Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

For

Donor Design Strategy for Triazine-Carbazole Blue Thermally Activated Delayed Fluorescence Materials

Xin Li, Jiuyan Li*, Di Liu,* Deli Li, Ruizhi Dong

State Key Laboratory of Fine Chemicals, College of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China. E-mail: jiuyanli@dlut.edu.cn, liudi@dlut.edu.cn.

Quantum Chemical Computation

All the simulations were performed using the Gaussian 09_D01 program package.[1] Detailed calculation approach affording $E_{0\text{-}0}$ (^{1}CT), $E_{0\text{-}0}$ (^{3}CT) and $E_{0\text{-}0}$ (^{3}LE) are shown in Equation S1 to S3.[2] More details of analysis data are shown in Table S1. The analysis of CT amount (q) of the investigated compounds was conducted using Multiwfn program.[3] Then the optimized Hartree-Fock percentage was confirmed by OHF%=42q relationship. The confirmation of E_{VA} (S_1, OHF) was fitted from a straight line between the E_{VA} (S_1) values yielded by two functions with the closest HF% to the OHF%. In relationship S3, the correction factor C is found to be 1.10, 1.18 and 1.30 for BMK, M06-2X and M06-HF, respectively. The natural transition orbital (NTO) analyses and the hole and electron overlap integral were also performed utilizing Multiwfn program.[3]

$$E_{0-0}(^1CT) = E_{VA}(S_1, OHF) - 0.24 \quad \text{(S1)}$$

$$E_{0-0}(^3CT) = E_{0-0}(S_1) - [E_{VA}(S_1, OHF) - \frac{E_{VA}(S_1, OHF)}{E_{VA}(S_1, BLYP)} E_{VA}(T_1, BLYP)] \quad \text{(S2)}$$

$$E_{0-0}(^3LE) = E_{VA}(T_1) / [E_{VA}(S_1, OHF) / E_{VA}(S_1, BLYP)] - 0.09 \quad \text{(S3)}$$

Parameters of Photo-physical Processes

According to transient decay curves and photoluminescence quantum yield measurement, we can obtain: [4,5]

$$\Phi_{PL} = \frac{k_r^s}{k_r^s + k_{nr}^s} \quad \text{(S4)}$$

$$\Phi_{PF} = \frac{k_r^s}{k_r^s + k_{nr}^s + k_{ISC}} = k_r^s \tau_{PF} \quad \text{(S5)}$$

$$\Phi_{ISC} = 1 - \Phi_{PF} \quad \text{(S6)}$$

$$\Phi_{RISC} = \frac{\Phi_{DF}}{\Phi_{ISC}} \quad \text{(S7)}$$

$$k_{PF} = \frac{1}{\tau_{PF}} \quad \text{(S8)}$$

$$k_{DF} = \frac{1}{\tau_{DF}} \quad \text{(S9)}$$

$$k_{TADF} = \frac{\Phi_{DF}}{\Phi_{ISC}\tau_{DF}} \quad \text{(S10)}$$

$$k_{nr}^{T} = k_{DF} - k_{RISC}\Phi_{PF} \quad \text{(S11)}$$

In which, ϕ_{PL}, ϕ_{PF}, ϕ_{TADF}, and ϕ_{ISC} represent photoluminescence quantum yield, quantum yield of prompt component, quantum yield of delayed component, intersystem crossing ratio, respectively. k_r^s, k_{nr}^s, k_{ISC}, k_{PF}, k_{DF}, k_{RISC}, k_{TADF} represent radiative, non-radiative, prompt process, delay process, intersystem crossing rate constants, reverse intersystem crossing constants, and thermally activated delayed fluorescence rate constants, respectively.

Supplementary tables

Table S1 The optimal HF exchange percentage (OHF) and the computational zero-zero energy levels for the investigated D-A molecules

Compounds	CT amount (q)	OHF (%)	$E_{VA}(S_1, OHF)$ (eV)	$E_{0\text{-}0}$ (^{1}CT) (eV)	$E_{0\text{-}0}$ (^{3}CT) (eV)	$E_{0\text{-}0}$ (^{3}LE) (eV)	ΔE_{ST} (eV)
tCPT	0.819	34.4	3.22	2.98	2.85	2.67	0.31
Ph-tCPT	0.891	36.2	3.24	3.00	2.91	2.74	0.26
o-PhCz-tCPT	0.868	36.5	3.22	2.98	2.89	2.78	0.20
p-PhCz-tCPT	0.934	39.2	3.24	3.00	2.98	2.76	0.24
3-PhCz-tCPT	0.929	39.0	3.15	2.91	2.88	2.73	0.18

Table S2 The hole and electron overlap integral in the optimized S_0, S_1 and T_1 geometry.

Compounds	tCPT	Ph-tCPT	*o*-PhCz-tCPT	*p*-PhCz-tCPT	3-PhCz-tCPT
$^0\langle\Psi_h\Psi_e\rangle$	0.1331	0.0959	0.0744	0.0381	0.0554
$^1\langle\Psi_h\Psi_e\rangle$	0.0884	0.1132	0.0538	0.0705	0.0684
$^3\langle\Psi_h\Psi_e\rangle$	0.3470	0.3420	0.3040	0.3374	0.3012

Table S3 The Photophysical properties of donor intermediate tCz and its derivatives.

Compound	λ_{abs} [a] [nm]	λ_{em} [a] [nm]	E_g [eV]	HOMO [eV] [b]	LUMO [eV] [b]
tCz	326,340	345,362	3.67	-5.45/-5.22	-1.78/-0.59
Ph-tCz	336,347	370	3.49	-5.47/-5.17	-1.98/-0.83
o-PhCz-tCz	327,340,351	374	3.48	-5.48/-5.22	-2.00/-0.94
p-PhCz-tCz	330,342,355	377	3.46	-5.45/-5.22	-1.99/-1.04
3-PhCz-tCz	335,348	379	3.45	-5.37/-5.00	-1.92/-0.82

[a] Absorption and fluorescence peak wavelengths in dilute toluene solution. [b] The left of the slash is

calculated from the cyclic voltammetry data and the right of slash is calculated from DFT calculation.

Table S4 Photophysical properties of the carbazole-triazine based emitters in doped films (10 wt% in DPEPO) at room temperature.

Compounds	Φ_{PL} [%]	Φ_{PF} [%]	Φ_{DF} [%]	τ_{PF} [ns] [a]	τ_{DF} [μs] [b]	k_r^s [10^7 s^{-1}]	k_{ISC} [10^7 s^{-1}]	Φ_{ISC}	k_{nr}^T [10^4 s^{-1}]	k_{RISC} [10^4 s^{-1}]	Φ_{RISC}	k_{TADF} [10^4 s^{-1}]	k_{CQ} [10^4 s^{-1}]
tCPT	76.2	61.3	14.9	7.8(80.5)	40.6(19.5)	7.9	5.0	0.387	1.5	1.5	0.505	0.95	1.5
Ph-tCPT	80.4	59.2	21.2	9.4(73.6)	44.5(26.4)	6.3	4.3	0.408	1.1	2.0	0.646	1.2	1.1
o-PhCz-tCPT	78.1	53.2	24.9	10.1(68.1)	33.1(31.9)	5.1	4.8	0.481	1.5	3.0	0.663	1.5	1.5
p-PhCz-tCPT	81.1	58.5	22.6	12.7(72.2)	41.9(27.8)	4.6	3.3	0.415	1.1	2.2	0.671	1.3	1.1
3-PhCz-tCPT	57.0	35.8	21.2	23.5(62.7)	5.5(37.3)	1.5	2.7	0.642	12	17	0.580	6.0	12.3

[a] The data in parentheses is the proportion of prompt fluorescence. [b] The data in parentheses is the proportion of delayed fluorescence.

Supplementary figures

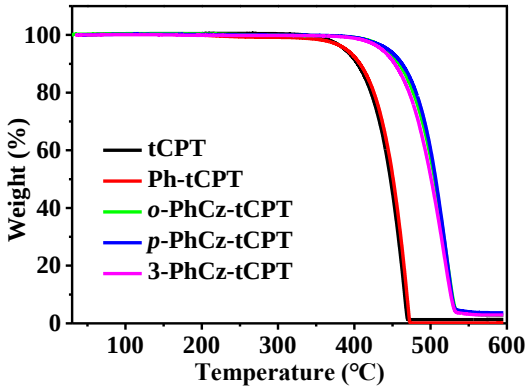

Fig. S1 The TGA curves of the investigated D-A molecules with a temperature rising rate of 10 ℃ min^{-1}.

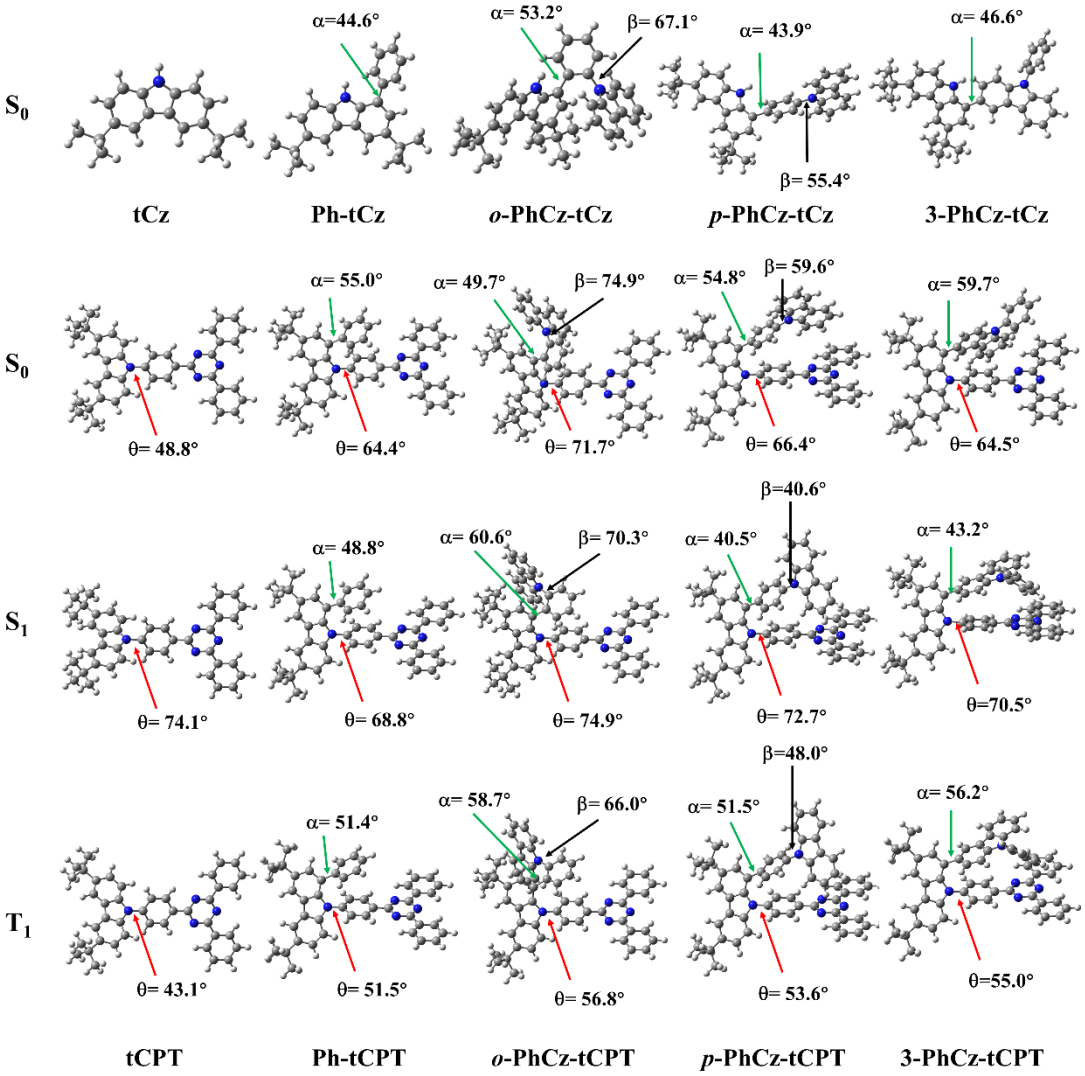

Fig. S2 The dihedral angel of tCz derivatives and the investigated D-A molecules at the ground state (S_0) and optimized singlet (S_1) and triplet (T_1) excited states.

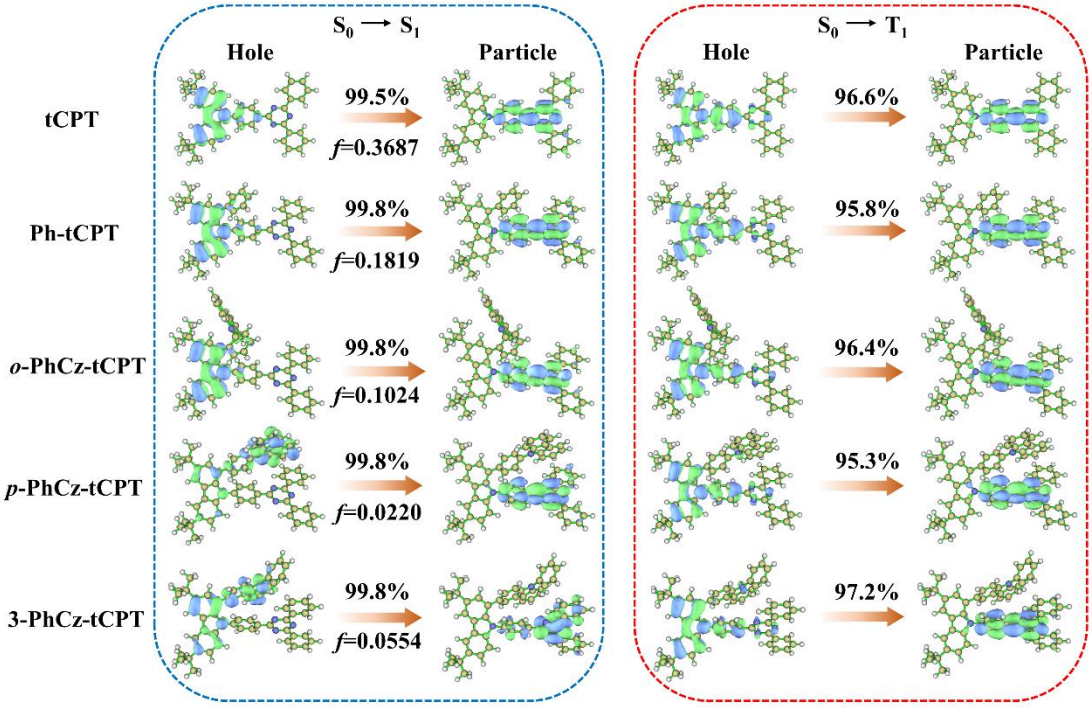

Fig. S3 The natural transition occupied (hole) and unoccupied (particle) orbital distributions, oscillator strengths (*f*) and eigenvalues of the investigated molecules.

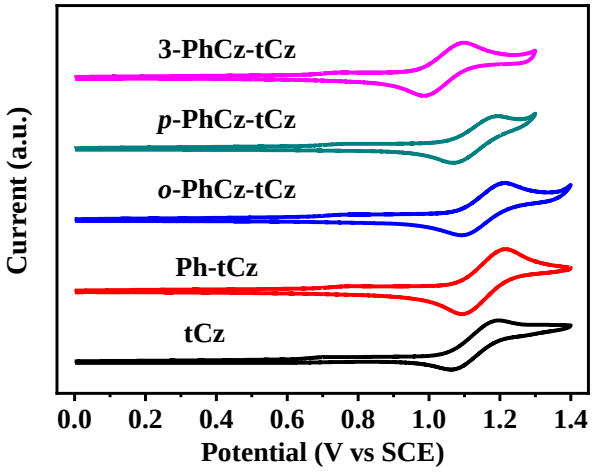

Fig. S4 The cyclic voltammograms for donor part tCz and its derivatives. The onset oxidation potentials of tCz and their derivatives are 1.05 V, 1.07 V, 1.08 V, 1.05 V and 0.97 V (relative to SCE reference) for tCz, Ph-tCz *o*-PhCz-tCz, *p*-PhCz-tCz and

3-PhCz-tCz, respectively, corresponding to the HOMO energies of -5.45, -5.47, -5.48, -5.45 and -5.37 eV. Their LUMO energies can be calculated from the HOMO energies and the E_gs obtained from the absorption spectra to be -1.78, -1.98, -2.00, -1.99, and -1.92 eV, respectively.

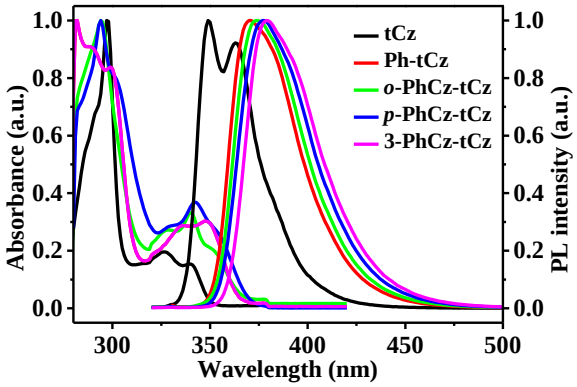

Fig. S5 UV-vis absorption and PL spectra of tCz and its derivatives measured in toluene at room temperature.

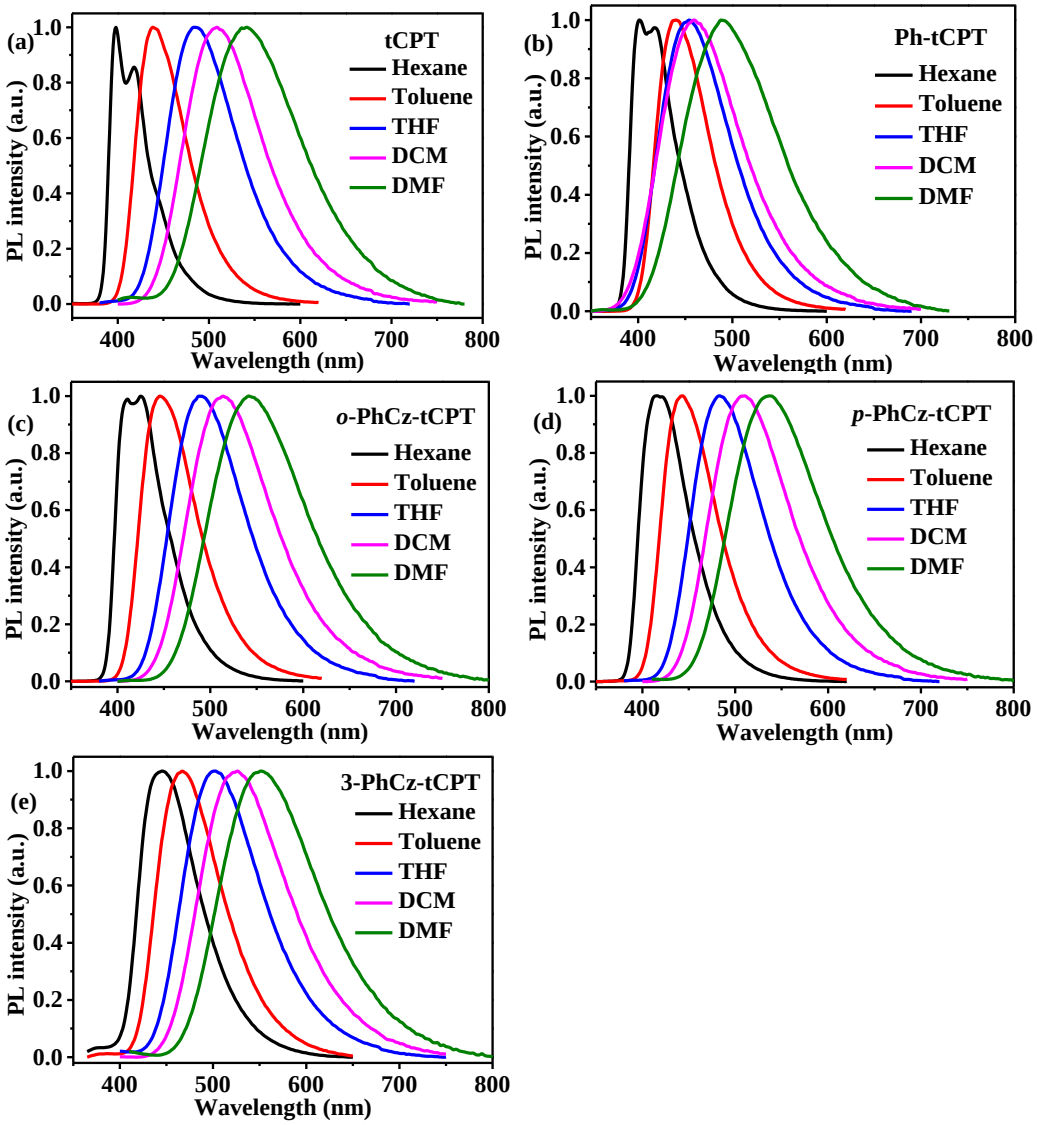

Fig. S6 PL spectra of the investigated D-A molecules in different solvents.

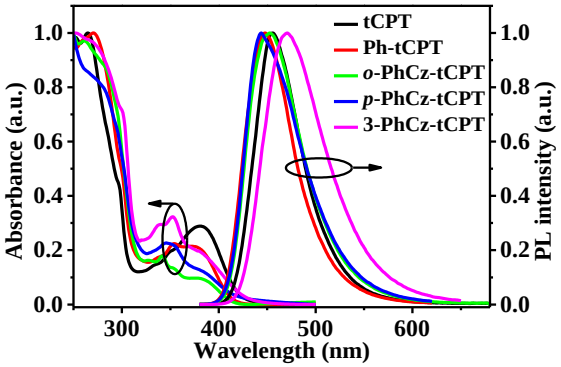

Fig. S7 Uv-vis absorption and PL spectra of the investigated D-A molecules in neat films at room temperature.

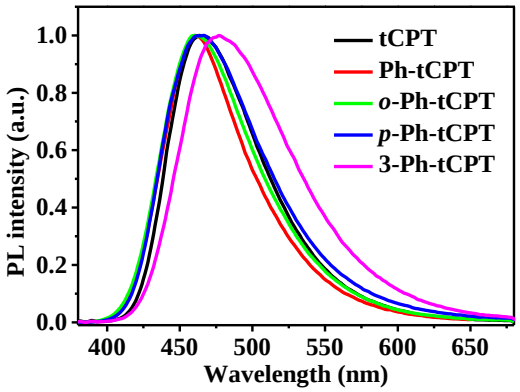

Fig. S8 PL spectra of the carbazole-triazine compound films doped in DPEPO (10 wt%).

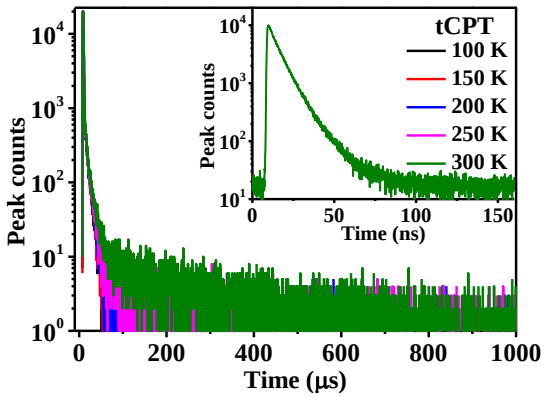

Fig. S9 Transient PL decay curves of tCPT doped in DPEPO film (10 wt%) measured from 100-300 K.

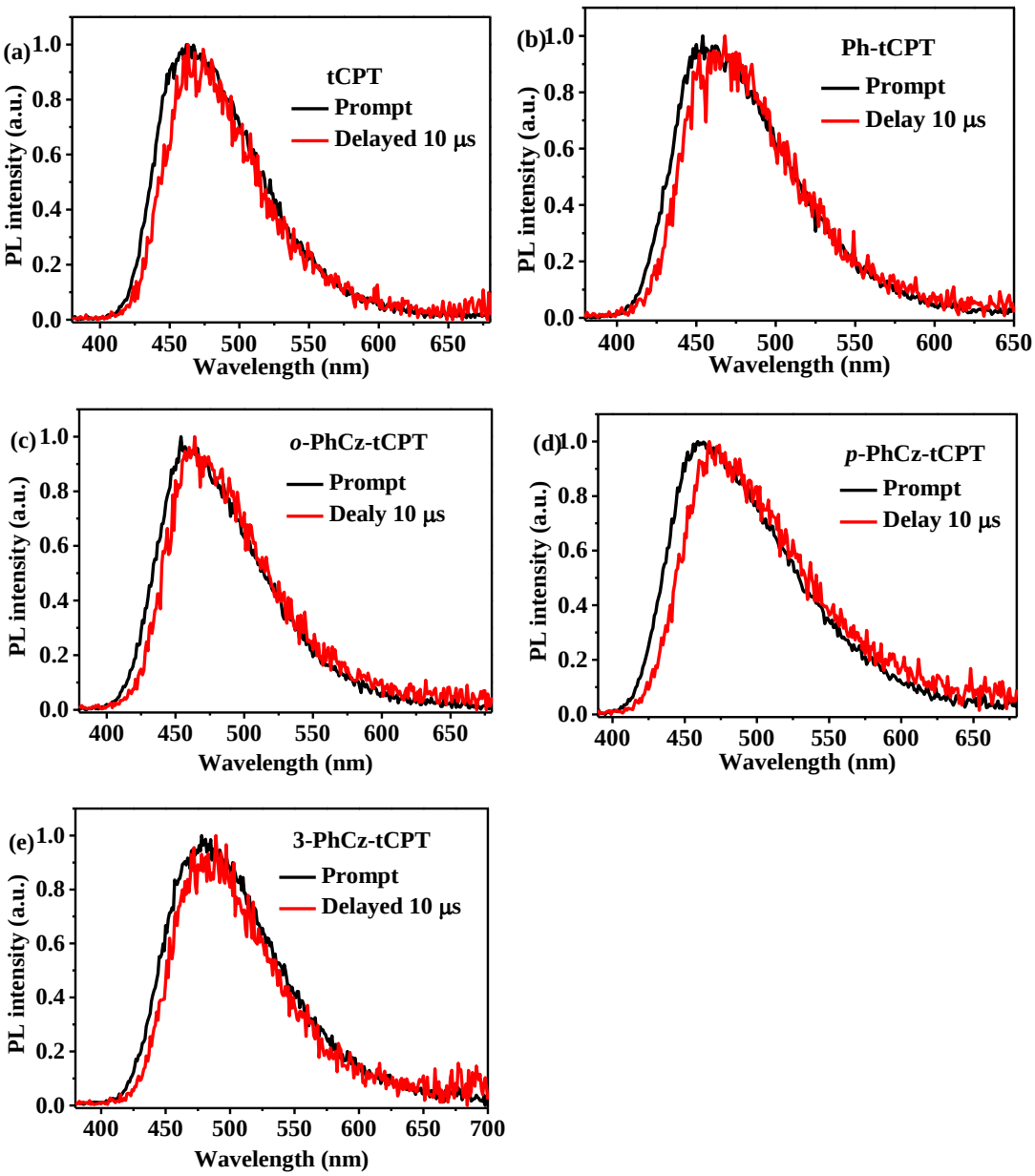

Fig. S10 The time-resolved spectra of the investigated D-A molecules doped in DPEPO films (10 wt%).

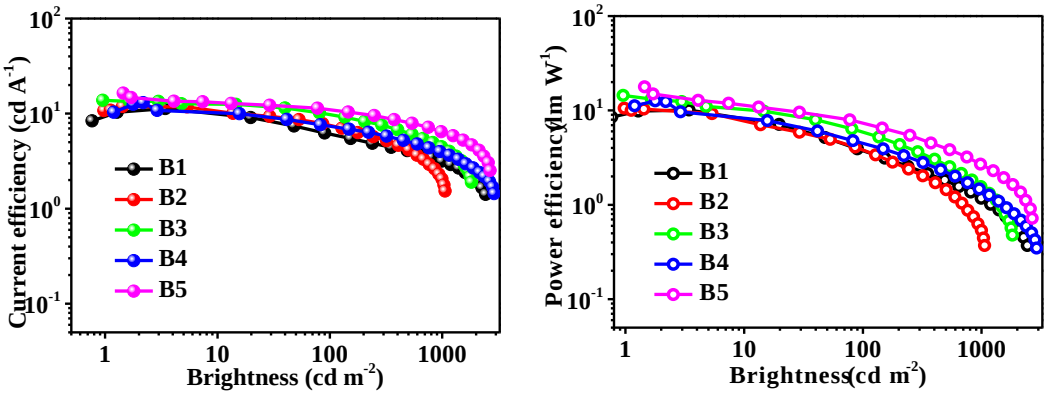

Fig. S11 Efficiency curves of the devices B1-5.

Reference

1 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, T. Keith, 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, Revision D_01. Gaussian, Inc., Wallingford CT, **2013**.

2 S. Huang, Q. Zhang, Y. Shiota, T. Nakagawa, K. Kuwabara, K. Yoshizawa, and C. Adachi, *J. Chem. Theory Comput.*, 2013, **9**, 3872-3877.

3 T. Lu, F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.

4 Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, *Adv. Mater.*, 2014, **26**, 7931-7958.

5 Q. Zhang, H. Kuwabara, W. J. Potscavage, Jr., S. Huang, Y. Hatae, T. Shibata, C. Adachi, *J. Am. Chem. Soc.*, 2014, **136**, 18070-18081.