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Electronic Supplementary Information

Tetraphenylpyrazine Decorated 1,3-Di(9H-carbazol-9-yl)benzene (mCP): A New AIE-

Active Host with Enhanced Performance of Organic Light-Emitting Diodes

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Experimental Section

Materials: All commercially available chemicals are purchased from Alfa Aesar, TCI, J&K chemistry or Beijing HWRK Chem Co., Ltd., Soochiral Chemical Reagent Co., Ltd. and used directly without further purification. Tetrahydrofuran (THF) and toluene are distilled from sodium benzopheone ketyl under dry nitrogen immediately before use.

Instrumentation: All ¹H and ¹³C NMR spectra are recorded with a Bruker AV 500 spectrometer in deuterated CDCl₃ using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra (HRMS) are tested using a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. UV-visible absorption spectra are measured with a SHIMADZU UV-2600 spectrophotometer. PL spectra are recorded on a HORIBA Flioromax-4 spectrofluorometer. Fluorescence quantum yields are measured using a Hamamatsu absolute photoluminescence quantum yield spectrometer C11347 Quantaurus-QY. Fluorescence lifetimes are determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. Thermogravimetric analysis (TGA) analysis was carried out on a TA TGA Q5000 absolute at a heating rate of 20 °C/min under dry nitrogen. differential scanning calorimetry (DSC) analysis was performed on a DSC Q1000 under dry nitrogen at a heating rate of 10 °C/min. Single crystal X-ray diffraction was carried out on a Gemini A Ultra diffractometer at 293K.

Synthesis of compounds 2, 3 and TPP-Br: Compounds 2, 3 and TPP-Br were prepared according to the reported procedures.¹

Synthesis of TPP-mCP: TPP-Br (920 mg, 2.0 mmol), compound **3** (1.34 g, 2.5 mmol), Pd(PPh₃)₄ (120 mg, 0.1 mmol) and K_2CO_3 (560 mg, 4.0 mmol) were added into a 250 mL two neck flask under nitrogen. Then 42 mL THF and 18 mL H₂O were injected via syringes and the mixture was refluxed overnight. After removing the solvent in vacuum, the mixture was dissolved in DCM and washed with water for three times. The organic phase was dried over MgSO₄ and concentrated. The crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. White solid of TPP-mCP was obtained in 76% yield. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.18-8.16 (m, 4H), 7.95 (d, 2H), 7.81-7.78 (m, 3H), 7.70-7.68 (m, 3H), 7.67-7.63 (m, 5H), 7.61-7.59 (m, 4H), 7.48-7.45 (m, 4H), 7.36-7.30 (m, 13H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 148.59, 148.49, 148.46, 147.43, 144.09, 140.58, 139.82, 139.22, 138.65, 138.34, 130.68, 129.88, 129.86, 128.82, 128.70, 128.41, 128.25, 127.00, 126.23, 124.30, 124.01, 123.65, 120.51, 120.41, 109.71. HRMS (MALDI TOF): *m/z* 790.3093 [M⁺], calcd for C₅₈H₃₈N₄ 790.3096.

Theoretical calculations

Theoretical calculation was carried out by using the Gaussian 09_B01 package. Density functional theory (DFT) calculation in the B3LYP/6-31G(d) basis set was performed to determine the ground state structure in the gas phase. Theoretical prediction for energy levels of the compounds was acquired based on the optimized structure. The M06-2x/6-31G(d) functional was utilized to gain insight into the character of the excited singlet states (S1) and triplet states (T1) by using the optimized structure mentioned above.

Device fabrication and characterization

Multilayer OLEDs were fabricated by the vacuum-deposition method. 95 nm indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15-20 Ω sq⁻¹ were subjected to a routine cleaning process of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol under ultrasonic bath and treated with O₂ plasma for 10 min. Organic layers and cathode were sequentially deposited on the ITO-coated glass substrates by thermal evaporation under high vacuum (< 5 × 10⁻⁴ Pa). And the deposition rates are 1.0 Å s⁻¹ for organic layers, 0.1 Å s⁻¹ for LiF layer and 3-5 Å s⁻¹ for Al cathode, respectively. The active area of each device was 9 mm². The electroluminescence spectra (EL),

the current density-voltage characteristics (J-V) and the current density-voltage-luminance curves characterizations (J-V-L) of the OLEDs were detected by a Photo Research SpectraScan PR-745 Spectroradiometer and a Keithley 2450 Source Meter and they are recorded simultaneously. All the device characterizations were carried out at room temperature under ambient conditions.

All the electroluminescent devices were fabricated in an uniform structure merely adjusting the doping concentration of dopant: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/hosts: x wt% dopants (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm). The detailed structures of the devices are as following: Device O1: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 6 wt% PO-01 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device O2: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 8 wt% PO-01 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device O3: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 10 wt% PO-01 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/AI (120 nm);

Device O5: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/mCP: 8 wt% PO-01 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device R1: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 3 wt% Ir(piq)₂acac (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device R2: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 6 wt% Ir(piq)₂acac (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device R3: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 8 wt% lr(piq)₂acac (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device R4: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/TPP-mCP: 10 wt% Ir(piq)₂acac (20

nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm);

Device R5: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/mCP: 3 wt% Ir(piq)₂acac (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/AI (120 nm).

Hole-only devices are in a structure of ITO/host (80 nm)/TAPC (10 nm)/Al and electron-only devices are in a structure of ITO/TmPyPB (10 nm)/host (80 nm)/LiF (1 nm)/Al.

Hole-only devices of yellow emitter are in a structure of ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA(5 nm)/host: 8 wt% PO-01 (20 nm)/TAPC (55 nm)/Al and electron-only devices of yellow emitter are in a structure of ITO/TmPyPB (35 nm)/host: 8 wt% PO-01 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al.

Energy transfer calculations

The efficiency of Förster energy transfer $\Phi_{\rm ET}$ can be obtained by²

$$\Phi_{ET} = \frac{K_{ET}}{K_{ET} + \frac{1}{\tau_D}} = \frac{1}{1 + \left(\frac{R_{DA}}{R_0}\right)^6}$$

The distance between the host to guest R_{DA} can be calculated by²

$$R_{DA} = \left(\left(N_G \right) \times \frac{4\pi}{3} \right)^{-\frac{1}{3}}$$

where $N_{\rm G}$ is the quantity of guest molecules in a unit volume, which is in direct proportion to the guest doping concentration. According to Samuel's work,³ the density of chromophores can be described as

$$N_G = \beta \times \rho \times N_A / M_C$$

where β is the fraction of guest present in the film, ρ is the density of the film (assumed to be 1 g cm⁻

 $^{\rm 3}$), N_A is the Avogadro's number and M_C is the molecular weight of the guest.

The Förster radius R_0 could be estimated by using the following equation⁴

$$R_0^6 = \frac{9000(\ln 10)k^2 \Phi_{PL}}{128\pi^5 N_A n^4} \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

where k^2 is orientation factor (k^2 is typically assumed to be 2/3 for the random orientation system), Φ_{PL} is the photoluminescence quantum yield of the donor in the absence of acceptor, N_A is Avogadro's

number, n is the refractive index of the medium, $\int_{0}^{\infty} F_{D}(\lambda)\varepsilon_{A}(\lambda)\lambda^{4}d\lambda$ is the spectral overlap integral between donor PL [$F_{D}(\lambda)$] and acceptor absorption [$\varepsilon_{A}(\lambda)$] in which $F_{D}(\lambda)$ is the donor's fluorescence normalized by area, $\varepsilon_{A}(\lambda)$ is the molar decadic extinction coefficient of the acceptor and λ is the wavelength.

Spectral Characterization

¹H and ¹³C NMR spectra of TPP-mCP



Fig. S1. ¹H and ¹³C NMR spectrums of TPP-mCP in CDCl₃. The solvent peaks are marked with asterisks.



Fig. S2. HRMS spectrum of TPP-mCP.



Fig. S3. AFM images of the neat films of TPP-mCP and mCP on silica wafers. Thickness of film: 30 nm.



Fig. S4. AFM images of the doped films of TPP-mCP and mCP on silica wafers with 8% wt PO-01.

Thickness of the films: 30 nm.



Fig. S5. AFM images of the doped films of TPP-mCP and mCP on silica waters 3% wt $Ir(piq)_2acac$. Thickness of the films: 30 nm.



Fig. S6. A) The time-resolved fluorescence spectra of TPP-mCP in THF solution and in solid film; concentration of soln: $10 \ \mu$ M; B) the time-resolved fluorescence spectra of mCP in THF solution and in solid film; concentration of solution: $10 \ \mu$ M.



Fig. S7. Fluorescence (black line) and phosphorescence (red line) spectra of TPP-mCP solution recorded





Fig. S8. Absorption spectra of PO-01 and Ir(piq)₂acac and PL spectrum of TPP-mCP.



Fig. S9. Chemical structures of HATCN, TAPC, TCTA and TmPyPB.



Fig. S10. A) Plots of external quantum efficiency versus luminance; B) changes in current density and luminance with the applied voltages; C) current efficiency–luminance–power efficiency of TPP-mCP-hosted devices O1, O2 and O3.



Fig. S11. A) Plots of external quantum efficiency versus luminance; B) changes in current density and luminance with the applied voltages; C) current efficiency–luminance–power efficiency of TPP-mCP-hosted devices R1, R2, R3 and R4.

device	Va (V)		η _{c^{b)} (c}	:d A⁻¹)	$\eta_{ m p^{c)}}$ (Im	ו W⁻¹)	$\eta_{ext}{}^{d}$	⁾ (%)	$\lambda_{\text{max}}{}^{e)}$ (nm)	CIE ^{e)} (x, y)	
01	2.6	3.0	3.4	84.97	69.47	99.73	64.19	26.94	22.03	562	(0.493, 0.506)
02	2.6	3.0	3.4	89.54	79.73	104.21	73.67	28.72	25.58	562	(0.495, 0.504)
03	2.6	3.0	3.4	76.37	70.00	88.39	64.68	26.30	24.11	566	(0.501, 0.497)
R1	2.8	3.4	4.4	15.68	13.57	16.96	9.69	20.87	17.64	624	(0.672, 0.323)
R2	2.6	3.0	3.8	14.51	13.06	16.25	10.80	19.66	17.39	626	(0.674, 0.323)
R3	3.0	4.0	5.8	11.00	9.69	11.17	5.25	18.97	16.71	626	(0.676, 0.321)
R4	2.6	3.2	4.2	12.78	11.57	14.69	8.66	17.86	16.18	628	(0.680, 0.319)

Table S1. Summary of the EL properties of the TPP-mCP-hosted devices.

^{a)} Voltage at 1, 100, and 1000 cd m⁻², respectively; ^{b)} Maximum forward-viewing η_c and η_c at 1000 cd m⁻²; ^{c)} Maximum forward-viewing η_p and η_p at 1000 cd m⁻²; ^{d)} Maximum forward-viewing η_{ext} and η_{ext} at 1000 cd m⁻²; ^{e)} Maximum wavelength and CIE coordinates at 10 mA cm⁻².

References

- M. Chen, H. Nie, B. Song, L. Li, J. Z. Sun, A. Qin and B. Z. Tang, *J. Mater. Chem. C*, 2016, *4*, 2901;
 b) L. Pan, W. Luo, M. Chen, J. Liu, L. Xu, R. Hu, Z. Zhao, A. Qin and B. Z. Tang, *Chin. J. Org. Chem.*, 2016, *36*, 1316; c) L. Pan, Y. Cai, H. Wu, F. Zhou, A. Qin, Z. Wang and B. Z. Tang, *Mater. Chem. Front.*, 2018, *2*, 1310; d) L. Pan, H. Wu, J. Liu, K. Xue, W. Luo, P. Chen, Z. Wang, A Qin and B. Z. Tang, *Adv. Optical Mater.*, 2019, 1801673.
- 2. H. Wang, B. Yue, Z. Xie, B. Gao, Y. Xu, L. Liu, H. Sun, Y. Ma, Phys. Chem. Chem. Phys., 2013, 15, 3527.
- 3. P. E. Shaw, A. Ruseckas, J. Peet, G. C. Bazan and I. D. W. Samuel, Adv. Funct. Mater., 2010, 20, 155.
- 4. Y. Kawamura, J. Brooks, J. J. Brown, H. Sasabe and C. Adachi, Phys. Rev. Lett., 2006, 96, 017404.