Supporting Information for

Efficient blue organic electrochemiluminescence luminophore based on a pyrenyl-phenanthroimidazole conjugate

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Note added after first publication: This supplementary information file replaces that originally published on 08 June 2022, in which the reference for the calculation of ECL efficiencies was omitted. This citation has now been added and the sentence explaining the calculation has been amended. This does not affect any results or conclusions of the paper.

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General information

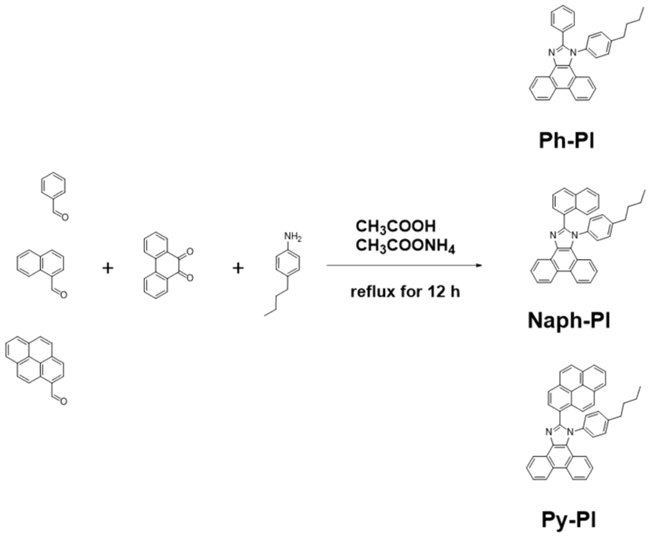
Instruments

^1H spectra were recorded in $CDCl_3$ using an Advance 500 MHz Bruker spectrometer. Mass spectra were obtained using a MALDI-TOF mass spectrometer from Bruker. UV-Vis spectra were recorded on a Jasco JP/V-730. Photoluminescence spectra were recorded on a Jasco FP-8300 spectrophotometer. All electrochemical experiments were performed using an electrochemical workstation (CH Instruments model 650B, model 440A, and Pine Research Instrumentation WaveDriver 200) with a conventional three-electrode cell. A glassy carbon electrode (dia. 3 mm) and a Pt wire was used as the working electrode and counter electrode, respectively. The electrochemical experiments were referenced with respect to a Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode or a Ag wire quasi-reference electrode. No matter which type of reference electrode was used, all potentials were calibrated by the addition of ferrocene as an internal standard, where $E°(Fc^+/Fc)$ = 640 mV vs. NHE. Before electrochemical experiments, the electrochemical cell was purged with inert N_2 gas to remove dissolved O_2 from the cell. The electrochemical experiments were conducted with continuous flushing of N_2 to the headspace of the cell. For spooling ECL spectroscopy, the three-electrode cell was connected to the slit of a monochromator (Acton Standard SP2150) combined with a CCD camera (PIXIS 100B). Electrochemical impedance spectroscopy (EIS) measurements were carried out to estimate the ohmic resistance using an IVIUM potentiostat. After measuring the value of ohmic resistance, the ohmic drop-corrected measurements were conducted for compensating the effect of ohmic potential drop in electrochemical experiments. Molecular structures in the ground state and charge distributions were calculated using Gaussian 09 Rev. with the DFT/B3LYP density functional and the 6-31G basis set.

ECL experiments

As same as for electrochemical experiments, all ECL measurements were conducted after sparging solutions with inert N_2 gas to avoid interference from dissolved O_2. ECL intensity was measured using an H-6780 photomultiplier tube (PMT) module (Hamamatsu photonics K.K., Tokyo, Japan) to obtain ECL-potential curves. An ECL cell was directly mounted on the PMT module with a homemade mounting support during the experiments. The ECL solutions were freshly prepared for each experiment. The glassy carbon working electrode was subsequently polished with 0.3 μm and 0.05 μm alumina powders (Buehler, IL, USA) on felt pads, and then sonicated in a 1:1 (v/v) mixture of deionized water and absolute ethanol for 10 min. Then, the electrode was blown by N_2 gas. Reductive-oxidation ECL data were measured by applying a single cathodic scan in the presence of 10 mM benzoyl peroxide (BPO) co-reactant at a scan rate of 100 mV/s. Oxidative-reduction ECL data were also collected by applying a single anodic sweep in the presence of 20 mM tripropylamine (TPrA) co-reactant at a scan rate of 100 mV/s. In addition, annihilation ECL data were obtained by pulsing the electrode between the potentials 100 mV beyond the diffusion-limited peak potentials for reduction and oxidation peaks with a pulse width of 0.1 s. The reported ECL values were obtained by averaging the values from at least three independent experiments.

Reagents and materials



Scheme S1 Synthetic routes for PI derivatives.

All chemicals were purchased from Tokyo Chemical Industry (TCI) and Alfa Aesar and were used as received.

Ph-PI. A mixture of benzaldehyde (0.212 g, 2 mmol), phenanthrene-9,10-dione (0.437 g, 2.1 mmol), 4-butylaniline (1.34 g, 9 mmol), and ammonium acetate (0.555 g, 7.2 mmol) in acetic acid (30 mL) was refluxed under nitrogen atmosphere for 12 h and was cooled. The resulting mixture was extracted with dichloromethane, washed with water, and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography (hexane:dichloromethane = 1:3). Yield: 50 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.79 (d, J = 10 Hz, 2H), 8.73 (d, J = 10 Hz, 2H), 7.77-7.22 (m, 15H), 2.18 (t, J = 10 Hz, 2H), 1.77-1.71 (m, 2H), 1.46-1.42 (m, 2H), 1.02 (t, J = 10 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 150.95, 144.76, 136.15, 130.04, 129.41, 129.22, 128.76, 128.74, 128.23, 128.14, 127.23, 126.19, 125.52, 124.79, 124.04, 123.14, 123.09, 122.74, 120.91, 35.37, 33.33, 22.22, 14.02. HRMS (FAB) m/z: calc. for $C_{31}H_{26}N_2$ $[M+H]^+$: 427.2096, found: 427.2167.

Naph-PI. Naph-PI was synthesized using 1-naphthaldehyde according to the synthesis of Ph-PI. Yield: 45%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.84 (d, J = 10 Hz, 2H), 8.77 (d, J = 5 Hz, 2H), 8.00-7.14 (m, 17H), 2.63 (t, J = 10 Hz, 2H), 1.21-1.56 (m, 2H), 1.33-1.29 (m, 2H), 0.93 (t, J = 10 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 150.51, 144.14, 135.48, 133.47, 133.17, 129.59, 129.47, 129.39, 128.15, 128.05, 127.29, 126.75, 126.22, 126.10, 126.02, 125.53, 124.90, 124.40, 124.07, 123.11, 121.09, 35.17, 33.07, 22.18, 13.89. HRMS (FAB) m/z: calc. for $C_{35}H_{28}N_2$ $[M+H]^+$: 477.2252, found: 477.2328.

Py-PI. Py-PI was synthesized using 1-pyrenecarboxaldehyde according to the synthesis of Ph-PI. Yield: 40%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.86 (d, J = 10 Hz, 2H), 8.80 (d, J = 10 Hz, 2H), 8.28-7.59 (m, 14H), 7.32-7.28 (m, 4H), 7.10 (d, J = 5 Hz, 2), 2.55 (t, J = 10 Hz, 2H), 1.54-1.48 (m, 2H), 1.25-1.22 (m, 2H), 0.84 (t, J = 10 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 150.98, 144.13, 135.51, 131.79, 131.36, 131.14, 130.88, 129.44, 128.63, 128.34, 128.28, 128.25, 127.34, 127.22, 126.27, 126.12, 125.59, 125.52, 124.95, 124.11, 123.77, 123.16, 123.14, 122.95, 121.16, 35.10, 32.95, 22.09, 13.81. HRMS (FAB) m/z: calc. for $C_{41}H_{30}N_2$ $[M+H]^+$: 551.2409, found: 551.2481.

Experimental section

Photophysical properties of PI derivatives

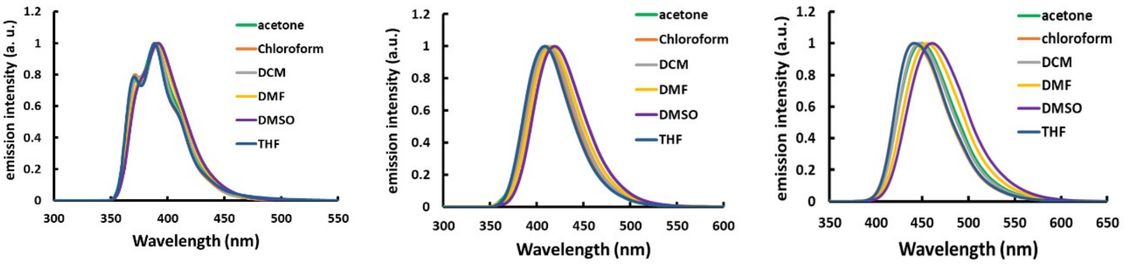


Fig. S1 Emission spectra of Ph-PI (left), Naph-PI (middle), and Py-PI (right) in various solvents at room temperature.

Table S1 Absorption and photoluminescence spectra of PI derivatives in acetonitrile.

	Ph-PI	**Naph-PI**	**Py-PI**
λ_{abs} (nm)[a]	305, 357	306, 358	307, 327, 345
ε ($M^{-1}cm^{-1}$)	18930, 6100	19220, 5910	18810, 25630, 36820
λ_{PL} (nm)[a]	390 (0.40) [b]	415 (0.70) [b]	454 (0.62) [b]

[a] Measured in acetonitrile (10 μM). [b] The photoluminescence quantum yields were calculated using DPA as a reference (0.95 in cyclohexane, 0.90 in acetonitrile).

CV data of PI derivatives

Table S2 CV data of PI derivatives in acetonitrile solvent.

		Ph-PI	**Naph-PI**	**Py-PI**
$E_{1/2}$[a] (V vs Fc^+/Fc)	**A/A^-**	–2.84 (E_{pc})	–2.68 (E_{pc})	–2.34
	A/A^+	0.87	0.91	0.85 (E_{pa})
HOMO, LUMO[b]		–5.46, –1.19	–5.48, –1.40	–5.47, –1.81
HOMO, LUMO[c]		–5.61, –2.16	–5.67, –2.31	–5.62, –2.54

[a] 1 mM luminophore. 0.1 M Bu_4NPF_6 in acetonitrile. Scan rate: 100 mV/s. N_2 atmosphere. [b] DFT calculation results in acetonitrile. [c] Experimental results: HOMO (eV) = − ($E_{ox,\ vs\ Fc/Fc+}$) − 4.8, LUMO (eV) = HOMO + $E_{g,opt}$ (optical band gap), $E_{g,opt}$ = The cross-point of normalized UV and PL spectra.[1]

ECL data of the luminophores

$$\Phi_{ECL} = \frac{\left[\frac{\int ECL\ intensity\ dt}{\int Current\ dt}\right]_x}{\left[\frac{\int ECL\ intensity\ dt}{\int Current\ dt}\right]_{st}} \times \Phi_{st}$$

The relative ECL efficiencies of luminophores were calculated using the above equation where *x* represents the luminophore, *st* represents the DPA reference compound, and $\Phi_{st} = 1$.[2]

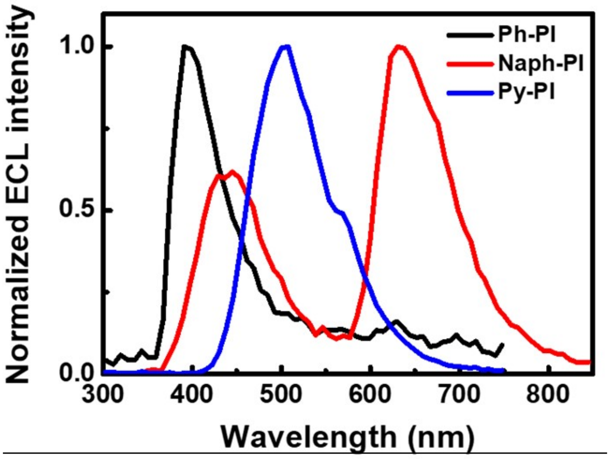


Fig. S2 Normalized annihilation ECL spectra of PI derivatives in acetonitrile containing 0.1 M Bu_4NPF_6. The annihilation ECL spectra were obtained by pulsing the electrode between the potentials 100 mV beyond the diffusion-limited peak potentials for reduction and oxidation peaks with a pulse width of 0.1 s. Exposure time: 6 s.

Table S3 Annihilation ECL data of PI derivatives.

	Ph-PI	**Naph-PI**	**Py-PI**
Applied potential[a] (V vs. Ag/Ag$^+$)	1.07 V and –2.87 V	1.11 V and –2.71 V	1.02 V and –2.24 V
λ_{ECL} (nm)[b]	391	436, 630	500, 569
Φecl[c]	0.0019	0.0131	0.0241

[a]Applied potential: peak potential ± 100 mV. [b]0.5 mM luminophore and 0.1 M Bu_4NPF_6 in acetonitrile solvent. Exposure time: 6 s. N_2 atmosphere. [c]ECL efficiencies were calculated relative to DPA taken as 1.

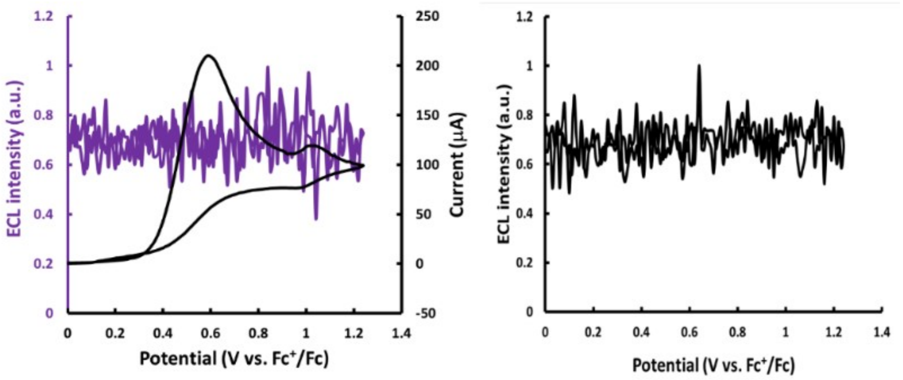


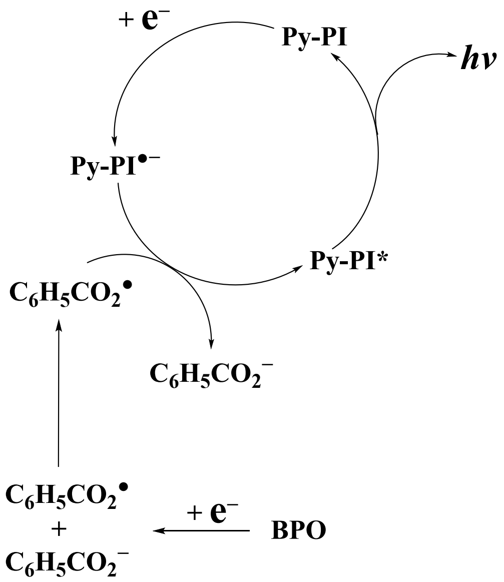
Fig. S3 Oxidative-reduction ECL data of Ph-PI (left, 0.5 mM Ph-PI, 0.1 M Bu_4NPF_6 and 20 mM TPrA in acetonitrile) and Bu_4NPF_6 (right, 0.1 M Bu_4NPF_6 and 20 mM TPrA in acetonitrile).

Table S4 Reductive-oxidation ECL data of PI derivatives.

	Ph-PI	**Naph-PI**	**Py-PI**
Φ_{ECL}[a]	0.05[b]	0.23[b]	3.30[b]
$P_{spooling\ ECL}$[c] **(V vs. Fc^+/Fc)**	–2.84	–2.70	–2.43
λ_{ECL} (nm)[a]	392	426	476

[a] 0.5 mM luminophore, 10 mM BPO (co-reactant), 0.1 M Bu_4NPF_6 in acetonitrile. Scan rate: 100 mV/s. [b] ECL efficiencies were calculated relative to DPA taken as 1. [c] Peak potentials where the strongest ECL emission observed in spooling ECL experiments (0.5 mM luminophore, 0.1 M Bu_4NPF_6, and 10 mM BPO in acetonitrile, Scan rate: 100 mV/s. Exposure time: 0.02 s.).

Reductive-oxidation ECL mechanism of Py-PI with BPO co-reactant



Scheme S2 Reductive-oxidation ECL mechanism of Py-PI with BPO co-reactant.[2-6]

References

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