# Supporting Information

Excimer Formation in Organic Emitter Films Associated with a Molecular Orientation Promoted by Steric Hindrance

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Experimental section

Synthesis:

1,6-Dibromopyrene (1), 9-anthracence boronic acid (2) and 4,4,5,5-tetramethyl-2-[1,1';3',1"]terphenyl-5'-yl-[1,3,2]dioxaborolane (6) were obtained according to the procedures reported elsewhere.[1] ^{13}C NMR data could not be obtained because of the very low solubilities of the three compounds.
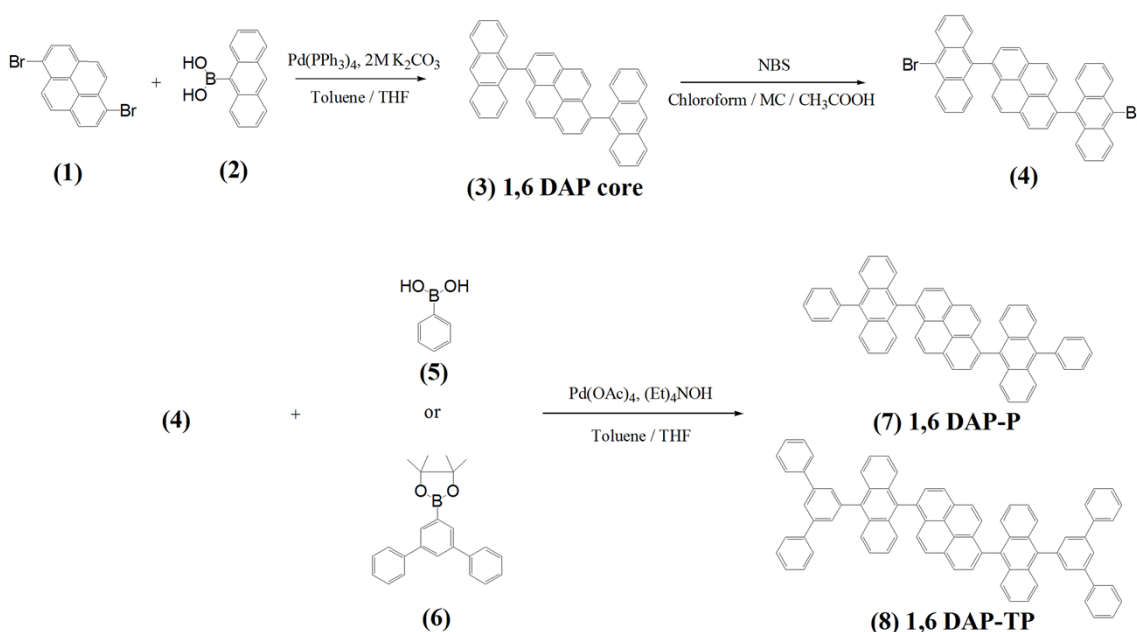
Scheme S1. Synthetic routes to the compounds.

1. 1,6-Di-anthracen-9-yl-pyrene (1,6 DAP core (3)): 1-bromopyrene (1) (2.00 g, 5.55 mmol), 9-anthracence boronic acid (2) (3.21 g, 14.44 mmol), and $Pd(PPh_3)_4$ (1.28 g, 1.11 mmol) were added to a 100 mL / 10 mL anhydrous toluene / THF solution. A 2 M K_2CO_3 solution (40 mL) dissolved in H_2O was added to the reaction mixture at 50°C. The mixture was refluxed for 5 h under nitrogen. After the reaction had finished, the mixture was filtered. The product was isolated using silica gel column chromatography with $CHCl_3$ as the solvent. The solvent was removed by evaporation. Recrystallization of the residue from $CHCl_3$ afforded a yellow product (3) (2.03 g, 65.8%). ^1H -NMR (300 MHz, THF-d_8, δ): 8.74(s, 2H), 8.40(d, 2H), 8.20(d, 4H), 8.06(d, 2H), 8.00(d, 2H), 7.50(t, 4H), 7.40(m, 6H), 7.27(t, 4H); HRMS (EI, m/z): [M]+ calcd. For C44H26, 554.2035; found, 554.2026. Anal. Calcd for C44H26: C 95.28, H 4.72; found: C 95.12, H 4.75.

2. 1,6-Bis-(10-bromo-anthracen-9-yl)-pyrene (4): Compound (3) (0.35 g, 0.63 mmol) and N-bromosuccinimide (NBS) (0.26 g, 1.45 mmol) were added to 300 mL $CHCl_3$, 300 mL CH_2Cl_2, and acetic acid (30 mL). The mixture was refluxed for 6 h. After the reaction had finished, the reaction mixture was extracted with $CHCl_3$ and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was re-dissolved in $CHCl_3$ and added to ethanol. The precipitate was filtered and washed with ethanol to obtain a yellow product (4) (0.34 g, 75.9%). ^1H-NMR (300 MHz, THF-d_8, δ): 8.73(d, 4H), 8.43(d,2H), 8.07(d, 2H), 8.03(d, 2H), 7.68(t, 4H), 7.43(m, 10H). EI+-Mass: 712.

3. 1,6-Bis-(10-phenyl-anthracen-9-yl)-pyrene (1,6 DAP-P (7)): Compound (4) (0.4 g, 0.56 mmol), phenyl boronic acid (5) (0.16 g, 1.34 mmol), $Pd(OAc)_2$ (0.046 g, 0.11 mmol), and (cyclohexyl)$_3$P (0.047 g, 0.17 mmol) were added to an anhydrous toluene (200 mL) / THF (10 ml) solution. Tetraethylammonium hydroxide (20 wt%) (15 mL) was added to the reaction mixture. A 0.5 g sample of (5) was added to the reaction mixture after refluxing for 1 h under nitrogen. The mixture was then refluxed for an additional 5 h. After the reaction had reached completion, the reaction mixture was extracted with $CHCl_3$ and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The product was isolated using silica gel column chromatography with $CHCl_3$. The solvent was removed by evaporation. Recrystallization of the residue from $CHCl_3$ afforded a yellow product (7) (0.26 g, 65.9%). ^1H-NMR (300 MHz, THF-d_8, δ): 8.45 (d, 2H), 8.13 (d, 2H), 8.06 (d, 2H), 7.81 (d, 4H), 7.73 (m, 10H), 7.49 (t, 6H), 7.38 (t, 4H), 7.26 (t, 4H); HRMS (EI, m/z): [M]+ calcd. For C56H34, 706.2661; found, 706.2669. Anal. Calcd for C56H34: C 95.15, H 4.85; found: C 94.87, H 5.01.

4. 1,6-Bis-(10-[1,1';3',1'']terphenyl-5'-yl-anthracen-9-yl)-pyrene (1,6 DAP-TP (8)): Compound (4) (0.3 g, 0.42 mmol), 4,4,5,5-tetramethyl-2-[1,1';3',1'']terphenyl-5'-yl-[1,3,2]dioxaborolane (6) (0.39 g, 1.09

mmol), Pd(OAc)$_2$ (0.034 g, 0.08 mmol), and (cyclohexyl)$_3$P (0.036 g, 0.13 mmol) were added to an anhydrous toluene (150 mL) / THF (5 ml) solution. Tetraethylammonium hydroxide (20 wt%) (15 mL) was added to the reaction mixture. A 0.5 g sample of (6) was added to the reaction mixture after refluxing for 1 h under nitrogen. The mixture was then refluxed for an additional 5 h. After the reaction had reached completion, the reaction mixture was extracted with CHCl$_3$ and water. The organic layer was dried with anhydrous MgSO$_4$ and filtered. The solution was evaporated. The product was isolated using silica gel column chromatography with CHCl$_3$. The solvent was removed by evaporation. Recrystallization of the residue from CHCl$_3$ afforded a yellow product (8) (0.15 g, 35.7%). ^{1}H-NMR (300 MHz, THF-d$_8$, δ): 8.47 (d, 2H), 8.21 (s, 2H), 8.15 (d, 2H), 8.08 (d, 2H), 8.00 (m, 16H), 7.53 (m, 14H), 7.43 (m, 8H), 7.29 (t, 4H); HRMS (EI, m/z): [M]+ calcd. For C80H50, 1011.3991; found, 1011.3994. Anal. Calcd for C80H50: C 95.02, H 4.98; found: C 94.55, H 5.10.
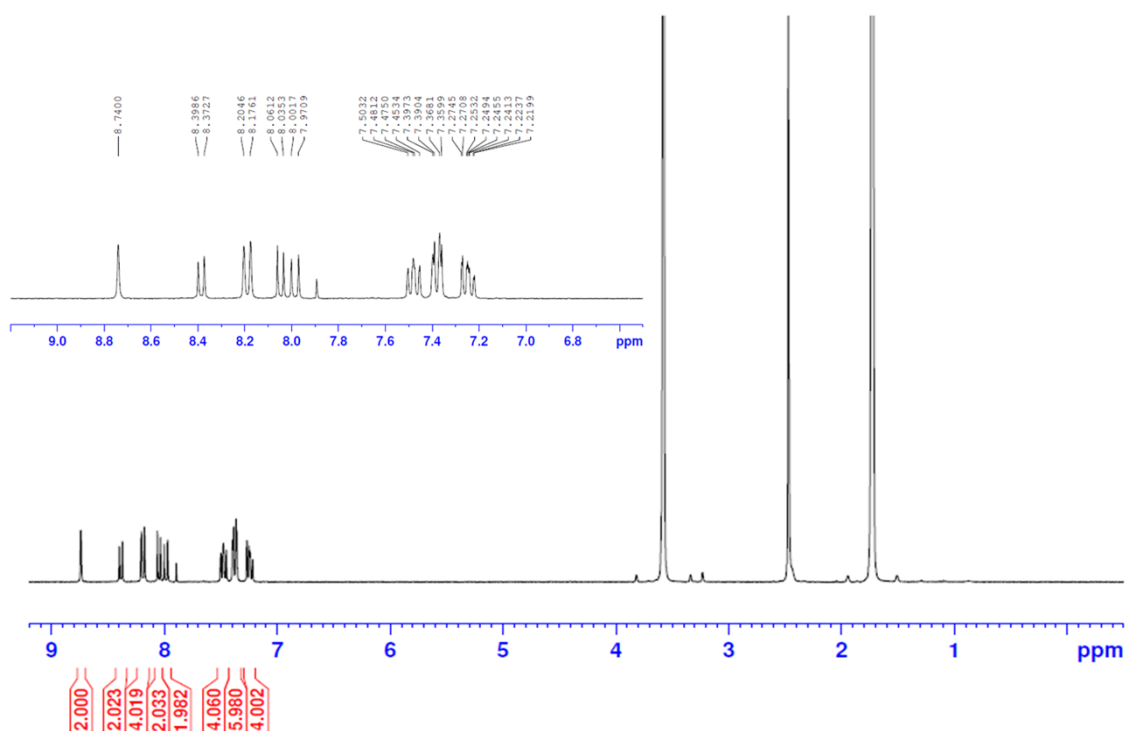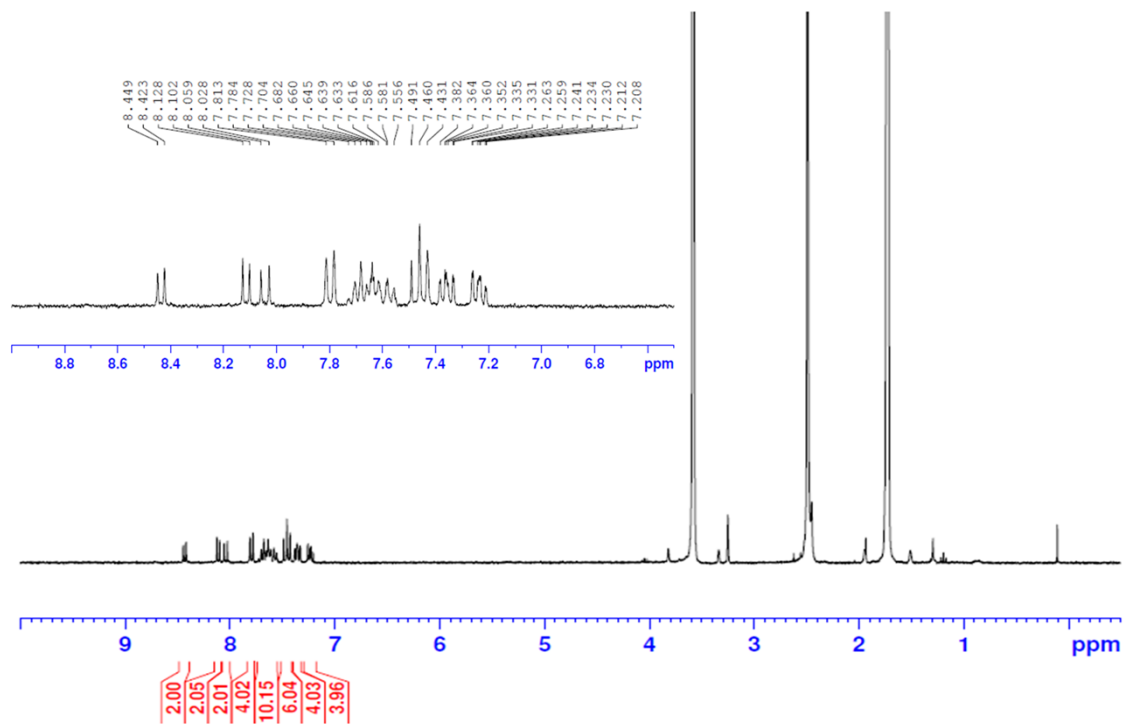

Fig. S1 ^{1}H NMR spectrum of the 1,6 DAP core.
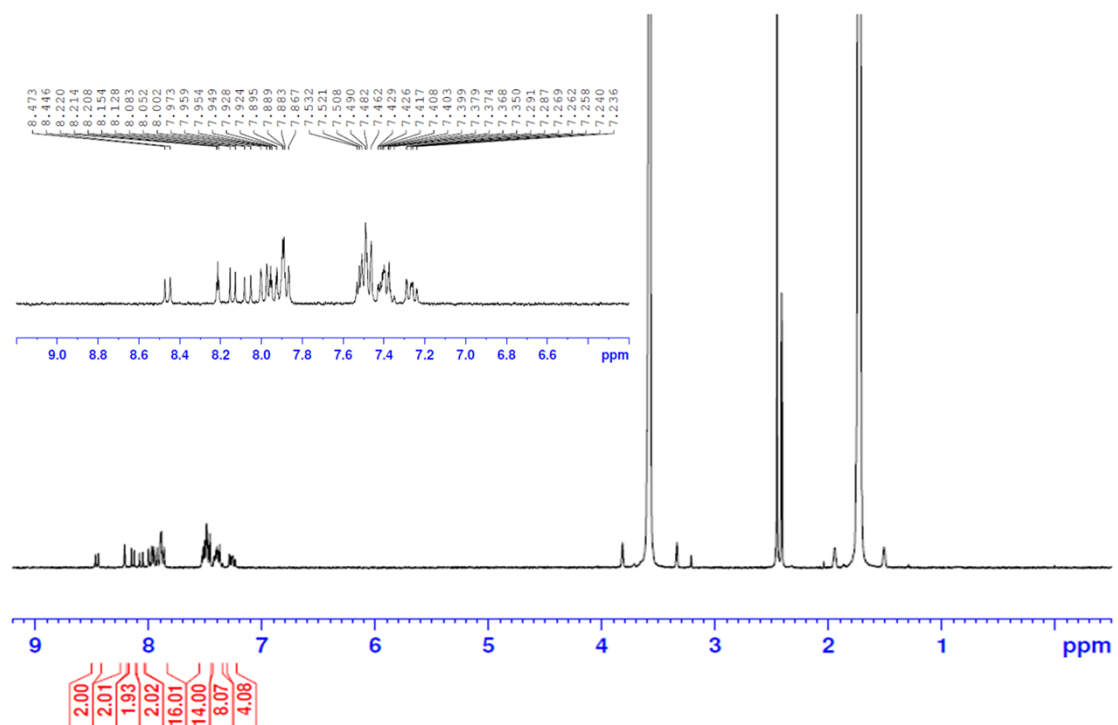
Fig. S2 ¹H NMR spectrum of 1,6 DAP-P.

Fig. S3 ¹H NMR spectrum of 1,6 DAP-TP.

General:

The ^{1}H-NMR spectra were recorded on Bruker Avance 300 spectrometers. The FAB[+]-mass and EI[+]-spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained using a Lambda 1050 UV/Vis/NIR spectrometer (PerkinElmer). A Perkin-Elmer luminescence spectrometer LS50 (Xenon flash tube) was used to collect the photoluminescence (PL) spectra.

The HOMO energy levels were determined by ultraviolet photoelectron yield spectroscopy (Riken Keiki AC-2). The LUMO energy levels were derived from the HOMO energy levels and the band gaps. We determined the optimized structures and dimer structure using density functional theory (DFT) at the B3LYP/6-31G (d) and ωB97XD/6-31G (d) levels of theory, respectively.

The variable angle spectroscopic ellipsometry (VASE) measurements of the films prepared from the synthesized materials on Si substrates were performed using a fast spectroscopic ellipsometer (M-2000U, J. A. Woollam Co., Inc.) at seven angles of incident light ranging from 45° to 75° in steps of 5°. At each angle, the experimental ellipsometric parameters Ψ and Δ were simultaneously obtained in steps of 1.6 nm throughout the spectral region from 245 to 1000 nm. VASE data were analyzed using the WVASE32 (J. A. Woollam Co., Inc) software. In the analysis, we assumed that the peak wavelength and the band width of each absorption band have the common values in the horizontal and vertical directions, which means that the absorption spectrum of each molecule does not depend on the molecular orientation.[2] In Table S1, we summarize the obtained values of the mean square errors (MSEs) of the fitting analysis, the orientation order parameter S, and $\langle\cos^2\theta\rangle$, where S is defined as $S = \dfrac{k_e - k_o}{k_e + 2k_o}$, θ is the angle between the normal direction of the substrate surface and the transition dipole moment of the molecule, and $\langle\cdots\rangle$ indicates the ensemble average. The MSE value of 1,6 DAP-TP is much larger than those of the other materials, probably because of a deviation of the above optical models from the real situation. The deviation is largest for 1,6 DAP-TP likely due to the strong molecular interactions among 1,6 DAP-TP molecules. Thus, for safety, we assume a very large error of k_e of 0.10 for 1,6 DAP-TP. Even with such a large error, our qualitative discussion of the system is not affected.

X-ray diffraction patterns were measured on a Bruker D8 Discover Diffractometer using a Cu Kα radiation source (Kα1 radiation, wavelength λ = 1.54060 Å). Time-resolved fluorescence lifetime experiments were performed using the time-correlated single photon counting (TCSPC) technique implemented in a FluoTime200 spectrometer (PicoQuant) equipped with a PicoHarp300 TCSPC board (PicoQuant) and a PMA182 photomultiplier (PicoQuant). The excitation source was a 377 nm picosecond pulsed diode laser (PicoQuant, LDH375) driven by a PDL800-D driver (PicoQuant) with a FWHM of ~70 ps. The decay time fitting procedure was carried out using the IRF implemented in the Fluofit software (PicoQuant).

The EL devices were prepared using tris(N-(naphthalen-2-yl)-N-phenyl-amino)triphenylamine (2-TNATA) as the hole injection layer (HIL) and N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine(NPB) as the hole transporting layer (HTL). The synthesized materials were used in the emitting layer (EML), 8-hydroxyquinoline aluminum (Alq_3) was used in the electron transporting layer (ETL), lithium fluoride (LiF) was used in the electron injection layer (EIL), and ITO was used as the anode and Al as the cathode. All organic layers were deposited under 10^{-6} Torr, with a rate of deposition of 1 Å s^{-1}, to give an emitting area of 4 mm^2. The LiF and aluminum layers were continuously deposited under the same vacuum conditions. The luminance efficiency data of the fabricated EL devices were obtained using a Keithley 2400 electrometer. Light intensities were obtained using a Minolta CS-1000A. The operational stabilities of the devices were measured under encapsulation in a glove box.

Single crystal X-ray diffraction data of compound 1,6 DAP-TP:

Single crystals suitable for X-ray analysis were obtained from a tetrachloroethane solution. Intensity data were collected at 103 K using a diffractometer equipped with an ADSC Quantun315 CCD detector using synchrotron radiation at a wavelength of 0.85 Å at the SPring-8 beamline BL38B1. A total of 8050 reflections were measured with a maximum 2Θ angle of 62.0°, of which 2995 were independent reflections (R_{int} = 0.0996). The collected diffraction data were processed using the HKL2000 software program. The structure was solved by direct methods (SHELXS-97[1]) and refined using the full-matrix least-squares method on F^2 (SHELXL-97[3]). The crystal contained a disordered tetrachloroethane molecule, i.e., (C41, C42, Cl1, Cl2, Cl3, Cl4), which was solved using an appropriate model. Thus, two sets of disordered atoms i.e. (C41A, C42A, Cl2A, Cl4A) and (C41B, C42B, Cl2B, Cl4B) were modeled and their occupancies were refined to be 0.48 and 0.52, respectively. All non-hydrogen atoms, except for a disordered solvent molecule, were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data were as follows: $C_{80}H_{50}$•2($C_2H_2Cl_4$); FW = 1346.87, crystal size 0.05 x 0.05 x 0.01 mm^3, Triclinic, P–1, a = 9.326(2) Å, b = 9.491(2) Å, c = 20.374(7) Å, α = 91.17(3), β = 103.492(11)°, γ = 115.22(2)° V = 1571.7(7) $Å^3$, Z = 1, D_c = 1.423 g cm^{-3}. The refinement converged to R_1 = 0.0820, wR_2 = 0.1960 (I > 2σ(I)), GOF = 0.813.

Table S1. The values of MSE, the orientation order parameter S, and $<\cos^2\theta>$ obtained by ellipsometry analysis.

	MSE	S	$<\cos^2\theta>$
1,6 DAP core	4.5	−0.17±0.04	0.22±0.03
1,6 DAP-P	5.4	−0.26±0.04	0.16±0.03
1,6 DAP-TP	13.0	−0.50 - −0.37[a]	0 - 0.09[a]

[a]Because of a possible deviation of the optical model from the real situation, we assume a very large error of k_e of 0.10 for 1,6 DAP-TP for safety.
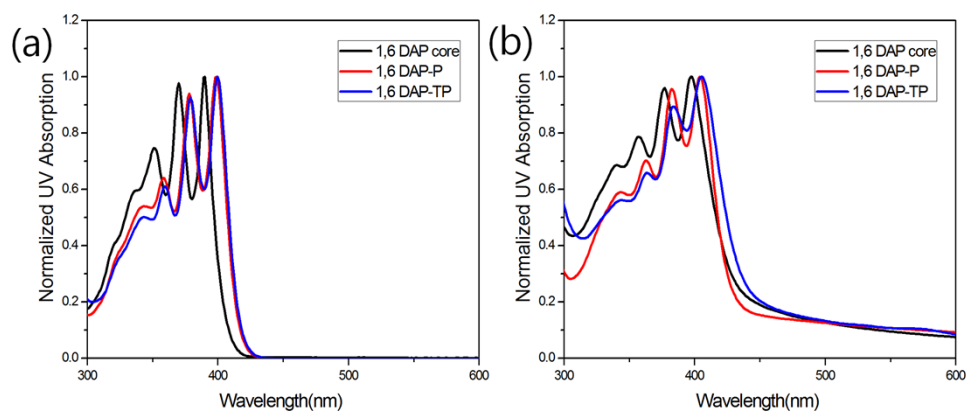

Fig. S4 (a) UV absorption spectra of the THF solution (1×10^{-5} M), (b) UV absorption spectra of the film prepared by evaporation onto glass (film thickness: 50 nm).
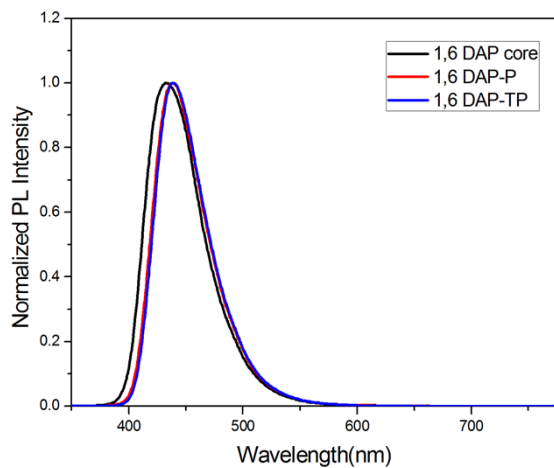
Fig. S5 PL spectra of the materials in a THF solution (1 x 10^{-5} M).
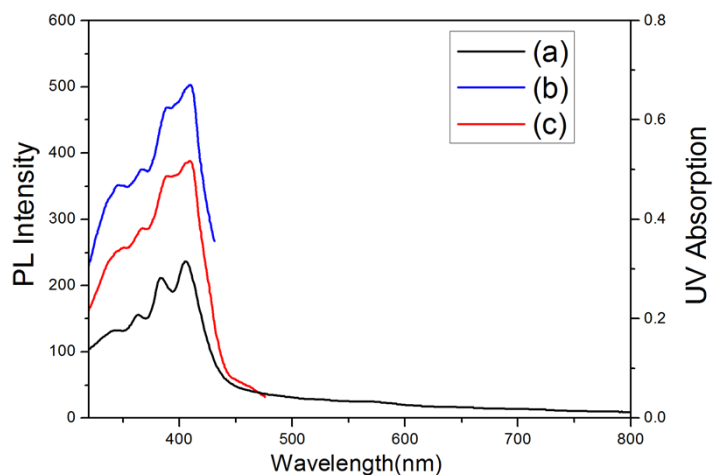
Fig. S6 UV absorption spectrum and excitation spectra of 1,6 DAP-TP film (thickness: 50nm): (a) UV absorption spectrum, (b) excitation spectrum monitored at 455 nm, (c) excitation spectrum monitored at 591 nm.
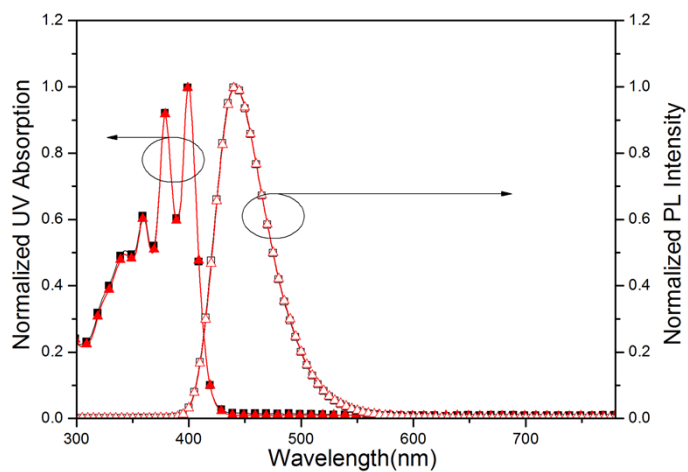

Fig. S7 UV absorption and PL spectra of 1,6-DAP-TP solution (squares, before deposition) and 1,6-DAP-TP deposited film solution (triangles, after deposition) (solvent: THF).
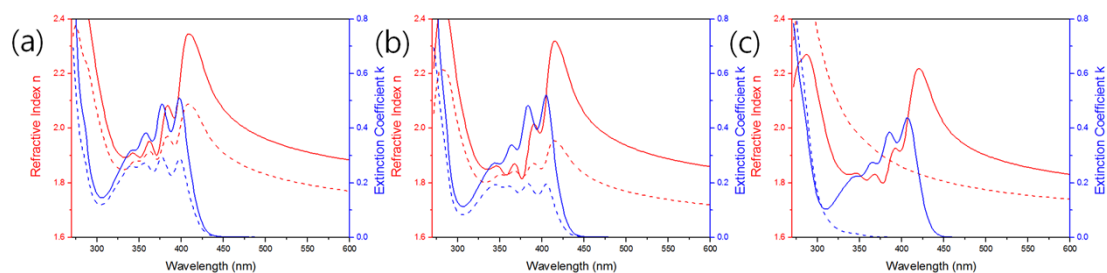
Fig. S8 Optical anisotropy of the films prepared from the (a) 1,6 DAP core, (b) 1,6 DAP-P, (c) 1,6 DAP-TP: anisotropic refractive indices n and extinction coefficients k. The solid lines (n_o and k_o) and dotted lines (n_e and k_e) indicate the horizontal (ordinary) and vertical (extraordinary) components of the optical constants, respectively.
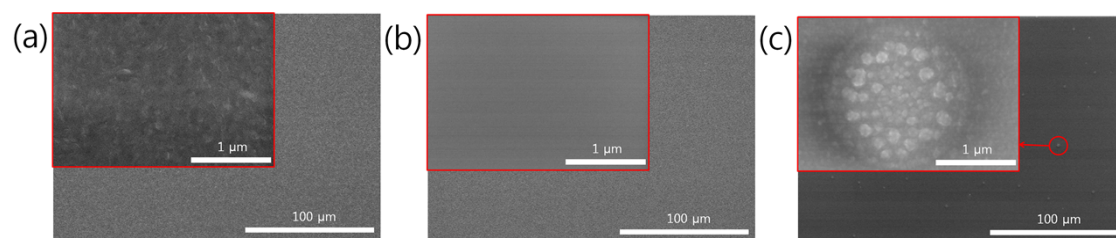

Fig. S9 SEM images of (a) 1,6 DAP core, (b) 1,6 DAP-P, (c) 1,6 DAP-TP: 200 nm films deposited on Si substrates
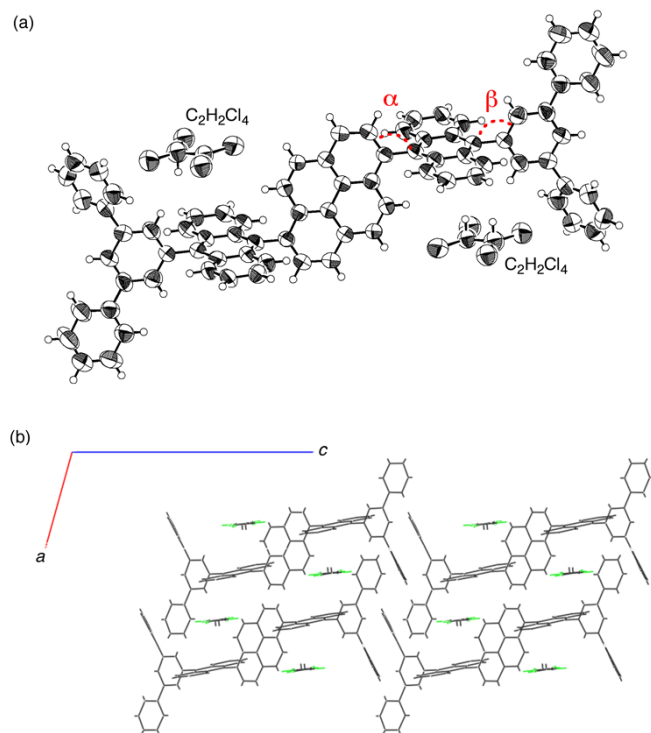
Fig. S10 The single crystal structure of 1,6 DAP-TP·2(C$_2$H$_2$Cl$_4$): (a) ORTEP drawing (50% probability for thermal ellipsoids) and (b) packing structure.
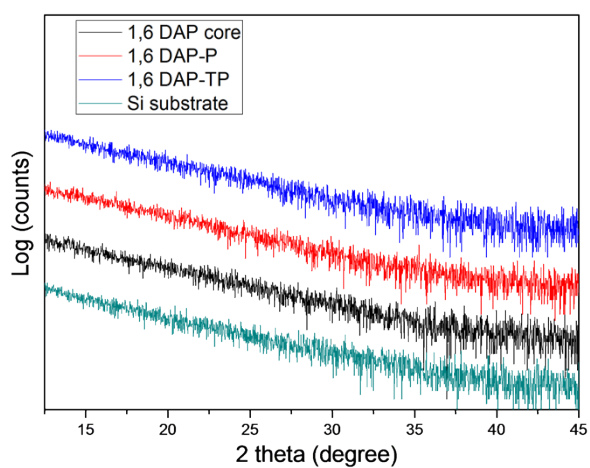

Fig. S11 In-plane XRD patterns obtained from 1,6 DAP core, 1,6 DAP-P, and 1,6 DAP-TP (200 nm films deposited on Si substrates)
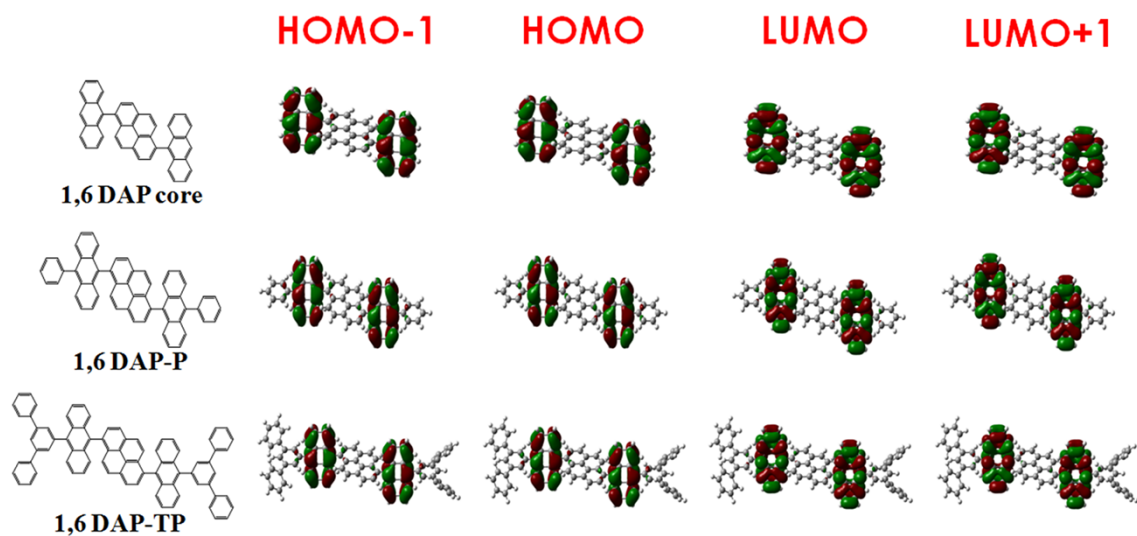
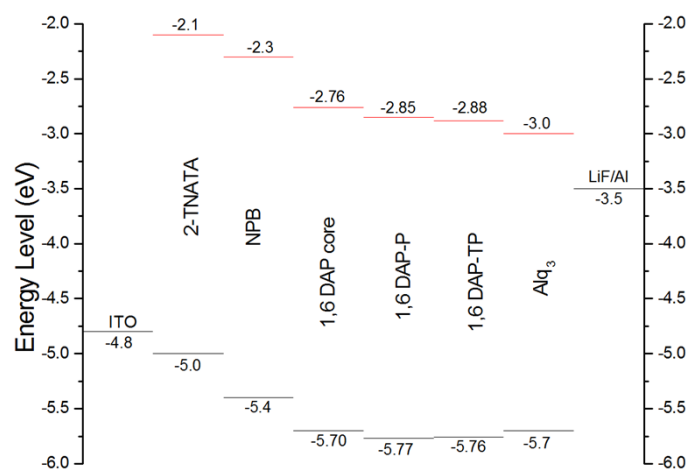**Fig**. S12 HOMO-1, HOMO, LUMO, and LUMO+1 shapes calculated at the B3LYP / 6-31G (d) level of theory.

Fig. S13 Energy diagrams of the organic compounds used in the OLED device.

[1] (a) B. Kim, Y. Park, J. Lee, D. Yokoyama, J. H. Lee, J. Kido, J. Park, *J. Mater. Chem. C.,* 2013, 1, 432. (b) Y. Park, J. Lee, D. H. Jung, S. Liu, Y. Lin, L. Chen, C. Wu, J. Park, *J. Mater. Chem.,* 2010, 20, 5930. (c) S. K. Kim, Y. I. Park, I. N. Kang, J. H. Lee, J. W. Park, *J. Mater. Chem.,* 2007, 17, 4670.

[2] D. Yokoyama, A. Sakaguchi, M. Suzuki and C. Adachi, *Org. Electron.*, 2009, 10, 127.

[3] Sheldrick, G. M. SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.