

## Supporting Information

### **A Pure Red Luminescent $\beta$ -Carboline-Substituted Biphenylmethyl Radical: Photophysics, Stability and OLEDs**

*Alim Abdurahman, Yingxin Chen, Xin Ai, Ablikim Obolda, Yu Gao, Shengzhi Dong,  
Bao Li, Bing Yang, Ming Zhang and Feng Li\**

#### **Contents**

|   |  |
|---|--|
| <b>S1.</b> Experimental section.....  |  |
| <b>S2.</b> MALDI-TOF mas spectra and FT-IR spectra of PyID-BTM.....                           |  |
| <b>Fig. S1 and S2</b>   |  |
| <b>S3.</b> Crystallographic data of PyID-BTM.....   |  |
| <b>Table S1</b>   |  |
| <b>S4.</b> Selected angles in the crystal of PyID-BTM.....                                    |  |
| <b>Table S2</b>   |  |
| <b>S5.</b> Therma and Electrochemical properties.....   |  |
| <b>Fig. S3, S4 and S5.</b>  |  |
| <b>S6.</b> Spin density distribution calculated using DFT.....                                |  |
| <b>Fig. S6.</b>   |  |
| <b>S7.</b> Measurements and calculations of molar extinction coefficients ( $\epsilon$ )..... |  |
| <b>Fig. S7 and S8</b>   |  |
| <b>S8.</b> Solvation Effect of PyID-BTM.....  |  |
| <b>Table S3</b>   |  |
| <b>S9.</b> Current efficiency (CE) and Power efficiency (PE) versus current density curves..  |  |

**Fig. S9**

**S10.** EL spectra of PyID-BTM-based OLEDs with different doping concentration at different voltages.....

**Fig. S10**

**S11.** EPR spectra of PyID-BTM before and after evaporation.....

**Fig. S11**

**S11.** Data of DFT and TD-DFT calculations.....

## S1. Experimental Section

General: All reagents and solvents were purchased from commercial sources and used as received unless otherwise stated. Chromatographic separations were carried out using silica gel (200-300 mesh). The  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra were obtained in deuterated dimethyl sulfoxide (DMSO) with a Bruker Avance-III 500 NMR spectrometer at ambient temperature. Fourier transform infrared spectroscopy (FTIR) spectra of radicals were recorded with Bruker VERTEX 80V. MALDI-TOF mass spectra were recorded on a Bruker Autoflex speed TOF/TOF mass spectrometer with DCTB as a matrix. EPR spectra were recorded on a Bruker ELEXSYS-II E500 CW-EPR spectrometer at ambient temperature. Thermal gravimetric analysis (TGA) was carried out on the Pyris1 TGA thermal analysis system at a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were performed using a RF-5301 PC spectrophotometer. The CV measurements were performed using an electrochemical analyzer (CHI660C, CH Instruments, USA). A glass carbon disk was used as the working electrode. A platinum wire acted as the counter electrode and Ag/Ag<sup>+</sup> acted as the reference electrode together with the redox couple ferrocenium/ferrocene as the internal standard at the rate of 50 or  $100\text{ mV}\cdot\text{s}^{-1}$ . Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in anhydrous dichloromethane (0.1 M) were used as the supporting electrolyte for negative and positive scan respectively. (The measured electrochemical data of CzBTM was slightly different from that reported previously. This may be due to the fact that the electrode used is

different from those used before). An Edinburgh fluorescence spectrometer (FLS980) was used for the fluorescence decay and absolute fluorescence measurements. The lifetime of the excited states was measured by the time-correlated single photon counting method (detected at the peak of the PL) under the excitation of a laser (375 nm) with a pulse width of 50 ps.

Magnetic measurements were performed on a Quantum Design 6.5 Tesla SQUID-VSM system with a temperature range of 2-300 K and an applied field of 1000 Oe. After correction of diamagnetic contributions from the sample, using tabulated constants, sample holder, and paramagnetic contamination, the magnetic data were fitted with Curie-Weiss law. " $\chi_m = C/(T-\theta)$ " where  $C$  is Curie constant and  $\theta$  is Weiss temperature.

Photostability of radicals was tested under irradiation with a 355 nm pulse laser (power density: 195.4 kW/cm<sup>2</sup>, pulse width: 8 ns, frequency: 10 Hz).

The single crystals suitable for X-ray structural analysis were obtained by slow evaporation from the chloroform/ethanol solution at room temperature. Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the  $\omega$ -scan mode with graphite-monochromator Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on  $F^2$ . The corresponding CCDC reference number (CCDC: 1831917) for PyID-BTM. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**OLED Fabrication and Measurements:** The OLEDs were fabricated through vacuum deposition of the materials at  $\approx 3\text{--}4 \times 10^{-6}$  mbar onto ITO-coated glass substrates having a sheet resistance of  $\approx 30 \Omega^{-2}$ . Ready-made indium tin oxide (ITO) glass substrates were purchased and cleaned with ethanol, acetone, toluene and isopropyl alcohol. After dried with  $\text{N}_2$ , they were treated with UV irradiation for 15 min. The  $\text{MoO}_3$  layer was deposited at a rate of  $0.2 \text{ \AA s}^{-1}$ . All the organic layers were deposited at  $0.4\text{--}0.6 \text{ \AA s}^{-1}$ . The evaporation rate of cathode LiF and Al metal layer were  $0.1 \text{ \AA s}^{-1}$  and  $0.6\text{--}1.2 \text{ \AA s}^{-1}$  respectively. The EL spectra, CIE coordinates, and The current density-voltage-luminance (J-V-L) characteristics of the devices were measured with a PHOTO RESEARCH SpectraScan PR 655 photometer and a KEITHLEY 2400 SourceMeter constant current source at room temperature.

**Lippert-Mataga calculation:** To further understand the effect of solvent polarity on the excited state of PyID-BTM, we used the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of solute:

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3} f(\epsilon, n)$$

where  $f$  is the orientational polarizability of the solvent,  $(v_a^0 - v_f^0)$  corresponds to the Stokes shifts when  $f$  is zero,  $\mu_e$  is the excited state dipole moment,  $\mu_g$  is the ground-state dipole moment;  $a$  is the solvent cavity (Onsager) radius ( $5.98 \text{ \AA}$ ), derived from the Avogadro number ( $N$ ), molecular weight ( $M$ ), and density ( $d=1.0 \text{ g/cm}^3$ );  $\epsilon$  and  $n$  are the solvent dielectric and the solvent refractive index, respectively;  $f(\epsilon, n)$  and  $a$  can be calculated respectively as follows:

$$f(\varepsilon - n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad a = \left(\frac{3M}{4N\pi d}\right)^{1/3}$$

The detailed data are listed in Table S1. In low-polarity solvents (slope value  $\sim 1321$ ,  $R = 0.52$ ), the corresponding  $\mu_e$  was estimated to be 5.3 D. In high-polarity solvents (slope value  $\sim 5295$ ,  $R = 0.96$ ), the corresponding  $\mu_e$  was estimated to be 10.6 D.

M1 was prepared according to the literature.<sup>1</sup>

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  10.63 (s, 1H), 7.35 (d,  $J = 7.7$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 6.99 (t,  $J = 7.4$  Hz, 1H), 6.93 (t,  $J = 7.3$  Hz, 1H), 3.86 (s, 2H), 3.31 (s, 1H), 2.98 (t,  $J = 5.6$  Hz, 2H), 2.59 (t,  $J = 5.5$  Hz, 2H). HRMS (ESI)  $m/z$ :  $[M + H]^+$  calcd for  $C_{11}H_4N_2$ : 172.1; found:171.89.

PyID was prepared according to the literature.<sup>1</sup>

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  11.60 (s, 1H), 8.90 (s, 1H), 8.34 (d,  $J = 5.2$  Hz, 1H), 8.24 (d,  $J = 7.8$  Hz, 1H), 8.11 (d,  $J = 5.2$  Hz, 1H), 7.65 – 7.51 (m, 2H), 7.25 (t,  $J = 7.4$  Hz, 1H). HRMS (ESI)  $m/z$ :  $[M + H]^+$  calcd for  $C_{11}H_8N_2$ : 168.07; found:167.96

Synthesis of PyID-BTM: Under an argon atmosphere, PyID (0.8 g, 4.76g) in dimethyl sulfoxide (10 ml) solution was added dropwise, with string, a dispersed of sodium hydride (60% in oil, 0.17 g, 7.14 mmol) in anhydrous dimethyl sulfoxide (40 ml). The reaction mixture was stirred for 20 min at room temperature before adding HBTM-Br (1.72 g, 3.82 mmol). And then the mixture was stirred for 4 h under 60 °C. After cooling to room temperature, the mixture was added in saturated ammonium chloride solution (100 ml). The precipitate was collected by suction filtration and

purified by column chromatography (ethyl acetate: petroleum ether = 1:8). Deep red solid PyID-BTM was obtained in 10% (0.21 g) yield. MALDI-TOF(M/S): Calcd for  $C_{24}H_{11}C_{16}N_2$ , 538.90; found, 538.90. Elem.Anal.Calcd for  $C_{24}H_{11}C_{16}N_2$ : C 55.70 , N 2.60 , H 2.24; found: C 55.55 , N 2.51 , H 2.20.

## References

- 1 C. Portmann, C. Prestinari, T. Myers, J. Scharfe, K. Gademann, *Chembiochem* **2009**, 10, 889.

## S2. MALDI-TOF mas spectra and FT-IR spectra of PyID-BTM

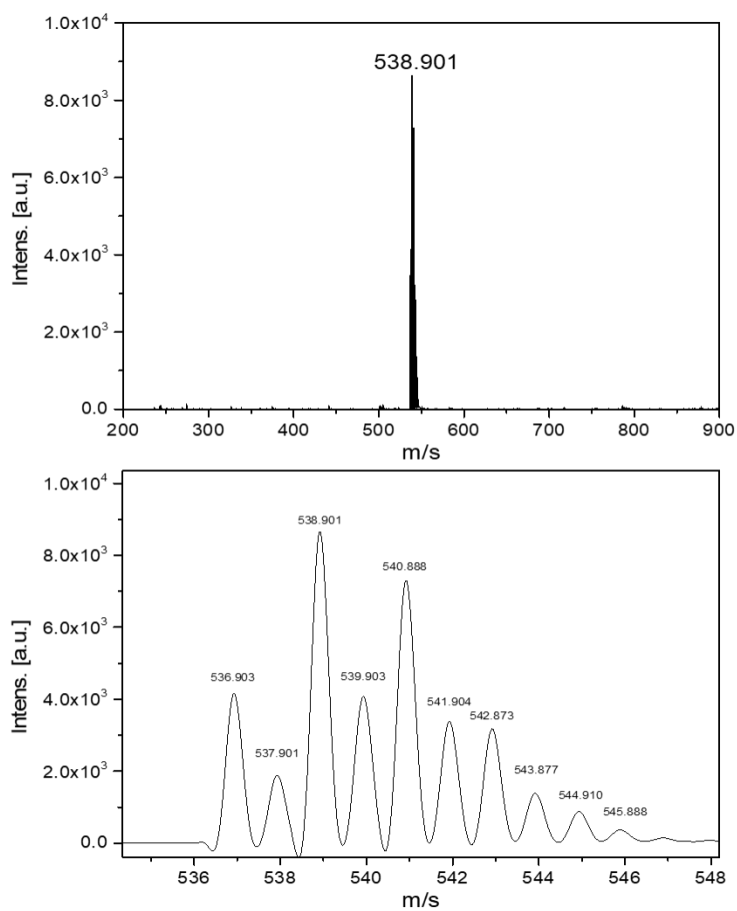


Fig. S1 MALDI-TOF mass spectra of PyID-BTM.

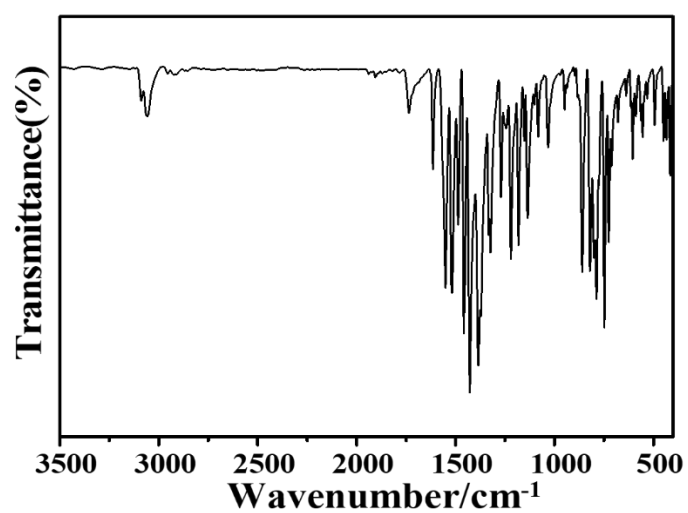


Fig. S2 FT-IR spectra of PyID-BTM.



### S3. Crystallographic data of PyID-BTM

**Table S1** X-Ray Crystallographic Data of PyID-BTM

|  |  |
|--|--|
| CCDC   | 1831917  |
| Empirical formula                              | C <sub>24</sub> H <sub>11</sub> Cl <sub>6</sub> N <sub>2</sub> |
| Formula weight                                 | 540.05   |
| Temperature                                    | 273(2) K   |
| Wavelength                                     | 0.71073 Å  |
| Crystal system                                 | Monoclinic   |
| Space group                                    | P 21/c   |
| a, Å   | 16.6879(5)   |
| b, Å   | 8.2499(2)  |
| c, Å   | 17.2222(5)   |
| alpha, deg                                     | 90   |
| beta, deg                                      | 107.7570(10)   |
| gamma, deg                                     | 90   |
| Volume, Å <sup>3</sup>                         | 2258.08(11)  |
| Z  | 4  |
| Calculated density, Mg/m <sup>3</sup>          | 1.589  |
| Absorption coefficient, mm <sup>-1</sup>       | 0.778  |
| F(000)   | 1084   |
| Crystal size, mm <sup>3</sup>                  | 0.0500x0.0300x0.0200   |
| Theta range for data collection, deg           | 2.76 to 28.29  |
| Limiting indices                               | -22<=h<=21, -10<=k<=10, -22<=l<=21                             |
| Reflections collected                          | 25386  |
| Independent reflections                        | 5592 [R(int) = 0.0449]   |
| Completeness to theta = 28.29°                 | 99.7 %   |
| Absorption correction                          | Semi-empirical from equivalents                                |
| Max. and min. transmission                     | 0.985 and 0.972  |
| Refinement method                              | Full-matrix least-squares on F <sup>2</sup>                    |
| Data / restraints / parameters                 | 5592 / 0 / 289   |
| Goodness-of-fit on F <sup>2</sup>              | 1.043  |
| Final R indices [I>2sigma(I)]                  | R1 = 0.0516, wR2 = 0.1296                                      |
| R indices (all data)                           | R1 = 0.1048, wR2 = 0.1669                                      |
| Largest diff. peak and hole, e.Å <sup>-3</sup> | 0.493 and -0.473   |

## S4. Selected angles in the crystal of PyID-BTM

Table S2 Selected angles in the crystal of PyID-BTM.

| Angles   | $\Phi(\text{PyID-BTM})$ |
|--|-------------------------|
| N1C7C8   | 118.14°                 |
| N1C7C6   | 118.7°                  |
| C6C7C8   | 123.15°                 |
| Dihedral angle between N1C6C8 plain ( $\beta$ -<br>carboline moieties) | 42.6°                   |
| (2,4,6-trichloropheny including C7)                                    | 49.5°                   |
| (2,4,6-trichloropheny including C6)                                    | 49.6°                   |

## S5. Thermo and Electrochemical properties

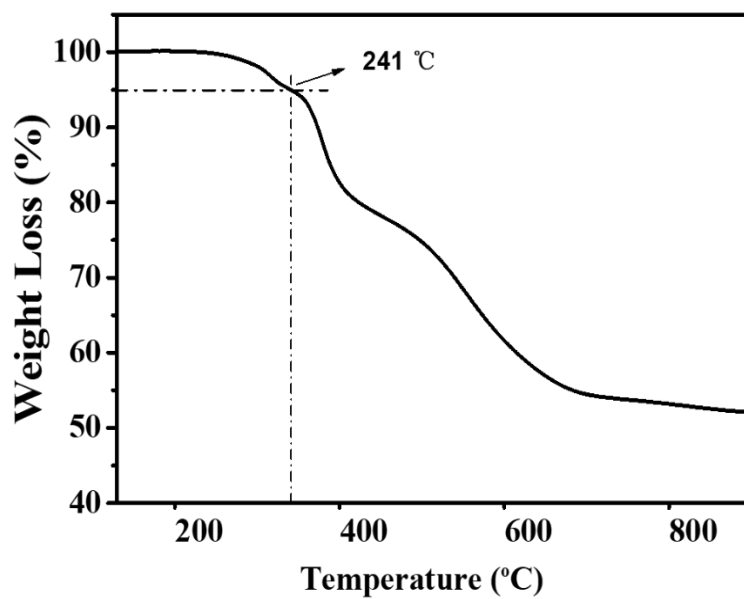


Fig. S3 TGA curve of PyID-BTM under nitrogen flow.

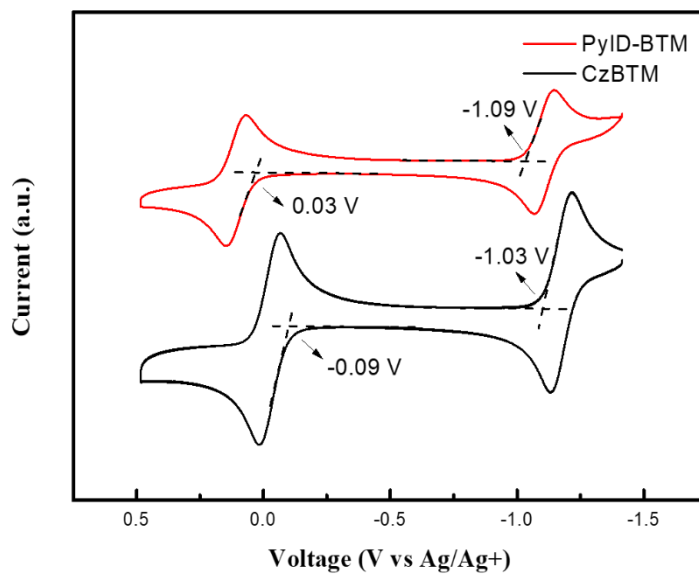
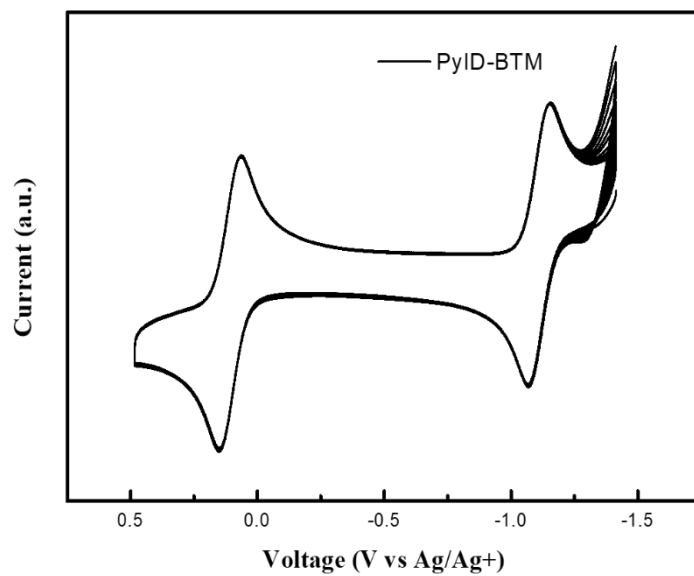
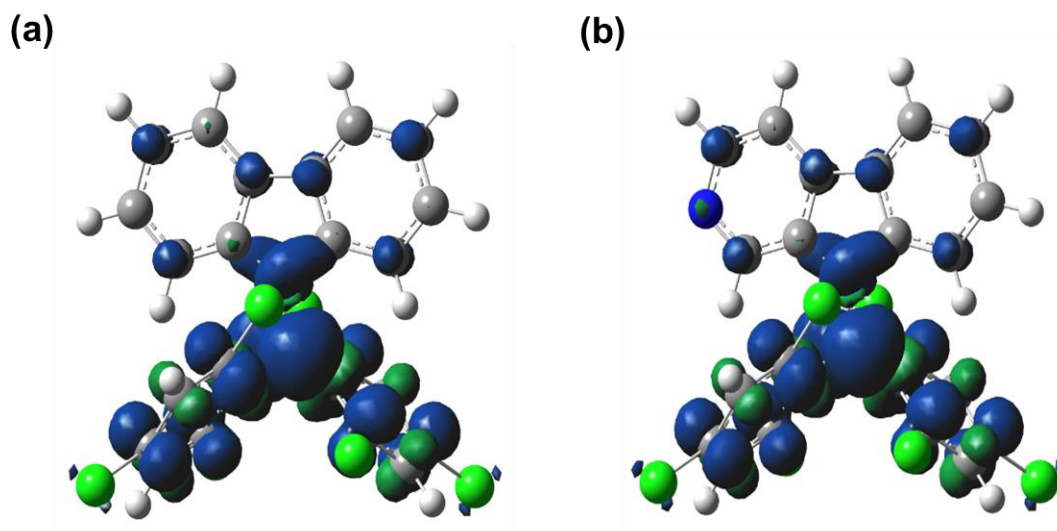


Fig. S4 Cyclic voltammograms of PyID-BTM and CzBTM in 0.1 M TBAPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 0.05 V s<sup>-1</sup>.



**Fig. S5** Multi-cycle CV measurements (20 cycles) of PyID-BTM in 0.1 M TBAPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 0.1 V s<sup>-1</sup>.

## S6. Spin density distribution calculated using DFT.



**Fig. S6** Spin density distribution of (a) CzBTM and (b) PyID-BTM using DFT methods (UB3LYP/6-31G(d,p)) with isovalue at 0.0015.

## S7. Measurements and calculations of molar extinction coefficients ( $\epsilon$ )

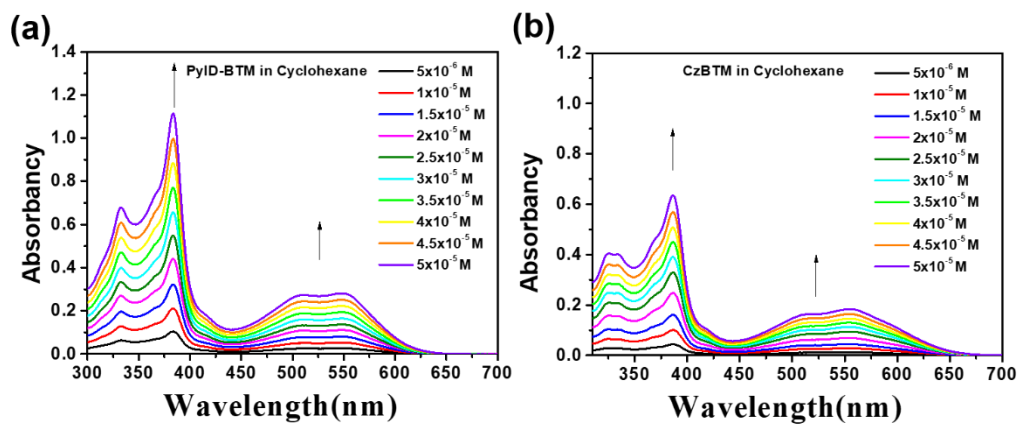


Fig. S7 UV-spectrum of (a) PyID-BTM and (c) CzBTM in cyclohexane at different concentration.

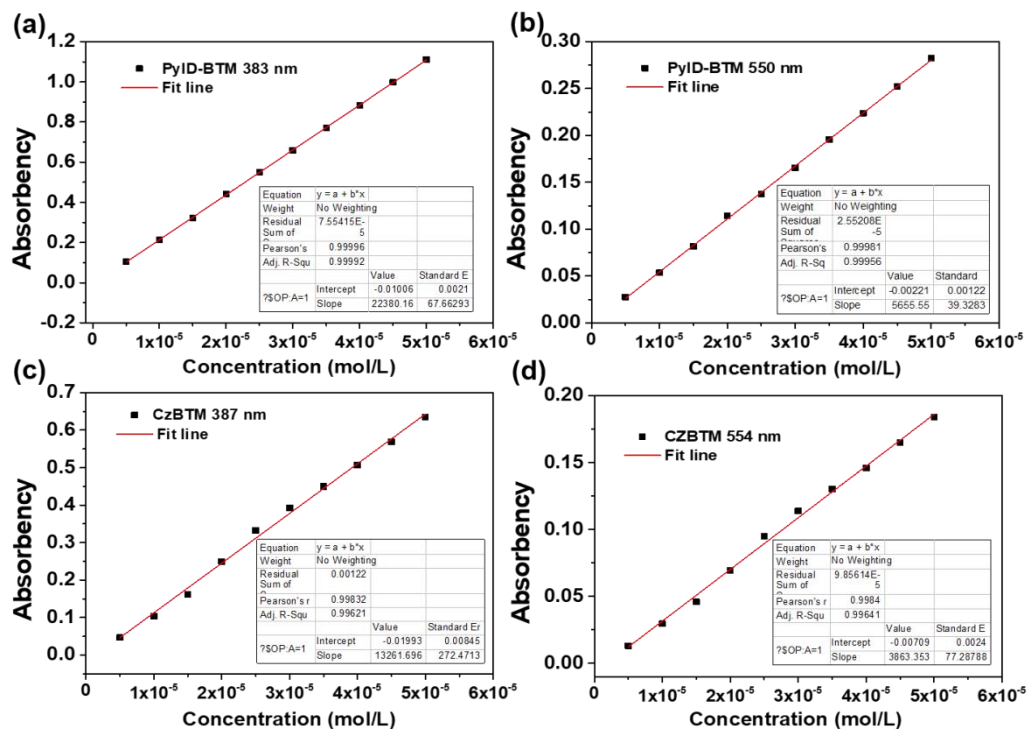


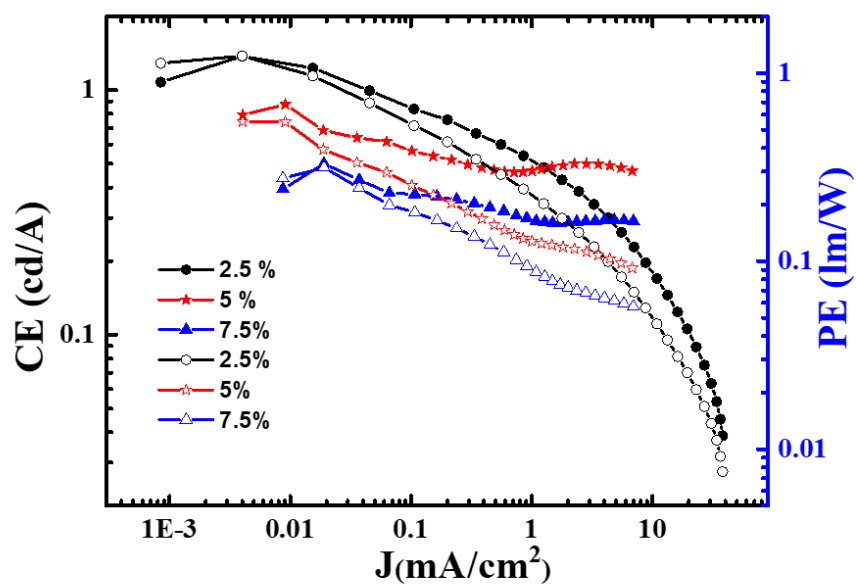
Fig. S8 Absorbency-concentration fitting line of PyID-BTM and CzBTM.

## S8. Solvation Effect of PyID-BTM

Table S3 Photophysical properties of PyID-BTM in different solvents.

| Solvent            | $\Delta f$ | $\nu_a$ (nm) | $\nu_b$ (nm) | $\nu_a-\nu_b$ (cm <sup>-1</sup> ) | FWHM (nm) | $\Phi_F$ (%) |
|--------------------|------------|--------------|--------------|-----------------------------------|-----------|--------------|
| Cyclohexane        | 0          | 548          | 664          | 3188                              | 81        | 19.51        |
| p-xylene           | 0.003      | 547          | 681          | 3597                              | 99        | 4.23         |
| Toluene            | 0.014      | 546          | 682          | 3652                              | 101       | 4.05         |
| butyl ether        | 0.096      | 544          | 678          | 3633                              | 101       | 3.63         |
| isopropyl ether    | 0.145      | 547          | 684          | 3661                              | 102       | 3.82         |
| chloroform         | 0.149      | 543          | 677          | 3645                              | 99        | 4.26         |
| diethyl ether      | 0.167      | 546          | 689          | 3801                              | 107       | 2.86         |
| Tetrahydrofuran    | 0.210      | 545          | 703          | 3973                              | 123       | 0.62         |
| dichloromethane    | 0.218      | 544          | 694          | 3973                              | 112       | 2.60         |
| Dimethyl formamide | 0.276      | 544          | 711          | 4494                              | 160       | 0.23         |
| Acetonitrile       | 0.305      | 541          | 711          | 4420                              | 139       | 0.3          |

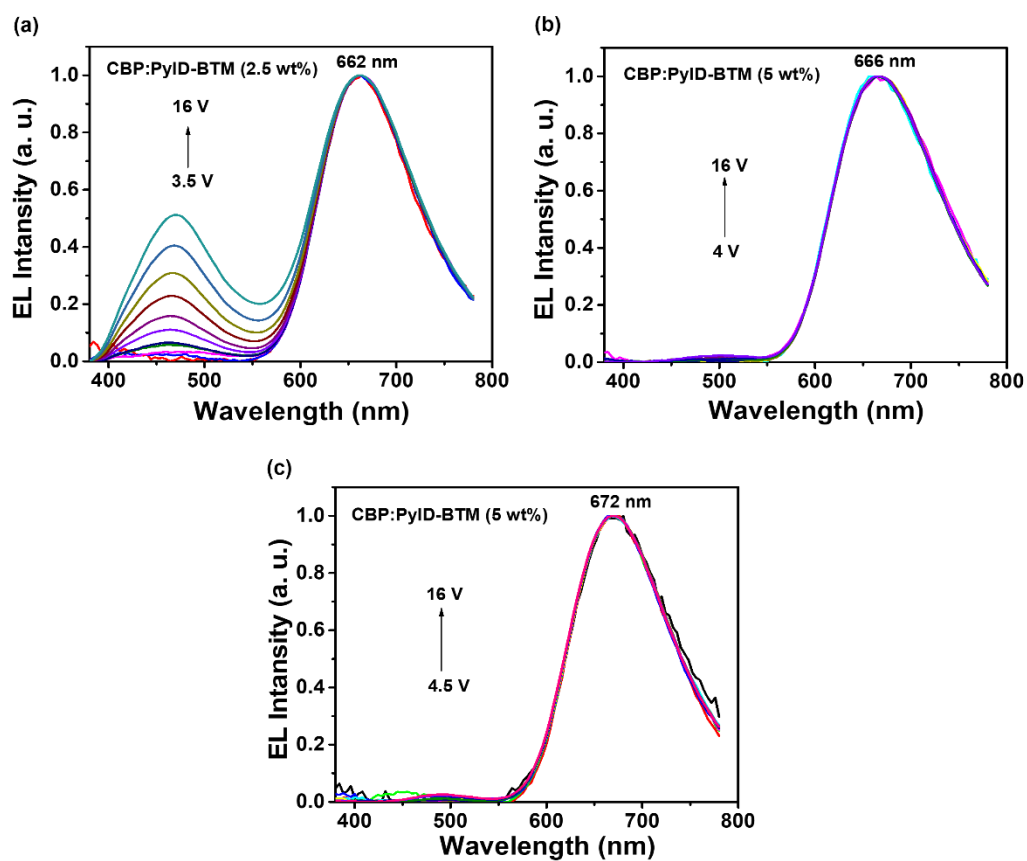
**S9. Current efficiency (CE) and Power efficiency (PE) versus current density curves.**



**Fig. S9** Current efficiency (CE) and Power efficiency (PE) versus current density curves.



### S10. EL spectra of PyID-BTM-based OLEDs with different doping concentration at different voltages



**Fig. S10** EL spectra of PyID-BTM-based OLEDs with different doping concentration at Different voltages

## S11. EPR spectra of PyID-BTM before and after evaporation

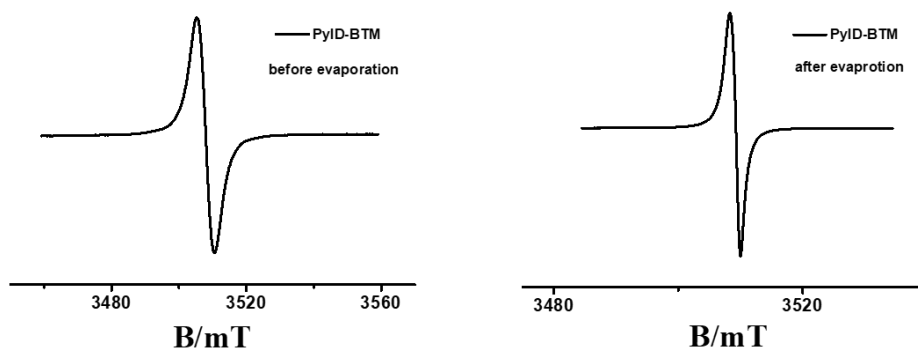


Fig. S11 EPR spectra of PyID-BTM powder measured at room temperature before and after evaporation.

## S12. Data of DFT and TD-DFT calculations

Cartesian coordinates of all the optimized geometries by DFT calculation

PYID-BTM (UB3LYP/6-31G(d))

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | 0.002721                | -0.072398 | 0.003823  |
| 2                | 6                | 0              | -1.284546               | -0.770775 | 0.093913  |
| 3                | 6                | 0              | -1.644863               | -1.830292 | -0.778867 |
| 4                | 6                | 0              | -2.271095               | -0.430025 | 1.058671  |
| 5                | 6                | 0              | -2.866231               | -2.492748 | -0.709559 |
| 6                | 6                | 0              | -3.504774               | -1.065331 | 1.139201  |
| 7                | 6                | 0              | -3.792494               | -2.097000 | 0.249920  |
| 8                | 1                | 0              | -3.095068               | -3.286594 | -1.408653 |
| 9                | 1                | 0              | -4.217303               | -0.774423 | 1.900243  |
| 10               | 6                | 0              | 1.289059                | -0.771506 | -0.085584 |
| 11               | 6                | 0              | 2.274830                | -0.436733 | -1.053734 |
| 12               | 6                | 0              | 1.648739                | -1.829439 | 0.789634  |
| 13               | 6                | 0              | 3.506405                | -1.076467 | -1.134671 |
| 14               | 6                | 0              | 2.867806                | -2.496230 | 0.719783  |
| 15               | 6                | 0              | 3.793190                | -2.106236 | -0.242934 |
| 16               | 1                | 0              | 4.217415                | -0.791037 | -1.899262 |
| 17               | 1                | 0              | 3.094930                | -3.289797 | 1.419805  |
| 18               | 17               | 0              | 1.950800                | 0.761656  | -2.290053 |
| 19               | 17               | 0              | 0.580703                | -2.320804 | 2.093597  |
| 20               | 17               | 0              | -0.574585               | -2.330455 | -2.077100 |
| 21               | 17               | 0              | -1.945114               | 0.772164  | 2.291715  |
| 22               | 17               | 0              | 5.337419                | -2.923138 | -0.335825 |
| 23               | 17               | 0              | -5.338367               | -2.909604 | 0.342930  |
| 24               | 6                | 0              | -0.880410               | 2.148956  | -0.733063 |
| 25               | 6                | 0              | 0.873394                | 2.166022  | 0.718709  |
| 26               | 6                | 0              | -1.888745               | 1.828725  | -1.645944 |
| 27               | 6                | 0              | -0.568134               | 3.501577  | -0.477698 |
| 28               | 6                | 0              | 1.880945                | 1.835360  | 1.628190  |
| 29               | 6                | 0              | 0.547747                | 3.515333  | 0.445310  |
| 30               | 1                | 0              | -2.132357               | 0.801916  | -1.898596 |
| 31               | 6                | 0              | -1.313006               | 4.488696  | -1.124276 |
| 32               | 6                | 0              | 2.578708                | 2.880061  | 2.230697  |
| 33               | 1                | 0              | 2.115741                | 0.807240  | 1.870588  |
| 34               | 6                | 0              | 1.259226                | 4.547810  | 1.063290  |
| 35               | 6                | 0              | -2.317037               | 4.068926  | -1.993259 |
| 36               | 1                | 0              | -1.118734               | 5.545106  | -0.968495 |

|    |   |   |           |          |           |
|----|---|---|-----------|----------|-----------|
| 37 | 6 | 0 | 2.280534  | 4.223281 | 1.950515  |
| 38 | 1 | 0 | 3.368169  | 2.644756 | 2.937948  |
| 39 | 1 | 0 | 1.011812  | 5.584944 | 0.857914  |
| 40 | 1 | 0 | -2.926934 | 4.801991 | -2.516303 |
| 41 | 1 | 0 | 2.845039  | 5.011576 | 2.438236  |
| 42 | 7 | 0 | 0.000489  | 1.322483 | -0.003647 |
| 43 | 7 | 0 | -2.597505 | 2.780374 | -2.258542 |

CzBTM (UB3LYP/6-31G(d))

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | 0.000037                | -0.069737 | -0.000077 |
| 2                | 6                | 0              | -1.285358               | -0.771511 | 0.092015  |
| 3                | 6                | 0              | -1.645172               | -1.832971 | -0.778698 |
| 4                | 6                | 0              | -2.271100               | -0.434724 | 1.059481  |
| 5                | 6                | 0              | -2.863322               | -2.501245 | -0.705615 |
| 6                | 6                | 0              | -3.502058               | -1.075350 | 1.143683  |
| 7                | 6                | 0              | -3.788359               | -2.108751 | 0.256201  |
| 8                | 1                | 0              | -3.090051               | -3.297370 | -1.402842 |
| 9                | 1                | 0              | -4.212993               | -0.787319 | 1.907353  |
| 10               | 6                | 0              | 1.285383                | -0.771541 | -0.092128 |
| 11               | 6                | 0              | 2.271350                | -0.434618 | -1.059335 |
| 12               | 6                | 0              | 1.644973                | -1.833204 | 0.778434  |
| 13               | 6                | 0              | 3.502284                | -1.075305 | -1.143412 |
| 14               | 6                | 0              | 2.863081                | -2.501555 | 0.705446  |
| 15               | 6                | 0              | 3.788346                | -2.108915 | -0.256094 |
| 16               | 1                | 0              | 4.213386                | -0.787161 | -1.906885 |
| 17               | 1                | 0              | 3.089600                | -3.297860 | 1.402537  |
| 18               | 17               | 0              | 1.948431                | 0.769220  | -2.290591 |
| 19               | 17               | 0              | 0.577980                | -2.328602 | 2.082441  |
| 20               | 17               | 0              | -0.578533               | -2.328118 | -2.083084 |
| 21               | 17               | 0              | -1.947832               | 0.768854  | 2.290893  |
| 22               | 17               | 0              | 5.332047                | -2.927679 | -0.353179 |
| 23               | 17               | 0              | -5.332100               | -2.927434 | 0.353424  |
| 24               | 6                | 0              | -0.877819               | 2.157269  | -0.730591 |
| 25               | 6                | 0              | 0.877864                | 2.157261  | 0.730528  |
| 26               | 6                | 0              | -1.879070               | 1.814812  | -1.641133 |
| 27               | 6                | 0              | -0.557262               | 3.508073  | -0.463820 |
| 28               | 6                | 0              | 1.879223                | 1.814748  | 1.640930  |
| 29               | 6                | 0              | 0.557164                | 3.508044  | 0.464013  |
| 30               | 1                | 0              | -2.106937               | 0.783680  | -1.877769 |

|    |   |   |           |          |           |
|----|---|---|-----------|----------|-----------|
| 31 | 6 | 0 | -1.272587 | 4.531034 | -1.091719 |
| 32 | 6 | 0 | 2.582322  | 2.851032 | 2.254031  |
| 33 | 1 | 0 | 2.107210  | 0.783606 | 1.877330  |
| 34 | 6 | 0 | 1.272396  | 4.530965 | 1.092058  |
| 35 | 6 | 0 | -2.290593 | 4.195895 | -1.980775 |
| 36 | 1 | 0 | -1.031601 | 5.571291 | -0.893933 |
| 37 | 6 | 0 | 2.290497  | 4.195835 | 1.980999  |
| 38 | 1 | 0 | 3.368439  | 2.606447 | 2.961842  |
| 39 | 1 | 0 | 1.031253  | 5.571222 | 0.894432  |
| 40 | 1 | 0 | -2.856704 | 4.979454 | -2.474703 |
| 41 | 1 | 0 | 2.856546  | 4.979347 | 2.475040  |
| 42 | 7 | 0 | 0.000065  | 1.323148 | -0.000110 |
| 43 | 6 | 0 | -2.582252 | 2.851124 | -2.254088 |
| 44 | 1 | 0 | -3.368292 | 2.606555 | -2.961990 |

---

### Excited states calculated by TD-DFT calculations

PyID-BTM (UB3LYP/6-31G(d))

Excited State 1: 2.058-A 2.2587 eV 548.92 nm f=0.1113 <S\*\*2>=0.809  
135B ->136B 0.98685

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3791.76162303

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.165-A 2.6204 eV 473.16 nm f=0.0199 <S\*\*2>=0.922  
135A ->137A 0.10657  
136A ->137A 0.59831  
129B ->136B -0.11358  
132B ->136B -0.22771  
134B ->136B 0.70452

Excited State 3: 2.166-A 2.6479 eV 468.23 nm f=0.0335 <S\*\*2>=0.923  
135A ->137A -0.10228  
136A ->137A -0.64970  
129B ->136B 0.20735  
132B ->136B 0.12449  
134B ->136B 0.66944

Excited State 4: 2.343-A 2.9308 eV 423.04 nm f=0.0068 <S\*\*2>=1.122

|             |          |
|-------------|----------|
| 135A ->138A | -0.12850 |
| 136A ->138A | 0.95504  |
| 135B ->138B | 0.19097  |

Excited State 5: 2.116-A 3.0474 eV 406.85 nm f=0.0042 <S\*\*2>=0.870

|             |          |
|-------------|----------|
| 135A ->139A | 0.10352  |
| 136A ->137A | -0.11154 |
| 136A ->139A | 0.82243  |
| 130B ->136B | -0.34260 |
| 131B ->136B | -0.26199 |
| 132B ->136B | -0.26246 |
| 133B ->136B | 0.12017  |

Excited State 6: 2.165-A 3.1313 eV 395.95 nm f=0.0072 <S\*\*2>=0.922

|             |          |
|-------------|----------|
| 136A ->139A | 0.11944  |
| 136A ->140A | 0.62765  |
| 130B ->136B | -0.41158 |
| 131B ->136B | 0.50462  |
| 132B ->136B | 0.23663  |
| 133B ->136B | -0.19623 |

Excited State 7: 2.225-A 3.1547 eV 393.01 nm f=0.0763 <S\*\*2>=0.988

|             |          |
|-------------|----------|
| 136A ->137A | -0.27264 |
| 136A ->139A | -0.17560 |
| 136A ->140A | 0.12933  |
| 136A ->141A | -0.17071 |
| 128B ->136B | 0.21922  |
| 129B ->136B | -0.16111 |
| 131B ->136B | 0.33786  |
| 132B ->136B | -0.39400 |
| 133B ->136B | 0.61122  |

Excited State 8: 2.413-A 3.2020 eV 387.20 nm f=0.0500 <S\*\*2>=1.205

|             |          |
|-------------|----------|
| 129A ->137A | 0.13425  |
| 130A ->139A | 0.10257  |
| 132A ->137A | 0.12829  |
| 134A ->138A | -0.10278 |
| 135A ->141A | -0.10892 |
| 136A ->137A | 0.18207  |
| 136A ->140A | -0.21299 |
| 136A ->141A | -0.35822 |
| 136A ->143A | -0.14821 |
| 128B ->136B | 0.50542  |
| 129B ->136B | 0.10790  |

|             |          |
|-------------|----------|
| 129B ->137B | -0.11443 |
| 130B ->136B | -0.13257 |
| 130B ->139B | -0.11859 |
| 132B ->136B | 0.46928  |
| 132B ->137B | -0.10710 |
| 133B ->136B | 0.15450  |
| 134B ->138B | -0.10550 |

Excited State 9: 2.598-A 3.2707 eV 379.07 nm f=0.0088 <S\*\*2>=1.437

|             |          |
|-------------|----------|
| 134A ->138A | -0.29760 |
| 135A ->144A | 0.12636  |
| 136A ->139A | -0.20777 |
| 136A ->140A | 0.19455  |
| 136A ->141A | 0.15868  |
| 136A ->144A | -0.16098 |
| 128B ->136B | -0.22752 |
| 129B ->136B | -0.16915 |
| 130B ->136B | -0.17253 |
| 131B ->136B | -0.34082 |
| 132B ->136B | 0.18902  |
| 133B ->136B | 0.50508  |
| 134B ->136B | 0.13489  |
| 134B ->138B | -0.30683 |
| 135B ->143B | -0.10496 |

Excited State 10: 2.300-A 3.2824 eV 377.72 nm f=0.0381 <S\*\*2>=1.073

|             |          |
|-------------|----------|
| 134A ->138A | 0.16983  |
| 136A ->137A | 0.12277  |
| 136A ->139A | 0.31891  |
| 136A ->141A | 0.13001  |
| 136A ->144A | 0.10916  |
| 128B ->136B | -0.17982 |
| 129B ->136B | 0.23640  |
| 130B ->136B | 0.40262  |
| 131B ->136B | 0.16409  |
| 132B ->136B | 0.41698  |
| 133B ->136B | 0.49601  |
| 134B ->138B | 0.19457  |

Excited State 11: 2.500-A 3.2979 eV 375.94 nm f=0.0558 <S\*\*2>=1.313

|             |          |
|-------------|----------|
| 134A ->138A | -0.27252 |
| 135A ->144A | 0.10070  |
| 136A ->137A | -0.18082 |
| 136A ->139A | 0.30894  |

|             |          |
|-------------|----------|
| 136A ->140A | -0.11985 |
| 136A ->144A | -0.13334 |
| 129B ->136B | -0.43705 |
| 130B ->136B | 0.47077  |
| 131B ->136B | 0.38846  |
| 133B ->136B | -0.10380 |
| 134B ->138B | -0.26998 |

Excited State 12: 2.161-A 3.3460 eV 370.55 nm f=0.0057 <S\*\*2>=0.918

|             |          |
|-------------|----------|
| 136A ->140A | 0.65462  |
| 136A ->141A | -0.20574 |
| 128B ->136B | 0.21656  |
| 130B ->136B | 0.46002  |
| 131B ->136B | -0.42629 |
| 132B ->136B | -0.10645 |

Excited State 13: 2.519-A 3.4606 eV 358.28 nm f=0.0361 <S\*\*2>=1.336

|             |          |
|-------------|----------|
| 134A ->138A | -0.36943 |
| 129B ->136B | 0.70680  |
| 130B ->136B | 0.14529  |
| 131B ->136B | 0.19234  |
| 132B ->136B | -0.37918 |
| 134B ->138B | -0.28056 |

Excited State 14: 2.603-A 3.6864 eV 336.33 nm f=0.1073 <S\*\*2>=1.444

|             |          |
|-------------|----------|
| 135A ->138A | 0.22476  |
| 136A ->138A | 0.11849  |
| 136A ->140A | 0.11183  |
| 136A ->141A | 0.69635  |
| 136A ->145A | -0.14869 |
| 128B ->136B | 0.35446  |
| 135B ->138B | -0.33681 |

Excited State 15: 3.264-A 3.7781 eV 328.17 nm f=0.0120 <S\*\*2>=2.414

|             |          |
|-------------|----------|
| 128A ->137A | -0.12128 |
| 130A ->139A | -0.25237 |
| 130A ->140A | -0.16486 |
| 131A ->139A | 0.23068  |
| 131A ->140A | -0.24896 |
| 132A ->140A | -0.11717 |
| 135A ->137A | 0.35202  |
| 136A ->137A | -0.15214 |
| 136A ->142A | 0.13720  |
| 128B ->137B | 0.16181  |



|             |          |
|-------------|----------|
| 129B ->136B | 0.28641  |
| 130B ->139B | 0.23213  |
| 130B ->140B | 0.17211  |
| 131B ->139B | -0.22856 |
| 131B ->140B | 0.23438  |
| 132B ->136B | 0.19305  |
| 132B ->140B | 0.10796  |
| 135B ->137B | -0.32915 |

Excited State 16: 3.047-A 3.8100 eV 325.42 nm f=0.0003 <S\*\*2>=2.072

|             |          |
|-------------|----------|
| 129A ->137A | 0.11549  |
| 130A ->139A | 0.20263  |
| 130A ->140A | 0.15012  |
| 131A ->139A | 0.11427  |
| 131A ->140A | -0.15015 |
| 132A ->137A | 0.11632  |
| 135A ->138A | -0.30167 |
| 136A ->138A | -0.16241 |
| 136A ->141A | 0.41006  |
| 136A ->142A | 0.10585  |
| 136A ->143A | -0.16058 |
| 128B ->136B | -0.15329 |
| 129B ->137B | -0.10904 |
| 130B ->139B | -0.20265 |
| 130B ->140B | -0.14348 |
| 131B ->139B | -0.10794 |
| 131B ->140B | 0.15328  |
| 135B ->138B | 0.52873  |

Excited State 17: 2.946-A 3.8375 eV 323.09 nm f=0.0074 <S\*\*2>=1.920

|             |          |
|-------------|----------|
| 130A ->139A | -0.23047 |
| 130A ->140A | -0.16444 |
| 131A ->139A | -0.16207 |
| 131A ->140A | 0.21096  |
| 132A ->139A | -0.10399 |
| 135A ->138A | -0.20607 |
| 136A ->138A | -0.12945 |
| 136A ->141A | 0.20783  |
| 136A ->142A | 0.16198  |
| 128B ->136B | 0.51915  |
| 129B ->137B | 0.13073  |
| 130B ->139B | 0.20687  |
| 130B ->140B | 0.14148  |
| 131B ->139B | 0.13237  |

|             |          |
|-------------|----------|
| 131B ->140B | -0.19037 |
| 132B ->137B | 0.11099  |
| 132B ->139B | 0.10418  |
| 135B ->138B | 0.37038  |

Excited State 18: 2.157-A 3.8467 eV 322.31 nm f=0.0059 <S\*\*2>=0.913  
136A ->142A 0.95237  
135B ->138B -0.12607

Excited State 19: 2.749-A 3.9669 eV 312.55 nm f=0.0132 <S\*\*2>=1.640  
133A ->138A 0.11395  
134A ->138A -0.17903  
135A ->144A -0.16330  
136A ->143A -0.14024  
136A ->144A 0.75931  
129B ->136B -0.12374  
129B ->138B -0.10879  
133B ->138B -0.12493  
134B ->138B -0.38945  
135B ->143B 0.18108  
135B ->144B 0.12614

Excited State 20: 2.286-A 4.0051 eV 309.56 nm f=0.0191 <S\*\*2>=1.056  
135A ->141A -0.10015  
136A ->143A 0.89751  
136A ->144A 0.11885  
136A ->145A -0.11633  
128B ->136B 0.12757  
135B ->138B 0.14422

CzBTM (UB3LYP/6-31G(d))

Excited State 1: 2.054-A 2.1841 eV 567.66 nm f=0.0884 <S\*\*2>=0.805  
134B ->136B 0.98732

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3775.72796568

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.071-A 2.2525 eV 550.44 nm f=0.0000 <S\*\*2>=0.822  
135B ->136B 0.98789

Excited State 3: 2.189-A 2.5933 eV 478.10 nm f=0.0459 <S\*\*2>=0.948  
134A ->137A 0.14669

|             |          |
|-------------|----------|
| 136A ->137A | 0.89734  |
| 130B ->136B | 0.26852  |
| 133B ->136B | -0.16207 |

Excited State 4: 2.101-A 2.9832 eV 415.61 nm f=0.0015 <S\*\*2>=0.854

|             |          |
|-------------|----------|
| 134A ->138A | 0.11167  |
| 136A ->138A | 0.92344  |
| 132B ->136B | -0.32141 |

Excited State 5: 2.143-A 3.0405 eV 407.78 nm f=0.0000 <S\*\*2>=0.898

|             |          |
|-------------|----------|
| 136A ->139A | 0.91110  |
| 131B ->136B | -0.34298 |

Excited State 6: 2.647-A 3.1103 eV 398.62 nm f=0.0219 <S\*\*2>=1.501

|             |          |
|-------------|----------|
| 134A ->144A | 0.14277  |
| 135A ->139A | -0.17378 |
| 135A ->140A | 0.26257  |
| 136A ->137A | 0.19986  |
| 136A ->144A | -0.17897 |
| 133B ->136B | 0.74607  |
| 134B ->144B | -0.15845 |
| 135B ->136B | -0.11875 |
| 135B ->139B | 0.24022  |
| 135B ->140B | -0.26009 |

Excited State 7: 2.456-A 3.2077 eV 386.53 nm f=0.0174 <S\*\*2>=1.258

|             |          |
|-------------|----------|
| 130A ->137A | -0.21617 |
| 131A ->139A | 0.12243  |
| 132A ->138A | 0.13538  |
| 133A ->137A | 0.10581  |
| 134A ->141A | 0.13970  |
| 136A ->139A | 0.11707  |
| 136A ->141A | 0.46339  |
| 136A ->143A | -0.22438 |
| 129B ->136B | 0.58891  |
| 130B ->137B | 0.18681  |
| 131B ->136B | 0.33716  |
| 131B ->139B | -0.11120 |
| 132B ->138B | -0.14590 |

Excited State 8: 2.364-A 3.2322 eV 383.59 nm f=0.0027 <S\*\*2>=1.147

|             |          |
|-------------|----------|
| 134A ->139A | 0.12685  |
| 136A ->139A | -0.23116 |
| 136A ->140A | 0.79280  |

|             |          |
|-------------|----------|
| 129B ->136B | 0.15053  |
| 131B ->136B | -0.42694 |
| 134B ->139B | -0.14819 |
| 134B ->140B | 0.13510  |

Excited State 9: 2.816-A 3.2399 eV 382.67 nm f=0.0716 <S\*\*2>=1.733

|             |          |
|-------------|----------|
| 134A ->137A | 0.12109  |
| 134A ->144A | 0.10699  |
| 135A ->139A | -0.23072 |
| 135A ->140A | 0.34293  |
| 136A ->137A | -0.28865 |
| 136A ->138A | -0.15064 |
| 136A ->144A | -0.12932 |
| 130B ->136B | 0.44110  |
| 132B ->136B | -0.31511 |
| 133B ->136B | -0.32940 |
| 134B ->144B | -0.12483 |
| 135B ->139B | 0.27565  |
| 135B ->140B | -0.29377 |

Excited State 10: 2.211-A 3.3156 eV 373.95 nm f=0.0129 <S\*\*2>=0.973

|             |          |
|-------------|----------|
| 135A ->139A | -0.10505 |
| 135A ->140A | 0.15097  |
| 136A ->138A | 0.30309  |
| 130B ->136B | 0.18454  |
| 132B ->136B | 0.85729  |
| 133B ->136B | -0.21690 |
| 135B ->140B | -0.10231 |

Excited State 11: 2.190-A 3.3541 eV 369.65 nm f=0.0040 <S\*\*2>=0.949

|             |          |
|-------------|----------|
| 136A ->139A | 0.25329  |
| 136A ->140A | 0.49768  |
| 136A ->141A | -0.21467 |
| 129B ->136B | -0.18267 |
| 131B ->136B | 0.73733  |
| 134B ->139B | -0.10590 |

Excited State 12: 2.466-A 3.3724 eV 367.64 nm f=0.0601 <S\*\*2>=1.270

|             |          |
|-------------|----------|
| 134A ->137A | 0.14768  |
| 135A ->139A | 0.19156  |
| 135A ->140A | -0.27042 |
| 136A ->137A | -0.19760 |
| 130B ->136B | 0.70578  |
| 133B ->136B | 0.45666  |

|             |          |
|-------------|----------|
| 135B ->139B | -0.16160 |
| 135B ->140B | 0.16693  |

Excited State 13: 2.427-A 3.6766 eV 337.23 nm f=0.0692 <S\*\*2>=1.222

|             |          |
|-------------|----------|
| 130A ->137A | 0.12752  |
| 132A ->138A | -0.10981 |
| 133A ->144A | -0.10316 |
| 136A ->140A | 0.11110  |
| 136A ->141A | 0.79650  |
| 136A ->143A | 0.16766  |
| 136A ->145A | 0.13152  |
| 129B ->136B | -0.32267 |
| 131B ->139B | 0.10274  |
| 132B ->138B | 0.12430  |

Excited State 14: 3.132-A 3.7491 eV 330.71 nm f=0.0163 <S\*\*2>=2.202

|             |          |
|-------------|----------|
| 131A ->138A | -0.29335 |
| 132A ->139A | -0.23860 |
| 132A ->140A | -0.12681 |
| 134A ->137A | -0.35155 |
| 136A ->137A | 0.11616  |
| 136A ->142A | -0.31157 |
| 129B ->137B | -0.14822 |
| 130B ->136B | 0.37062  |
| 131B ->138B | 0.27276  |
| 132B ->139B | 0.20430  |
| 132B ->140B | 0.15272  |
| 133B ->136B | -0.11239 |
| 134B ->137B | 0.42153  |

Excited State 15: 2.252-A 3.7625 eV 329.52 nm f=0.0018 <S\*\*2>=1.018

|             |          |
|-------------|----------|
| 134A ->137A | -0.16884 |
| 136A ->142A | 0.92959  |
| 134B ->137B | 0.13475  |

Excited State 16: 3.044-A 3.8397 eV 322.90 nm f=0.0131 <S\*\*2>=2.066

|             |          |
|-------------|----------|
| 130A ->137A | 0.17200  |
| 130A ->138A | -0.13171 |
| 131A ->139A | -0.31759 |
| 131A ->140A | -0.16533 |
| 132A ->138A | -0.35148 |
| 136A ->145A | -0.10333 |
| 129B ->136B | 0.54649  |
| 130B ->137B | -0.20330 |

|             |          |
|-------------|----------|
| 131B ->139B | 0.25842  |
| 131B ->140B | 0.18987  |
| 132B ->138B | 0.32369  |
| 133B ->137B | 0.11045  |
| 134B ->139B | -0.11554 |

Excited State 17: 2.666-A 3.9067 eV 317.36 nm f=0.0105 <S\*\*2>=1.527

|             |          |
|-------------|----------|
| 129A ->140A | -0.10552 |
| 133A ->144A | 0.15633  |
| 134A ->139A | 0.13370  |
| 134A ->140A | -0.15597 |
| 134A ->141A | 0.13439  |
| 136A ->140A | -0.15509 |
| 136A ->141A | 0.14815  |
| 136A ->143A | 0.70734  |
| 136A ->145A | -0.11518 |
| 128B ->136B | -0.14821 |
| 132B ->138B | -0.10784 |
| 133B ->144B | -0.14286 |
| 134B ->139B | -0.29648 |
| 134B ->140B | 0.22305  |
| 134B ->141B | -0.12021 |
| 135B ->146B | 0.10144  |

Excited State 18: 2.364-A 3.9699 eV 312.31 nm f=0.0229 <S\*\*2>=1.147

|             |          |
|-------------|----------|
| 134A ->140A | 0.10508  |
| 136A ->141A | -0.12410 |
| 136A ->143A | 0.50171  |
| 128B ->136B | 0.63496  |
| 129B ->136B | 0.26711  |
| 134B ->139B | 0.30262  |
| 134B ->140B | -0.22844 |

Excited State 19: 2.750-A 3.9980 eV 310.11 nm f=0.0066 <S\*\*2>=1.641

|             |          |
|-------------|----------|
| 134A ->144A | -0.18977 |
| 136A ->144A | 0.78281  |
| 133B ->136B | 0.12091  |
| 133B ->139B | 0.11049  |
| 133B ->140B | -0.11690 |
| 134B ->144B | 0.26613  |
| 135B ->139B | 0.30040  |
| 135B ->140B | -0.24942 |

Excited State 20: 2.867-A 4.0049 eV 309.58 nm f=0.0003 <S\*\*2>=1.805

|             |          |
|-------------|----------|
| 134A ->139A | 0.10012  |
| 134A ->140A | -0.12709 |
| 135A ->137A | 0.85655  |
| 135A ->144A | -0.11008 |
| 136A ->140A | -0.11693 |
| 136A ->143A | -0.17630 |
| 128B ->136B | 0.28837  |
| 134B ->139B | -0.20484 |
| 134B ->140B | 0.15518  |