Allochroic thermally activated delayed fluorescence diodes through field-induced solvatochromatic effect

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Allochroic organic light-emitting devices (AOLEDs) characterized by field-dependent emissive color variation are promising as visible signal response units for intelligent applications. Most of the AOLEDs were realized by changing their recombination zones or inter- and intramolecular energy transfer, rendering the limited repeatability, stability, and electroluminescence (EL) performance. We report a novel thermally activated delayed fluorescence (TADF) diode that featured a successive and irreversible emission color change from bluish green to deep blue during voltage increase, which uses the significant influence of host polarity on the emission color of TADF dyes, namely, solvatochromatic effect. Its host 3,6-di-tert-butyl-1,8-bis(diphenylphosphoryl)-9H-carbazole (tBczHDPO) was designed with remarkable field-dependent polarity reduction from 7.9 to 3.3 D by virtue of hydrogen bond-induced conformational isomerization. This TADF device achieves the best EL performance among AOLEDs, to date, with, for example, an external quantum efficiency beyond 15%, as well as the unique irreversible allochroic characteristic for visible data storage and information security.

INTRODUCTION

Allochroic organic light-emitting devices (AOLEDs) are one kind of unique OLED with variable emission color dependent on applied voltages; therefore, they can convert electrical signals to light color signals (1, 2). On that basis, AOLEDs are perfect for naked-eye information recognition, making them promising in nearly all display applications. The early AOLEDs were designed with two emissive layers (EMLs) with different colors, whose recombination zones can be switched or shifted between EMLs for the electroluminescent (EL) spectral variation (3–6). In contrast, through restraining energy transfer, Berggren et al. (7) achieved the ordinal emissions from different domains in EMLs of polymer blend–based OLEDs, forming another kind of AOLEDs with changeable intra- and/or intermolecular energy transfer. In actuality, it is a common phenomenon for OLEDs that recombination location shift (RLS) and energy transfer modulation (ETM) during voltage increase are often accompanied by slight spectral change due to its optical effect and emission ratio variation (8–10). However, these allochroic devices inevitably suffered from poor repeatability and weak EL performance. Therefore, in recent years, some new strategies were developed to realize field-induced allochroic behaviors, including emitters with multiple radiative transition channels [for example, carbon dots (11)] and voltage-dependent dynamic molecular structure rearrangement (12). Nevertheless, the involvement of excitons in these allochroic processes inevitably exacerbates quenching and reduces EL performance and repeatability. The great challenge is still that allochroic devices with applicable EL performance, such as brightness beyond 1000 cd m⁻² and external quantum efficiencies (EQEs) of more than 10%, are absent.

Thermally activated delayed fluorescence (TADF) devices rapidly gained attention owing to their advantages in 100% exciton harvesting, low cost, and environmental friendliness (13), in which emitters are characterized by donor-acceptor systems with strong intramolecular charge transfer (CT) for triplet-singlet exciton upconversion through reverse intersystem crossing (14–18). Within 10 years of the first reported TADF diode, the performance of TADF devices is already comparable to electrophosphorescence analogs, displaying their great potential for practical applications (19–22). It is noteworthy that the emissions from all TADF dyes show the remarkable bathochromic shifts along with the increase of the solvent polarity, namely, the so-called solvatochromatic effect, which should be attributed to the stronger stabilization effect of higher polar solvents on their CT-featured excited states in contrast to ground states (Scheme 1A) (23). In OLEDs with doping-type EMLs, their host matrices actually serve as the solid solvents of emitters; therefore, the molecular polarities of host materials should markedly influence the emission colors of TADF devices (24). The remarkable emission bathochromic shifts of TADF diodes when slightly increasing doping concentrations, even from 1 to 3%, actually reveal the high sensitivity of TADF emission to environmental polarity (25). In contrast to their phosphorescent and fluorescent counterparts, TADF dyes are featured with efficiently radiative CT excited states, establishing the basis for their potential applications in high-efficiency AOLEDs. In our previous work, a significant bathochromic shift of emission peaks from 460 to 472 nm, corresponding to deep blue and greenish blue, were observed for conventional blue TADF dye bis[4-(9,9-dimethyl-9,10-dihydroacridine)phenyl]sulfone (DMAC-DPS)–based devices (26) when using host materials with gradually increased polarities, which inspired us to develop TADF AOLEDs on the basis of solvatochromism (27). Herein, we report 3,6-di-tert-butyl-1,8-bis(diphenylphosphoryl)-9H-carbazole (tBczHDPO) as a host with hydrogen bond–controlled polarity variation to fabricate a proof-of-concept TADF AOLED with the unique host-leading irreversible green-to-blue emission color change and the state-of-the-art EL performance (for example, the maximum EQE beyond 15%) (Fig. 1A), paving a way to practically applicable AOLEDs.

RESULTS

Polarity bistability

TBCzHDPO is designed as a carbazole–phosphine oxide (PO) hybrid. The intramolecular hydrogen bond (IHB) between N–H of its carbazole core and the oxygen atoms of its two diphenylphosphine oxide (DPPO) groups can fix its conformation as an endo type with stronger thermodynamic stability, which is confirmed by its single-crystal structure. Theoretically, tBczHDPO can adopt three main conformation types with two outward, one outward–one inward, and two inward P=O...
bonds, corresponding to symmetrical and asymmetrical exo types and endo types, respectively. However, the symmetrical exo-type conformer is the most thermodynamically unstable because of its high total energy and large energy barrier of conformation transformation (fig. S1). In this case, the actual preferential conformations of tBCzHDPO are the endo and asymmetrical exo types. The latter is referred to simply as exo type. The density functional theory (DFT) simulation indicates the low polarity of endo-type tBCzHDPO by a level of ~3 D. In contrast, its exo-type conformation with a markedly increased polarity of ~8 D is the major conformer in as-deposited solid films on account of its two equivalent conformational isomers (Fig. 1B, fig. S1A, and table S1). The total energy of its endo conformer is 11.7 kJ mol⁻¹, lower than that of the exo conformer, revealing the higher thermodynamical stability of the former. Furthermore, the energy barrier of ~15 kJ mol⁻¹ for exo-to-endo transformation is surmountable. Therefore, tBCzHxPO and its mono-PO analog 3,6-di-tert-butyl-1-(diphenylphosphoryl)-9H-carbazole (tBCzHSPO), collectively named tBCzHₓPO, are designed with IHB-controlled binary polar states. The main difference is that the polarities of the exo and endo conformers for tBCzHSPO are comparable as 3 to 4 D.

Polar state transformation

Time-dependent DFT (TDDFT) calculation of the nature transition orbitals (NTOs) (28) in singlet excitations for tBCzHSPO and tBCzHDPO indicated the influence of conformation variation on electronic characteristics of their exo- and endo-type isomers (fig. S2). For ground state (S₀) → singlet excited state (S₁) transitions, the comparison between the exo and endo conformers shows the decreased contributions from DPPO groups to their "particle" locations, giving rise to a remarkable S₁ energy reduction by 0.21 and 0.08 eV, corresponding to red shifts of 19 and 8 nm, respectively, which is in accord with DFT-simulated frontier molecular orbital (FMO) energy gaps (fig. S3). The solid-state emissions of tBCzHₓPO vacuum-evaporated films before and after annealing show the identical situation. Photoluminescence (PL) spectra of the as-prepared films are peaked at 392 and 385 nm for tBCzHSPO and tBCzHDPO, respectively. After annealing at 200°C for 30 min, the remarkable emission bathochromic shift by ~10 nm can be observed for these films (fig. S4B). In this sense, the shorter emission peak wavelengths of the as-prepared tBCzHₓPO films before annealing indicate the predominant ratio of their exo-type isomers with the higher S₁ excited energy. In actuality, when preparing thin films through high-temperature evaporation and rapid cooling, it is rational that the high-energy condition for evaporation is beneficial to overcome the rotational energy barrier. Therefore, the exo conformers should be dominant in the as-deposited films according to statistics. Significantly, the bathochromic emissions of annealed tBCzHₓPO films manifest the exo-to-endo transformation by heating, ascribed to the higher thermodynamic stability of their endo-type isomers. The role as driving force for heat is further demonstrated with differential scanning calorimetry, by which tBCzHₓPO films reveal the distinct glass-state transition accompanied by the exo-to-endo transformation (fig. S5 and table S1). To figure out the effect of IHB on conformation variation, the solid-state PL spectra of the vacuum-evaporated films based on the N-methyl–substituted derivative 3,6-di-tert-butyl-1-(diphenylphosphoryl)-9H-carbazole and 3,6-di-tert-butyl-1,8-bis(diphenylphosphoryl)-9-methyl-carbazole (tBCzMₓPO) (29) without IHB were simultaneously measured to show the almost unchanged emissions before and after annealing, despite the similar exo-to-endo S₁ excited energy reduction and thermodynamic stabilization of tBCzMₓPO (fig. S2). Therefore, IHB is the crucial force to fix endo-type conformations of tBCzHₓPO during annealing and to induce monodirectional exo-to-endo transformation.
It can be expected that conformation switch of tBCzHDPO between its exo and endo isomers in the doped thin film would markedly change the matrix polarity of its dopants. To confirm the possibility of conformational transformation under an electrical field, we fabricated tBCzHxPO-based light-emitting devices with the configuration of indium tin oxide (ITO)/MoO3 (6 nm)/4,4′-bis[N-(1-naphthyl)-N-phenylamino]-1,1′-biphenyl (NPB) (40 nm)/1,3-bis(N-carbazolyl) benzene (mCP) (5 nm)/tBCzHxPO (20 nm)/bis{2-[di(phenyl)phosphino]phenyl}ether oxide (DPEPO) (5 nm)/4,6-bis(diphenylphosphoryl) dibenzothiophene (DBTDPO) (30 nm)/LiF (1 nm)/Al (100 nm) through vacuum evaporation, in which NPB and DBTDPO were adopted as hole-transporting layer and electron-transporting layer (ETL), respectively, whereas mCP and DPEPO with the appropriate FMO energy levels were used to improve the carrier injection and the confinement of charge carrier recombination in tBCzHxPO layers (scheme S2). Along with the voltage increase from 5.5 to 9.5 V, both tBCzHSPO and tBCzHDPO show the voltage-dependent EL spectra with red shifts of 12 and 24 nm (Fig. 1C). As indicated by optical analysis, exo-type conformations of tBCzHxPO are dominant in their as-deposited films. The joule heat generated by electricity is basically proportional to the product of voltage and current density (\(J\)), namely, power density, therefore facilitating the exo-to-end transformation as the same mechanism of the annealing effect on tBCzHxPO films.
To further verify the effect of electrical field on conformation variation of tBCzHxPO, we fabricated their single-layer devices with configuration of ITO/MoO$_3$ (6 nm)/tBCzHxPO (100 nm)/LiF (1 nm)/Al (fig. S6B). For the first circle of voltage increase from 0 to 20 V, the typical semiconductor volt-ampere characteristics were recognized with conductive voltages of 4.3 and 7.9 V for tBCzHSPO and tBCzHDPO, respectively. Then, in the second circle, their conductive voltages decreased to 2.8 and 1.5 V, respectively, and their $J$ markedly increased, reflecting improved ordered intermolecular packing after the first circle. Commonly, the hole and electron injecting abilities are roughly determined by the energy levels of the highest occupied and the lowest unoccupied molecular orbitals (LUMOs), respectively. In this sense, tBCzHDPO with the deeper LUMO should be superior to tBCzHSPO in electron injection (figs. S3 and S6A). However, the higher conductive voltage of tBCzHDPO-based devices in the first circle reflected the equally crucial influence of aggregation characteristics on carrier injection in the thick films. Besides the reduced FMO energy gaps of the endo-type conformers for carrier injection balance, in contrast to the exo-isomers, the endo types of tBCzHxPO are more symmetrical to enhance the regular alignment and intermolecular interaction for the improvement of carrier injection and transport, indicating the correlation between the increased $J$ in the second circle and the exo-to-endo transformation in the first circle.

**Photophysical properties**

tBCzHxPO show the optical properties in dilute solution almost identical to those of tBCzMsPO (fig. S4A) (29). Their high triplet excited energy ($T_1$) beyond 2.9 eV can support the positive energy transfer to DMAC-DPS, rendering the pure blue emissions and high photoluminescence quantum yields beyond 70% from their DMAC-DPS-doped vacuum-evaporated thin films (Fig. 1D). It is noteworthy that the PL emission peaks of DMAC-DPS in tBCzHDPO and 3,6-di-tert-butyl-1,8-bis(diphenylphosphoryl)-9-methyl-carbazole (tBCzMDPO) matrices are 8 nm longer than those in tBCzHSPO and 3,6-di-tert-butyl-1-(diphenylphosphoryl)-9-methyl-carbazole (tBCzMSPO). These bathochromic shifts of dopant emissions rationally manifest...
the existence of the high-polarity states in tBCzHDPO and tBCzMDPO films and their significant influences on emission color. Furthermore, the emission profiles of these films are only dependent on the DPPO group numbers of their host matrices. In contrast to tBCzHxPO, without influence of IHB, the conformation population of tBCzMxPO should roughly follow the statistic probability. Therefore, the exo-type conformation of tBCzMDPO would be the major conformers in its films, whose polarities are almost the same as that of exo-type tBCzHDPO (fig. S7). In this sense, the identical emission of DMAC-DPS in tBCzHDPO validates the predominance of the exo-type isomers for the host in its as-deposited films, in accord with the situation of its nondoped films.

**Device performance**

Inspired by the electric field–induced conformation variation of tBCzHxPO, we created five-layer devices with the configuration of ITO/MoO3 (6 nm)/NPB (40 nm)/mCP (5 nm)/host:DMAC-DPS (10 wt %, 20 nm)/DPEPO (5 nm)/DBTDPO (30 nm)/LiF (1 nm)/Al (100 nm) in which mCP and DPEPO served as exciton-blocking layers (Fig. 2A and scheme S2). tBCzHDPO and tBCzMDPO endowed their devices with a reduced onset voltage of 3.0 V, 0.5 V lower than those of tBCzHSPO- and tBCzMSPO-based devices, which were in accord with the deeper LUMO of the former for more efficient electron injection (Fig. 2B and table S2). At a voltage range of 4.0 to 4.5 V, for commercial lithium batteries, the luminescence of tBCzHDPO- and tBCzMDPO-based devices can increase to an applicable range of 25 to 100 cd m⁻². tBCzHDPO realized the highest efficiencies among these hosts, with maxima of 30.4 cd A⁻¹ for current efficiency, 38.2 lumen W⁻¹ for power efficiency, and 15.2% for EQE, which were comparable to the five-layer DMAC-DPS–based counterparts using the most popular blue TADF host DPEPO (Fig. 2C and fig. S8) (27). Therefore, tBCzHDPO-based devices can be integrated into the lithium battery–driven portable equipment.

EL spectra of the devices at 4.0 V are identical to PL spectra of the corresponding DMAC-DPS–doped films, with the peaks at 476 nm for tBCzHDPO and tBCzMDPO and 464 nm for tBCzHSPO and tBCzMSPO (Fig. 2D). Significantly different from the other hosts with the stable EL spectra during voltage change, emissions of tBCzHDPO-based devices markedly shift from 480 nm at 3.5 V to 460 nm at 10 V,
corresponding to the Commission Internationale de L’Eclairage (CIE)
coordinates of (0.175, 0.303) for bluish green and (0.168, 0.192) for
depth blue. Consequently, as designed, tBcZHDPO supports its devices with
the field-induced allochroic phenomenon (Fig. 2E). It is interesting that
the devices show continuous allochroic behavior in direct proportion
to voltage input with emission peaks varying from 480 to 460 nm, with
an interval of 4 nm for each increase of 1 V, similar to the solvatochromic
characteristics of DMAC-DPS (26). This reveals the gradually transformed
and uniformly dispersed low-polarity states of tBcZHDPO molecules
in EMLs, which is identical to the solvatochromic behaviors of CT
molecules under continuously reduced solvent polarities (30). Furthermore,
the operation time to realize the emission change, namely, response
time, was in reverse proportion to driving voltage and exponentially
dependent on power density (fig. S9). This accurate correspondence be-
tween the voltage and emission peaks establishes the basis for pur-
poseful and controllable multilevel color regulation as one of the main
challenges for AOLEDs.

It is particularly noteworthy that the allochroic process of tBcZHDPO-
based TADF devices is irreversible, which is opposite to most of organic
and inorganic (31, 32) color-variable LEDs (Fig. 3A). During the first
circle of voltage increase from 4 to 8 V, the emission peak successively
shifts from 476 to 464 nm, whereas for the second circle, the EL emis-
sion becomes invariable with a stable peak wavelength at 464 nm and
unchanged profiles identical to those at 8 V in the first circle. Because
distortion. Therefore, when a photo- and electrostable TADF dye was
applied as write operation to change E Le m i s s i o n i n t o b l u e w i t h a
blue emission that peaked at 476 nm is set as 0. Then, a voltage of 8 V is
read (4 V) circle, the 0 and 1 signals can be read out for many times in continuous succession with-
out any distortions, corresponding to a typical WORM memory mode.

The intensity of light signal is in reverse proportion to the times of read
operation because of the device degradation due to the photo-
and electro-oxidation of DMAC-DPS (33). In this sense, the reading num-
ber is mainly dependent on the EL lifetime of the device rather than data
distortion. Therefore, when a photo- and electrostable TADF dye was
available, the memory lifetime can be markedly improved.

By virtue of an ordinary photometer with a resolution of 4 nm, the
multilevel data storage at the maximum of senary scale can be realized
to increase capacity exponentially, considering the emission peak vari-
ation from 480 to 460 nm with an interval of 4 nm. In particular, on
account of the “electro-write photo-read” (EWPR) mode and the
diversified and strict correspondence between write operation voltage
and emission peak, data can be dually encrypted in electrical input
and optical output. Furthermore, this memory has a self-destruction
function to enhance information safety. For this memory, the read volt-
age should be lower than the write voltage. Otherwise, all the bits would
be written as 1 during the “read” process, which erases the stored
information (scheme S3).

DISCUSSION

We have demonstrated a novel green-to-blue AOLED based on solva-
tochromic behavior of the TADF dye DMAC-DPS through field-
induced conformational transformation of its host tBcZHDPO from
high- to low-polar states. The IHB is used to fix the low-polarity con-
formation after field removal, giving rise to the unique irreversible allo-
chroic mode for nonvolatile visible data storage and information
security. This kind of host-leading allochroic process, rather than the
other exciton-involved allochroic mechanisms, significantly mitigates
exciton quenching during emission change. Consequently, EL perform-
ance of the tBcZHDPO-based device is comparable to the state-of-the-art
values of homochromous analogs, making it competent to commercial
applications. Further increasing color changing range can be realized
through widening of the polarity difference of the binary polar states. This
work demonstrates the great potential and superiority of TADF diodes
for allochroic applications and the feasible host-control strategy.

MATERIALS AND METHODS

Fabrication and characterization of OLEDs

Before loading it into a deposition chamber, the ITO substrate was
cleaned with detergents and deionized water, dried in an oven at 120°C
for 4 hours, and treated with ultraviolet ozone for 20 min. Devices were
fabricated by evaporating organic layers at a rate of 0.1 to 0.3 nm s⁻¹
onto the ITO substrate sequentially at a pressure below 1 × 10⁻⁶ mbar.
A layer of LiF with 1-nm thickness was deposited onto the ETL at a rate of
0.1 nm s⁻¹ to improve electron injection. Finally, a 100-nm-thick
layer of Al was deposited at a rate of 0.6 nm s⁻¹ as the cathode. The
emission area of the devices was 0.09 cm², as determined by the overlap
area of the anode and the cathode. The EL spectra and CIE coordinates
were measured using a PR-655 spectroradiometer. The current density–
voltage and brightness-voltage curves of the devices were measured
using a Keithley 4200 source meter and a calibrated silicon photodiode.
All the measurements were performed at room temperature in a glove
box. For each structure, four devices were fabricated in parallel to confirm
the performance repeatability. To make the conclusions reliable, the
data reported herein were mostly close to the average results (fig. S10).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/
content/full/3/9/e1700904/DC1
Experimental section
Gaussian simulation results
Optical properties of the PO molecules
Thermal and morphological properties of tBcZHxPO
Electrical properties of tBcZxPO
Polarity variation of tBcZxPO isomers
Device structure and electroluminescence process
Encryption mechanism
Device performance
Movie indicating the allochroic process
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scheme S3. Encryption flow chart of EWPR-type memory based on irreversible AOLEDs.
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fig. S12. $^{13}$C NMR spectrum of tBCzHPO.
fig. S13. $^{31}$P NMR spectrum of tBCzHPO.
fig. S14. $^{1}H$ NMR spectrum of tBCzHPO.
fig. S15. $^{31}$P NMR spectrum of tBCzHSPO.
fig. S16. $^{31}$P NMR spectrum of tBCzHDPO.

REFERENCES AND NOTES


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