**Supporting Information**

**Solution-Processed Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes Using New Polymeric Emitter Containing Non-conjugated Cyclohexane Units**

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**Fig. S1** (a) Optimized geometry, (b) HOMO and LUMO spatial distribution, and (c) energy level diagram for DMAC-TRZ calculated by DFT (B3LYP/6-31G) using Gaussian 09W.
Fig. S2 Photoluminescence (PL) spectra of P(DMTRZ-Cp) in solvents with different polarities.

Fig. S3 Differential scanning calorimetry curve for P(DMTRZ-Cp).
Table S1 Photophysical properties of the P(DMTRZ-Cp)-doped with mCP.

<table>
<thead>
<tr>
<th>Polymer Emitter</th>
<th>$\tau_p^a$ (ns)</th>
<th>$\tau_d^a$ (μs)</th>
<th>$\Phi_p / \Phi_d / \Phi_{pl}$</th>
<th>$k_p^c$ (s$^{-1}$)</th>
<th>$k_d^d$ (s$^{-1}$)</th>
<th>$k_{isc}^e$ (s$^{-1}$)</th>
<th>$k_{risc}^f$ (s$^{-1}$)</th>
<th>$k_{nrT}^g$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(DMTRZ-Cp)</td>
<td>12.2</td>
<td>1.8</td>
<td>0.21/0.32/0.53</td>
<td>8.22x10$^7$</td>
<td>5.56x10$^5$</td>
<td>4.03x10$^7$</td>
<td>1.07x10$^6$</td>
<td>3.20x10$^4$</td>
</tr>
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</table>

$^a$ PL lifetimes of the prompt ($\tau_p$) and delayed ($\tau_d$) decay components (film). $^b$ Absolute photoluminescence quantum yield using an integrating sphere in the solution and film states without degassing (prompt, $\Phi_p$) and under nitrogen (delayed: $\Phi_d$, total: $\Phi_{pl}$). $^c$ Prompt fluorescence decay rate constant. $^d$ Delayed fluorescence decay lifetime. $^e$ The radiative decay rate constant of the singlet excited state. $^f$ The rate constant for intersystem crossing (ISC) from the singlet excited state to the triplet excited state. $^g$ The rate constant for reverse intersystem crossing (RISC) from the triplet excited state to the singlet excited state. $^h$ The non-radiative (nr) decay rate constant of the triplet excited state.

To further understand the fundamental mechanism of the TADF polymeric emitter, the kinetic parameters of the polymeric emitter-doped film in mCP were determined from the experimental data (Table S1). The prompt ($\Phi_p$) and delayed ($\Phi_d$) fluorescence quantum yields were determined by the ratio of emission area in the transient PL spectra based on total photoluminescence quantum yield ($\Phi_{pl}$). Prompt ($\tau_p$) and delayed ($\tau_d$) fluorescence lifetimes are obtained by fitting the transient PL curve. Through this values, prompt ($k_p$) and delayed ($k_d$) fluorescence decay rate constants (where $k_p = 1/\tau_p$ and $k_d = 1/\tau_d$) were obtained. The radiative decay rate constants of the singlet excited state ($k_{rS}^i$), the rate constant for intersystem crossing ($k_{isc}$, $S_1 \rightarrow T_1$), the rate constant for reverse intersystem crossing ($k_{risc}$, $T_1 \rightarrow S_1$) were calculated using the following equations.

$$k_{rS}^i = k_p \cdot \Phi_p$$  
$$k_{isc} = k_p \cdot (1-\Phi_p)$$  
$$k_{risc} = (k_p \cdot k_d / k_{isc}) \cdot (\Phi_d / \Phi_p)$$
From the equations (1)-(3), the non-radiative (nr) decay rate constant of the triplet excited state ($k_{nrT}$) can be obtained.

$$k_{nrT} = k_d - k_{RISC} \Phi_p$$  \hspace{1cm} (4)

This value was based on the assumption that the non-radiative decay rate constant of the singlet excited state ($k_{nrS}$) is zero at 300 K.$^{1,2}$

All the kinetic parameters including PL characteristics are summarized in Table S2 and it demonstrate that the P(DMTRZ-Cp) polymeric emitter-doped film with mCP shows comparable rate constant values.$^{1,3-10}$

Fig. S4 PL spectra of the mCP film and P(DMTRZ-Cp): mCP blend film (5 wt% and 25 wt%).
**Fig. S5** Normalized electroluminescence (EL) spectra of devices based on P(DMTRZ-Cp) (25 wt%) as functions of different applied voltages.

**Fig. S6** (a) Current density-voltage-luminance (J-V-L) curves, (b) current efficiency-luminance-power efficiency curves, (c) external quantum efficiency (EQE)-current density ($\eta_{\text{ext}}$-$J$) curves and (d) electroluminescence (EL) spectra at 1000 cd/m$^2$ of TADF-OLEDs fabricated using the new P(DMTRZ-Cp) polymer emitter at different concentrations (5, 10, 15 wt%).
Fig. S7 AFM (a) height and (b) phase images of mCP:P(DMTRZ-Cp) (25 wt%) blended film.

To investigate the surface homogeneity of the emitting layer, an AFM image of a blend film (mCP: P(DMTRZ-Cp) (25 wt%)) was measured. High uniformity and smoothness were expected to be sufficient to act as a light emitting layer.

Notes and references


