Asian Journal of
Organic Chemistry

Supporting Information

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Yuanrong Shan,[a] Takeshi Yasuda,[b] Takaki Kanbara,[a] Junpei Kuwabara*[a][c]

[a] Y. Shan, Prof. T. Kanbara, Prof. J. Kuwabara
Institute of Pure and Applied Sciences
University of Tsukuba
1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

[b] Dr. T. Yasuda
Research Center for Macromolecules and Biomaterials,
National Institute for Materials Science (NIMS),
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.

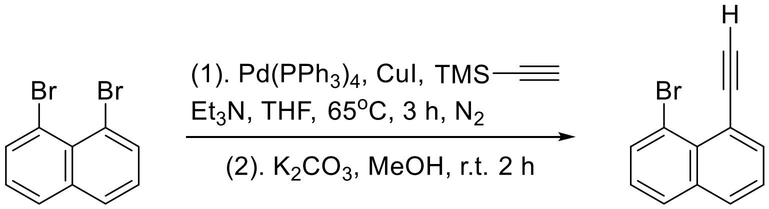
[c] Prof. J. Kuwabara
Tsukuba Research Center for Energy Materials Science (TREMS), Institute of Pure and Applied Sciences,
University of Tsukuba
1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
E-mail: kuwabara@ims.tsukuba.ac.jp

General, Measurement, and Materials.

^{1}H NMR spectra were recorded using Bruker AVANCE-400 NMR spectrometer and AVANCE-600 NMR spectrometer. Elemental analyses were carried out using a Yanaco CHN coder MT-6 or MT-5. Crystal structure determination intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation. MALDI-TOF-MS spectra were recorded on an AB SCIEX TOF/TOF (TM) 5800 system. UV-Vis absorption spectra in solution and film state were recorded on a Hitachi U-3900H and Hitachi U-3010 spectrophotometer, respectively. The photoluminescence (PL) spectra in the solution state and the thin film state were recorded Hitachi F-2700 fluorescence spectrophotometer and a JASCO FP-6500, respectively. The PL quantum yields (PLQY) of the emission were measured using a Hamamatsu Photonics C9920-02 absolute PL quantum yield spectrometer. The HOMO energy levels were estimated by photoelectron yield spectroscopy (PYS) using an AC-3 spectrometer (Riken Keiki). The surface morphology of films was examined with an atomic force microscope (AFM) (Hitachi High-Tech Corporation, AFM5100N and AFM5000II). Dry solvents were purchased from Kanto Chemical. Green light-emitting spiro-copolymer (Livilux™ SPG-01T, CAS 1430803-21-6, average M_n >100,000, E_{HOMO} = -5.38 eV, E_{LUMO} = -2.81

eV) was purchased from Sigma-Aldrich. The other reagents were purchased from Tokyo Chemical Industry Co., Ltd. (TCI), Sigma-Aldrich and FUJIFILM Wako Pure Chemical Corporation.

Synthesis of 1-bromo-8-ethynylnaphthalene.[S1]



A mixture of 1,8-dibromonaphthalene (2860 mg, 10.0 mmol), Pd(PPh$_3$)$_4$ (580 mg, 0.500 mmol), CuI (190 mg, 1.00 mmol), trimethylsilylacetylene (1520 μL, 11.0 mmol) and triethylamine (4 mL) in dried THF (6 mL) was stirred at 65 °C for 3 h under nitrogen atmosphere. After the reaction, the crude product was extracted with CHCl$_3$ and dried with sodium sulfate. The intermediate product with a TMS group was isolated by column chromatography on silica gel using hexane as an eluent (brown oil). To the intermediate product, potassium carbonate (2764 mg, 20.0 mmol) in methanol (30 mL) were added and stirred at r.t. for 2 h. After the reaction, the crude product was extracted with CHCl$_3$ and dried with sodium sulfate. The product was isolated by column chromatography on silica gel using hexane as an eluent. After evaporation, 1-bromo-8-ethynylnaphthalene was obtained (1499 mg, total yield 65%, brown solid).

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.89 (dd, 1H, *J* = 1.6, 7.2 Hz), 7.84 (d, 2H, *J* = 7.6 Hz), 7.80 (dd, 1H, *J* = 0.8, 8.4 Hz), 7.42 (t, 1H, *J* = 7.8 Hz), 7.28 (t, 1H, *J* = 7.6 Hz), 3.58 (s, 1H).

NMR Spectroscopy

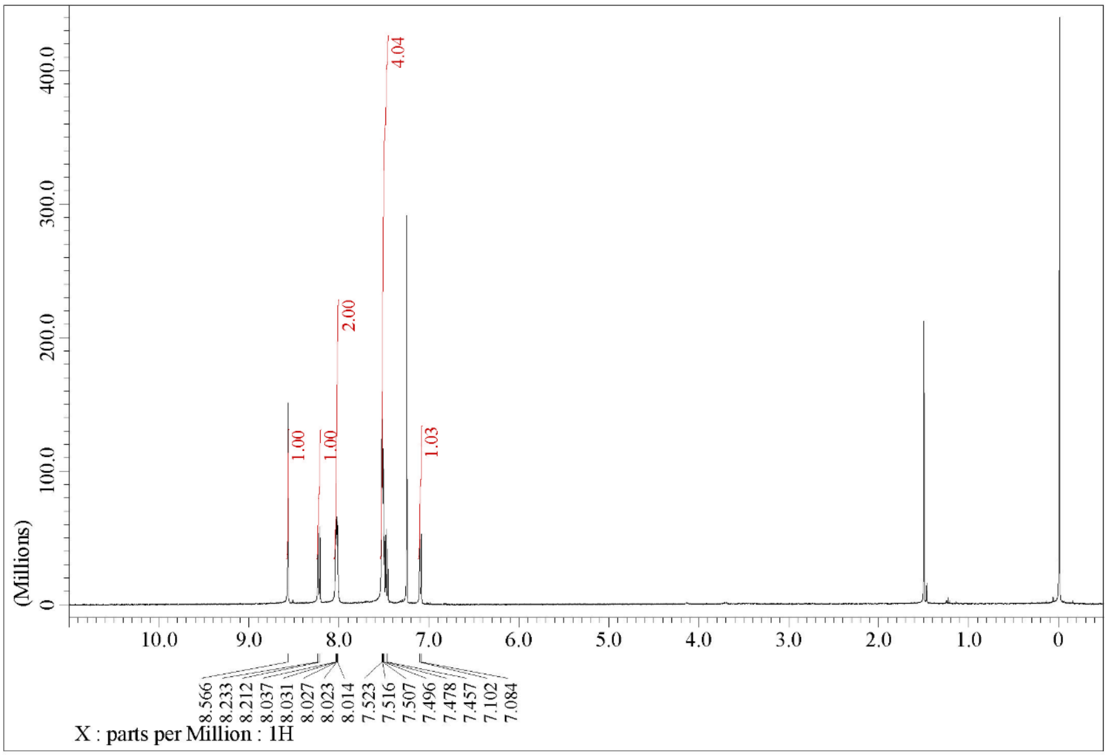


Figure S1. ^{1}H NMR spectrum of the diimine intermediate prepared from1,5-naphthalenediamine and benzaldehyde (400 MHz, $CDCl_3$, r.t.)

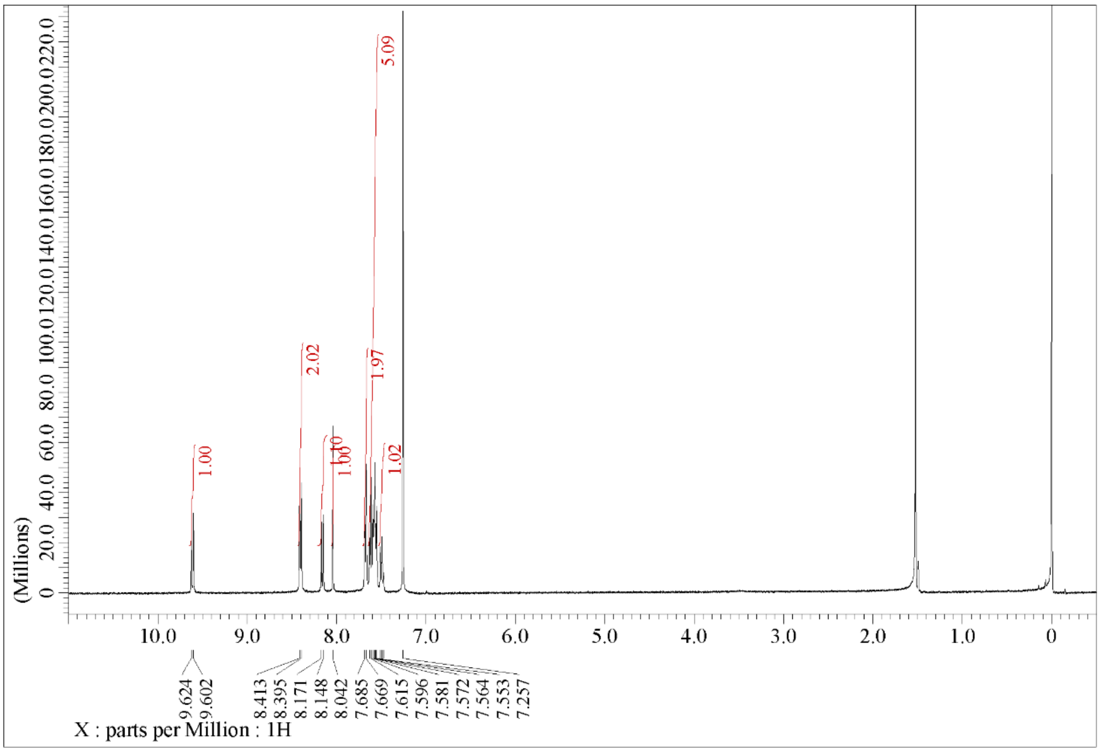


Figure S2. ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$, r.t.)

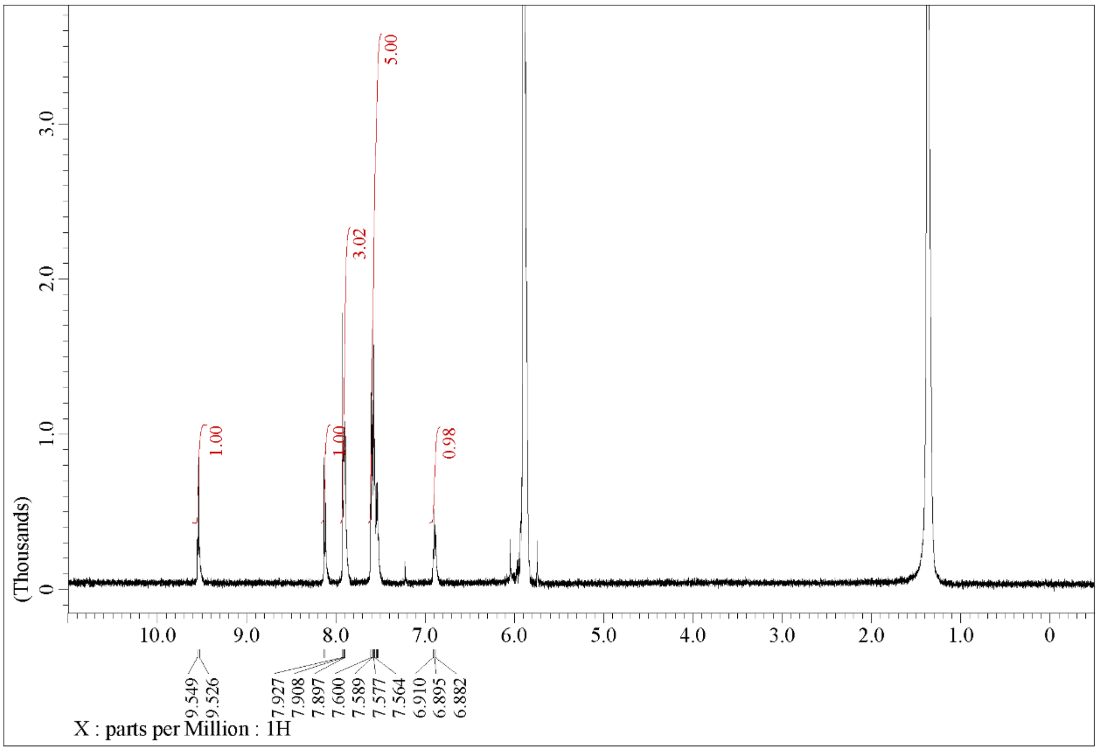


Figure S3. ^{1}H NMR spectrum of **1b** (600 MHz, $CDCl_2CDCl_2$, 373 K)

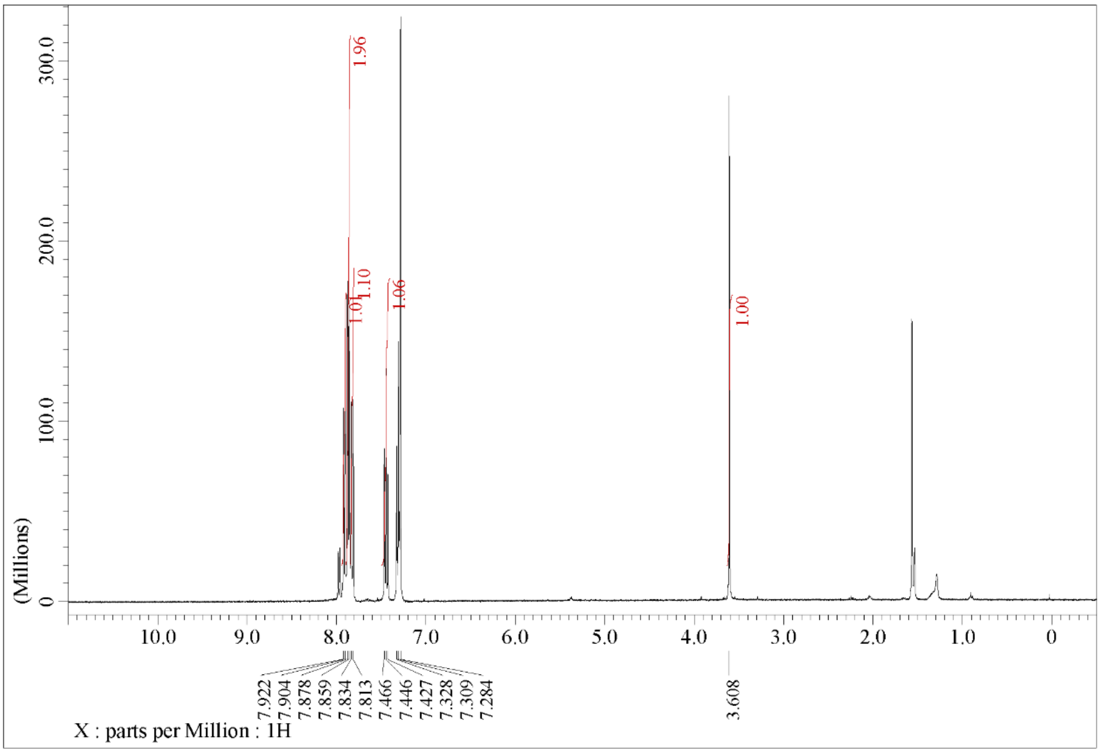


Figure S4. ¹H NMR spectrum of 1-bromo-8-ethynylnaphthalene (400 MHz, $CDCl_3$, r.t.)

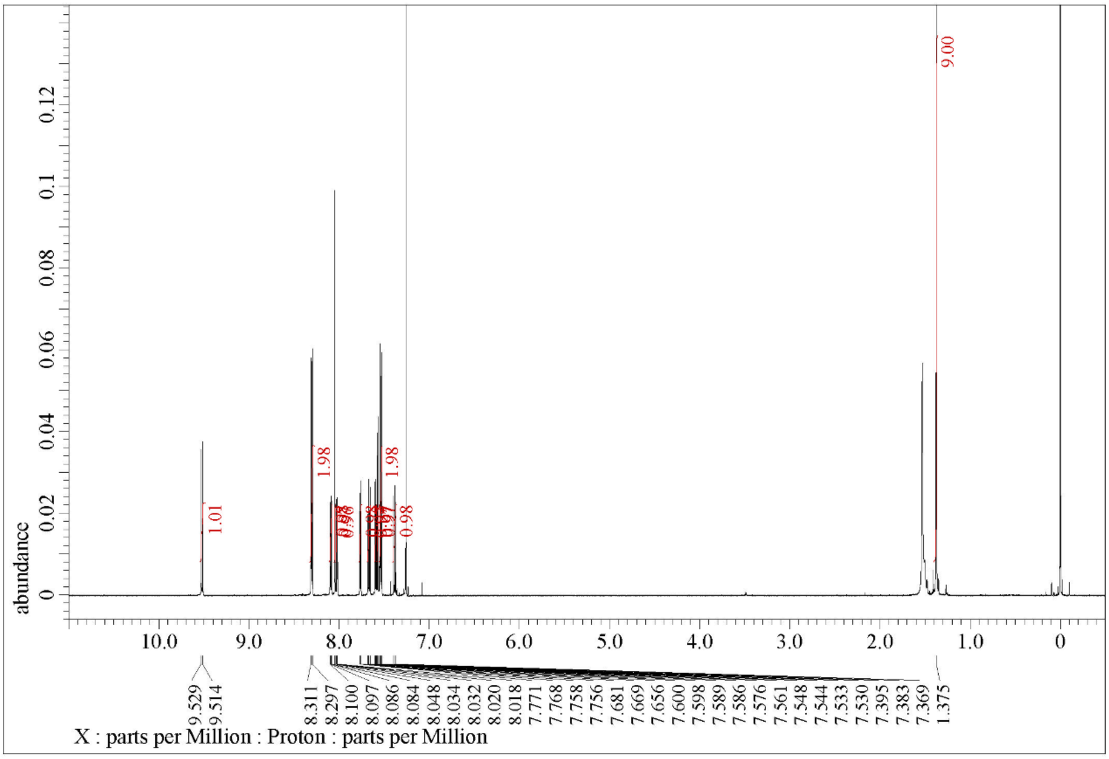


Figure S5. ¹H NMR spectrum of **1c** (600 MHz, $CDCl_3$, r.t.)

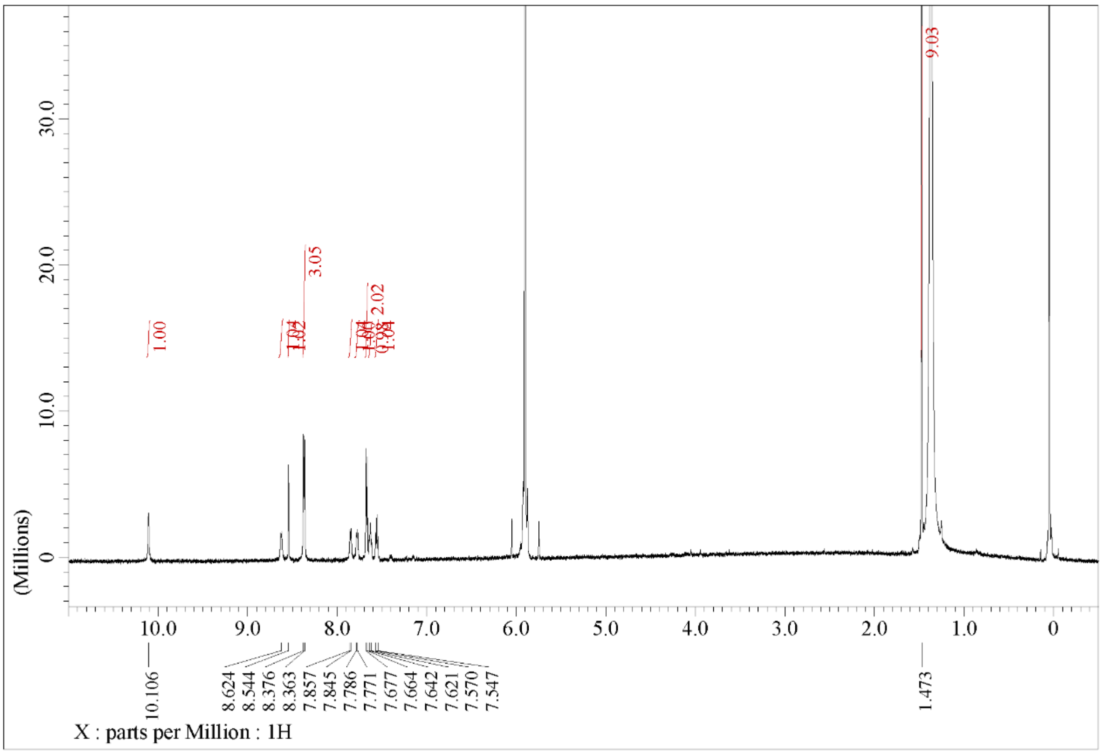
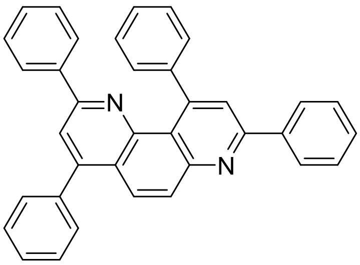


Figure S6. ^{1}H NMR spectrum of **2** (600 MHz, $CDCl_2CDCl_2$, 373 K)



HOMO -6.38 eV, LUMO -2.83 eV, Optical HOMO/LUMO gap 3.55 eV

Figure S7. The chemical structure and energy levels of a tetraphenyl-1,7-phenanthroline. [S2]

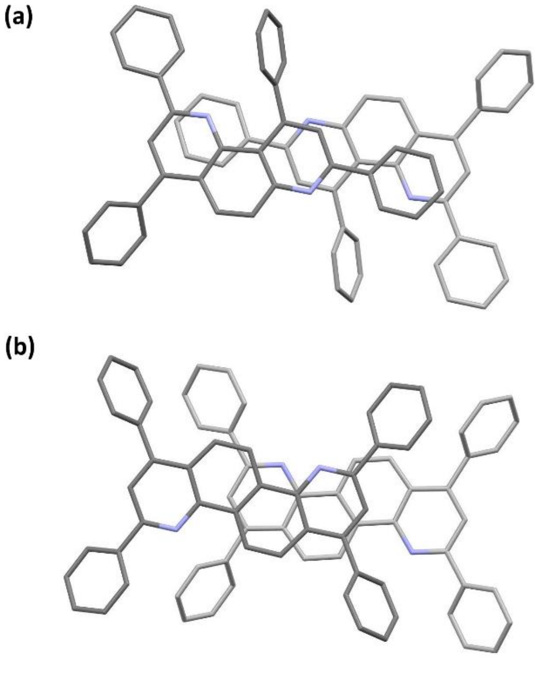


Figure S8. Stacking structures of (a) the tetraphenyl-1,7-phenanthroline [S2] and (b) **1a** in crystalline state.

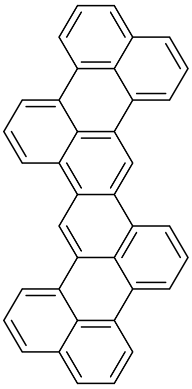


Figure S9. The chemical structure of the reference compound. [S3]

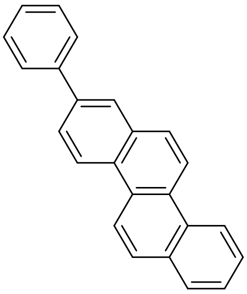


Figure S10. The chemical structure of the reference compound. [S4]

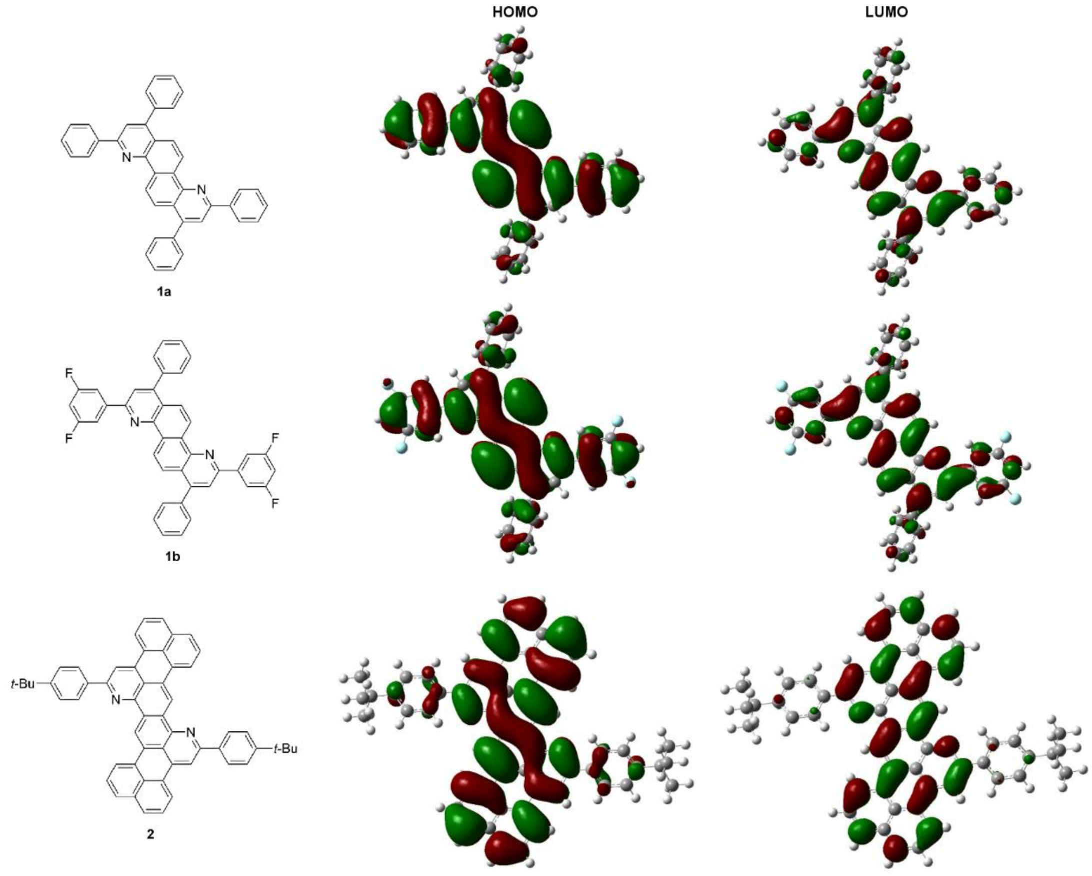
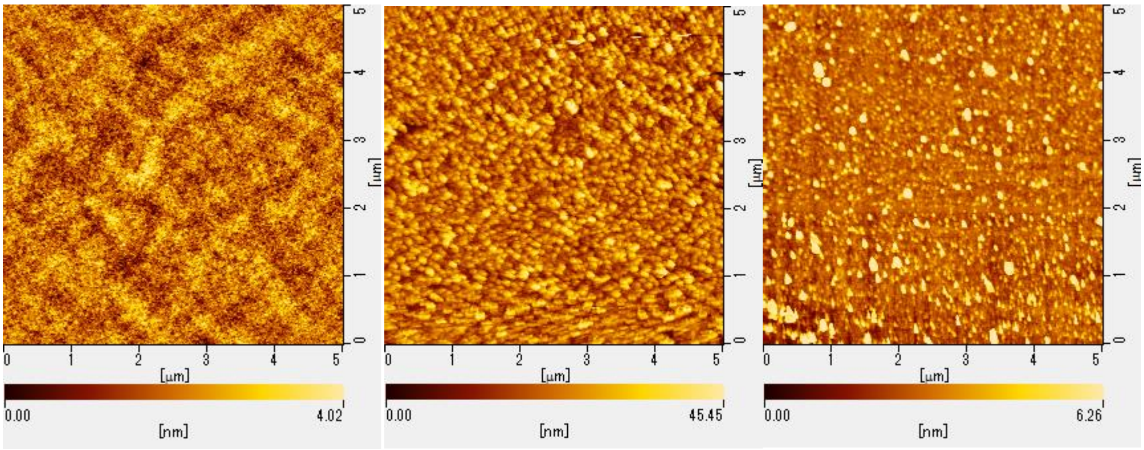


Figure S11. Frontier molecular orbitals for compounds **1a**, **1b** and **2,** orbitals by DFT calculation，at the level of B3LYP/6-31G(d).



1a RMS 0.6208 nm **1b** RMS 6.978 nm **2** RMS 0.9960 nm

Figure S12. AFM images of a vacuum-deposited film of **1a**, **1b**, and **2**.

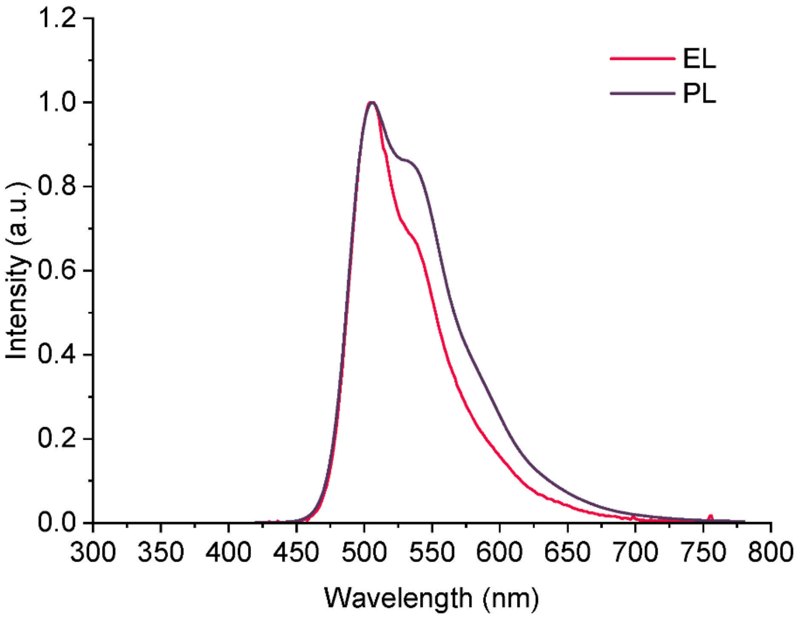


Figure S13. PL spectrum from the thin film of Green light-emitting spiro-copolymer (GP) and EL spectrum from GP in the OLEDs with **1a** in Figure 6.

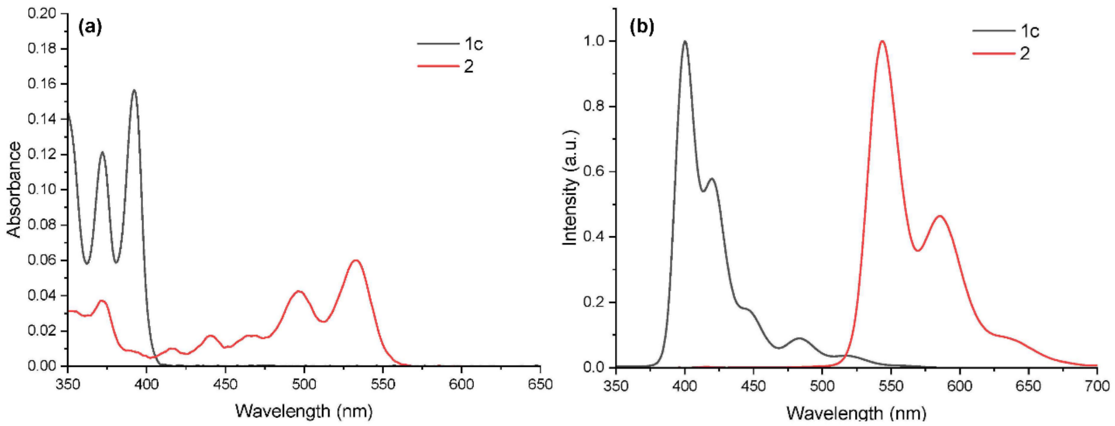
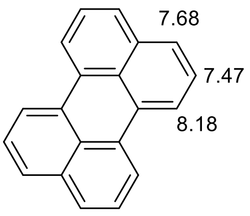
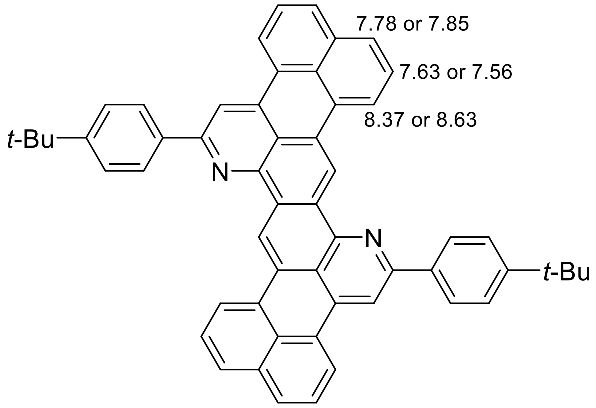


Figure S14. (a)UV-vis absorption and (b) photoluminescence spectra of **1c** and **2** (in toluene, 5.0 × 10^{-6} M).



Perylene



2 (ppm)

Figure S15. Chemical shift values of perylene[S5] and **2** in ^{1}H NMR.

Table S1. Calculated frontier molecular orbitals energy for compounds **1a**, **1b** and **2**, obtained by DFT calculation at the level of B3LYP/6-31G(d).

	E_g / eV	HOMO / eV	LUMO / eV
1a	3.05	-5.50	-1.75
1b	3.09	-5.78	-2.04
2	2.23	-4.84	-2.34

Table S2. Crystallographic data of **1a**.

	1a
CCDC No	2393382
Chemical formula	$C_{40}H_{26}N_2$
Formula weight	534.66
Crystal system	triclinic
Space group	P-1 (#2)
a [Å]	10.5687(6)
b [Å]	11.4271(6)
c [Å]	11.6197(7) Å
α [°]	87.2700
β [°]	76.9590
γ [°]	89.0390
V [$Å^3$]	1365.54(13)
Z value	2
μ(MoKα) [cm^{-1}]	0.754
F_{000}	560.00
D_{calc}	1.300
crystal dimensions	0.176 x 0.096 x 0.090
No. of data	15746
No. of unique data	5990
No. of variables	379
R (I > 2.00σ(I))	0.0394
R (All reflections)	0.0461
R_W (All reflections)	0.1052
GOF	1.045

References

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