-EQE plots.

Figure[^]4 Comparison of EL spectra and PL spectra of a)[^]CZCO and b)[^]CZ2CO.

Scheme[^]1 Factors of the molecular structure that can reduce the FWHM of the emission profile, grey line: stretching vibration energy level, blue line: bending or rocking vibration energy level.

Table[^]1 Summary of the photophysical data of CZCO and CZ2CO.<W=3>

Compound	$E_g^{[a]}$	HOMO/LUMO	$\lambda_{PL}^{[c]}$	$\lambda_{abs}^{[c]}$	FWHM	Δv	$\Phi_{PL}^{[d]}$	$\tau^{[d]}$	$E_{S1}/E_{T1}^{[e]}$
	[eV]	[eV]	[nm]	[nm]	[nm/eV]	[nm]	[%]	[ns/ μ s]	[eV]
ZCO	2.90	5.73/-2.83	430	410	32/0.21	20	75	2.93/3	8/2.55 92.8
CZ2CO	2.76	-5.78/-3.02	440	434	16/0.10	6	84	3.28/43	2.82/2.45 1.8

[a][^]Optical energy gap estimated from the absorption onset, [b][^]Measured by cyclic voltammetry/calculated from LUMO<M->HOMO= E_g , [c][^]Measured in toluene solution, [d][^]Measured in solid thin film, [e][^]Measured in toluene solution at 77[^]K.

Table[^]2 Summary of performance of type I and type II devices.<W=3>

Device	EML	$V_{on}^{[a]}$	$\lambda_{EL}^{[b]}$	FWHM	CE ^[c]	PE ^[c]	EQE ^[d]	CIE ^[b]
		[V]	[nm]	[nm/eV]	[cd [^] A ^{^-M-} >1]	[lm [^] W ^{^-M-} >1]	[%]	
Type I	CZCO	3.4	432	35/0.22	6/4.2	7.1/2.3	.6/6.0/5.9	54,0.047)
	CZ2CO	3.4	445	23/0.14	4/7.6	5.9/4.1	9.9/3.9	54,0.061)
Type II	CZCO	3.8	432	44/0.28	3.6/13.6	7.9/7.9	1/26.8/24.3	54,0.051)
	CZ2CO	3.8	445	26/0/16	16.4/7.0	5.1/3.5	25.6/1.4/10.1/22	(0.157,0.074) .4

[a] Voltage at $1 \text{ cd}^{\text{M} \rightarrow 2}$, [b] Measured at 9 V , [c] Device efficiency at maximum, $100 \text{ cd}^{\text{M} \rightarrow 2}$, [d] Device efficiency at maximum, $1 \text{ cd}^{\text{M} \rightarrow 2}$, $100 \text{ cd}^{\text{M} \rightarrow 2}$ and $1000 \text{ cd}^{\text{M} \rightarrow 2}$.