Supporting Information

Exploiting Racemism Enhanced Organic Room-Temperature Phosphorescence to Demonstrate Wallach’s Rule in the Lighting Chiral Chromophores

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**Supplementary Method:**

**Fabrication of devices.**

The materials used in OLED device fabrication were commercially available. To fabricate devices, the ITO-coated glass was used as an anode and sequentially cleaned as standard operation. A 35 nm thick hole injection layer of PEDOT : PSS film was spin-coated on the cleaned ITO substrate and then annealed at 120 °C for 20 min in a vacuum oven. 1,1′-bis(di-4-tolylaminophenyl) cyclohexane (TAPC, 40 nm), 1,3-Bis(carbazol-9-yl)benzene (mCP, 7 nm), BINAP (20 nm), TmPyPB (40 nm), CsF (1.2 nm), and aluminum (120 nm) were continuously deposited using resistive evaporation, respectively. The device area was 0.16 cm² for all samples in this work. The thicknesses of spin-coating and evaporation were monitored with a quartz crystal thickness/ratio monitor (model STM-100/MF, Sycon). The J-V-R characteristics were measured using the Keithley 236 system and a calibrated silicon photodiode. Irradiance and luminance were calculated assuming a Lambertian distribution. Electroluminescence (EL) spectra and CIE coordinate were measured using CS-1000 spectroradiometer.
Supplementary Discussion:

Derivations of intrinsic fluorescence and phosphorescence yield.

Under the assumption that the net intersystem crossing yield \((x)\), which includes the effect resulting from triplet-triplet annihilation (TTA), is the same in both photoluminescence (PL) and electroluminescence (EL), \(x\) can be calculated from the following equation:

\[
\alpha \left( \frac{1-x}{x} \right) = \frac{I_F}{I_P}
\]

\[
\alpha \left( \frac{25 \times (1-x)}{75 + 25x} \right) = \frac{E_F}{E_P}
\]

where \(\alpha\) denotes the ratio for radiative rate of fluorescence versus phosphorescence. \(I_F\) and \(I_P\) denote the PL intensity of fluorescence and phosphorescence, respectively. \(E_F\) and \(E_P\) denote the EL intensity of fluorescence and phosphorescence. Therefore, \(x\) can be solved by dividing eqs 1 with eqs 2. The net intersystem crossing yield \((x)\) can be expressed in following equation:

\[
x = \frac{3}{\frac{I_F}{I_P} - 1}
\]

The ratio for PL of fluorescence versus phosphorescence is set to be 18.23, which is deduced from the ratio of area from the PL fluorescence and phosphorescence of rac-BINAP. As for the ratio for EL of fluorescence versus phosphorescence, the value is set to be 0.58, which is determined from the ratio for area for the EL fluorescence versus phosphorescence under 3.6V operated voltage. Under low operated voltage, TTA is hindered as much as possible. \(x\) is thus deduced to be 9.8%. The intrinsic fluorescence and phosphorescence yield can thus be obtained by dividing the respective quantum yield with 1-x and x.
Derivations for the ratio variation of fluorescence versus RTP in Electroluminescence (EL).

In EL mechanism, the energy originates from the migrations of electrons and holes, i.e., hopping between molecules. Thus, we assume that the energy transporting molecules serve as the energy source (ES). On the other hand, molecules undergoing TTA (rac-BINAP in this case) serve as annihilators (A). The initial reaction pathways are depicted as follows:

\begin{align}
1ES \rightarrow 1ES^* & \quad \text{Singlet Exciton excitation (exc)} \\
1ES \rightarrow 3ES^* & \quad \text{Triplet Exciton excitation (exc)} \\
1ES^* \rightarrow 1ES & \quad \text{Singlet Exciton quenching} \\
3ES^* \rightarrow 1ES & \quad \text{Triplet Exciton quenching}
\end{align}

(R1) (R2) (R3) (R4)

Here, \( k_{\text{exc}}, k_{\text{qf}}, \) and \( k_{\text{qp}} \) denotes the constants of excitation rate, quenching rate of the singlet exciton and triplet exciton, respectively. \( 1ES, 1ES^*, \) and \( 3ES^* \) represent the non-excited energy source, singlet exciton, and triplet exciton respectively. Accordingly, the corresponding time-resolved differential equations without any energy transfer processes are depicted below:

\begin{align}
\frac{d[1ES]}{dt} &= k_{\text{qp}} [3ES^*] + k_{\text{qf}} [1ES^*] - 4k_{\text{exc}} [1ES] \\
\frac{d[1ES^*]}{dt} &= -k_{\text{qf}} [1ES^*] + k_{\text{exc}} [1ES] \\
\frac{d[3ES^*]}{dt} &= -k_{\text{qp}} [3ES^*] + 3k_{\text{exc}} [1ES]
\end{align}

(R4) (R5) (R6)

Next, we list all the possible energy transfer processes, including the annihilation pathways in triplet-triplet annihilation (TTA) and singlet-triplet annihilation (STA) processes depicted as follows:

\begin{align}
1ES^* + 1A \rightarrow 1ES + 1A^* & \quad \text{Singlet Energy Transfer to ground-state annihilator (SET)} \\
3ES^* + 1A \rightarrow 1ES + 3A^* & \quad \text{Primary Triplet Energy Transfer to ground-state annihilator (TET1)} \\
3ES^* + 3A^* \rightarrow 1ES + 3A^{**} & \quad \text{Secondary Triplet Energy Transfer to triplet excited annihilator (TET2)} \\
3A^* + 3A^{**} \rightarrow 1A + 1A^* & \quad \text{Primary (intermolecular) Triplet-Triplet Annihilation (TTA1)} \\
3A^{**} \rightarrow 1A^* & \quad \text{Secondary (intramolecular) Triplet-Triplet Annihilation (TTA2)} \\
1A^* + 3A^* \rightarrow 1A + 3A^{**} & \quad \text{Singlet-Triplet Annihilation (STA)} \\
1A^* \rightarrow 3A^* & \quad \text{Intersystem crossing process (ISC)} \\
1A^* \rightarrow 3A^{**} & \quad \text{Excited singlet decay of Annihilator (FA)} \\
3A^* \rightarrow 1A & \quad \text{Excited triplet decay of annihilator (PA)}
\end{align}

(R5) (R6) (R7) (R8) (R9) (R10) (R11) (R12) (R13)

where \( 1A, 1A^*, 3A^*, \) and \( 3A^{**} \) represent the annihilator (A) in its ground-state, first singlet excited-state, first triplet excited-state, and highly triplet excited-state, respectively. \( k \) with
We then employ steady-state approximations for the equations list above:

\[ 0 = [^{1}ES] + [^{1}ES^*] + [^{3}ES^*] - [^{1}ES]_0 \]  

balance (14)

\[ 0 = [^{1}A] + [^{1}A^*] + [^{3}A^*] - [^{1}A]_0 \]  

balance (15)

\[ 0 = \frac{d[^{1}ES]}{dt} = -k_{sp} [^{1}ES^*] - k_{SET} [^{1}ES^*] [^{1}A] + k_{exc} [^{1}ES] \]  

\[ ^{1}S^* \] (16)

\[ 0 = \frac{d[^{1}ES^*]}{dt} = -k_{sp} [^{3}ES^*] - k_{TET1} [^{3}ES^*] [^{3}A] - k_{TET2} [^{3}ES^*] [^{3}A^*] + 3k_{exc} [^{1}ES] \]  

\[ ^{3}S^* \] (17)

\[ 0 = \frac{d[^{1}A]}{dt} = k_{TET1} [^{1}ES^*] [^{1}A] - 2k_{TAL} [^{1}A^*] - k_{SET} [^{1}ES^*] [^{1}A^*] - k_{STA} [^{1}A^*] + k_{exc} [^{1}A] \]  

\[ ^{3}A \] (18)

\[ 0 = \frac{d[^{3}A^*]}{dt} = k_{TET2} [^{3}ES^*] [^{3}A^*] - k_{TAL} [^{3}A^*] + k_{STA} [^{3}A^*] - k_{exc} [^{3}A^*] - k_{KA} [^{1}A] \]  

\[ ^{3}A^* \] (19)

\[ 0 = \frac{d[^{1}A^*]}{dt} = k_{SET} [^{1}ES^*] [^{1}A] + k_{TET1} [^{1}ES^*] [^{1}A^*] + k_{TET2} [^{1}ES^*] [^{1}A^*] - k_{STA} [^{1}A^*] - k_{exc} [^{1}A^*] - k_{KA} [^{1}A] \]  

\[ ^{1}A^* \] (20)

Followed by the above equations, the derivations are listed below:

From eqs. 16

\[ k_{exc} [^{1}ES] - k_{sp} [^{1}ES^*] + k_{SET} [^{1}ES^*] [^{1}A] \]  

(21)

From eqs. 17

\[ k_{TET1} [^{3}ES^*] [^{3}A] = 3k_{exc} [^{1}ES] - k_{sp} [^{3}ES^*] - k_{TET2} [^{3}ES^*] [^{3}A^*] \]  

(22)
From eqs. 18
\[ k_{\text{TET}}[\text{ES}][\text{A}] = k_{\text{TET}}[\text{ES}][\text{A}] - 2k_{\text{TTA}}[\text{ES}][\text{A}] - k_{\text{STA}}[\text{ES}][\text{A}] + k_{\text{ISC}}[\text{A}] \] (23)

From eqs. 19
\[ k_{\text{TET}}[\text{ES}][\text{A}] = k_{\text{TTA}}[\text{ES}][\text{A}] - k_{\text{STA}}[\text{ES}][\text{A}] \] (24)

From eqs. 20
\[ k_{\text{PA}}[\text{A}] = k_{\text{SET}}[\text{ES}][\text{A}] + k_{\text{TTA}}[\text{ES}][\text{A}]^2 - k_{\text{STA}}[\text{ES}][\text{A}] - k_{\text{ISC}}[\text{A}] \] (25)

Combine eqs. 23 with 24
\[ k_{\text{TTA}}[\text{ES}][\text{A}] = k_{\text{TET}}[\text{ES}][\text{A}] - 2k_{\text{TTA}}[\text{ES}][\text{A}]^2 - k_{\text{PA}}[\text{A}] + k_{\text{ISC}}[\text{A}] \]

Then combine with eqs. 22
\[ k_{\text{TTA}}[\text{A}] = 3k_{\text{exc}}[\text{ES}] - k_{\text{ES}}[\text{ES}][\text{A}] + k_{\text{TTA}}[\text{ES}][\text{A}] - 2k_{\text{TTA}}[\text{ES}][\text{A}]^2 - k_{\text{PA}}[\text{A}] + k_{\text{ISC}}[\text{A}] \]

Then combine with eqs. 24
\[ k_{\text{TTA}}[\text{A}] = 3k_{\text{exc}}[\text{ES}] - k_{\text{ES}}[\text{ES}][\text{A}] - 2k_{\text{TTA}}[\text{ES}][\text{A}]^2 - k_{\text{PA}}[\text{A}] + k_{\text{ISC}}[\text{A}] \] (26)

Considering 25% of singlet excitons and 75% of triplet excitons in EL system, the overall energy source intensity \( I_{\text{exc}} \) can be described as:
\[ k_{\text{exc}}[\text{ES}] + 3k_{\text{exc}}[\text{ES}] = I_{\text{exc}} \] (27)

We then combine eqs. 27 with eqs. 26 to obtain eqs. 28.
\[ \frac{3}{4} I_{\text{exc}} - k_{\text{ES}}[\text{ES}] = 2k_{\text{TTA}}[\text{ES}][\text{A}]^2 + 2k_{\text{TTA}}[\text{ES}][\text{A}] - k_{\text{STA}}[\text{ES}][\text{A}] - k_{\text{ISC}}[\text{A}] \] (28)

Further, we define the fluorescence intensity to be \( I_F \), which is then combined with eqs. 20.
\[ I_F = k_{\text{PA}}[\text{A}] + k_{\text{TTA}}[\text{A}] + k_{\text{TTA}}[\text{ES}][\text{A}] - k_{\text{STA}}[\text{ES}][\text{A}] - k_{\text{ISC}}[\text{A}] \] (29)

Next, we define the phosphorescence intensity to be \( I_P \)
\[ I_P = k_{\text{PA}}[\text{A}] + k_{\text{TTA}}[\text{ES}][\text{A}] + k_{\text{TTA}}[\text{ES}][\text{A}] - k_{\text{STA}}[\text{ES}][\text{A}] - k_{\text{ISC}}[\text{A}] \] (30)

Using eqs. 28, we then obtain the quadratic dependent function for \( I_{\text{exc}} \) versus \( I_P \)
\[ \frac{3}{4} I_{\text{exc}} - k_{\text{ES}}[\text{ES}] - 2k_{\text{TTA}}[\text{ES}][\text{A}] + k_{\text{STA}}[\text{ES}][\text{A}] + k_{\text{ISC}}[\text{A}] = 2k_{\text{TTA}} \left( \frac{I_P}{k_{\text{PA}}[\text{A}] + k_{\text{TTA}}[\text{ES}][\text{A}] - k_{\text{STA}}[\text{ES}][\text{A}] - k_{\text{ISC}}[\text{A}]} \right) \] (31)

In order to simplify the correlation between \( I_{\text{exc}} \) and \( I_F \), we made two assumptions to conduct steady-state approximation. First, under low excitation intensity, TTA should have less effect to the phosphorescence intensity. Accordingly, the following relationship should hold.
\[ 2k_{\text{TTA}}[\text{ES}][\text{A}] + 2k_{\text{TTA}}[\text{ES}][\text{A}] < < k_{\text{PA}}[\text{A}] \]
which is applied to eqs. 28, giving eqs. 32.

\[
\frac{3}{4}I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] = 2k_{\text{TATA}}\left[3A^*\right] + 2k_{\text{TATA}}\left[3A''\right] - k_{\text{STA}}\left[3A^*\right] + k_{\text{ISC}}\left[3A''\right] - k_{\text{PA}}\left[3A''\right]
\]

\[
\frac{3}{4}I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] + k_{\text{STA}}\left[3A^*\right] + k_{\text{ISC}}\left[3A''\right] - k_{\text{PA}}\left[3A''\right] \approx k_{\text{PA}}\left[3A^*\right]
\] (32)

Therefore

\[
k_{\text{TATA}}\left(\frac{\frac{3}{4}I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] + k_{\text{STA}}\left[3A^*\right] + k_{\text{ISC}}\left[3A''\right] - k_{\text{PA}}\left[3A''\right]}{k_{\text{PA}}}\right)^2 \approx k_{\text{TATA}}\left(\frac{3A^*}{k_{\text{PA}}}\right)^2 = k_{\text{TATA}}\left[3A^*\right]^2
\] (33)

Combining eqs 33 with eqs.20

\[
k_{\text{PA}}\left[3A^*\right] = k_{\text{TATA}}\left[3A^*\right] + k_{\text{TATA}}\left[3A''\right] + k_{\text{SET}}\left[3S^*\right]\left[3A\right] - k_{\text{STA}}\left[3A^*\right] - k_{\text{ISC}}\left[3A''\right]
\]

As a result, a quadratic dependent function for \(I_F\) can be obtained under low current intensity (eqs. 34):

\[
I_F = k_{\text{PA}}\left[3A^*\right]\phi_a = \phi_a\left(3I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] + k_{\text{STA}}\left[3A^*\right] + k_{\text{ISC}}\left[3A''\right]\right)^2 + k_{\text{TATA}}\left[3A^*\right]^2 + k_{\text{SET}}\left[3ES^*\right]\left[3A\right] - k_{\text{STA}}\left[3A^*\right] - k_{\text{ISC}}\left[3A''\right]
\] (34)

Second, under high excitation intensity (i.e. high current density), TTA should have large effect to the phosphorescence intensity (annihilation dominant region). Accordingly, the following relationship holds.

\[
2k_{\text{TATA}}\left[3A^*\right]^2 + 2k_{\text{TATA}}\left[3A''\right] >> k_{\text{PA}}\left[3A^*\right]
\]

which is applied to eqs. 28, giving eqs. 35.

\[
\frac{3}{4}I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] = 2k_{\text{TATA}}\left[3A^*\right]^2 + 2k_{\text{TATA}}\left[3A''\right] - k_{\text{STA}}\left[3A^*\right] + k_{\text{ISC}}\left[3A''\right] - k_{\text{PA}}\left[3A''\right]
\]

\[
\frac{3}{4}I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] + k_{\text{STA}}\left[3A^*\right] + k_{\text{ISC}}\left[3A''\right] + k_{\text{PA}}\left[3A''\right] \approx 2k_{\text{TATA}}\left[3A^*\right]^2 + 2k_{\text{TATA}}\left[3A''\right]
\] (35)

Gather the above eqs. 35 and eqs. 20, a linear dependent function for fluorescence intensity \(I_F\) can be obtained under high current density.

\[
I_F = k_{\text{PA}}\left[3A^*\right]\phi_a \approx \phi_a\left(\frac{3}{4}I_{\text{exc}} - k_{\text{pq}}\left[3ES^*\right] - k_{\text{STA}}\left[3A^*\right] - k_{\text{ISC}}\left[3A''\right] \right) + k_{\text{PA}}\left[3A''\right]
\] (36)

Eqs. 31, 34 and 36 are used as the fitting functions to the experimental data shown in Fig. 5d in the main text. The fitting procedures were performed by Origin 2016.

As described above, strictly speaking, the “Quadratic” (eqs. 34) and “Linear” (eqs. 36) components of fluorescence and “Quadratic” phosphorescence (eqs. 31) intensities are not pure linear and quadratic character because of the existence of \(3ES^*\) and \(3ES^*\), which are proportional to the excitation intensity.
Supportive data for Characterization.

Supplementary Figure 1. $^1$H NMR of R-BINAP.

Supplementary Figure 2. $^1$H NMR of S-BINAP.
Supplementary Figure 3. $^{13}$C NMR of R-BINAP in CDCl$_3$.

Supplementary Figure 4. $^{13}$C NMR of S-BINAP in CDCl$_3$. 
Supplementary Figure 5. $^{13}$C NMR of rac-BINAP in CDCl$_3$.

Supplementary Figure 6. $^{31}$P NMR of R-BINAP in CDCl$_3$. 
Supplementary Figure 7. $^{31}$P NMR of S-BINAP in CDCl$_3$.

Supplementary Figure 8. $^{31}$P NMR of rac-BINAP in CDCl$_3$. 
CHEMICAL ANALYSIS TEST REPORT

Product Name: 1,1’-[(1R)-[1,1’-binaphthalene]-2,2’-diyl]bis[1,1-diphenyl]phosphine

Product No.: 110231
Cas No.: 76189-55-4
Lot No.: NFYF0921

Column: Welch Xtiame C18 0.46 cm I.D. x15 cm L, 5 μm
Injection: 2 μl
Mobile phase: B: MeOH(0.05%NH3) (v/v)
Gradient: NA
Flow rate: 1.0ml/min
Wave length: UV 254nm
Temperature: 30°C
Sample solution: 2.0 mg/ml in DCM20%M80%
HPLC equipment: Shimadzu UPLC 30A QA&QC-HPLC-11

<Chromatogram>

<Peak Table>

| Peak No. | Time  | Area  | Area % | Plate number | Tailing | Resolution |
|---------|------|-------|--------|--------------|---------|------------|
| 1       | 2.161| 28775 | 0.801  | 1505         | 1.669   | --         |
| 2       | 2.785| 20272 | 0.565  | 3530         | 1.353   | 3.042      |
| 3       | 3.441| 2129  | 0.059  | 2612         | --      | 2.873      |
| 4       | 4.211| 3535876| 98.465| 4441         | 1.249   | 2.949      |
| 5       | 5.040| 431   | 0.012  | 7781         | 0.932   | 3.444      |
| 6       | 6.974| 3498  | 0.097  | 3230         | 1.437   | 5.377      |

Supplementary Figure 9. HPLC of R-BINAP.
**Supplementary Figure 10.** HPLC of S-BINAP.
Supplementary Figure 11. Chiral Analysis report of rac-BINAP.

| Peak No. | Time  | Area   | Area % | Plate number | Tailing | Resolution |
|----------|-------|--------|--------|--------------|---------|------------|
| 1        | 10.027| 6399262| 45.199 | 3076         | 1.083   | --         |
| 2        | 13.538| 7758726| 54.801 | 3082         | 1.069   | 4.135      |
Chiral Analysis report for
1,1''-[(1R)-[1,1'-binaphthalene]-2,2'-diyl]bis[1,1-diphenylphosphine]

Product Name: 1,1''-[(1R)-[1,1'-binaphthalene]-2,2'-diyl]bis[1,1-diphenylphosphine]

**Remark:**

| Original product | 1,1''-[(1R)-[1,1'-binaphthalene]-2,2'-diyl]bis[1,1-diphenylphosphine] |
|------------------|---------------------------------------------------------------------|
| Product No.      | 110231                                                               |
| Cas No.          | 76189-55-4                                                          |
| Lot No.          | NFYF0921                                                            |

Supplementary Figure 12. Chiral Analysis report of R-BINAP.
Chiral Analysis report for 1,1'-(1S)-[1,1'-binaphthalene]-2,2'-diyl]bis[1,1-diphenylphosphine]

Product Name: 1,1'-(1S)-[1,1'-binaphthalene]-2,2'-diyl]bis[1,1-diphenylphosphine]

Remark:

| Original product | 1,1'-(1S)-[1,1'-binaphthalene]-2,2'-diyl]bis[1,1-diphenylphosphine] |
|------------------|---------------------------------------------------------------------|
| Product No.      | 110232                                                              |
| Cas No.          | 76189-56-5                                                          |
| Lot No.          | NFYF0922                                                            |

Supplementary Figure 13. Chiral Analysis report of S-BINAP.
**Supplementary Figure 14.** The crystal geometry of (a) rac-BINAP, (b) R-BINAP, and (c) S-BINAP depicted with thermal ellipsoids shown at 50% (hydrogen atoms are omitted for clarity). Note that in rac-BINAP, the left molecule is R-form, and the right one is S-form with atom number in corresponding order. As for the rac-BINAP crystal, it is worth to note that R- and S-BINAP show the same structure parameters except for its chirality in the racemic environment. However, both R- and S-BINAP in racemic environment show different values with respect to their homochiral crystal (see Table S1 in detail).

**Supplementary Table 1.** Selected bond lengths [Å] and angles [°] of BINAP

| parameters   | rac-BINAP | R-BINAP | S-BINAP |
|--------------|-----------|---------|---------|
| **bond lengths (Å)** |           |         |         |
| C1-C2        | 1.499     | 1.508   | 1.496   |
| P1-C3        | 1.839     | 1.851   | 1.836   |
| P2-C4        | 1.839     | 1.841   | 1.848   |
| P1-C5        | 1.833     | 1.840   | 1.830   |
| P1-C6        | 1.836     | 1.843   | 1.831   |
| P2-C7        | 1.836     | 1.831   | 1.833   |
| P2-C8        | 1.833     | 1.839   | 1.834   |
| **angles (°)**      |           |         |         |
| C1-C3-P1     | 118.79    | 118.79  | 118.17  |
| C2-C4-P2     | 118.79    | 118.35  | 118.48  |
| C3-P1-C3     | 102.77    | 102.18  | 101.76  |
| C3-P1-C6     | 100.83    | 100.37  | 103.27  |
| C4-P2-C7     | 100.83    | 103.57  | 100.35  |
| C4-P2-C8     | 102.77    | 102.07  | 101.79  |
| **torsion (°)**    |           |         |         |
| C4-C2-C1-C3  | 93.31     | 91.74   | 91.66   |

*All the corresponding parameters of R-/S-form is identical to each other in rac-BINAP, and the items listed is represented by R-form.*
**Supplementary Table 2.** Structure data of rac-BINAP, R- BINAP, and S- BINAP single crystals.

| Name            | rac-BINAP     | R-BINAP     | S-BINAP     |
|-----------------|---------------|-------------|-------------|
| Formula         | C₄₄H₃₂P₂     | C₄₄H₃₂P₂   | C₄₄H₃₂P₂   |
| Temperature/K   | 173           | 173         | 173         |
| Crystal system  | monoclinic    | monoclinic  | monoclinic  |
| Space group     | C2/c          | P2₁         | P2₁         |
| a=             | 19.492(3)     | 9.130(3)    | 9.1246(10)  |
| b=             | 9.1725(13)    | 18.817(5)   | 18.7595(18) |
| c=             | 19.047(3)     | 9.997(3)    | 9.9821(10)  |
| α=             | 90            | 90          | 90          |
| β=             | 107.888(3)    | 103.090(7)  | 103.180(3)  |
| γ=             | 90            | 90          | 90          |
| Cell Volume (Å³)| 3240.8(8)     | 1673.0(8)   | 1663.7(3)   |
| Z               | 4             | 2           | 2           |
| Density (g/cm³)| 1.276         | 1.236       | 1.243       |
| F(000)          | 1304.0        | 652.0       | 652.0       |
| Crystal size (mm³)| 0.28 × 0.15 × 0.11 | 0.19 × 0.15 × 0.12 | 0.6 × 0.25 × 0.12 |
| Radiation       | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| CCDC number     | 1968817       | 1968818     | 1968819     |

**Supplementary Figure 15** Short contacts between the two molecules of the same layer in (a) rac-BINAP, (b) R-BINAP and (c) S-BINAP.
Supplementary Figure 16. TGA curves and differential scanning calorimetry (DSC) analysis of (a,d) rac-BINAP, (b,e) R-BINAP, and (c,f) S-BINAP.
Supportive data for Photophysical properties.

**Supplementary Figure 17.** (a) The emission of S-BINAP in single crystals: (black circle) steady-state emission acquired by cw 360 nm excitation, (cyan circle) the prompt fluorescence acquired by pulse excitation (360 nm) and ICCD opened at t=0 with 50 ns gate width, (blue and red line) the spectrum deconvolution of the steady state emission. (orange circle) The phosphorescence detected by ICCD opened at t = 1.55 ms (S-BINAP) with 200 μs gate width. (b) The decay dynamics of the RTP of R-BINAP. The rate constant \( k_{\text{obs}} \) and \( k_{\text{TT}} \) are deduced from the fitting with eq. 1.

**Supplementary Figure 18.** The excitation spectra of rac-BINAP in crystal.
Supplementary Figure 19. R-BINAP and S-BINAP displayed subtle differences in the spectral shapes of the CPL signals (particularly, at extreme wavelengths around 500 nm) with $|\text{gem}| \approx (1.46-1.65) \times 10^{-3}$ that were nearly mirror images of each other.
### Supplementary Table 3. Photophysical properties of the reported metal-free red phosphors from literature

| Compound | λ_{em} (nm) | Φ (%) | τ_{p} (ms) | Reference |
|----------|-------------|-------|------------|-----------|
| 1        | 611         | 0.05  | 5.1        | [3]       |
| 2        | 600         | 0.05  | 5.6        | [3]       |
| 3        | 600         | 0.0057| 84         | [3]       |
| 4        | 600         | 0.046 | 3.6        | [3]       |
| 5        | 600         | 0.021 | 70         | [3]       |
| 6        | 650         | 0.5   | 0.15       | [4]       |
| 7        | 660         | -     | 1.5        | [4]       |
| 8        | 642         | 2.8   | 0.55       | [5]       |
| 9        | 643         | 3.6   | 0.59       | [5]       |
| 10       | 624         | 5.4   | 0.7        | [5]       |
| 11       | 667         | 3.4   | 0.5        | [5]       |
| 12       | 580         | 1     | 0.6        | [6]       |
| 13       | 602         | 14.6  | 0.605      | [7]       |
| 14       | 635         | 12.5  | 12.7       | [8]       |
| 15       | 600         | 6.1   | 32.8       | [9]       |
| 16       | 675         | 21.7  | 1.1        | [10]      |

**rac-BINAP** | 680 | 0.42 | 18.1 | This work

Note that for structures of the molecules list in literature are shown in **Supplementary Figure 20** below.

**Supplementary Figure 20.** The reported molecular structures with red phosphorescence from literature (see **Supplementary Table 3**)
**Supplementary Figure 21** Lifetime measurement for the fluorescence of crystal BINAP series.

**Supplementary Table 4.** Fitting Parameters of Dynamic of BINAP Series.

| Crystal  | Delayed Fluorescence | Phosphorescence | α       | $[T_i]$ | $k_{obs}$ | $k_{TT}$ |
|----------|----------------------|-----------------|---------|---------|----------|----------|
|          | Short /μs$^a$ | Long /ms | Short /μs$^a$ | Long /ms | (a.u.) | (M) | (s$^{-1}$) | (s$^{-1}$M$^{-1}$) |
| rac-BINAP | (0.996)$^b$ 598 | (0.004)$^b$ 8.57 | – | 18.1 | 0.96 | 1 | 52 | 8.5 |
| S-BINAP  | (0.992)$^b$ 553 | (0.008)$^b$ 4.92 | (0.896)$^b$ 616 | (0.104)$^b$ 12.0 | 1.02 | 1 | 56 | 2200 |
| R-BINAP  | (0.991)$^b$ 531 | (0.009)$^b$ 4.61 | (0.913)$^b$ 705 | (0.087)$^b$ 11.3 | 1.04 | 1 | 56 | 2600 |

$^a$The short component of lifetime denotes the component fitted to be among hundreds of μs.

$^b$The number in the parentheses denotes the pre-exponential factor.
Supplementary Table 5. Photophysical properties of RTP from BINAP series.

| Molecules   | $k_{\text{obs}}$ (s$^{-1}$)$^a$ | $k_{\text{TT}}$ (s$^{-1}$M$^{-1}$)$^a$ | ISC (%) | efficiency $\Phi_{p, \text{intrinsic}}$ (%) | $k_{p, r}$ (s$^{-1}$)$^b$ | $k_{p, nr}$ (s$^{-1}$)$^c$ |
|-------------|-------------------------------|---------------------------------|--------|---------------------------------|-----------------|-----------------|
| rac-BINAP   | 52                            | 8.5                             | 9.8    | 4.3                             | 2.2             | 50              |
| R-BINAP     | 56                            | 2600                           | NA     | NA                             | NA              | NA              |
| S-BINAP     | 56                            | 2200                           | NA     | NA                             | NA              | NA              |

Note that NA denotes “not available”.

$^a$ Rate constants deduced from fit shown Fig. 3a and Supplementary Figure 17b.

$^b$ The radiative rate ($k_{p, r}$) is calculated by $k_{p, r} = \Phi_{p, \text{intrinsic}} \times k_{\text{obs}}$.

$^c$ The non-radiative rate ($k_{p, nr}$) is calculated by $k_{\text{obs}} - k_{p, r}$.

Supplementary Figure 22. Lifetime measurements for the delayed fluorescence of crystal BINAP series. Note that for all BINAP series, the fast decay component was irresolvable and was attributed to the signal of fluorescence of BINAP. Please see Supplementary Table 4 for the fitting results.
Supplementary Figure 23. The temporal evolution of both RTP and delayed fluorescence in single crystals at denoted time delay acquired by intensified charge coupled detector (ICCD) with 360 nm ND:YAG for excitation. The gate width was set to be 200 μs for each acquisition time.

Supplementary Figure 24. Steady-state (a) absorption and (b) PL spectra (λ_ex = 300 nm) of BINAP series in thin film. (c) The emission of rac-BINAP in thin film: (black circle) steady-state emission acquired by continuously 360 nm excitation. (cyan circle) The prompt fluorescence acquired by pulse excitation (360 nm) and detected by intensified charge coupled detector (ICCD) opened at t=0 with 50 ns gate width. (orange circle) The phosphorescence detected by ICCD opened at t = 10 μs with gate width of 100 μs. (blue and red solid lines) The fluorescence (blue) and phosphorescence (red) spectra convoluted from the steady state emission.
Supplementary Figure 25 Lifetime measurements for (a) rac-BINAP, (b) S-BINAP, and (c) R-BINAP in thin film at 298 K. Figures in the left are the nanosecond-scaled lifetime measurements ($\lambda_{ex} = 360$ nm), while figures in the middle and right are micro- to millisecond-scale lifetime measurement ($\lambda_{ex} = 376$ nm).

Comparing with the population decay of RTP measured in single crystals, all the decay curves of BINAPs measured in thin films show similar temporal evolution. This can be rationalized by the amorphous arrangement of BINAPs in thin films, while the crystals of BINAPs possess specific and ordered packing structure, resulting in the different population decay for the racemic versus homochiral crystals.

Supplementary Table 6. The summary of lifetime of BINAP series in thin film.

| compound | $\tau_{510\text{nm}}$ (short) | $\tau_{510\text{nm}}$ (long) | $\tau_{670\text{nm}}$ |
|----------|------------------------------|------------------------------|-----------------|
| rac-BINAP | $\tau_1 = 0.41$ ns | $\tau_1 = 0.28$ ms | $\tau_1 = 3.47$ ms |
|          | $\tau_2 = 1.48$ ns | $\tau_2 = 10.00$ ms | $\tau_2 = 8.64$ ms |
| S-BINAP  | $\tau_1 = 0.52$ ns | $\tau_1 = 0.21$ ms | $\tau_1 = 3.33$ ms |
|          | $\tau_2 = 1.51$ ns | $\tau_2 = 9.98$ ms | $\tau_2 = 8.64$ ms |
| R-BINAP  | $\tau_1 = 0.41$ ns | $\tau_1 = 0.23$ ms | $\tau_1 = 3.13$ ms |
|          | $\tau_2 = 1.37$ ns | $\tau_2 = 10.01$ ms | $\tau_2 = 8.03$ ms |
**Supplementary Figure 26.** The energy level diagram and molecular structures for materials utilized for BINAP device fabrication in this study.

![Energy Level Diagram](image)

**Supplementary Figure 27.** Cyclic voltammogram for BINAP series. The energy levels of HOMO are determined by the onset of the oxidation curves of cyclic voltammogram (HOMO = \(-[E_{OX}-E_{(Fc/Fc^+)}]+4.8\) eV = \(-[1.44-0.45+4.8]\) = -5.79 eV); the energy gaps are then deduced from the optical absorption onset recorded at 375 nm (3.31 eV). (LUMO = -2.48 eV).

![Cyclic Voltammogram](image)
Supportive Figures for Devices Characterization.

Supplementary Figure 28. Electroluminescence performance of device 2 based on R-BINAP: (a) EL spectrum under different operated voltages; (b) The CIE coordinates; (c) current density-voltage-luminance curve; (d) external quantum efficiency- current density curve; (e) current efficiency - current density curve; (f) power efficiency - current density curve.
Supplementary Figure 29. Electroluminescence performance of device 3 based on S-BINAP: (a) EL spectrum under different operated voltages; (b) The CIE coordinates; (c) current density-voltage-luminance curve; (d) external quantum efficiency-current density curve; (e) current efficiency - current density curve; (f) power efficiency - current density curve.
**Supplementary Table 7.** The comparison of devices performances between reported RTP-OLEDs and this work.

| Compound | Device configuration | $\lambda_{EL}$ (nm) | EQE (%) | CE max (cd·A$^{-1}$) | CIE (x,y) | $L_{max}$ (cd·m$^{-2}$) | Ref. |
|----------|----------------------|---------------------|---------|---------------------|----------|--------------------------|------|
| a | ITO / NPb(40 nm) / TSPBA(10 nm) / CBP:10% a (20 nm) / TPBi(50 nm) / LiF (1 nm) / Al (10 nm) | 427 | 0.6 | 1.0 | - | 1700 | [11] |
| b | ITO / PEDOT:PSS / PVK:PBD:b/TmPyPB / Liq / Al | 510 | - | - | - | 194 | [12] |
| c | ITO / PEDOT:PSS / TPD/PVK: e/PBD / CsF / Al | - | 0.0254 | - | - | - | [13] |
| d | ITO / PEDOT:PSS / TPD / PVK: d / PBD / CsF / Al | - | 0.00558 | - | - | - | [13] |
| e | ITO / NPD (30 nm) / mCP (10 nm) / 1% e:CzSte (30 nm) / TPBi (60 nm) / LiF (0.8 nm) / Al (80 nm) | 450 | 1 | - | - | - | [14] |
| f | ITO / PEDOT:PSS / NPb / f / BCP / Alq3 / LiF / Al | - | - | - | 0.31, 0.44 | 20 | [15] |
| g | ITO / PEDOT:PSS / NPb / g/ BCP/Alq3/ LiF / Al | - | - | - | 0.29, 0.35 | 110 | [15] |
| h | ITO / PEDOT:PSS / TAPC / mCP / TPBi:27QNX:h / TSP01 / TPBi / LiF / Al | 583 | 0.11 | - | - | 22.4 | [16] |
| i | PEDOT:PSS / TCTA-i / TPBi / Cathod | 510 | - | - | - | 570 | [17] |
| j | ITO / NPb (25 nm) / TCTA (10 nm) / 10% j:TRZ-BIM (20 nm) / TPBi (40 nm) / LiF (1 nm) / Al (100 nm) | 570 | 11.5 | 33.8 | 0.46, 0.52 | 18500 | [18] |
| k | TAPC/CBP:K/BPen | 464,569,601 | 0.2 | - | - | - | [19] |
| l | ITO / MoO3 (3 nm) / mCP (10 nm) / T (100 nm) / TBPi (20 nm) / LiF (0.5 nm) / Al (100 nm) | 510,586 | 1.59 | 3.18 | 0.371, 0.441 | 934 | This work |
| m | ITO / PEDOT:PSS (35nm) / TAPC (40nm) / mCP (7nm) / rac-BINAP (20nm) / TmPyPB (40nm) / CsF (1.2nm) / Al (120nm) | 425,587 | 1.36 | 3.33 | 0.373, 0.376 | 781 | This work |
| n | ITO / PEDOT:PSS (35nm) / TAPC (40nm) / mCP (7nm) / S-BINAP (20nm) / TmPyPB (40nm) / CsF (1.2nm) / Al (120nm) | 482,580 | 1.58 | 3.51 | 0.453, 0.386 | 1026 | This work |

*The data didn’t appear in the corresponding paper. *the paper can’t offer a precise mechanism for the phenomenon of TRZ-BIM enhanced RTP. Note that the structures of compounds demonstrated in literature are shown in the Supplementary Figure 30 below.
Supplementary Figure 30. The reported molecular structures used in OLEDs. Please refer to Supplementary Table 7.
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