Electronic Supplementary Information

Mechanochromic luminescence and color-tunable light-emitting devices of triphenylamine functionalized benzo[*d,e*]benzo[4,5]imidazo[2,1-*a*] isoquinolin-7-one

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1. Experimental section

General information

All reagents and solvents are purchased from commercial sources and used as received without further purification. 3-bromobenzo[*d,e*]benzo[4,5]imidazo[2,1-*a*] isoquinolin-7-one is synthesized according to the reported method.[1-2] ^{1}H NMR and ^{13}C NMR spectra are measured on a Bruker AV 400 NMR spectrometer with $Si(CH_3)_4$ as the internal standard. Mass spectra are recorded on a Thermo Electron Corporation Finnigan LTQ mass spectrometer. Elemental analysis is carried out with an Elementar Vario EL CHN elemental analyzer. The UV–vis absorption spectra is measured on an ultra-violet visible diode-array spectrophotometer (Agilent 8453). The photoluminescence (PL) spectra, quantum efficiency, and transient lifetime are measured on a fluorescence spectrophotometer (FLS980, Edinburgh). The solution of 3-TPA-BBI in 1,2-dichloroethane (1.0 g/100 mL) is spin-coated onto the quartz plate to provide the film. During the heating process, the film is heated for 10 minutes at the given temperature (80-130 ^{o}C) or for 5 s at 150 ^{o}C. Then the films are cooled to room temperature for measurements. The X-ray diffraction (XRD) measurements are obtained through a diffractometer (Ultima IV) with an X-ray source of Cu Kα at 40 kV and 40 mA, at a scan rate of 2° (2θ) per 1 min. Single crystal XRD measurement is carried out on a single crystal X-ray diffractometer (Oxford Gemeni S Ultra) with Cu Kα radiation (λ = 1.54178 Å) at 193 K. Ultraviolet photoemission spectroscopy (UPS) analysis are carried out using a VG ESCALAB 220i-XL surface analysis system equipped with a He-discharge lamp providing He-I photons of 21.22 eV with a base vacuum of 10^{-10} Torr. CCDC 1879174 provides supplementary crystallographic data for this paper.[3]

Device fabrication and measurement

In a general procedure, indium-tin oxide (ITO)-coated glass substrates are pre-cleaned and dried carefully and treated by UV ozone for 20 min. A 50 nm poly(3,4-ethylenedioxythiophene) doped with poly(styrene-4-sulfonate) (PEDOT:PSS) aqueous solution is spin-coated onto the ITO substrate and baked at 150 ^{o}C for 10 min. Then the emission layer of 3-TPA-BBI in 1,2-dichloroethane (1.0 g/100 mL) is spin-coated onto the PEDOT:PSS layer to fabricate orange OLED. After heated the substrate at 150 ^{o}C for 5 s, the emitting layer is converted to a yellow-emissive layer to fabricate yellow OLED. Subsequently, the substrate is transferred into an evaporation chamber with a base vacuum of 5 × 10^{-6} Torr, where a 50 nm thick 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-*1H*-benzimidazole) (TPBI) is deposited at a rate of 1.0 Å/s by thermal evaporation. Finally, 1-nm thick LiF and 100-nm thick Al are evaporated at evaporation rates of 0.1 and 5 Å/s, respectively. The current-voltage characteristics of the devices are characterized with a Keithley 2400 Sourcemeter. The electroluminescent spectra, luminance Commission Internationale de l'Éclairage (CIE) color coordinates are measured on a Spectrascan PR650 photometer.

Lippert-Mataga calculation

To obtain the change in the dipole moment upon excitation ($\Delta\mu$), we use the Lippert-Mataga equation, Eq. (1), which express the Stokes shift as a function of the solvent polarity parameter $\Delta f(\varepsilon, n)$.[4]

$$\Delta\nu = \nu_a - \nu_f = \left(2\Delta\mu^2 / hca^3\right)\Delta f\left(\varepsilon,\ n\right) + A \qquad (1)$$

Where $\Delta f(\varepsilon, n)$ is calculated from Eq. (2):

$$\Delta f\left(\varepsilon,\ n\right) = \left[\left(\varepsilon-1\right)/\left(2\varepsilon+1\right)\right] - \left[\left(n^2-1\right)/\left(2n^2+1\right)\right] \qquad (2)$$

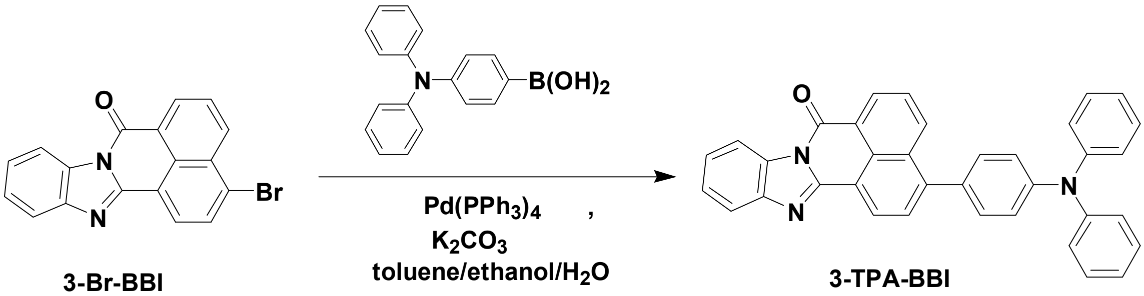
Here, $\Delta\nu$ corresponds to the Stokes shift (in cm^{-1}) between the maxima of absorption and fluorescence emission. The other terms are: h corresponds to the Plank's constant (6.6 × 10^{-34} J s), c is the velocity of light in the vacuum (3.0 × 10^{8} m s^{-1}) and α is the solute cavity radius (in meter), respectively. In Eq. (2), n and ε are the refractive index and the static dielectric constant of the solvent, respectively.

From Fig. S1, the slope value is calculated to be 14527 cm^{-1} for 3-TPA-BBI. From the single crystal structure, α is estimated to be 0.9575 nm. Accordingly, the $\Delta\mu$ value of 3-TPA-BBI is calculated to be 33.8 D.

Theory calculations

All density functional theory (DFT) calculations are performed using Gaussian 09 program package. The molecular model is selected from the single crystal structure. The molecular structure at ground state is optimized at the B3LYP/6-31G(d) level.

Synthesis of 3-(4-diphenylaminophenyl)-benzo[*d,e*]benzo[4,5]imidazo[2,1-*a*] isoquinolin-7- one (3-TPA–BBI)



Scheme S1. Synthesis route of 3-TPA-BBI

To a solution of 3-bromobenzo[*d,e*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-one (10 mmol), 4-(diphenylamino)phenyl boronic acid (10 mmol) in 100 mL of toluene and 40 mL of ethanol, aqueous K_2CO_3 solution (2.0 M, 10 mL) is added. After the reaction mixture is purged with N_2 for 10 min, Pd[PPh_3]$_4$ (1 mmol) is added. Then the reaction mixture is heated under reflux for 24 h under N_2. The cooled mixture is poured into 100 mL water, and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layer is washed with saturated aqueous NaCl solution (2×40 mL) , dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue is purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1-5:1) as eluent to afford 3-TPA-BBI as yellow solid. The yield is 74.2%. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm): 8.86 (d, *J*=5.2 Hz, 1H), 8.82 (d, *J*=4.8 Hz, 1H), 8.58-8.56 (m, 1H), 8.50 (d, *J*=5.6 Hz, 1H), 7.90-7.88 (m, 2H), 7.80-7.66 (m, 2H), 7.49-7.47(m, 2H), 7.41(d, *J*=5.8

Hz, 2H), 7.33(t, *J*=5.2 Hz, 3H), 7.23-7.215(m, 6H), 7.10 (t, *J*=5.2 Hz, 4.8 Hz, 2H).^{13}C NMR(100 MHz, $CDCl_3$) δ(ppm): 160.89, 149.41, 148.15, 147.37, 144.69, 143.93, 134.16, 132.22, 131.67, 130.97, 130.70, 129.45, 128.22, 126.87, 126.64, 125.79, 125.23, 124.96, 123.53, 122.61, 119.84, 119.21, 115.87. MS (MALDI-TOF) [m/z]: Calcd for $C_{36}H_{23}N_3O$, 513.57; Found: 513.86. Anal. Calcd. for $C_{36}H_{23}NO_3$ (%): C, 84.19; H, 4.51; N, 8.18; O, 3.12. Found: C, 84.22; H, 4.50; N 8.16.

Single crystals

The needle–like yellow crystals of 3-TPA-BBI are grown from dichloromethane/ethanol (v:v = 1:1) solution by slow evaporation at room temperature.

2. Figures

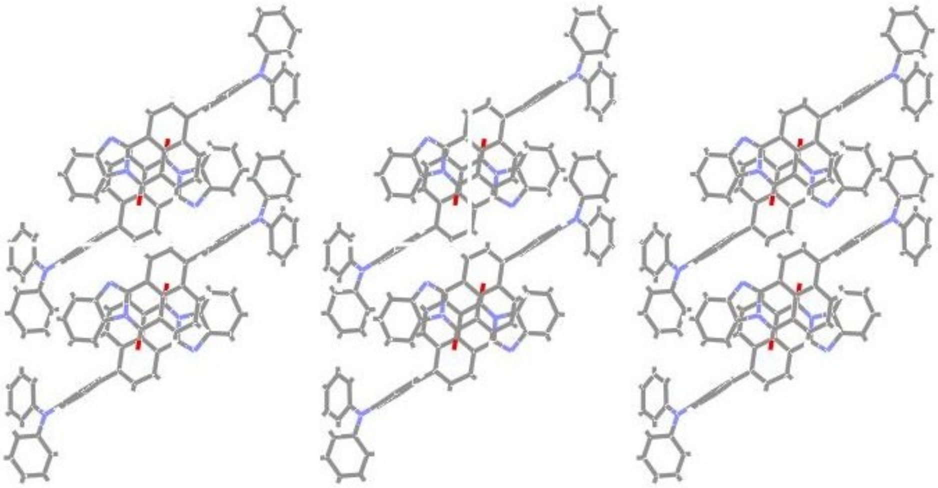


Fig. S1 Molecular interactions in crystal cell of 3-TPA-BBI.

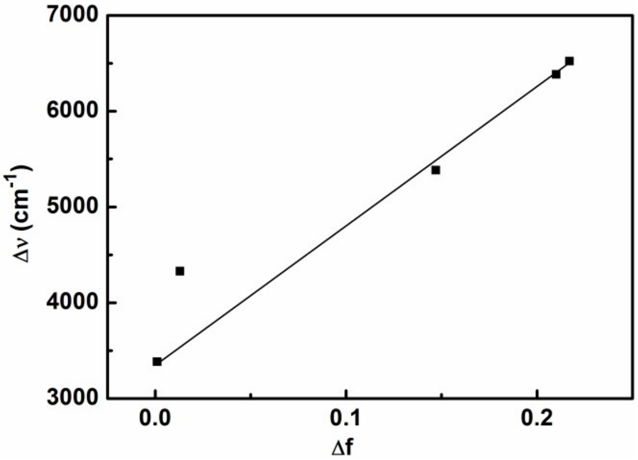


Fig. S2 Lippert-Mataga plots of 3-TPA-BBI.

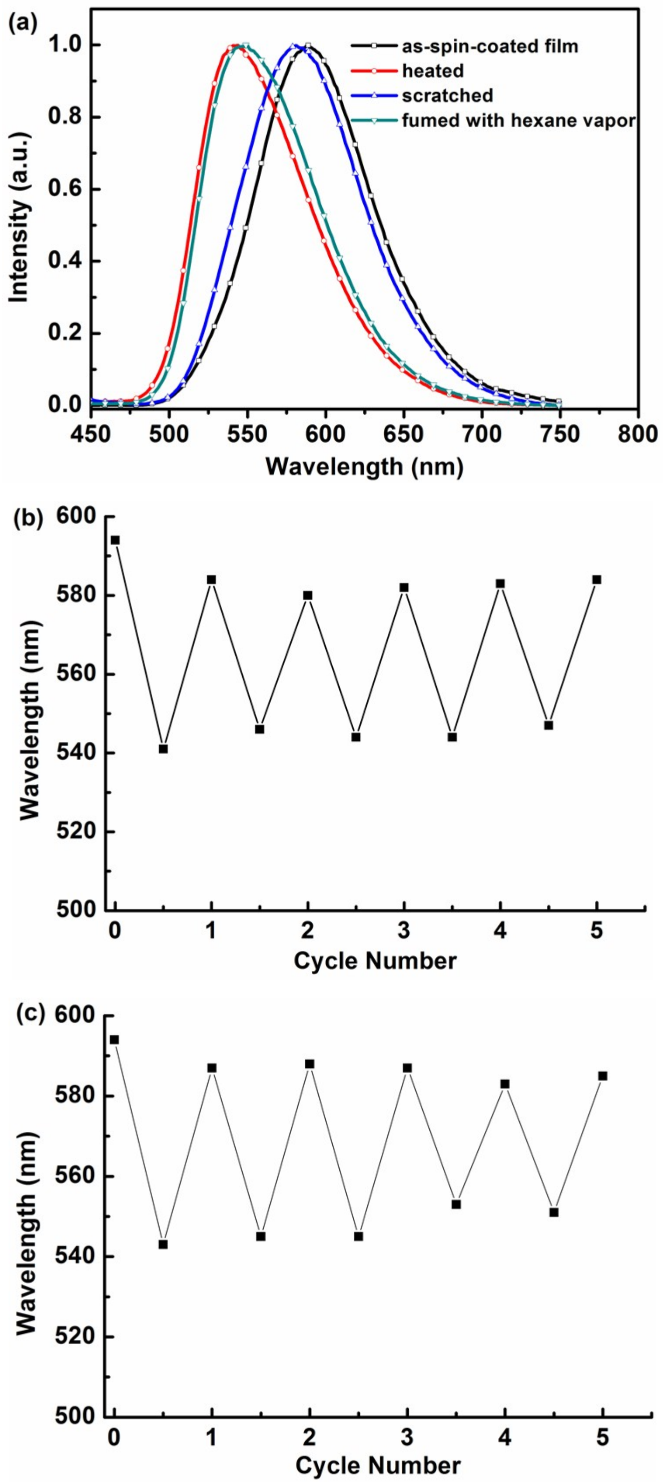


Fig. S3 (a) PL spectra of 3-TPA-BBI in film under different conditions; (b) Fluorescent emission peak wavelength of 3-TPA-BBI upon treated by heating and scratching; (c) Fluorescent emission peak wavelength of 3-TPA-BBI upon treated by fuming with hexane and scratching. The chemical structure of 3-TPA-BBI does not change before and after stimuli as confirmed by ^{1}H NMR measurements.

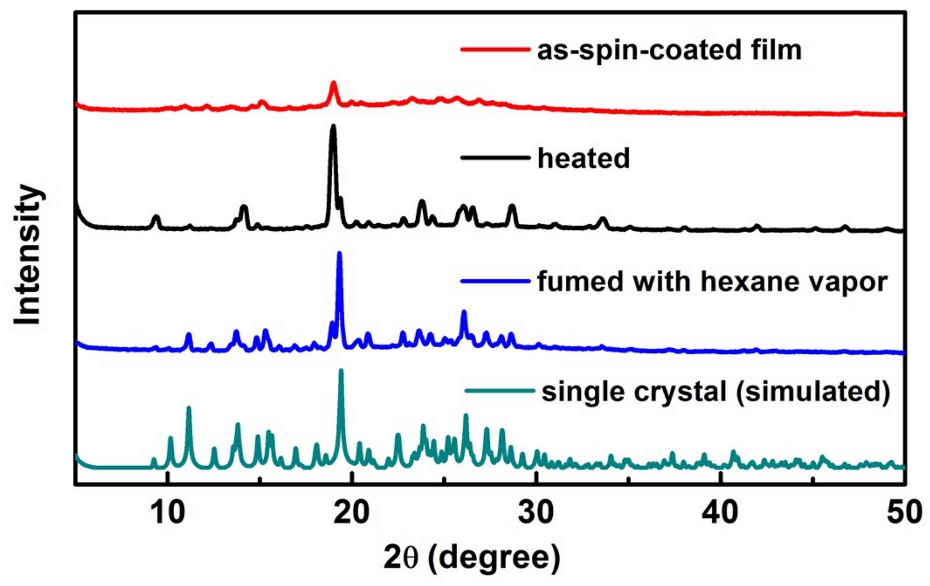


Fig. S4 XRD spectra of 3-TPA-BBI in different states.

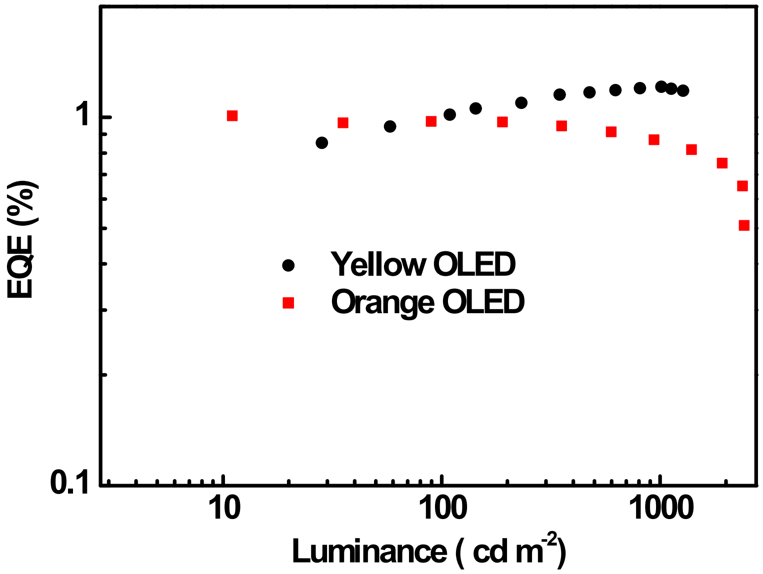


Fig. S5 Luminance-EQE characteristics of the OLEDs based on 3-TPA-BBI.

3. Tables

Table S1. Crystal data and structure refinement for 3-TPA-BBI.

Formula	$C_{36}H_{23}N_3O$
CCDC No.	1879174
Formula weight	513.57
Space group	P 2_1/c
Temperature	193(2)
Wavelength /Å	1.542
Crystal system	Monoclinic
a/Å	8.6951(4)
b/Å	7.5970(3)
c/Å	38.1721(18)
α/°	90.00
β/°	90.378(4)
γ/°	90.00
Volume/Å^3	2521.47(19)
Z	4
Calculated density /Mg m^{-3}	1.353
M(mm^{-1})	0.646
F(000)	1072
Crystal size/mm^3	0.61 × 0.05 × 0.02
No. of reflns collected	4607
No. of unique reflns	3639
Goodness-of-fit on F^2	1.053
R_1 , wR_2 [I>2σ(I)]	0.0696, 0.1802
R_1, wR_2 *(all data)*	0.0869, 0.1931

Table S2. Spectral properties of 3-TPA-BBI in different solvents.

Solvent	$\Delta f(\varepsilon, n)$	λ_{abs} (nm)	λ_{em} (nm)	Δv ($\mathrm{cm^{-1}}$)
hexane	0.001	306, 432	506	3385
toluene	0.013	310, 439	542	4329
chloroform	0.147	314, 451	611	5384
THF	0.210	308, 438	608	6384
DCM	0.217	301, 445	627	6523

Table S3. Temperature-dependent PL characteristics of 3-TPA-BBI in films.

	80 °C	90 °C	100 °C	110 °C	120 °C	130 °C	150 °C
λ_{abs} (nm)	319, 459	319, 459	319, 459	319, 395	319, 395	319, 395	319, 395
λ_{PL} (nm)	594	594	597	586	548	550	545
Φ_{PL}	0.445	0.517	0.529	0.562	0.674	0.595	0.605
τ_1 (ns)	2.16 (17.94%)	1.73 (15.02%)	2.05 (17.73%)	1.87 (16.69%)	3.11 (27.49%)	2.45 (26.23%)	3.98 (45.82%)
τ_2 (ns)	9.02 (82.06%)	8.98 (84.98%)	9.08 (82.27%)	8.60 (83.31%)	8.32 (72.51%)	7.95 (73.77%)	13.36 (54.18%)
τ_{avg} (ns)	8.68	8.74	8.75	8.32	7.67	7.40	6.80
k_r (10^7 $\mathrm{s^{-1}}$)	5.13	5.91	6.04	6.76	8.78	8.03	8.90
k_{nr} (10^7 $\mathrm{s^{-1}}$)	6.39	5.52	5.38	5.27	4.25	5.47	5.81

Table S4. Theoretically calculated and experimentally measured energy levels of 3-TPA-BBI

Form	E_g (eV)	HOMO (eV)	LUMO (eV)
Ground [a]	2.77	-5.16	-2.39
Orange film	2.25	-5.45	-3.20
Yellow film	2.37	-5.49	-3.12

[a] Theoretically calculated and energy levels of 3-TPA-BBI.

Table S5. EL of the fabricated devices based on 3-TPA-BBI.

	V_{on} (V)	LE (cd A^{-1})	Max luminance (cd m^{-2})	Max EQE (%)	λ_{EL} (nm)	CIE (x, y)
Orange Device	5.0	1.4	2429	1.01	608	(0.56, 0.42)
Yellow Device	4.5	2.7	1273	1.22	568	(0.48, 0.51)

4. References

(1) Verma, M.; Luxami, V.; Paul, K. *Eur. J. Med. Chem*, 2013, **68**, 352.

(2) Jiang, W.; Tang, J.; Qi, Q.; Wu, W.; Sun, Y.; Fu, D. *Dyes Pigments* **2009**, *80*, 279-286.

(3) CCDC 1879174 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(4) Ye, J.; Chen, Z.; Fung, M. K.; Zheng, C.; Ou, X.; Zhang, X.; Yuan,Y.; Lee, C.-S. *Chem. Mater.*, **2013**, *25*, 2630-2637.