Supporting Information

For

Efficient and thermally stable non-doped red OLEDs based on a “bird-like” donor-acceptor fluorophore with aggregation induced emission enhancement and intramolecular charge transfer

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Experimental Details:

Materials:
All the solvents for UV and FL analyses were used as spectroscopic grade. Column chromatography was performed on silica gel (100-200 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel F-254 plates (0.25 mm, E. Merck). Phenothiazine, 2-Ethylhexylbromide, Methyl 6-bromo-2-naphthoate, Sodium cyanide, DIBAL-H (1 M in heptanes), 9,9-dihexylfluorene and tetrakis-triphenylphosphine) palladium(0) were purchased from Sigma Aldrich and used as received for the synthesis of monomer and copolymers.

Instrumentation:
\textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a 400 MHz Bruker spectrophotometer using CDCl\textsubscript{3} with tetramethylsilane (TMS, d = 0) as the internal standard. Mass spectra were recorded on a MALDI-mass Bruker ultraflextreme spectrometer by using a 4-HCCA (a-cyano-4-hydroxycinnamic acid) matrix. Elemental analysis was carried out using a Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer.
Fourier transform infrared (FT-IR) spectra of the compounds were recorded on an ABB BOMEM MB3000 spectrometer using KBr pellets. UV-visible absorbance spectra were recorded on a Varian Cary 50 Bio UV-visible spectrophotometer. Fluorescence spectra of the monomer and copolymers were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Cyclic voltammetry measurements were done using CHI 600D electrochemical work stations using Ag/AgCl, platinum disc and platinum wire as reference, working and counter-electrodes respectively. Cyclic voltammetry was performed by coating a thin layer of PTNAA luminogen on a platinum disc electrode and measurements were performed in acetonitrile medium with tetrabutylammonium hexafluorophosphate (0.1 M [Bu₄N] PF₆) as a supporting electrolyte. Dynamic light scattering (DLS) experiments were performed on a Malvern, DLS instrument. Fluorescence lifetime experiments were conducted on EDINBURGH (UK) and FLS 980 TCSPC instruments. Atomic force micrographs (AFM) were obtained on a RUSSIA model: NTEGRA PRIMA instrument under ambient conditions using NT-MDT solver software for analysis, Ireland. The high resolution scanning electron microscopy (HRSEM) analysis were performed using HITACHI S-4800. Samples for AFM and SEM were prepared by spin coating 300 microliters of the chloroform solution (2 mg mL⁻¹) and over the surface area of 1.8 cm² of an ITO coated glass substrate to simulate the end use device conditions. The absolute quantum yield of PTNAA was collected by measuring the total light output in all directions in an integrating sphere using EDINBURGH (UK) and FLS 980 TCSPC instruments. GIXRD studies were performed on films of the PTNAA coated on ITO substrates using a Bruker AX D8 advance X-ray diffractometer with a Cu Ka wavelength of 1.5406 Å. Density functional theory (DFT) calculations were performed using the B3LYP functional. The basis set used for the C, H, and N atoms was 6-31 Gs.

**OLEDs fabrication and measurement:** OLEDs of PNAA were fabricated using indium tin oxide (ITO) with a sheet resistance of 10 Ω square⁻¹. The substrates were cleaned by a series of ultrasonic processing with acetone, detergent, and deionized water in an ultrasonic solvent bath. After cleaning in the solvent bath they were then baked in a heating chamber at 120 °C and treated with oxygen plasma for 25 min before use. The PEDOT-PSS (10–40 nm) solution was spin-coated on cleaned ITO substrates and baked
in a heating chamber at 200 °C for one hour. After the above process 300 mL of PTNAA in CHCl₃ (solution with 1 mg/mL concentration) were spin-coated at 2000 rpm for 60 seconds to get uniform film (with thickness 100–150 nm) and the aluminium was coated at 105 Torr. Current–voltage (I–V) characteristics were studied using a Keithley 2400 sourcemeter. Luminescence–voltage (L–V) characteristics of the OLEDs were performed using a NUCLEONIX type 168 PMT housing with drawer assembly. Electroluminescence spectra of the OLEDs were further measured using a Carey Eclipse fluorescence spectrophotometer. Commission Internationale de l’Eclairage (CIE) color coordinate values of the thin films of the LEDs were standardized using a Konica Minolta CS-100 Chromameter in automated mode.

**Synthesis procedure of PTNAA monomer:**

![Synthetic route to AIE monomer of PTNAA](image)

**Scheme 1** Synthetic route to AIE monomer of PTNAA (i) DIBAL-H in THF, 0 to 25 °C, for 12 hr; (ii) SOCl₂, ZnCl₂, DME, 0 °C for 2 hrs and then RT for 12 hrs; (iii) NaCN, aq CH₃CN, reflux for 12 hrs...
(iv) Ethylhexyl-bromide, DMF, NaH stirred for 12 hrs at RT; (v) 1,2-dichloroethane, POCl₃, DMF reflex for 12 hrs; (vi) KOT-Bu/methanol, for 24 hrs at RT.

(6-bromonaphthalen-2-yl) methanol: (NA-OH)

To a completely-dried 250 mL, round bottom flask was added methyl 6-bromo-2-naphthoate (10 g, 3.8 x 10⁻² mol) and anhydrous THF (50 mL) under a nitrogen atmosphere. The solution was cooled to 0 °C and slowly charged into a solution of DIBAL-H (1 M in heptane, 13.5 mL (11.38 g), 8.0 x 10⁻² mol) was added dropwise to the reaction mixture. The reaction mixture was heated up to room temperature and agitated overnight. The reaction mixture was quenched slowly by pouring into a HCl (4N aq. 30 mL) at 0 °C. The reaction mixture was stirred for 45 min and the organic layer was separated using separating funnel. The organic layer was washed with HCl (4N aq. 20 mL), NaHCO₃ (5% aq. 75 mL), and washed with brine solution (50 mL). The organic layer was concentrated over MgSO₄, filtrated by Celite and concentrated to dryness. EtOAc (10 mL) and hexanes (80 mL) were added to the resultant product. Filtration by filter paper and drying under vacuum gave (NA-OH) as a white solid (~ 8.45 g, 3.58 x 10⁻² mol, yield = 94%). Spectral data for (NA-OH):

¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.71 – 7.58 (m, 3H), 7.44 (dd, J = 22.3, 8.6, 1.7 Hz, 2H), 4.76 (s, 2H), 1.72 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.84, 132.96, 130.78, 128.76, 128.56, 128.51, 126.39, 125.14, 124.26, 118.81, 64.22. Elemental analysis: Calculated (%) for C₁₁H₉BrO: C, 55.72; H, 3.83, Br, 33.70; Found: C, 54.97; H, 3.78; Br, 33.69.
Figure S1 $^1$H and $^{13}$C NMR spectrum of NA-OH
2-bromo-6-(chloromethyl) naphthalene: (NA-Cl)

To a 250 mL round bottom flask was added (6- bromonaphthalen-2-yl) methanol (NA-OH) (5.212 x 10^{-2} mol), ZnCl\(_2\) (115 mg, 0.085 x 10^{-2} mol) and DME (70 mL). The reaction mixture was cooled to 0°C and SOCl\(_2\) (3.1 mL (5g), 4.24 x 10^{-2} mol) was slowly added. The resulting mixture was stirred at 0°C for 2 hours, and then at room temperature overnight. The solvent was removed by rotary evaporation. Hexanes (100 mL) were added to the crude product. Filtration by filter paper and drying under vacuum gave NA-Cl as a white solid (5.14 g, 2.0 x 10^{-2} mol, yield = 95%). Spectral data for NA-Cl:

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (s, 1H), 7.74 – 7.60 (m, 3H), 7.48 (m, \(J = 16.3, 8.6, 1.7\) Hz, 2H), 4.66 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 134.33, 133.11, 130.57, 128.88, 128.80, 128.57, 126.77, 126.41, 126.30, 119.52, 45.26. Elemental analysis: Calculated (%) for C\(_{11}\)H\(_8\)BrCl: C, 51.70; H, 3.16, Br, 31.27; Found: C, 51.43; H, 3.21; Br, 31.19.
Figure S2 $^1$H and $^{13}$C NMR spectrum of NA-Cl.
2-(6-bromonaphthalen-2-yl)acetonitrile (NA-CN) (1):

To a 250 mL round bottom flask was added 2-bromo-6-(chloromethyl)naphthalene (NA-Cl) (5 g, 1.95 \times 10^{-2} \text{mol}) and NaCN (1.15 g, 2.34 \times 10^{-2} \text{mol}), CH\text{\textsubscript{3}}CN (75 mL) and H\text{\textsubscript{2}}O (15 mL) The mixture was refluxed overnight under nitrogen. After cooling to room temperature, finally H\text{\textsubscript{2}}O (70 mL) was added to the flask. The resulting organic layer was separated and the solvent was removed by rotary evaporation. Then H\text{\textsubscript{2}}O (100 mL) and Methylene chloride (500 mL) was added to the mixture. The organic layer was separated, dried over MgSO\textsubscript{4}, filtered through Celite and concentrated to dryness. The crude product was washed with CH\text{\textsubscript{2}}Cl\text{\textsubscript{2}}/hexanes (1:20 v/v). The organic compound was filtered by using filter paper and drying under vacuum gave NA-CN as a light yellow solid (4.54 g, 1.853 \times 10^{-2} \text{mol}, yield = 95\%). Spectral data for NA-CN:

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.00 (d, \(J = 1.2\) Hz, 1H), 7.81 – 7.67 (m, 3H), 7.59 (dd, \(J = 8.7, 1.9\) Hz, 1H), 7.40 (dd, \(J = 8.5, 1.6\) Hz, 1H), 3.90 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 133.77, 131.77, 130.26, 129.85, 129.36, 128.16, 127.80, 126.85, 126.55, 120.58, 117.53, 23.83. Elemental analysis: Calculated (%) for C\textsubscript{12}H\textsubscript{8}BrN: C, 58.56; H, 3.28, Br, 32.47; Found: C, 58.49; H, 3.31; Br, 32.36. These spectral data match those previously reported for this compound.\textsuperscript{1,2}
Figure S3 $^1$H and $^{13}$C NMR spectrum of NA-CN
(2-ethylhexyl)-10H-phenothiazine (PT-Al)

A 100 mL 3-neck flask was added with phenothiazine (5 g, $2.51 \times 10^{-2}$ mol), NaH (0.8 g, $3.26 \times 10^{-2}$ mol), and 50 mL of DMF. The resulting mixture was stirred for 30 min. Further, 2-Ethylhexylbromide (6.29 g, $3.26 \times 10^{-2}$ mol) was added and the reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched by water and extracted three times with chloroform. The combined organic fractions were washed with brine and dried over MgSO4. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and n-hexane/ethylacetate (9/1; v/v) as the eluent to give PT-Al as a yellow viscous liquid (6.7 g, $2.15 \times 10^{-2}$ mol, yield = 86%). Spectral data for PT-Al:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.14 – 6.99 (m, 4H), 6.87 – 6.76 (m, 4H), 3.67 (d, $J = 7.0$ Hz, 2H), 1.91 (dt, $J = 12.3$, 6.1 Hz, 1H), 1.35 (m, $J = 30.2$, 23.4, 7.4, 1.5 Hz, 8H), 0.83 (t, $J = 7.5$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.96, 127.71, 127.22, 126.05, 122.49, 116.03, 51.17, 35.97, 30.93, 28.78, 24.25, 23.26, 14.24, 10.71. Elemental analysis: Calculated (%) for C$_{20}$H$_{25}$NS: C, 77.12; H, 8.09, N, 4.50, S, 10.29; Found: C, 76.98; H, 8.14, N, 4.39, S, 9.67.
Figure S4 $^1$H and $^{13}$C NMR spectrum of PT-Al
10-(2-ethylhexyl)-10H-phenothiazine-3,7-dicarbaldehyde (PT-(CHO)$_2$ (2))

A 100 mL 2-neck flask was added with a solution of 10-(2-ethylhexyl)-10H-phenothiazine (5.00 g, 1.60 x 10$^{-2}$ mol) and dry DMF (5.87 g, 0.080 mol) in 1,2-dichloroethane (DCE) (50 mL), phosphorus oxychloride (11.9 mL (19.62 g), 12.8 x 10$^{-2}$ mol) was added slowly at 0 °C. Then the reaction mixture was heated to reflux and maintained for overnight. The reaction mixture was quenched with addition of water and extracted three times with chloroform. The combined organic fractions were washed with brine solution and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and ethylacetate/hexane (1/9; v/v) as the eluent to give the two different products, 10-(2-ethylhexyl)-phenothiazine-3-carbaldehyde and 10-(2-ethylhexyl)-10H-phenothiazine-3,7-dicarbaldehyde (3.17 g, 0.93 x 10$^{-2}$ mol, yield = 54% of PT(CHO)$_2$.

Spectral data for PT(CHO)$_2$:

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.76 (s, 2H), 7.62 (dd, $J = 8.4, 1.9$ Hz, 2H), 7.56 (d, $J = 1.8$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 3.78 (dd, $J = 7.2, 1.1$ Hz, 2H), 1.85 (dt, $J = 12.5, 6.4$ Hz, 1H), 1.41 – 1.27 (m, 4H), 1.22 – 1.13 (m, 4H), 0.79 (dt, $J = 10.7, 7.3$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 189.93, 149.77, 132.15, 129.94, 128.89, 125.75, 116.38, 51.94, 36.15, 30.49, 28.43, 23.86, 22.95, 13.93, 10.41.

Elemental analysis: Calculated (%) for C$_{22}$H$_{25}$NO$_2$S: C, 71.90; H, 6.86, N, 3.81, S, 8.73; Found: C, 71.87; H, 5.79, N, 3.63, S, 8.56.
Figure S5 $^1$H and $^{13}$C NMR spectrum of PT(CHO)$_2$

(2Z,2’Z)-3,3’-(10-(2-ethylhexyl)-10H-phenothiazine-3,7-diyl)bis(2-(6-bromonaphthalene-2-yl)acrylonitrile) (PTNAA)
A mixture of compound PT-(CHO)_2 (2.00 g, 0.54 x 10^{-2} mol), NaCN (3.34 g, 1.36 x 10^{-2} mol) and methanol were placed in a 100-mL two-neck round bottom flask at room temperature. A catalytic amount of potassium tert-butoxide in methanol was added slowly into this reaction mixture. After 24 h, the product was filtered and dried. The crude solid was further purified by column chromatography on silica gel eluted with dichloromethane/hexane 3:2 afforded PTNAA as a red solid (4.04 g, 0.49 mol, yield = 91%). Spectral data for PTNAA:

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 7.2 Hz, 2H), 7.93 (d, J = 5.2 Hz, 2H), 7.87 – 7.75 (m, 2H), 7.73 – 7.59 (m, 6H), 7.57 – 7.47 (m, 3H), 7.44 – 7.33 (m, 2H), 7.19 (s, 1H), 6.87 (m, J = 17.7, 10.5, 5.2 Hz, 2H), 6.58 (d, J = 8.6 Hz, 1H), 3.79 – 3.60 (m, 2H), 1.95 – 1.74 (m, 1H), 1.42 – 1.17 (m, 8H), 0.84 – 0.74 (m, 6H); ^13C NMR (100 MHz, CDCl_3) δ 146.74, 143.02, 140.84, 134.21, 132.34, 131.77, 130.43, 129.99, 129.81, 128.98, 128.74, 127.96, 127.04, 125.80, 123.54, 121.01, 118.20, 116.29, 108.94, 51.31, 36.22, 30.60, 28.53, 23.93, 23.05, 13.97, 10.48. MALDI mass m/z: Calculated for C_{46}H_{37}Br_{2}N_{3}S; 823.68; found, 823.16. Elemental analysis: Calculated (%) for C_{46}H_{37}Br_{2}N_{3}S: C, 67.08; H, 4.53, Br, 19.40, N, 5.10, S, 3.89; Found: C, 66.74; H, 4.57, Br, 19.31, N, 4.96, S, 3.73.
**Figure S6** $^1$H and $^{13}$C NMR spectrum of PTNAA.
**Figure S7** HPLC of PTNAA monomer.

**Figure S8** Maldi-TOF mass spectrometrum of PTNAA monomer.
Figure S9 Absorption spectrum of PTNAA monomer in varying polarity of the solvents.

Lippert- mataga study:

Solvatochromism is a characteristic behavior of dipolar molecules. In general, different polarity of solvent provides a useful framework for study of solvent dependent spectral shift. Using Lippert-mataga study the influence of different polarity of solvents environment on photophysical property of organic luminogen can be understood. Lippert- mataga study reveals that the interactions between the solvent and dipole moment of solute, the equation can be given as follows.

\[ \frac{h c (v_a - v_f)}{a^3} = \frac{2 (\mu_e - \mu_g)}{a^3} \left[ \frac{\varepsilon - 1}{2 \varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \]

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

\[ \mu_g = (m_2 - m_1/2) \left[ hca^3/2m_1 \right]^{1/2} \]

\[ \mu_e = (m_1 + m_3/2) \left[ hca^3/2m_1 \right]^{1/2} \]

Where \( h \) is the Planck’s constant (6.625x10^{-7} ergs), \( c \) is the velocity of light (2.997x10^{10} cm/s), \( \varepsilon \) is the Radius of the cavity in which the fluorophore resides, derived from the Avogadro number (N), molecular weight(M), and density (d=1.0 g/cm^3); \( v_a \) and \( v_f \) is wavenumber (cm^{-1}) of the absorption and
emission respectively; $\nu_0$ and $\nu_f$ are corresponds to the stokes shift when $f$ is Zero; $\mu_e$ is the excited state dipole moment, $\mu_g$ is the ground state dipole moment; $f$ is the orientation polarizability of the solvent; $\varepsilon$ and $n$ are the solvent dielectric and the solvent refractive index, respectively. The detailed data are listed in Table S1.

**Table S1.** Detailed study of absorption and emission peak position of PTNAA in different polar solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\varepsilon$</th>
<th>$n$</th>
<th>$f(\varepsilon, n)$</th>
<th>$\lambda_a$ (nm)</th>
<th>$\lambda_f$ (nm)</th>
<th>Stroke shift ($\lambda_a - \lambda_f$) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>1.9</td>
<td>1.375</td>
<td>0.0012</td>
<td>446</td>
<td>548</td>
<td>4436</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>1.49</td>
<td>0.014</td>
<td>441</td>
<td>559</td>
<td>4786</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>4.34</td>
<td>1.35</td>
<td>0.167</td>
<td>439</td>
<td>567</td>
<td>5143</td>
</tr>
<tr>
<td>Ethylacetate</td>
<td>6.02</td>
<td>1.372</td>
<td>0.200</td>
<td>437</td>
<td>573</td>
<td>5431</td>
</tr>
<tr>
<td>Tetrahydrofurane</td>
<td>7.58</td>
<td>1.40</td>
<td>0.210</td>
<td>438</td>
<td>577</td>
<td>5500</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>8.93</td>
<td>1.42</td>
<td>0.217</td>
<td>433</td>
<td>581</td>
<td>5883</td>
</tr>
<tr>
<td>N’N-Dimethyl formamide</td>
<td>37</td>
<td>1.427</td>
<td>0.276</td>
<td>435</td>
<td>585</td>
<td>5784</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
<td>1.35</td>
<td>0.284</td>
<td>443</td>
<td>588</td>
<td>5825</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>37.5</td>
<td>1.34</td>
<td>0.305</td>
<td>434</td>
<td>593</td>
<td>6178</td>
</tr>
</tbody>
</table>

Where, $\varepsilon$ and $n$ are the solvent dielectric and the solvent refractive index, respectively; $f$ is the orientational polarizability of the solvent; $\lambda_a$ and $\lambda_f$ absorption maximum and emission maximum respectively.

**Table S2.** Spectral properties of PTNAA monomer

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (Abs) (nm)</th>
<th>$\lambda_{\text{max}}$ (Emi) (nm)</th>
<th>$\phi_{\text{PL}}$ (Solution) ($\varepsilon$)</th>
<th>$\phi_{\text{PL}}$ (Thin film, Exc)</th>
<th>$\phi_{\text{PL}}$ (Solution)</th>
<th>$\phi_{\text{PL}}$ (Thin film, Exc)</th>
<th>$\phi_{\text{PL}}$ (Thin film, (T$_1$/T$_2$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTNAA</td>
<td>328, 442</td>
<td>573 (442)</td>
<td>605 (483)</td>
<td>6.47/2.06</td>
<td>57.7</td>
<td>71.9</td>
<td></td>
</tr>
</tbody>
</table>

$\lambda_{\text{max}}$ (Abs), absorption maxima for solutions and thin films in nm; $\phi$($\varepsilon$), extinction coefficient in dL g$^{-1}$ cm$^{-1}$; $\lambda_{\text{max}}$ (Emi), emission maxima for solutions and thin films in nm; $T_1/T_2$, lifetime of different decay channels from fluorescence lifetime experiment in ns for thin films; $\phi_{\text{PL}}$ (SOL) and $\phi_{\text{PL}}$ (TF), solution and thin film absolute PL quantum yields (in %) were measured using an integrating sphere.
Figure S10. (a) AFM micrograph of spun thin films from chloroform solution of PTNAA (inset GIXRD traces), (b) HRSEM micrograph ((scale bar for image is 2 μm).

Figure S11. Absorptin spectrum of PTNAA in varying percentage addition of water fraction in THF-aggregated states.
Figure S12. DLS traces of PTNAA monomer with varying percentage compositions of water /THF mixtures.

Figure S13. (a) TGA curve: (b) DSC curve of PTNAA (Scan rate = 10° C min⁻¹ under the nitrogen).
Figure S14: Cyclic voltammetry traces of PTNAA
Figure S15 (a) Luminescence voltage traces (L-V), Current voltage traces (J-V)

Table S3. Device characteristics of PTNAA copolymers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO a (eV)</th>
<th>LUMO b (eV)</th>
<th>$E_{\text{ele}}/E_{\text{opt}}/E_{\text{theo}}$ c (eV)</th>
<th>$\eta_c^\text{max}$ (cd/A)</th>
<th>$\eta_p^\text{max}$ (Lm/W)</th>
<th>$I_{L_{\text{max}}}$ (cd/m²)</th>
<th>Turn-on Voltage (V)</th>
<th>$a_{\text{CIE}}^{\text{EL}}$</th>
<th>$a_{\text{CIE}}^{\text{PL}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTNAA</td>
<td>-5.80</td>
<td>-3.54</td>
<td>2.26/2.37/2.41</td>
<td>13.7</td>
<td>9.6</td>
<td>23931</td>
<td>4.1</td>
<td>(0.54, 0.43)</td>
<td>(0.57, 0.38)</td>
</tr>
</tbody>
</table>

aHighest Occupied Molecular Orbital. bLowest Unoccupied Molecular Orbital. c$E_{\text{ele}}/E_{\text{opt}}$, Electrochemical band gap/Optical band gap. $d\eta_c^\text{max}$, Luminous efficiency. $e\eta_p^\text{max}$, Power efficiency. $fL_{L_{\text{max}}}$, Maximum luminance. gCIE coordinates for EL. hCIE coordinates for PL.
**Computational details:**

The gas-phase density functional theory (DFT) calculations (B3LYP/ 6-31G* level) were carried out in order to gain a clear insight into the intramolecular charge transfer character of PTNAA at the molecular level and implemented in the Gaussian 09 package.\textsuperscript{S1-S3} All the optimized structures were identified by a frequency analysis and were shown to be all positive frequencies. On the principle of gas-phase optimized ground geometry, the absorption spectra in tetra hydro furan (THF) were calculated by the time-dependent density functional theory (TD-DFT) method which was employed to investigate ground to excited-state transitions using Gaussian 09 program along with B3LYP/6-31G* levels of theory.\textsuperscript{S4} The energy optimized structures (Fig. S12), adopted a bird-like structure.

![Optimized geometry of PTNAA (bird-like structure) by using B3LYP/6-31G* level of theory.](image-url)
Figure S17. Theoretically calculated absorption spectra of PTNAA Monomer at B3LYP/6-31G* level.

Table S4 Summary of the excited state electronic transitions obtained from the TD-DFT calculations at the B3LYP/6-31G* level

<table>
<thead>
<tr>
<th>Model systems</th>
<th>States</th>
<th>Absorption (nm)</th>
<th>Energy (eV)</th>
<th>Oscillator strength ($F$)</th>
<th>Dominant contribution$^a$ (%)</th>
<th>Exp. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTNAA</td>
<td>S1</td>
<td>393</td>
<td>3.15</td>
<td>1.61</td>
<td>HOMO→LUMO (84%), H-1→L+1 (7%); H-2→LUMO (53%), H-1→L+1 (28%);</td>
<td>328, 442</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>306</td>
<td>4.05</td>
<td>1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-polymer</td>
<td>S1</td>
<td>396</td>
<td>3.13</td>
<td>2.51</td>
<td>HOMO→LUMO (73%), H-1→L+1 (8%); H-2→LUMO (32%), H-1→L+1 (26%);</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>318</td>
<td>3.90</td>
<td>1.06</td>
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$^a$ denotes HOMO and L denotes LUMO.
References


