

## Supplementary Information

# **Efficient Thermally Activated Delayed Fluorescence Based on Carbonitrile-Substituted Pyridine and Carbazole**

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## General experimental information

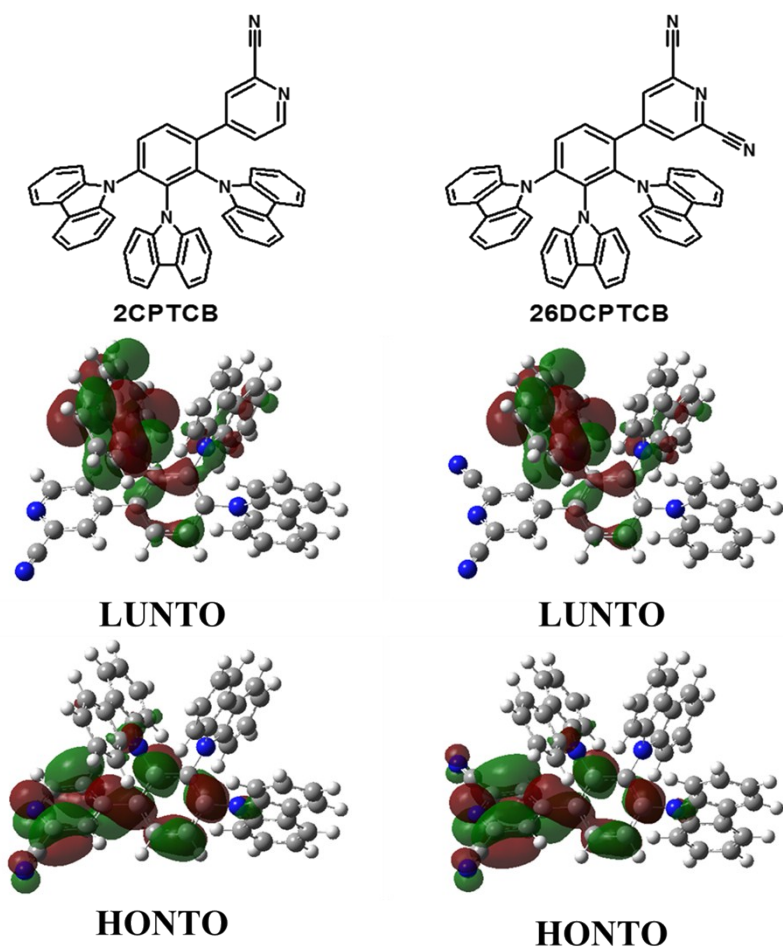
All reagents for synthesis were purchased from Energy Chemical Co. and used as received without further purification. Detailed synthetic routes of the objective compounds are outlined in the synthesis section.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 500M spectrometer. Mass spectra were obtained using a Waters SQII mass detector. TGA figures were undertaken by using a Netzsch TG 209 unit under nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 209 under  $\text{N}_2$  flow at a heating and cooling rate of  $10\text{ }^\circ\text{C min}^{-1}$ . CV was performed on a CHI600D electrochemical workstation with a Pt working electrode and a Pt wire counter electrode at a scanning rate of  $100\text{ mV s}^{-1}$  against a  $\text{Ag}/\text{Ag}^+$  ( $0.1\text{ m}$  of  $\text{AgNO}_3$  in acetonitrile) reference electrode with a nitrogen-saturated anhydrous acetonitrile solution of  $0.1\text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate. UV-vis absorption spectra were measured by using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured by using a Horiba Fluorolog luminescence spectrometer. PLQYs of the doped films were measured by using an integrating sphere on a Hamamatsu absolute PL quantumyield spectrometer C11347. Transient PL was measured with an Edinburgh FL920 fluorescence spectrophotometer.

## Theoretical Calculation

All of the simulations were performed using the Gaussian 09\_B01 program package <sup>(1)</sup>. Density functional theory (DFT) and Time-dependent density functional theory (TD-DFT) calculations were performed at the B3LYP/6-31G (d) and TD-M06-2x/6-31G\* level, respectively, to investigate their ground states geometries, FMOs distributions and energy level, oscillator strength, as well as energy of excited state at molecular level. Natural transition orbital (NTO) analysis was conducted to unveil the excited state properties of the investigated compounds in TD-M06-2x/6-31G\* level in toluene solutions employing polarized continuum model (PCM) model.

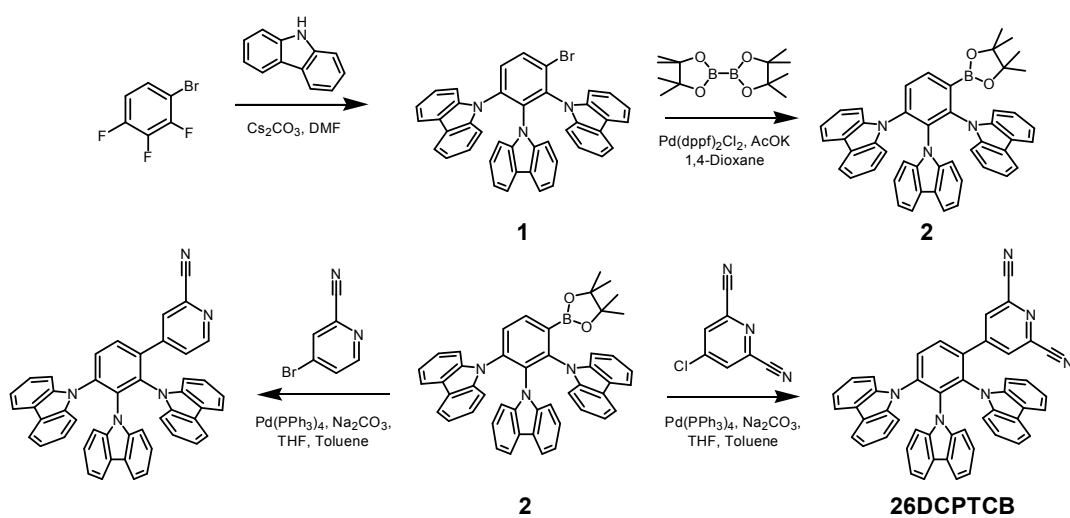
**Table S1.** The fitted parameters and computed results of compounds 2CPTCB and 26DCPTCB.

Compound	HOMO (eV)	LUMO (eV)	oscillator strength	$S_1$ (eV)	$T_1$ (eV)	$\Delta E_{ST}$ (eV)
<b>2CPTCB</b>	-4.958	-1.839	0.0166	3.925	3.538	0.387
<b>26DCPTCB</b>	-5.051	-2.247	0.0143	3.646	3.416	0.230



**Figure S1.** Calculated natural transitional orbits (NTOs) distribution of 2CPTCB and 26DCPTCB.

### Synthesis



**Scheme S1.** Synthetic routes of 2CPTCB and 26DCPTCB

*Synthesis of Compound (1)*: 2,3,4-Trifluorobromobenzene (2.52 g, 12.0 mmol), 9H-carbazole (6.68 g, 40.0 mmol), caesium carbonate (16.3 g, 50.0 mmol) and N,N-dimethylformamide (120 mL) were added into a 250 mL three-necks flask. Then the mixture was heated to 150 °C and stirred for 24 h. The reaction mixture was poured into 300 mL of water and extracted with dichloromethane (100 mL × 3). The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was purified through column chromatography on silica gel to afford the target compound as white crystal (4.77 g, yield: 61%). MS (APCI<sup>+</sup>, m /Z): calcd. for C<sub>42</sub>H<sub>26</sub>BrN<sub>3</sub>: 651.1; found: 652.1. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.23 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.80-7.75 (m, 2H), 7.74-7.69 (m, 2H), 7.33-7.28 (m, 4H), 7.11-6.98 (m, 10H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.79-6.71 (m, 2H), 6.68-6.60 (m, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, δ): 139.73, 138.85, 138.48, 137.38, 136.99, 135.70, 134.14, 131.19, 125.40, 125.18, 124.95, 124.24, 123.61, 123.42, 123.38, 120.31, 120.07, 120.00, 119.86, 119.79, 119.22, 110.71, 110.30, 109.85.

*Synthesis of Compound (2)*: Compound 1 (5.21 g, 8 mmol), bis(pinacolato)diboron (3.02 g, 12.0 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.44 g, 0.6 mmol), potassium acetate (1.96 g, 20.0 mmol) and 1,4-dioxane (50 mL) were added into a 150 mL three-necks flask. Then the mixture was heated to refluxing and stirred overnight. After being cooled, the reaction mixture was poured into 300 mL of water and extracted with dichloromethane (100 mL × 3). The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was purified through column chromatography on silica gel to afford the target compound as white powder (2.78 g, yield: 53%). MS (APCI<sup>+</sup>, m /Z): calcd. for C<sub>48</sub>H<sub>38</sub>BN<sub>3</sub>O<sub>2</sub>: 699.3; found: 700.3. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.26 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.78-7.74 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.25-7.22 (m, 2H), 7.13 (dd, *J* = 6.1, 2.9 Hz, 2H), 7.05-6.99 (m, 8H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 2H), 6.67-6.62 (m, 2H), 0.82 (s, 12H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, δ): 141.90, 141.26, 139.88, 139.27, 138.80, 135.99, 132.93, 129.58, 125.30, 125.24, 124.95, 124.26, 123.53, 123.31, 120.03, 119.84, 119.58, 119.42, 119.34, 119.17, 110.24, 109.99, 109.84, 84.02, 24.31.

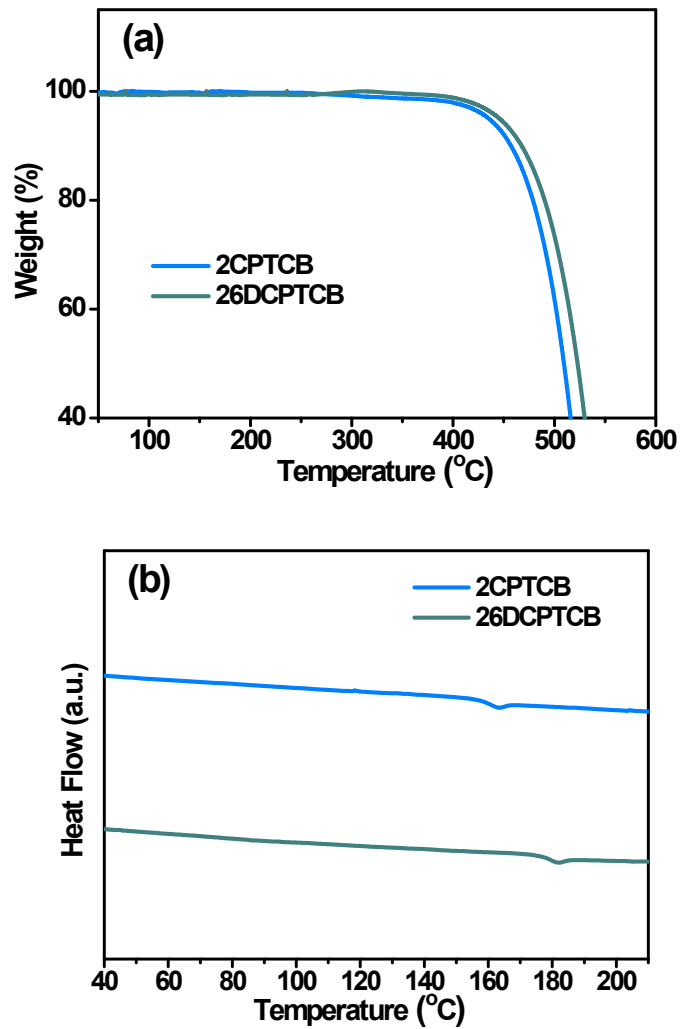
*Synthesis of 2CPTCB*: 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,2,3-tri(9H-carbazol-9yl)benzene (0.84 g, 1.2 mmol), 4-bromopyridine-2-carbonitrile (0.26 g, 1.4 mmol), sodium carbonate (0.42 g, 3 mmol), tetrahydrofuran (15 mL), toluene (30 mL) and distilled water (20 mL) were successively added into a 150 mL three-necks flask. After degassing for 10 min, tetrakis(triphenylphosphine)palladium (46 mg, 0.04 mmol) was added quickly. Then the mixture was refluxed for 24 h under argon protection. The reaction mixture was poured into 300 mL of water and extracted with dichloromethane (100 mL × 3). The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was purified through column chromatography on silica gel to afford the target compound as light yellow powder (6.2 g, yield: 77%). Highly purified product was then obtained via vacuum sublimation. MS (APCI<sup>+</sup>, m /Z): calcd. for C<sub>48</sub>H<sub>29</sub>N<sub>5</sub>: 675.2; found: 675.2. Anal. calcd.

for C<sub>48</sub>H<sub>29</sub>N<sub>5</sub>: C 85.31, H 4.33, N 10.36; found: C 85.26, H 4.41, N 10.33. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.22 (d, *J* = 4.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.83-7.76 (m, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.48 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 6.9, 1.7 Hz, 2H), 7.11-7.01 (m, 4H), 7.01-6.86 (m, 9H), 6.76 (t, *J* = 7.2 Hz, 2H), 6.62 (t, *J* = 7.5 Hz, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, δ): 150.96, 147.40, 139.68, 139.04, 138.90, 138.40, 137.95, 135.40, 134.65, 134.14, 131.03, 130.81, 127.29, 125.45, 125.35, 125.27, 124.41, 123.73, 123.47, 123.35, 120.49, 120.47, 120.11, 120.03, 119.91, 119.36, 116.70, 110.00, 109.81, 109.72.

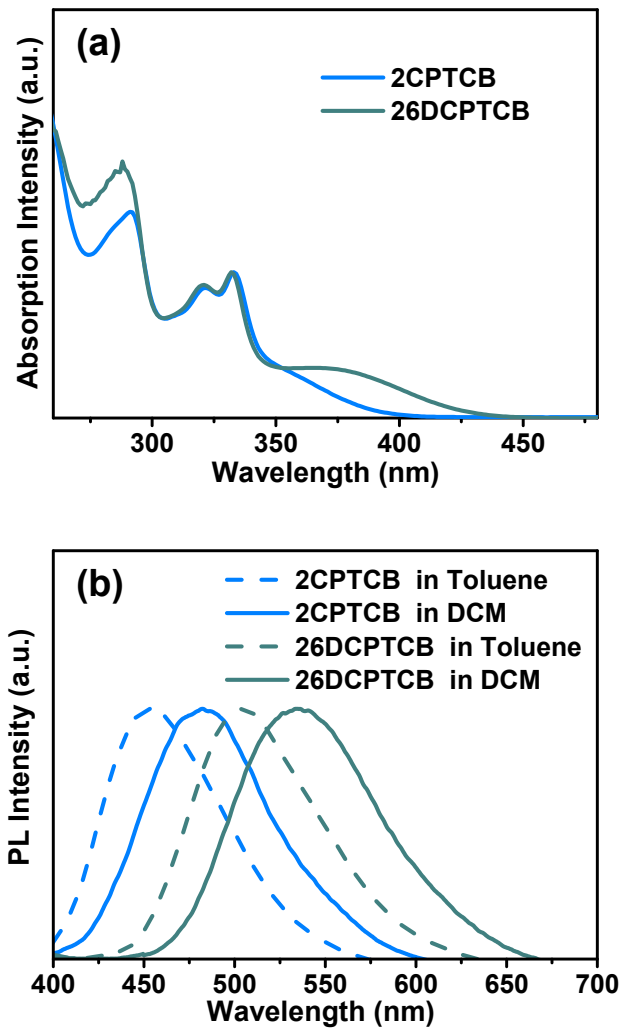
*Synthesis of 26DCPTCB*: This compound was synthesized according to the procedure as described above for the synthesis of 2CPTCB by combining 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,2,3-tri(9*H*-carbazol-9yl)benzene and 4-chloropyridine-2,6dicarbonitrile, giving a light green solid in 64% yield. Highly purified product was then obtained via vacuum sublimation. MS (APCI<sup>+</sup>, *m*/*Z*): calcd. for C<sub>49</sub>H<sub>28</sub>N<sub>6</sub>: 700.2; found: 700.2. Anal. calcd. for C<sub>49</sub>H<sub>28</sub>N<sub>6</sub>: C 83.98, H 4.03, N 11.99; found: C 83.92, H 4.11, N 11.96. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.15 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.83-7.77 (m, 2H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.33 (s, 2H), 7.27-7.24 (m, 2H), 7.12-6.99 (m, 6H), 6.97 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.79 (t, *J* = 7.5 Hz, 2H), 6.66 (t, *J* = 8.0 Hz, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, δ): 149.39, 139.83, 139.49, 138.96, 138.32, 135.84, 135.82, 135.02, 134.98, 131.31, 130.35, 129.57, 125.75, 125.54, 124.61, 123.82, 123.58, 123.46, 121.08, 120.69, 120.52, 120.16, 120.10, 119.53, 114.91, 109.85, 109.70, 109.52.

### Device Fabrication and Characterization

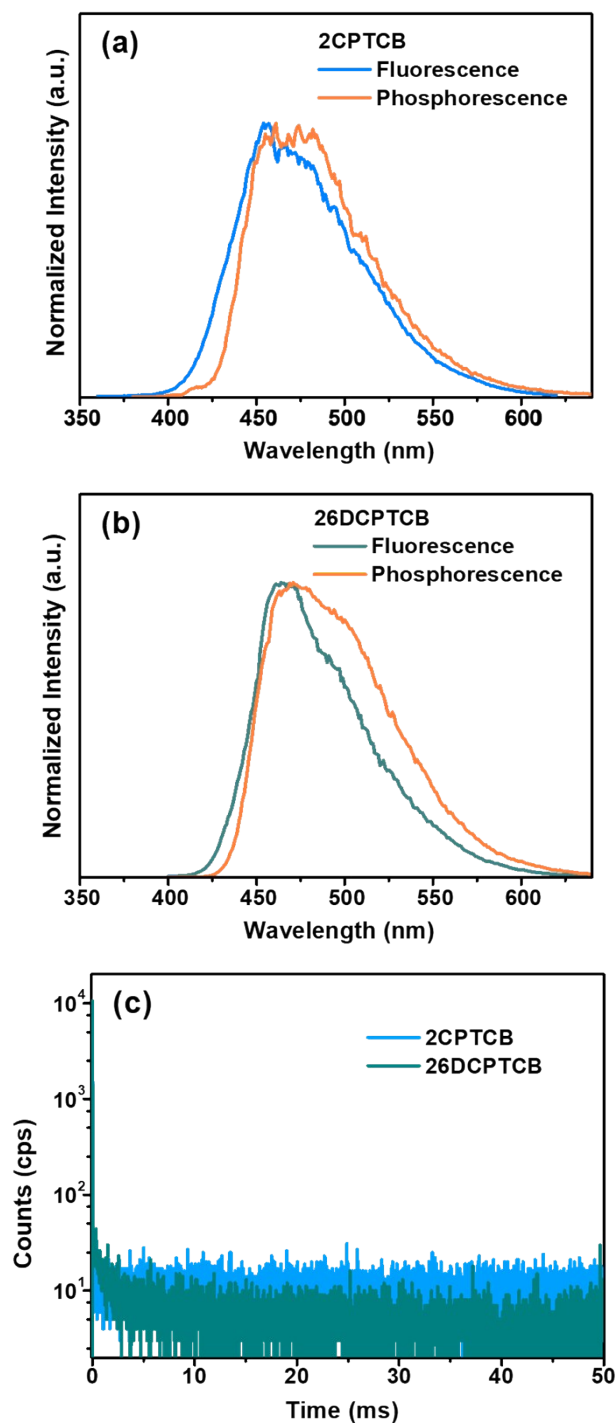
The substrates were cleaned with ultra-purified water and then dry-cleaned for 10 min by exposure to UV-ozone. In next step, the organic layers, LiF and Al were vacuum deposited successively (10<sup>-5</sup> Pa). Deposition rates were 1 Å s<sup>-1</sup> for organic materials except light emitting dopant, 0.1 Å s<sup>-1</sup> for LiF, and 1.5 Å s<sup>-1</sup> for Al, respectively. EL spectra and luminance were taken by using Photo Research PR-655 spectroradiometer. The current density–voltage characteristics were measured with a Keithley source measure unit 2400.



**Figure S2.** (a) Differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) thermograms of 2CPTCB and 26DCPTCB.

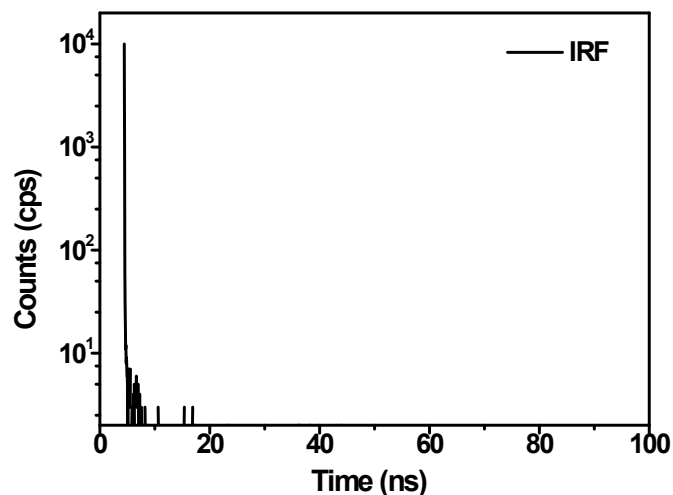


**Figure S3.** (a) UV-vis absorption of 2CPTCB and 26DCPTCB in dichloromethane solution and (b) PL spectra of 2CPTCB and 26DCPTCB in toluene and dichloromethane solutions.

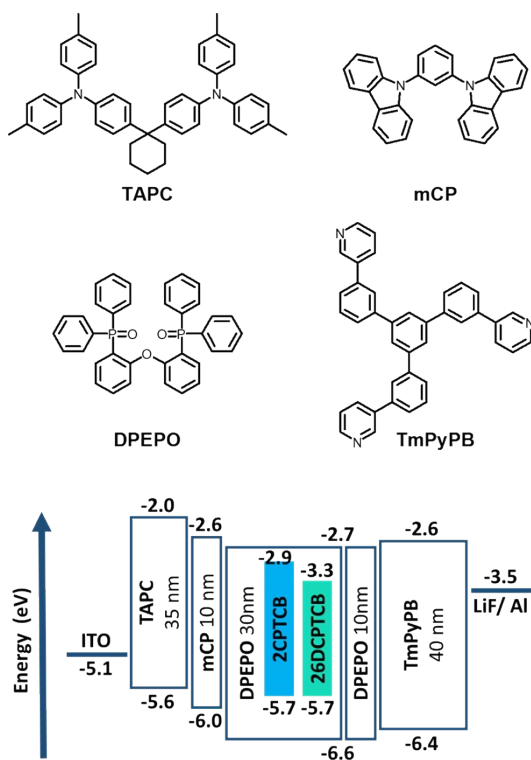


**Figure S4.** Low temperature PL spectra of (a) 2CPTCB, (b) 26DCPTCB and (c) their transient PL decay in toluene solution at 77 K (the phosphorescence spectra were recorded after 1ms delayed time).

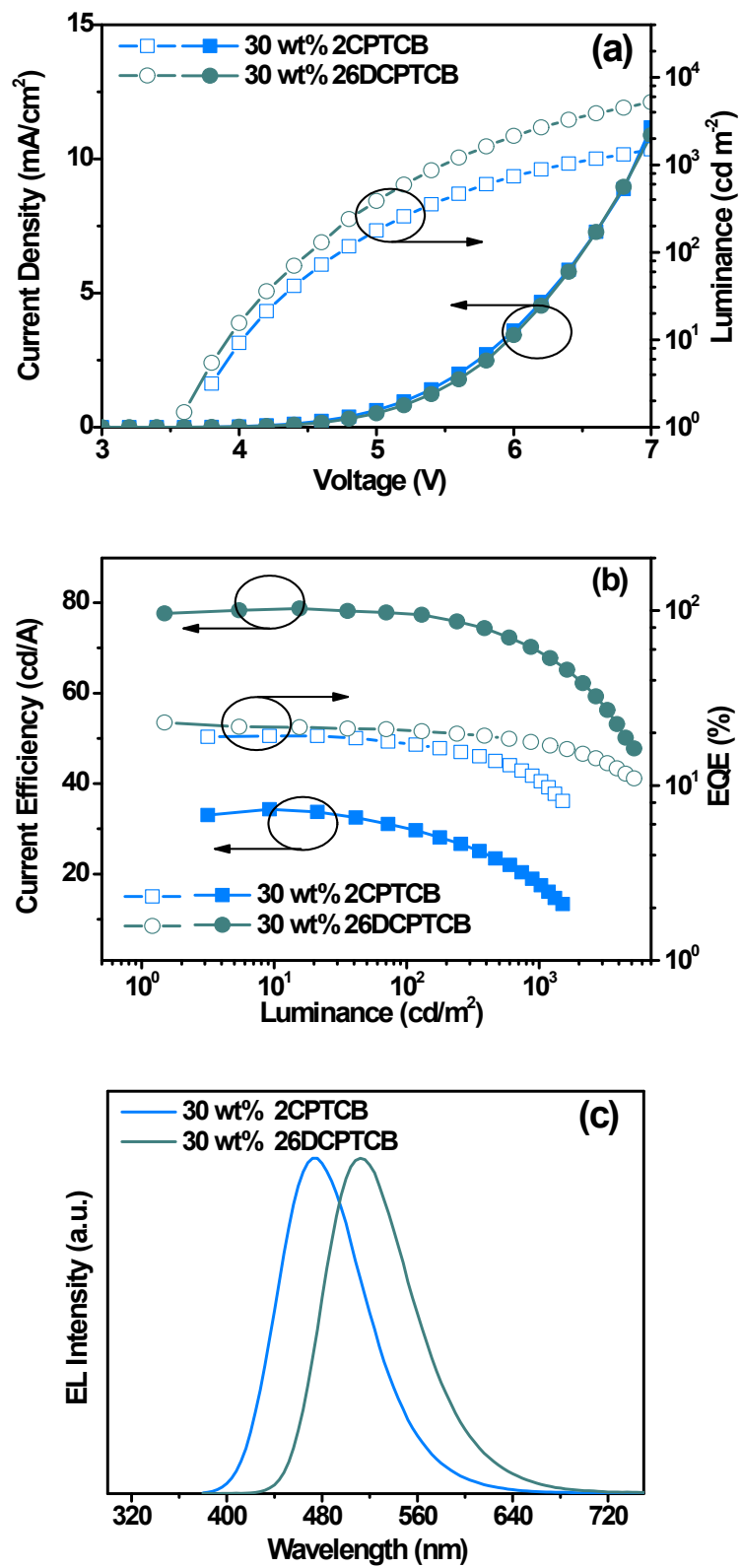




**Figure S5.** The instrument response function (IRF) curve for PL decay measurement at room temperature under vacuum condition.



**Figure S6.** Chemical structures of materials used for device fabrication and energy level diagrams of the devices.



**Figure S7.** (a) Current density-voltage-luminance characteristics, (b) current efficiency

and EQE versus current density characteristics and (c) EL spectra of devcies based on 2CPTCB and 26DCPTCB with doping concentration of 30 wt%.

**Table S2.** Electroluminescence characteristics of OLED devices

Emitter	Doping Concentration (w%)	$V_{on}^{(a)}$ (V)	Maximum CE <sup>(b)</sup> (cd/A)	Maximum PE <sup>(c)</sup> (lm/W)	Maximum EQE (%)	at 100 cd/m <sup>2</sup>			at 1000 cd/m <sup>2</sup>			CIE <sup>(d)</sup> (x, y)
						CE (cd/A)	PE (lm/W)	EQE (%)	CE (cd/A)	PE (lm/W)	EQE (%)	
<b>2CPTCB</b>	20	3.8	32.1	25.5	21.1	28.9	19.6	19.4	15.6	7.5	10.8	(0.15, 0.19)
	30	3.8	33.8	27.4	19.2	30.1	20.2	17.4	18.1	8.9	10.7	(0.16, 0.23)
<b>26DCPTCB</b>	20	3.6	80.7	69.8	27.6	76.0	51.1	25.1	63.7	34.4	20.0	(0.22, 0.49)
	30	3.6	78.4	67.8	22.9	77.4	54.5	20.9	68.1	39.8	17.4	(0.25, 0.52)

(a) Turn-on voltage at 1 cd m<sup>-2</sup>; (b) current efficiency; (c) power efficiency; (d) CIE at 2.5 mA cm<sup>-2</sup>.

## References:

- (S1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford, CT, **2010**.