Supporting Information

One-pot heteroannulation toward phosphaperylene diimides with high luminescence and out-of-plane anisotropy

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1. Materials and Measurements

¹H NMR, ¹³C NMR ³¹P NMR spectra were recorded in deuterated solvents on a Bruker AVIII 500 MHz NMR Spectrometer or Bruker AVANCE 400 MHz NMR Spectrometer. ¹H NMR and ¹³C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer.

Absorption spectra were measured with Shimadzu (UV-3600) UV-Vis-NIR spectrophotometer in a 1-cm quartz cell. TGA spectra were measured with Pyris 1 TGA. Emission spectra were measured with Jasco FP-660 Spectrofluorometer and Horiba Fluoromax4 Spectrofluorometer. The absolute photoluminescence quantum yields of fluorescence were collected by HAMAMATSU Quantaurus-QY instrument in air. The data of transient fluorescence/phosphorescence decay spectra were determined with HAMAMATSU Quantaurus-Tau spectrometer C11367. Cyclic voltammetry (CV) was performed with a CHI620E electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode at a scanning rate of 100 mV/s. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in CH_2CI_2 was employed as the supporting electrolyte. The plot includes the signal of the ferrocene as an internal potential marker. CH_2CI_2 was freshly distilled prior to use.

Single crystals data collections were performed on MM007HF Saturn724+ diffractometer, using Cu Ka radiation (1.5418 Å). Using Olex2, these structures were solved with the ShelXS and refined with the ShelXL-2014 refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

All chemicals were purchased from commercial suppliers (for example, J&K Corp.) and used without further purification unless otherwise specified.

2. Synthesis and Characterization

The starting material 4CIPDI (1) was synthesized according to literature.[1]

A Schlenk flask was charged with **1** (445 mg, 0.5 mmol), $Pd(dppf)Cl_2$ (55 mg, 0.075 mmol) and KOAc (981 mg, 10 mmol). Then, phenylphosphine (1.1 g, 10 wt% in *n*-hexane) was added through syringe under an argon atmosphere after 10 mL toluene was injected. The mixture was heated to 110 °C and was stirred overnight. After cooling down to room temperature, the mixture was diluted with chloroform, and was added with 2 mL H₂O₂ and stirred for additional 0.5 h. The solution was further dried with Na₂SO₄ and concentrated under reduced pressure distillation to remove the solvent, and then the mixture was purified by column chromatography on silica gel, eluted with ethyl acetate/CH₂Cl₂ to afford corresponding oxide compounds. Eluted with EtOAc: DCM (1: 20 v/v), the Rf values of compound **4**, *cis*-**5** and *trans*-**5** are measured to be 0.55, 0.10 and 0.68, respectively.

4 (red solids, yield: 32%): ¹H NMR (400 MHz, C₂D₂Cl₄, 298 K, ppm): δ = 8.80 (d, 2H), 8.72 (d, *J* = 7.9 Hz, 2H), 8.57 (d, *J* = 7.9 Hz, 2H), 7.77 (dd, *J*₁ = 7.6 Hz, *J*₂ = 13.4 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.45 (m, 2H), 4.95 (t, *J*_{H-F} = 15.48 Hz, 4H); ¹³C NMR (125 MHz, C₂D₂Cl₄, 373.2 K, ppm): δ = 162.47, 162.03,140.57, 140.40, 135.52, 134.46, 133.87, 132.93, 131.38, 130.91, 130.82, 129.65, 129.55, 125.13, 124.21, 124.14, 123.29, 38.85, (t, *J*_{C-F} = 22.9 Hz); ³¹P NMR (162 MHz, C₂D₂Cl₄, ppm): δ = 36.95; HRMS (MALDI (N), 100%) m/z calcd for C₃₈H₁₅F₁₄N₂O₅P: 876.0500, found 876.0495.

cis-5 (red solids, yield: 22%): ¹H NMR (400 MHz, C₂D₂Cl₄, 298 K, ppm): δ = 8.83 (d, 4H), 7.84 (dd, J₁ = 7.9 Hz, J₂ = 13.8 Hz, 4H), 7.66 (t, J = 7.3 Hz, 2H), 7.49 (m, 4H), 4.97 (t, J_{H-F} = 15.24 Hz, 4H); ¹³C NMR (125 MHz, C₂D₂Cl₄, 373.2 K, ppm): δ = 161.96, 140.66, 140.48, 135.29, 134.29, 133.60, 133.51, 130.82, 130.74, 129.82, 129.71, 124.84, 39.10; ³¹P NMR (162 MHz, C₂D₂Cl₄, ppm): δ = 42.70; HRMS (MALDI (N), 100%) m/z calcd for C₄₄H₁₈F₁₄N₂O₆P₂: 998.0422, found 998.0412.

trans-5 (red solids, yield: 3%): ¹H NMR (400 MHz, C₂D₂Cl₄, 298 K, ppm): δ = 8.82 (s, 4H), 7.81 (dd, J₁ = 7.5 Hz, J₂ = 13.6 Hz, 4H), 7.67 (t, J = 7.4 Hz, 2H), 7.50 (m, 4H), 4.94 (t, J_{H-F} = 15.24 Hz, 4H); ¹³C NMR (125 MHz, C₂D₂Cl₄, 373.2 K, ppm): δ =161.93, 140.87, 14070, 135.09, 134.35, 134.24, 133.65, 133.55, 132.12, 130.75, 130.66, 129.89, 129.79, 126.77, 125.94, 124.79, 124.71, 39.05; ³¹P NMR (162 MHz, C₂D₂Cl₄, ppm): δ = 42.70; HRMS (MALDI (N), 100%) m/z calcd for C₄₄H₁₈F₁₄N₂O₆P₂: 998.0422, found 998.0417.

3. Thermodynamic Properties



Fig. S1 TGA curves of 4, cis-5, and trans-5 under nitrogen flow.

4. Cyclic Voltammetry Measurement



Fig. S2 cyclic voltammograms in deaerated CH_2Cl_2 solution containing Bu_4NPF_6 (0.1 mol L⁻¹). compound **4** is identified by red trace, *cis*-**5** is identified by green trace, *trans*-**5** is identified by blue trace, and the reference PDI is identified by black trace.

5. Photophysical Properties



Fig. S3 UV-vis absorption spectra in 10⁻⁵ M CHCl₃ solution, compound **4** is identified by red trace, *cis*-**5** is identified by green trace, *trans*-**5** is identified by blue trace, and the reference PDI is identified by black trace.



Fig. S4 Photodegradation study of a) **4**, b) *cis*-**5**, and c) *trans*-**5**. Absorption spectra (10^{-5} M, toluene) were measured in a 1-cm quartz cell, continuously irradiated with UV light (6 W × 2, λ = 365 nm); d) The evolution of relative absorbance at the respective lowest energy absorption peak with the radiation time.

All phosphaperylene diimides derivatives demonstrated high photostability over a long time of UV irradiation. The absorption spectrum of **4** and *trans*-**5** hardly changed after 5h UV irradiation (365nm), while *cis*-**5** showed excellent photostability within 1 h UV irradiation but suffered a mild photodegradation soon afterward.



Fig. S5 3D emission spectra of 4 in CHCl₃ (10⁻⁵ M), color scale: from purple to blue to green to yellow to red to black.



Fig. S6 3D emission spectra of *cis*-5 in CHCI₃ (10⁻⁵ M), color scale: from purple to blue to green to yellow to red to black.



Fig. S7 Time-resolved photoluminescence decay curves of phosphaperylene diimides derivatives in CHCl₃ (10⁻⁵ M)

Table S1 Optical and electrochemical properties of phosphaperylene diimides derivatives

Compound	λ _{max} [nm] ^[a]	ε [М ⁻¹ сm ⁻¹] [а]	λ _{em} [nm] ^[a]	E _{LUMO} [eV] ^[b]	E _{HOMO} [eV] ^[c]	E _g [eV] ^[d]	φ _{fl} <i>[%]</i> (λ _{ex} =485 nm) ^[a]	τ (ns) (λ _{ex} =485 nm) ^[a]
PDI	525	88200	535	-3.95	-6.23	2.28	91.0	
4	548	55050	561	-4.24	-6.42	2.18	85.4	6.72
cis-5	563	37050	578	-4.41	-6.54	2.13	94.0	8.75
trans-5	563	37350	579	-4.42	-6.54	2.12	93.5	8.68

[a] λ_{abs} , ε_{max} , λ_{onset} , λ_{em} , Φ_{fl} and τ were measured in CHCl₃ (1.0 × 10⁻⁵ M). [b] Estimated from the onset potential of the first reduction wave and calculated according to $E_{LUMO} = -(4.8 + E_{onset})^{e}$ eV. [c] Calculated according to $E_{HOMO} = (E_{LUMO} - E_g)$ eV. [d] Obtained from the edge of the absorption in CHCl₃ solution according to $E_g = (1240/\lambda_{onset})$



Fig. S8 Images obtained by optical microscopy of the microfibers of 4 (a) and *cis*-5 (b). The width and length of the fibers are indicated in blue. Scale bars: $50 \mu m$.

6. X-ray Crystallographic Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. The single crystal X-ray crystallographic data were summarized in Table S1.

Compound	4	cis- 5	trans-5
CCDC number	2106285	2106292	2106293
Empirical formula	C38H15F14N2O5P	C45H20Cl2F14 N2O6P2	C47H21Cl9F14N2O6P2
Formula weight	876.49	1083.47	1356.65
Crystal system	Monoclinic	Monoclinic	Monclinic
Space group	P1 21/c 1	P1 21/c 1	C2/c
a (Å)	17.4624(4)	17.5562(11)	34.0447(12)
b (Å)	9.90830(10)	11.4446(5)	5.7951(2)
c (Å)	19.9540(3)	20.8876(13)	26.8127(10)
α (°)	90	90	90
β (°)	106.936(2)	97.757(6)	94.674(4)
γ (°)	90	90	90
Volume (ų)	3302.76	4158.4	5272.4
Density (mg/m³)	1.763	1.731	1.709
Crystal size (mm ³)	0.3×0.2×0.1	0.128×0.125×0.021	0.426×0.117×0.032
Z	4	4	4
Data / restraints /	6695/0/541	9502/228/704	6054/2/366
parameters			
Goodness-of-fit on F ²	1.048	1.017	1.059
Final R [I>2sigma(I)]	R1=0.0479, wR2=0.1292	R1=0.0762, wR2=0.1623	R1=0.0891, wR2=0.2578
R indices (all data)	R1=0.0611, wR2=0.1401	R1=0.1553, wR2=0.2013	R1=0.0891 , wR2=0.2724

Table S2. Single-crystal XRD data of phosphaperylene diimides derivatives.

7. Theoretical Calculation

The Density functional theory (DFT) calculations were performed with the Gaussian 16 program² suite employing the PBE0³ exchange-correlation functional and the 6-311G(d) basis set for all atoms. Optimized geometries of top and side views by DFT at the PBE0/6-311G(d) level were calculated. To simplify the calculation, methyl groups are introduced at the imide positions.

UV-vis absorption spectra of compounds were calculated using time-dependent density functional theory (TDDFT) employing the PBE0 functional and 6-311G(d) basis set and the effect of the solvent (chloroform) was taken into account by using polarizable continuum model (PCM).⁴ UV-vis peak present 80 lowest-energy roots determined by the TDDFT calculations.

For the nuclear independent chemical shift (NICS) calculations, the Gauge Independent Atomic Orbitals method (GIAO)⁵ was employed for chemical shifts calculations at the same level as the geometry

optimization. NICS were calculated at the center of each ring for NICS(0). The magnetic NICS index is defined as the negative of the chemical shift computed at ghost atoms, generally located at ring centers or above the plane of the ring.⁶ Any ghost atom can be viewed as a magnetic sensor at which one computes the local magnetic shielding caused by the circulation of the electrons in the ring. Thus, a significant negative NICS value in interior positions of the rings indicate the presence of so-called induced diamagnetic ring currents and is synonym of aromaticity. On the contrary, a positive NICS value denotes induced paramagnetic ring currents and is synonym of antiaromaticity.



Fig. S9 Calculated UV-vis absorption spectra of modle 4, cis-5 and trans-5 by TDDFT.



Fig. S10 Electrostatic potential surface and dipole moment of *trans*-**5** calculated at the PBE0/6-311G(d) level of theory (color code: red = -18.8 kcal mol⁻¹, blue = +18.8 kcal mol⁻¹).



Fig. S11 Calculated frontier molecular orbitals of compound 4.



Fig. S12 Calculated frontier molecular orbitals of cis-5.



Fig. S13 Calculated frontier molecular orbitals of trans-5.

Model	HOMO (eV)	LUMO (eV)	E _g ((eV))
4	-6.62	-3.85	2.77
cis-5	-6.81	-4.06	2.75
trans-5	-6.81	-4.06	2.75

Model	Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Weight(%)
4	S1	2.29	541	0.6237	$\begin{array}{c} 139{\rightarrow}140\\ \text{HOMO} \rightarrow \text{LUMO} \end{array}$	99
cis-5	S1	2.22	558	0.4952	$\begin{array}{c} 170 {\rightarrow} 171 \\ \text{HOMO} {\rightarrow} \text{LUMO} \end{array}$	99
trans-5	S1	2.22	558	0.4952	170→171 HOMO → LUMO	99

Table S4 Parameters of representative excited states of phosphaperylene diimides derivatives

8. References

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9. NMR Spectra



Fig. S14 ¹H NMR of 4 recorded in C₂D₂Cl₄.



Fig. S15 ¹H NMR of *cis*-5 recorded in C₂D₂Cl₄.



Fig. S16 ¹H NMR of *trans*-5 recorded in C₂D₂Cl₄.



Fig. S17 ¹³C NMR of 4 recorded in $C_2D_2Cl_4$.





Fig. S19 ¹³C NMR of *trans*-5 recorded in C₂D₂Cl₄.



Fig. S20 ³¹P NMR of 4 recorded in $C_2D_2Cl_4$.



Fig. S21 ³¹P NMR of *cis*-5 recorded in C₂D₂Cl₄.



Fig. S22 ³¹P NMR of *trans*-5 recorded in C₂D₂Cl₄.