Electronic Supplementary Information

Regulation of singlet and triplet excitons in a single emission layer: Efficient fluorescent/phosphorescent hybrid white organic light-emitting diodes

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SI-I: Solvatochromism for HLCT character- Lippert-Mataga plot

The solvatochromic effect using Lippert-Mataga plot has been displayed in Figure 3 (Tables S1 & S2). When solvent polarity was increased the blue emitters exhibit a larger red shift which supports charge transfer in these molecules. The properties of ground state ($S_0$) and the lowest singlet excited state ($S_1$) can be better understood through solvatochromic experiment. We use the Lippert-Mataga equation to explore the influence of solvent environment on the optical property of our materails, the model can describes the interaction between the solvent and the dipole moment of solute:

$$hc(\tilde{\nu}_a - \tilde{\nu}_f) = hc(\tilde{\nu}^{vac}_a . hc \tilde{\nu}^{vac}_f) + 2 (\mu_e - \mu_g)^2 / \alpha_0^2 f(\varepsilon, n)$$

where $f$ is the orientational polarizability of the solvent, $\tilde{\nu}_a . \tilde{\nu}_f$ 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, derived from the Avogadro number ($N$), molecular weight ($M$), and density ($d = 1.0 \text{ g cm}^{-3}$); $\varepsilon$ and $n$ are the solvent dielectric and the solvent refractive index, respectively; $f(\varepsilon, n)$ and $a$ can be calculated respectively as follows:

$$f(\varepsilon, n) = [(\varepsilon - 1/2 \varepsilon + 1) - \frac{1}{2} (n^2 - 1/2n^2 + 1)]$$

$$a = (3M / 4N\pi d)^{1/3}$$

The relationships between stokes shift and solvent polarity are presented in Figure 3. The ground state dipole ($\mu_g$) of blue emitting materials, DDIBNPPi and DDIBPPI could be estimated from density functional theory (DFT) calculation as, 4.67 and 8.5 D, respectively which is attributed by local exciton (LE) transition and $\mu_e$ in high polar solvents is 23.9 and 24.1 D, respectively. The non-linear correlation of Stokes shift $\nu_s$ solvent polarity function reveal that there is transformation of fitted line between ethyl ether and methylene chloride: non-linear correlation supports the presence of both locally excited state (LE) and charge transfer excited state (CT).
**Figure S1** Solvatochromic a) absorption and b) emission spectra of DDIBNPPI and DDIBPPIN.

**SI-II: Potential energy scan (PES)**

The ground ($S_0$) and excited ($S_1$) state geometries of DDIBNPPI and DDIBPPIN were optimized with DFT/B3LYP/6–31G (d, p) and TD-DFT/B3LYP/6-31G (d, p) methods, respectively, using Gaussian-09 (Figure S2). The three key twist angles ($θ^o$): PPI-$θ^o$ (between phenanthrimidazole core and styryl spacer, LIN-$θ^o$ (between styryl linker and phenyl linker) and DPI-$θ^o$ (between diphenyl imidazole and phenyl linker) play a key role in electron overlap of frontier molecular orbitals in ground and excited states. The ground and excited state energy of DDIBNPPI and DDIBPPIN reveal that
PPI-θ° was limited at room temperature (13.3 eV and 14.5 eV) (DDIBNPPI 65.8°/69.3°: DDIBPPIN-74.6°/77.2°); LIN-θ° (DDIBNPPI-70.1°/73.4°: DDIBPPIN-76.8°/79.1°); DPI-θ° (DDIBNPPI-86.7°/89.8°: DDIBPPIN-98.7°/99.1°) and rises steeply when the twist angle was out of this range (Figure S2). The larger twist angle (DPI-θ°) of DDIBPPIN compared to DDIBNPPI is due to the stronger repulsion between the bulky substituent at azomethine nitrogen of diphenyl imidazole fragment with linker fragment. The excited state (S₁) twist angles, PPI-θ°, LIN-θ° and DPI-θ° of DDIBNPPI and DDIBPPIN are increased compared to ground state (S₀) twist angles. Only small change in geometry of DDIBPPIN from S₀→S₁ was observed compared to DDIBNPPI, which facilitate the suppression of non-radiation for the enhancement of ηPL.¹ From the potential energy surface of the twisted geometry of DDIBPPIN at ground and excimer at excited states (Figure S3) reveal that the DDIBPPIN needs very small relaxation energy to form excimer of excited state corresponding to slightly increased interplanar separation of PPI from linker fragment (1.34 Å to 1.35Å: 98.7° to 99.1°: Figure. S3) and then only small energy needs to return to equilibrium geometry at ground state. At this point, the DDIBPPIN with rigid geometry from initial state to excimer indicating that the minimized non-radiative energy dissipation contributes to the enhanced emission. Hence, the lifetime of excitons are increased due to the suppression of non-radiative pathway and DDIBPPIN shows higher photoluminescence efficiency.³⁶
Figure S2 Molecular structure, ground and excited state geometries with dihedral angles of DDIBNPP and DDIBPPIN.
**Figure S3** Potential energy surface scan (PES) diagram of (a) DDIBNPPI and (b) DDIBPPIN.

**SI-III: Charge–Transfer indexes**

The excited state properties of DDIBNPPI and DDIPPIN were discussed briefly in SI-III: charge-transfer indexes (Figure S4-S7).

The hole–particle pair interactions have been related to the distance covered during the excitations one possible descriptor $\Delta r$ intex could be used to calculate the average distance which is weighted in function of the excitation coefficients.

$$\Delta r = \frac{\sum_{i} k_{i}^{2} |\langle \phi_{i} | r | \phi_{i} \rangle - \langle \phi_{i} | r | \phi_{i} \rangle|}{\sum_{i} k_{i}^{2}} \quad \text{.................. (S1)}$$

where $|\langle \phi_{i} | r | \phi_{i} \rangle|$ is the norm of the orbital centroid. $\Delta r$–index will be expressed in Å.
The density variation associated to the electronic transition is given by

\[ \Delta \rho(r) = \rho_{EX}(r) - \rho_{GS}(r) \]  

(S2)

where \( \rho_{GS}(r) \) and \( \rho_{EX}(r) \) are the electronic densities of to the ground and excited states, respectively. Two functions, \( \rho_+(r) \) and \( \rho_-(r) \), correspond to the points in space where an increment or a depletion of the density upon absorption is produced and they can be defined as follows:

\[
\rho_+(r) = \begin{cases} 
\Delta \rho(r) & \text{if } \Delta \rho(r) > 0 \\
0 & \text{if } \Delta \rho(r) < 0
\end{cases}
\]  

(S3)

\[
\rho_-(r) = \begin{cases} 
\Delta \rho(r) & \text{if } \Delta \rho(r) < 0 \\
0 & \text{if } \Delta \rho(r) > 0
\end{cases}
\]  

(S4)

The barycenters of the spatial regions \( R_+ \) and \( R_- \) are related with \( \rho_+(r) \) and \( \rho_-(r) \) and are shown as

\[
R_+ = \frac{\int \rho_+(r) dr}{\int \rho_+(r) dr} = (x_+, y_+, z_+) 
\]  

(S5)

\[
R_- = \frac{\int \rho_-(r) dr}{\int \rho_-(r) dr} = (x_-, y_-, z_-) 
\]  

(S6)

The spatial distance (\( D_{CT} \)) between the two barycenters \( R_+ \) and \( R_- \) of density distributions can thus be used to measure the CT excitation length

\[
D_{CT} = |R_+ - R_-| 
\]  

(S7)

The transferred charge (\( q_{CT} \)) can be obtained by integrating over all space \( \rho_+ (r) \). Variation in dipole moment between the ground and the excited states (\( \mu_{CT} \)) can be computed by the following relation:

\[
\| \mu_{CT} \| = D_{CT} \int \rho_+(r) dr = D_{CT} \int \rho_-(r) dr 
\]  

(S8)

\[
= D_{CT} q_{CT} 
\]  

(S9)

The difference between the dipole moments \( \| \mu_{CT} \| \) have been computed for the ground and the excited states \( \Delta \mu_{ES-GS} \). The two centroids of charges (\( C^+/C^- \)) associated to the positive and
negative density regions are calculated as follows. First the root–mean–square deviations along the three axis \((\sigma_{aj}, j = x, y, z; a = + \text{ or } -)\) are computed as

\[
\sigma_{aj} = \sqrt{\frac{\sum p_a(r)}{\sum \rho_a(r_i)}} \quad \text{................................ (S10)}
\]

The two centroids \((C_+ \text{ and } C_-)\) are defined as

\[
C_+(r) = A_+ e\left(-\frac{(x-x_+)^2}{2\sigma_{1x}^2} - \frac{(y-y_+)^2}{2\sigma_{1y}^2} - \frac{(z-z_+)^2}{2\sigma_{1z}^2}\right) \quad \text{.................. (S11)}
\]

\[
C_-(r) = A_- e\left(-\frac{(x-x_-)^2}{2\sigma_{1x}^2} - \frac{(y-y_-)^2}{2\sigma_{1y}^2} - \frac{(z-z_-)^2}{2\sigma_{1z}^2}\right) \quad \text{.................. (S12)}
\]

The normalization factors \((A_+ \text{ and } A_-)\) are used to impose the integrated charge on the centroid to be equal to the corresponding density change integrated in the whole space:

\[
A_+ = \frac{\int \rho_+(r) dr}{\int e(-\frac{(x-x_+)^2}{2\sigma_{1x}^2} - \frac{(y-y_+)^2}{2\sigma_{1y}^2} - \frac{(z-z_+)^2}{2\sigma_{1z}^2}) dr} \quad \text{.................. (S13)}
\]

\[
A_- = \frac{\int \rho_-(r) dr}{\int e(-\frac{(x-x_-)^2}{2\sigma_{1x}^2} - \frac{(y-y_-)^2}{2\sigma_{1y}^2} - \frac{(z-z_-)^2}{2\sigma_{1z}^2}) dr} \quad \text{.................. (S14)}
\]

H index is defined as half of the sum of the centroids axis along the D–A direction, if the D–A direction is along the X axis, H is defined by the relation:

\[
H = \frac{\sigma_{+x} + \sigma_{-x}}{2} \quad \text{.................. (S15)}
\]

The centroid along X axis is expected. The \(t\) index represents the difference between \(D_{CT}\) and H:

\[
t = D_{CT} - H \quad \text{................. (S16)}
\]
Figure S4 Natural transition orbital pairs with (HONTOs and LUNTOs) transition character analysis for singlet states ($S_1$-$S_{10}$) and triplet states ($T_1$-$T_{10}$) of DDIBNPPI [$f$-oscillator strength and % weights of hole-particle].
Figure S5 Natural transition orbital pairs with (HONTOs and LUNTOs) transition character analysis for singlet states ($S_1$-$S_{10}$) and triplet states ($T_1$-$T_{10}$) of DDIBPPIN [$f$-oscillator strength and % weights of hole-particle].
Figure S6: Hole and particle distribution [S₁–S₄ states: green- increasing electron density and blue-decreasing electron density] and Computed contour plots of transition density matrices (TDM) of DDIBNPI for [S₁–S₄ states: density=transition=n /Op(6/8=3)].
Figure S7 Hole and particle distribution [S₁–S₄ states: green - increasing electron density and blue - decreasing electron density and Computed contour plots of transition density matrices (TDM) of DDIBPPIN for [S₁–S₄ states: density=transition=n /IOp(6/8=3)].
Figure S8 $^1$H NMR spectrum of (E)-2-(2-4-(1-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-4,5-diphenyl-H-imidazole-2-yl)-[1,1-biphenyl]-4-yl)vinyl-1-yl(naphthalene-1-yl)-1H-phenanthro[9,10-d]imidazole (DDIBNPPPI)

Figure S9 $^{13}$C NMR spectrum of (E)-2-(2-4-(1-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-4,5-diphenyl-H-imidazole-2-yl)-[1,1-biphenyl]-4-yl)vinyl-1-yl(naphthalene-1-yl)-1H-phenanthro[9,10-d]imidazole (DDIBNPPPI)
**Figure S10** $^1$H NMR spectrum of (E)-4-(2-(2-(-4'-1(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-4,5-diphenyl-1H-imidazole-2-yl)-[1,1'-biphenyl]-4-yl)vinyl)-1H-phenanthro[9,10-d]imidazole-1-yl)-1-naphthonitrile(DDIBPPIN)

![NMR spectrum](image1)

**Figure S11** $^{13}$C NMR spectrum of (E)-4-(2-(2-(-4'-1(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-4,5-diphenyl-1H-imidazole-2-yl)-[1,1'-biphenyl]-4-yl)vinyl)-1H-phenanthro[9,10-d]imidazole-1-yl)-1-naphthonitrile(DDIBPPIN)

![NMR spectrum](image2)
Figure S12 MALDI-TOF mass spectra of DDINPPI (a) and DDIBPIN (b).
Table S1 Photophysical properties of DDIBNPPI in different solvents.

| Solvents           | $\varepsilon$ | $n$  | $f(\varepsilon,n)$ | ET(30) | $\lambda_{ab}$ (nm) | $\nu_{ab}$ (cm$^{-1}$) | $\lambda_{flu}$ (nm) | $\nu_{flu}$ (cm$^{-1}$) | $\nu_{ss}$ (cm$^{-1}$) | $\Delta G$ (kcal/mol) | $\Delta(\Delta G_{hex}-\Delta G_{sol})$ (kcal/mol) | $\lambda$ (kcal/mol) |
|-------------------|---------------|------|---------------------|--------|----------------------|-------------------------|----------------------|-------------------------|------------------------|----------------------|-------------------------------------------------|-----------------------|
| Hexane            | 1.88          | 1.37 | 0.000411            | 32.4   | 204                  | 49019.61                | 371                  | 26954.18                | 21065.43               | 108.59               | -26.07                                           | 31.54                 |
| dioxane           | 2.22          | 1.42 | 0.021437            | 36.0   | 214                  | 46728.97                | 392                  | 25510.2                 | 20218.77               | 103.25               | -20.73                                           | 30.33                 |
| Carbon tetrachloride | 2.23       | 1.46 | 0.011075            | 39.1   | 221                  | 45248.87                | 384                  | 26041.67                | 18207.2                | 101.89               | -19.37                                           | 27.45                 |
| Benzene           | 2.28          | 1.42 | 0.026639            | 34.3   | 229                  | 43668.12                | 394                  | 25380.71                | 19287.41               | 98.69                | -16.17                                           | 26.14                 |
| Chloroform        | 4.81          | 1.44 | 0.148262            | 39.1   | 235                  | 42553.19                | 424                  | 23584.91                | 18105.98               | 94.53                | -12.01                                           | 27.11                 |
| ethyl acetate     | 6.09          | 1.41 | 0.186569            | 38.1   | 242                  | 41322.31                | 428                  | 23364.49                | 18065.94               | 92.45                | -9.93                                            | 25.67                 |
| THF               | 7.52          | 1.40 | 0.209634            | 37.4   | 248                  | 40322.58                | 430                  | 23255.81                | 18405.42               | 90.87                | -8.35                                            | 24.39                 |
| dichloromethane   | 9.08          | 1.42 | 0.218349            | 40.7   | 251                  | 39840.64                | 430                  | 23255.81                | 19067.33               | 90.18                | -7.66                                            | 23.70                 |
| acetonitrile      | 37.5          | 1.34 | 0.305378            | 45.6   | 256                  | 39062.5                 | 439                  | 22779.04                | 20011.24               | 88.39                | -5.87                                            | 23.27                 |
Table S2 Photophysical properties of DDIBPPIN in different solvents.

| Solvents       | ε    | n    | f(ε,n)     | ET(30) | λ_{ab} (nm) | ν_{ab} (cm^{-1}) | λ_{flu} (nm) | ν_{flu} (cm^{-1}) | ν_{ss} (cm^{-1}) | ΔG (kcal/mol) | Δ(ΔG_{hex}-ΔG_{sol}) (kcal/mol) | λ (kcal/mol) |
|----------------|------|------|------------|--------|-------------|------------------|-------------|------------------|-----------------|---------------|-------------------------------|--------------|
| Hexane         | 1.88 | 1.37 | 0.000411   | 32.4   | 215         | 46511.63         | 384         | 26041.67         | 20469.96        | 103.70        | -21.18                         | 29.26        |
| dioxane       | 2.22 | 1.42 | 0.021437   | 36.0   | 220         | 45454.55         | 392         | 25510.20         | 18944.34        | 101.43        | -18.91                         | 28.51        |
| Carbon tetrachloride | 2.23 | 1.46 | 0.011075   | 39.1   | 226         | 44247.79         | 384         | 26041.67         | 20206.12        | 100.46        | -17.94                         | 26.02        |
| Benzene       | 2.28 | 1.42 | 0.026639   | 34.3   | 230         | 43478.26         | 394         | 25380.71         | 19209.99        | 98.42         | -15.90                         | 25.87        |
| Chloroform    | 4.81 | 1.44 | 0.148262   | 39.1   | 237         | 42194.09         | 400         | 25000.00         | 17800.46        | 96.04         | -13.52                         | 24.57        |
| ethyl acetate | 6.09 | 1.41 | 0.186569   | 38.1   | 241         | 41493.78         | 404         | 24752.48         | 19704.76        | 94.68         | -12.16                         | 23.93        |
| THF           | 7.52 | 1.40 | 0.209634   | 37.4   | 245         | 40816.33         | 406         | 24630.54         | 19207.51        | 93.54         | -11.02                         | 23.13        |
| dichloromethane | 9.08 | 1.42 | 0.218349   | 40.7   | 249         | 40160.64         | 420         | 23809.52         | 19561.41        | 91.43         | -8.91                          | 23.37        |
| acetonitrile  | 37.5 | 1.34 | 0.305378   | 45.6   | 254         | 39370.08         | 411         | 24330.90         | 20701.12        | 91.04         | -8.52                          | 21.49        |