Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

ELECTRONIC SUPPLEMENTARY INFOMATION

Control of electrochemical and photophysical properties of *N*-substituted benzo[*ghi*]perylene derivatives

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Synthesis

DABPIm. DAP (60 mg, 0.24 mmol), *p*-chloranil (131 mg, 0.53 mmol) and maleic anhydride (941 mg, 9.6 mmol) were added in dried vessel, and the mixture was heated with stirring at 225 ºC for 3 days. After cooling to room temperature, the mixture was washed with an excessive amount of chloroform and methanol. The crude and 4-heptylamine (750 mg, 6.5 mmol) were added to DMF (30 mL), and the mixture was heated at 150 ºC for 16 h. After cooling to room temperature, the mixture was eluted in cool water. The suspension was filtered off, and the crude was chromatographed on basic silica, eluting with chloroform/methanol/triethylamine = 100/10/1. Finally, DABPIm was purified by recycle gel permeation chromatography. Yellow powder; yield: 15.5 mg (14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.60 (2H, d, J = 5.4 Hz), 9.58 (2H, d, J = 9.3 Hz), 8.39 (2H, d, J = 9.3 Hz), 8.30 (2H, d, J = 5.4 Hz), 4.49 (1H, quint, J = 5.1 Hz), 2.31-2.25 (2H, m), 1.85-1.81 (2H, m), 1.44 (4H, q, J = 7.8 Hz), 0.98 (6H, t, J = 7.8 Hz), ^{13}C NMR (100 MHz, CDCl3) δ (ppm) 169.1, 147.7, 146.3, 135.2, 128.3, 126.4, 123.9, 123.7, 123.4, 120.7, 119.3, 51.8, 34.7, 20.17, 13.9. High resolution MALDI-TOF MS: m/z calcd: 468.169 [M+Na] found: 468.166. mp > 290 ºC. FT-IR (KBr) $\tilde{\nu}$ (Int.): 2959 (w), 2866 (w), 1758 (m), 1698 (s), 1617 (w), 1579 (m), 1557 (w), 1360 (s), 1260 (w), 1150 (w), 1062 (w), 854 (m), 799 (w), 755 (w), 607 (w), 548 (w).

TABPIm. DAP (100 mg, 0.39 mmol), 4-phenyl-1,2,4-triazoline-3,5-dione (345 mg, 2.0 mmol) and *p*-chloranil (100 mg, 0.40 mmol) were dissolved in toluene (20 mL), and the mixture was stirred at 150 ºC for 18 h. After cooling to room temperature, the solvent was removed under reduced pressure. Then, the residue was chromatographed on basic silica, eluting with chloroform/methanol/triethylamine = 100/10/1 to give TABPIm (68 mg,

40%) as a purple solid. ^{1}H NMR ($CDCl_3$) δ: 8.72 (2H, d, J = 5.6 Hz), 8.67 (2H, d, J = 9.0 Hz), 7.71 (2H, d, J = 9.0 Hz), 7.61-7.57 (4H, m), 7.52-7.51 (3H, m). High resolution MALDI-TOF MS: m/z calcd: 427.107 [M] found: 467.046. mp > 290 ºC. FT-IR (KBr) $\tilde{\nu}$ (Int.): 3114 (w), 3016 (w), 2920 (w), 2849 (w), 1757 (s), 1708 (s), 1579 (m), 1484 (m), 1394 (s), 1339 (s), 1260 (w), 1139 (m), 1022 (m), 851 (s), 759 (s), 689 (w), 642 (w) 540 (w), 501 (w).

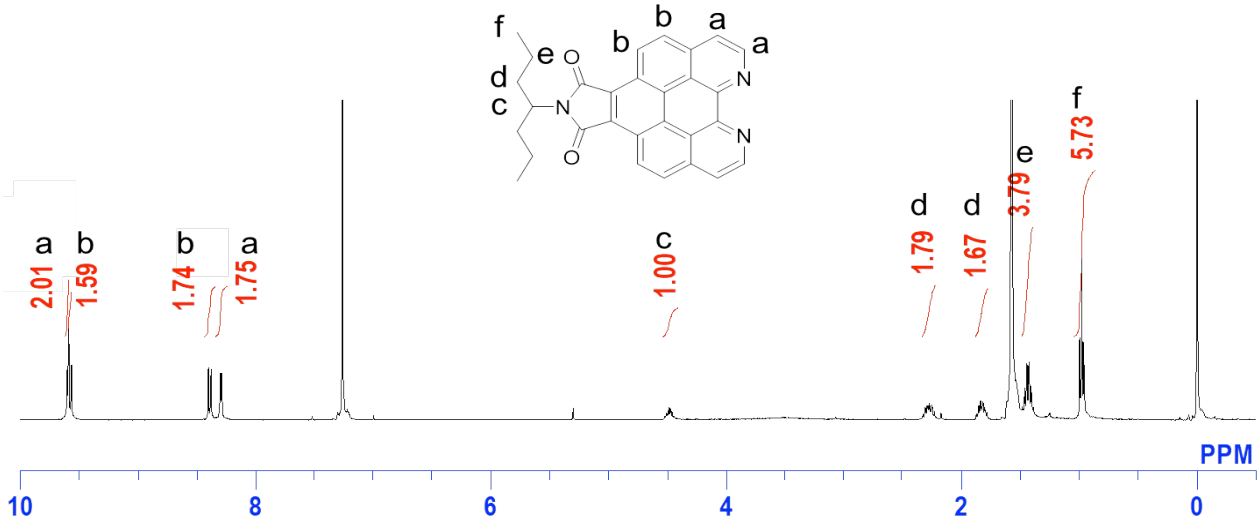


Fig. S1 ^{1}H NMR spectrum of DABPIm (400 MHz, $CDCl_3$).

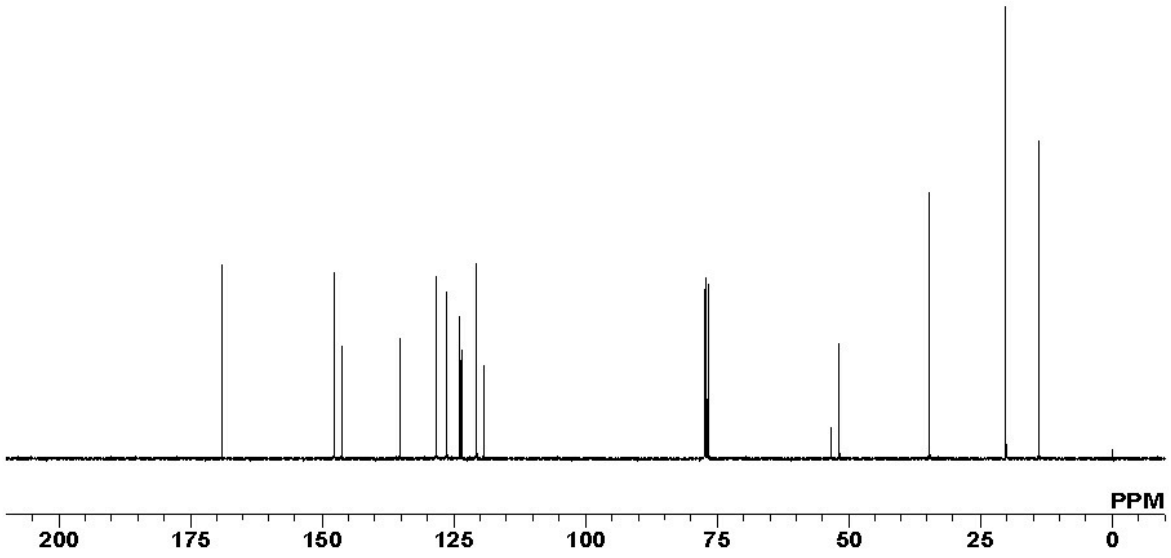


Fig. S2 ^{13}C NMR spectrum of DABPIm (100 MHz, $CDCl_3$).

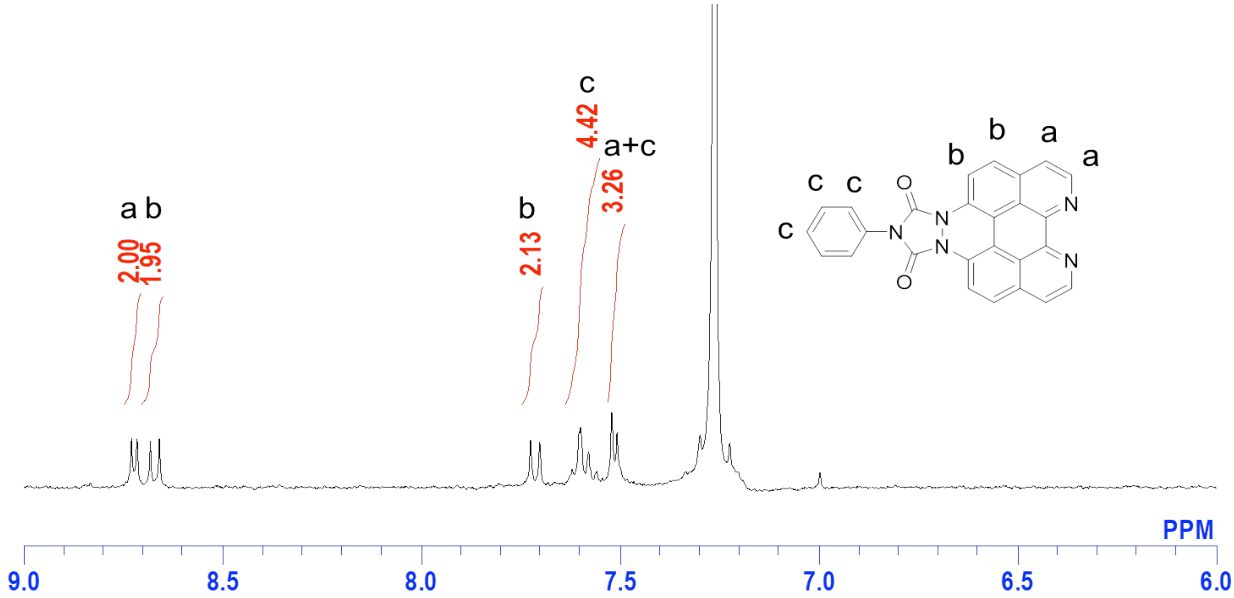


Fig. S3 ^{1}H NMR spectrum of TABPIm (400 MHz, $CDCl_3$).

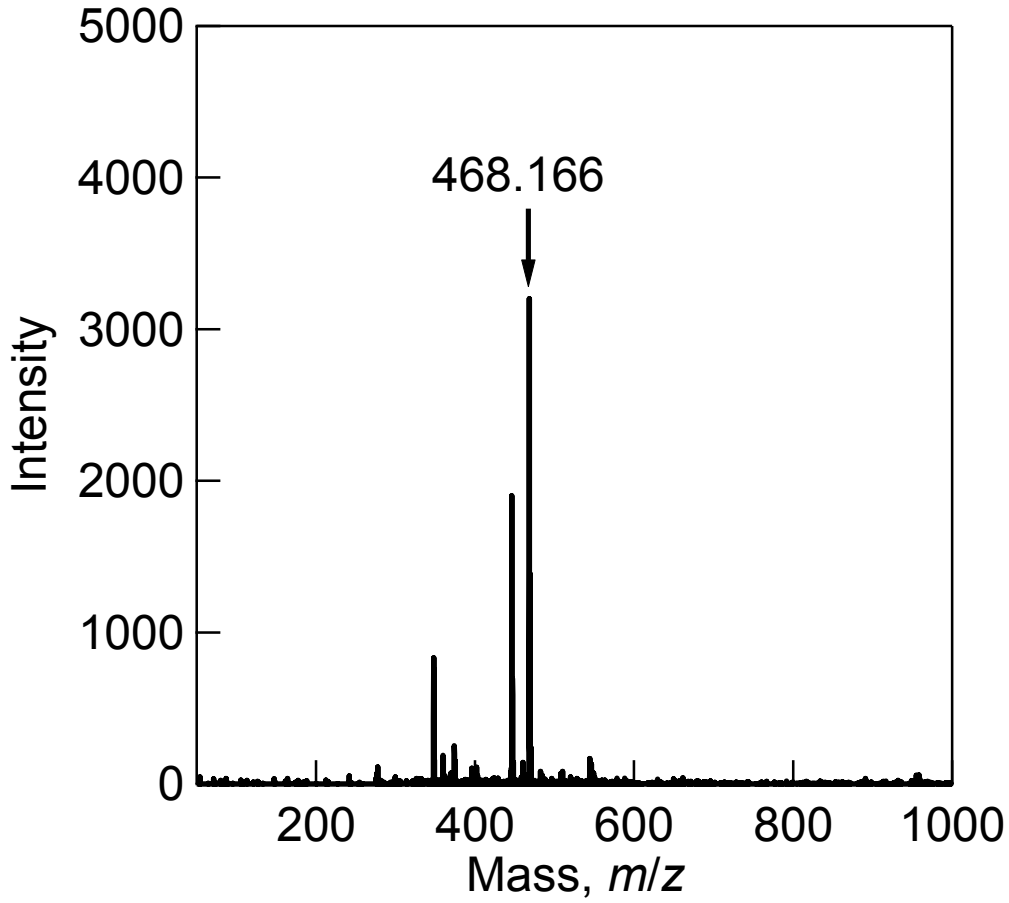


Fig. S4 High resolution MALDI-TOF mass spectrum of DABPIm.

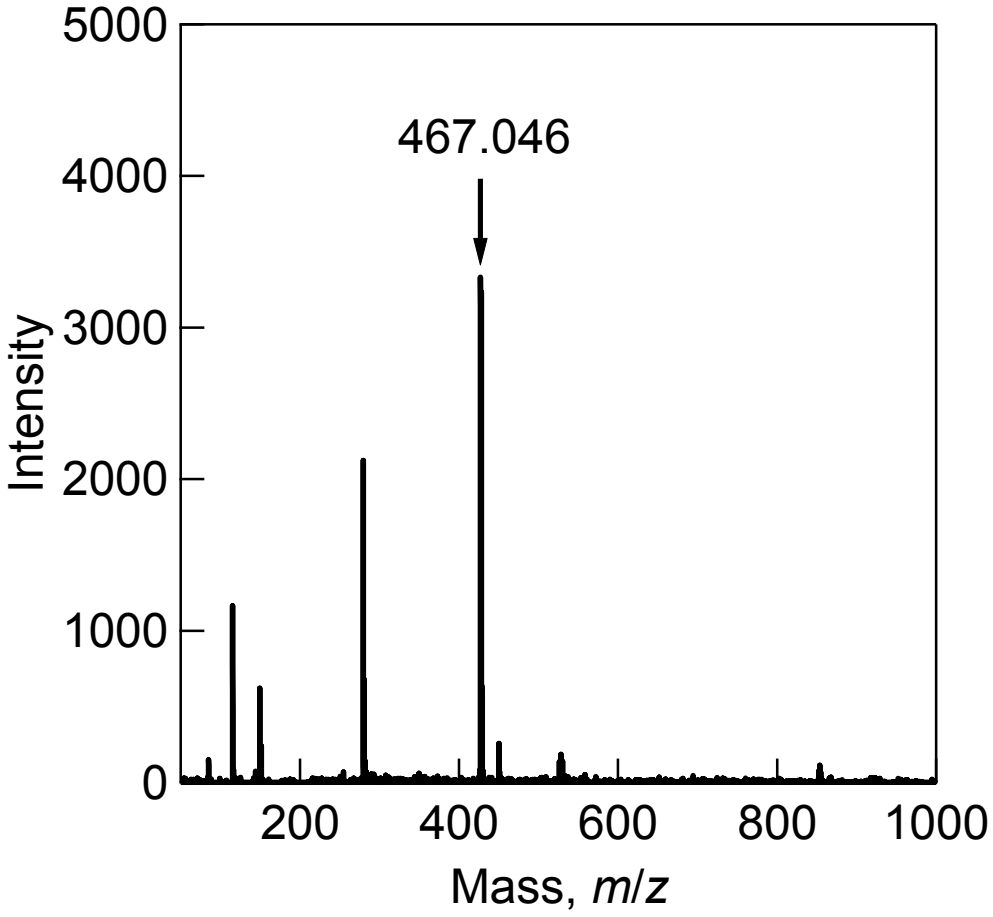


Fig. S5 High resolution MALDI-TOF mass spectrum of TABPIm.

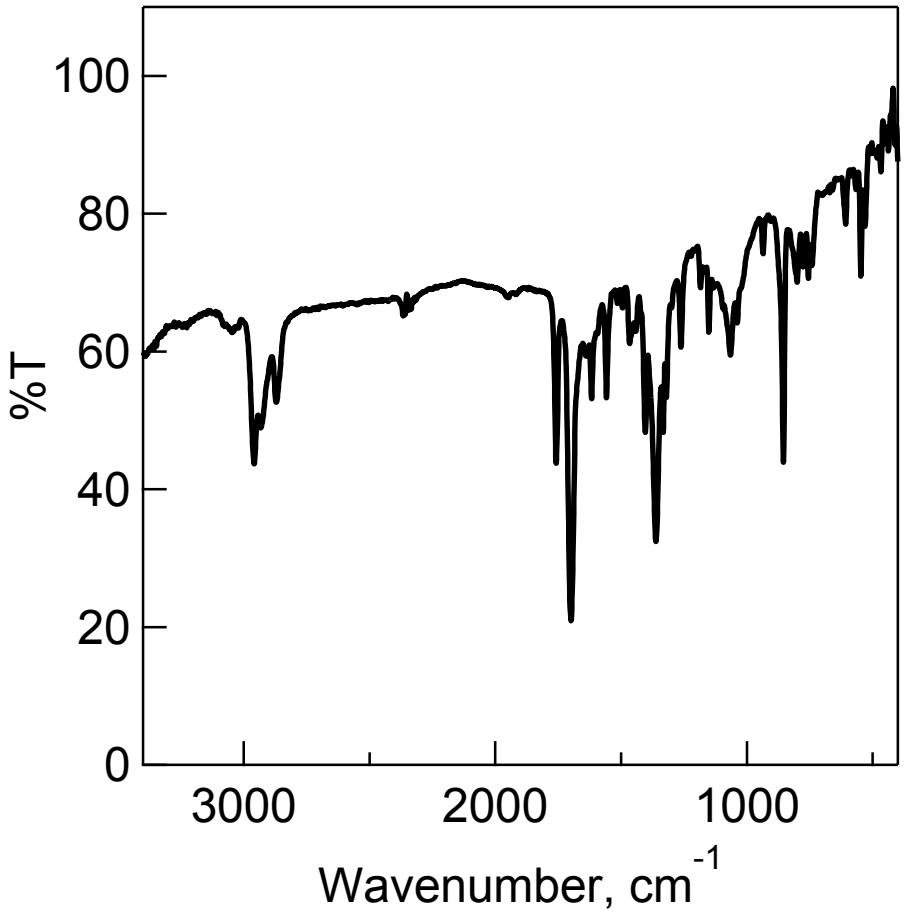


Fig. S6 FT-IR spectrum of DABPIm.

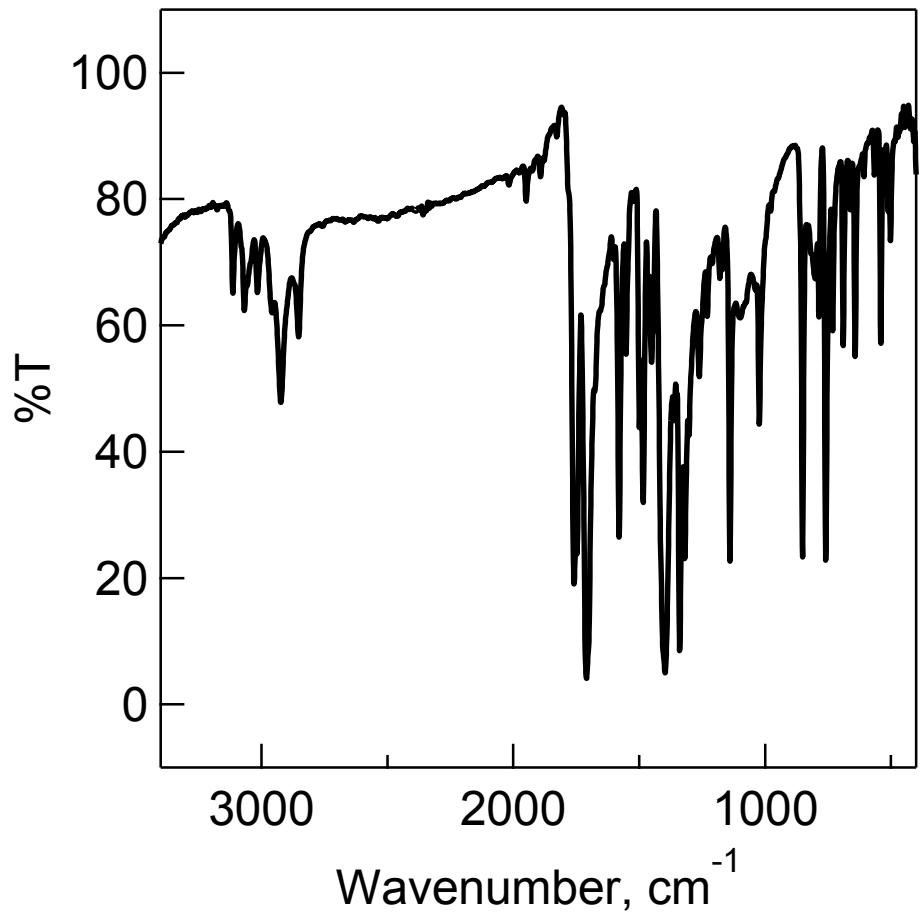
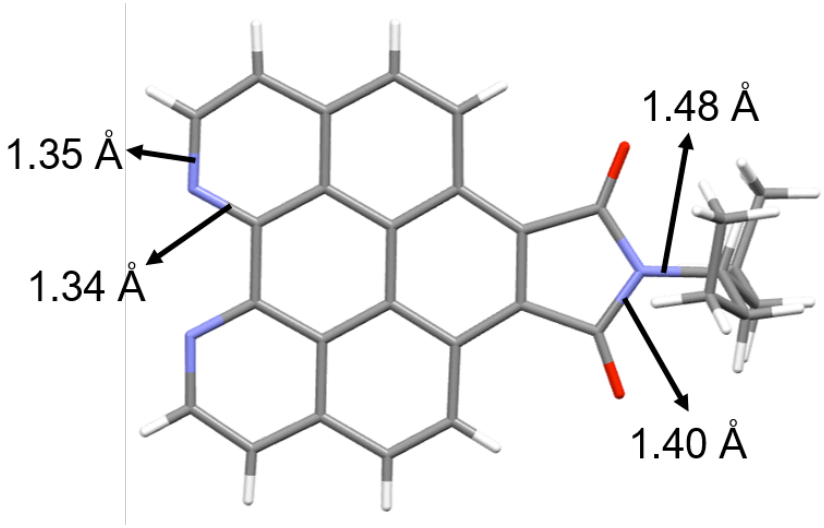


Fig. S7 FT-IR spectrum of TABPIm.

(A)



(B)

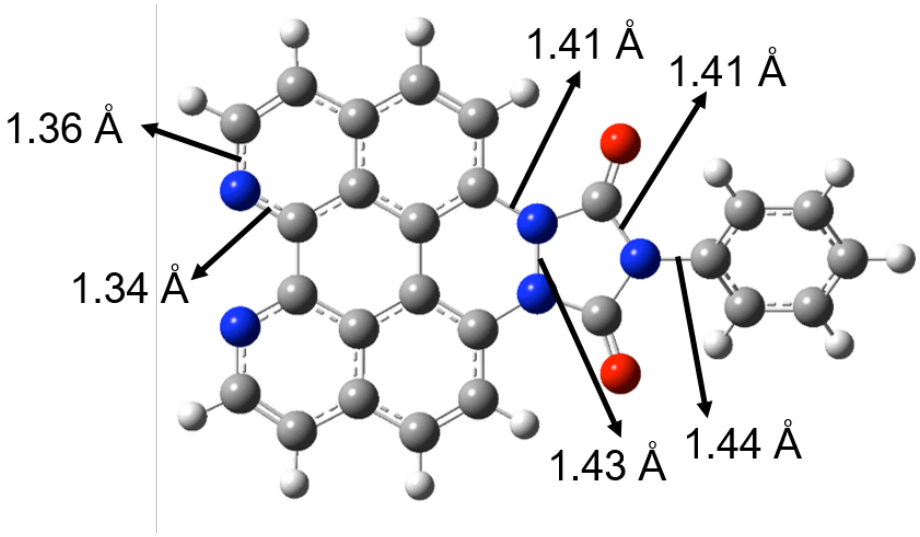


Fig. S8 Structural analyses of DABPIm and TABPIm. (A) ORTEP diagram of DABPIm evaluated by X-ray analysis. (B) Optimized structure calculated in B3LYP/6-31+G(d) level of TABPIm.

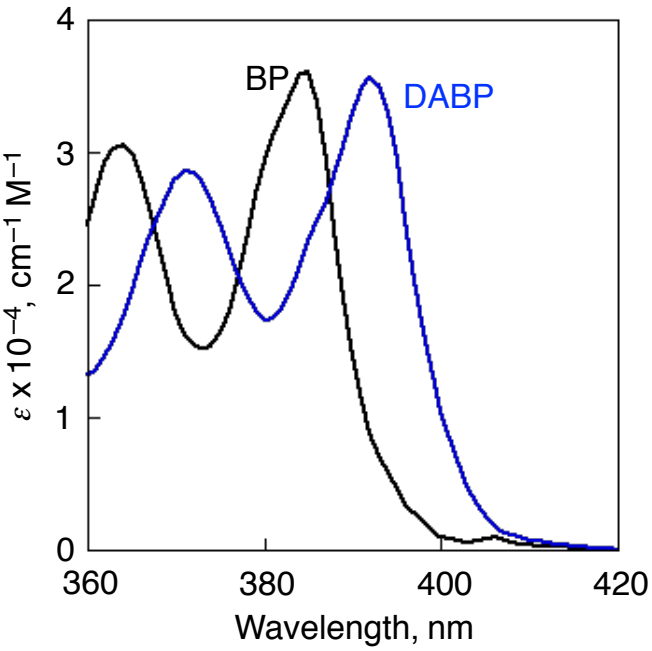


Fig. S9 Absorption spectra of BP (black) and DABP (blue) in CH_2Cl_2.

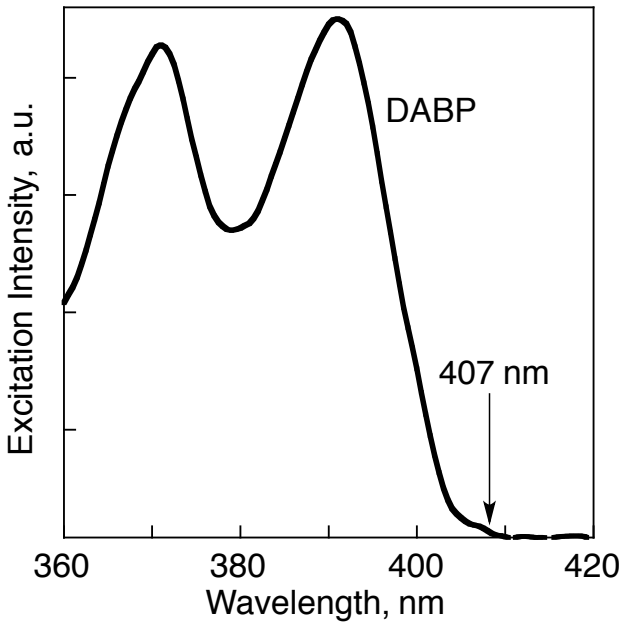


Fig. S10 Excitation spectrum of DABP in CH_2Cl_2. Observed at 430 nm.

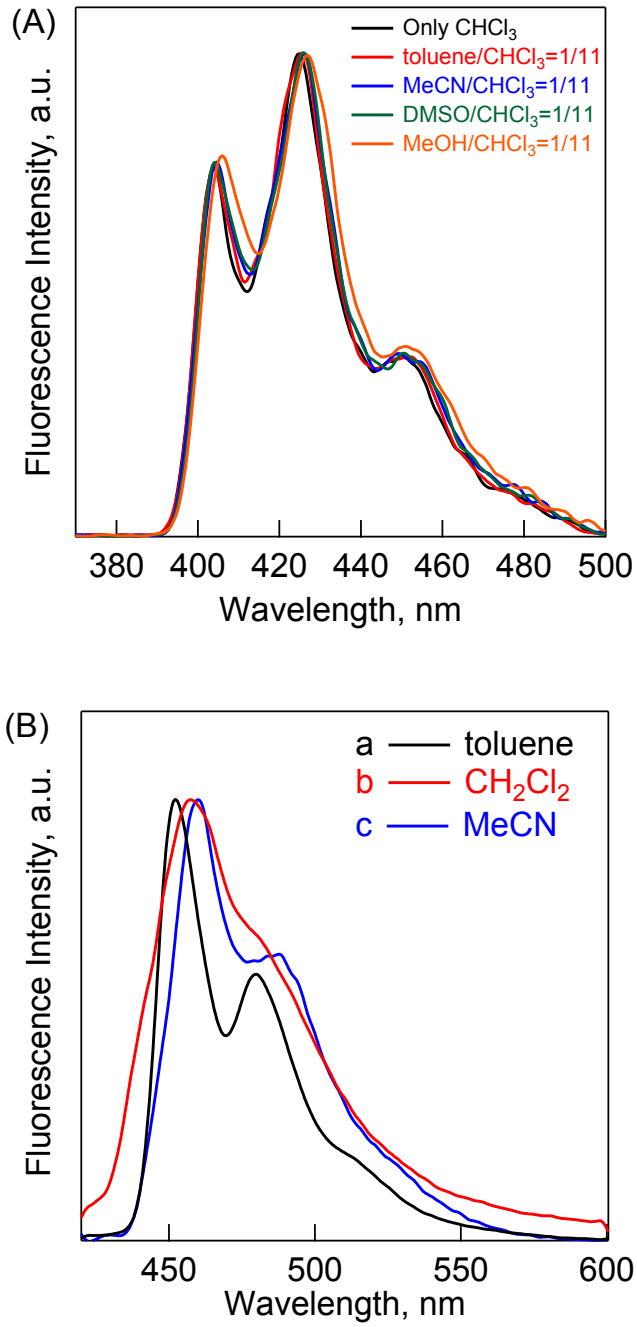


Fig. S11 Fluorescence spectra of (A) DABP and (B) DABPIm in various solvents. Excitation wavelength: 300 nm for DABP and 404 nm for DABPIm.

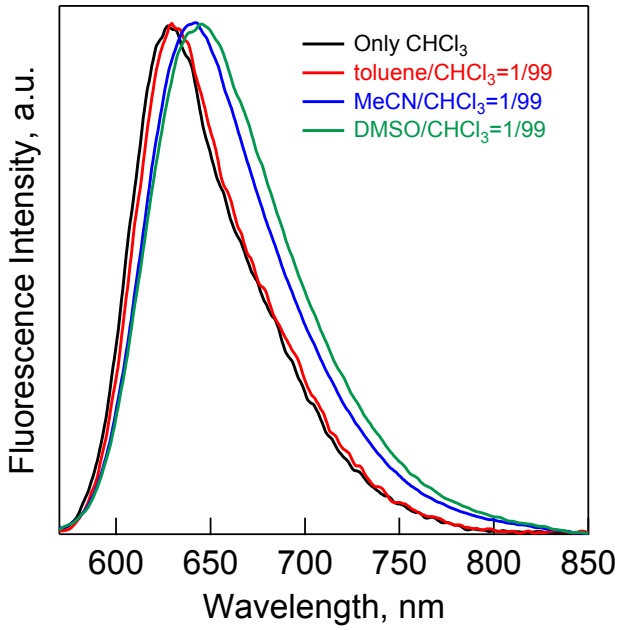


Fig. S12 Fluorescence spectra of TABPIm in various mixed solvents. Excitation wavelength: 550 nm.

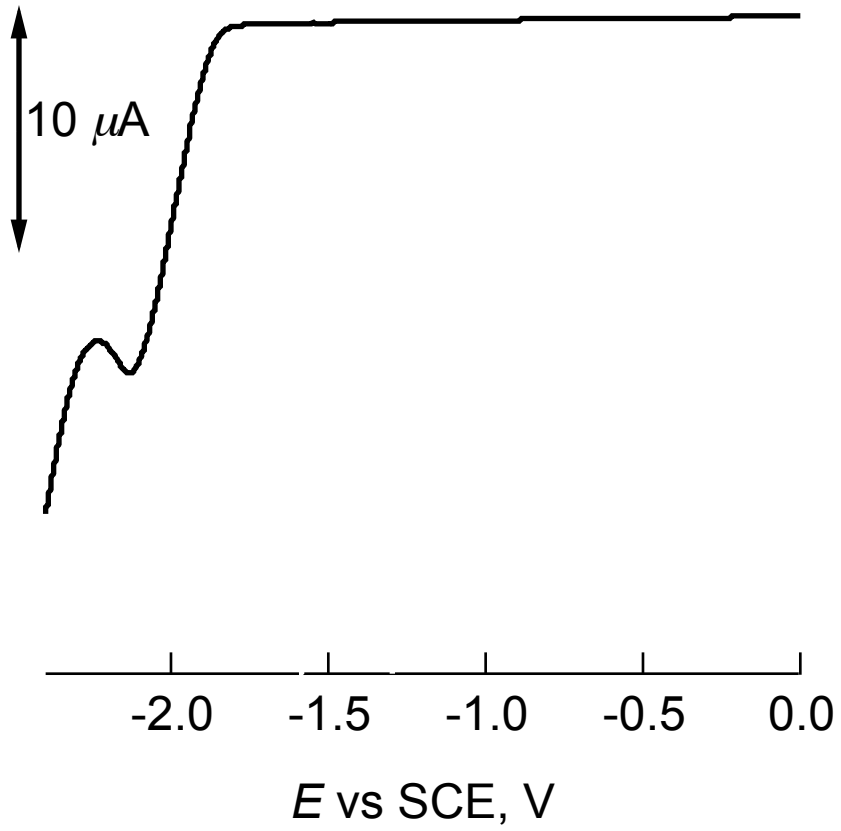


Fig. S13 Differential pulse voltammogram of BP in CH_2Cl_2 with 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. Scan rates: 10 mV s^{-1}.

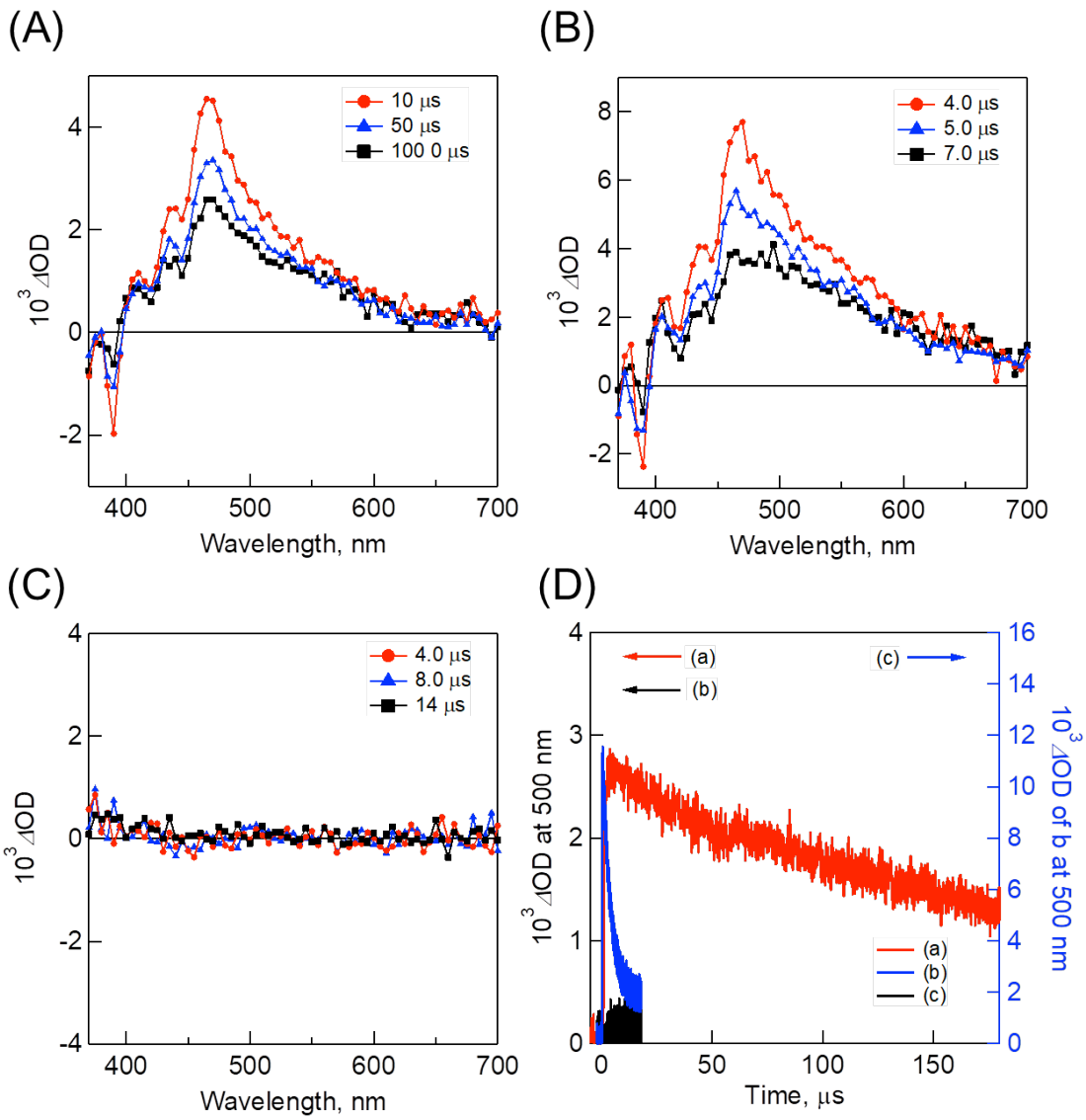


Fig. S14 (A) Nanosecond transient absorption spectra of DABPIm (10 μM) oxygen in Ar-saturated toluene solution. (B) Nanosecond transient absorption spectra of DABPIm (7.0 μM) in air-bubbled toluene solution for a few minutes. (C) Nanosecond transient absorption spectra of DABPIm (7.0 μM) in O_2 saturated-toluene solution. The observation wavelength is 500 nm. The excitation wavelength is 355 nm. (D) The corresponding time profiles of (a) transient absorption spectra in Ar-saturated toluene solution: τ = 260 μs, (b) transient absorption spectra in O_2 saturated-toluene solution and (c) transient absorption spectra in air-bubbled toluene solution: τ = 4.0 μs at 500 nm.

In Ar-saturated toluene solution of DABPIm (ESI Fig. S14A), we can see the long-lived triplet-triplet absorption (τ = 260 μs). This is in sharp contrast with no transient signal in O_2-saturated toluene solution of DABPIm (ESI Fig. S14B) because of occurrence of efficient

quenching process. Moreover, we also measured transient spectra of air-bubbled toluene solution for a few minutes to examine the quenching process in the appropriate concentrated condition of O_2 (ESI Fig. S14C). In this case we can see the excellent quenching process of triplet excited states (τ = 4.0 μs), whereas monotonous quenching process of T-T absorption without additional photochemical pathways was clearly observed.

From the kinetic point of view, the fraction of the triplet state quenched by oxygen was estimated to be 0.99 even under air-saturated condition. The quenching fraction in O_2-saturated toluene solution should be definitely close to unity. These contents surely indicate that the quenching process is attributable to energy transfer from triplet excited states of BP derivatives to O_2. Based on these discussions, we have concluded that the quantum yields of intersystem crossing listed in Table 3 should be correct. This content was revised in left column, page 6 and added in ESI Fig. 14.

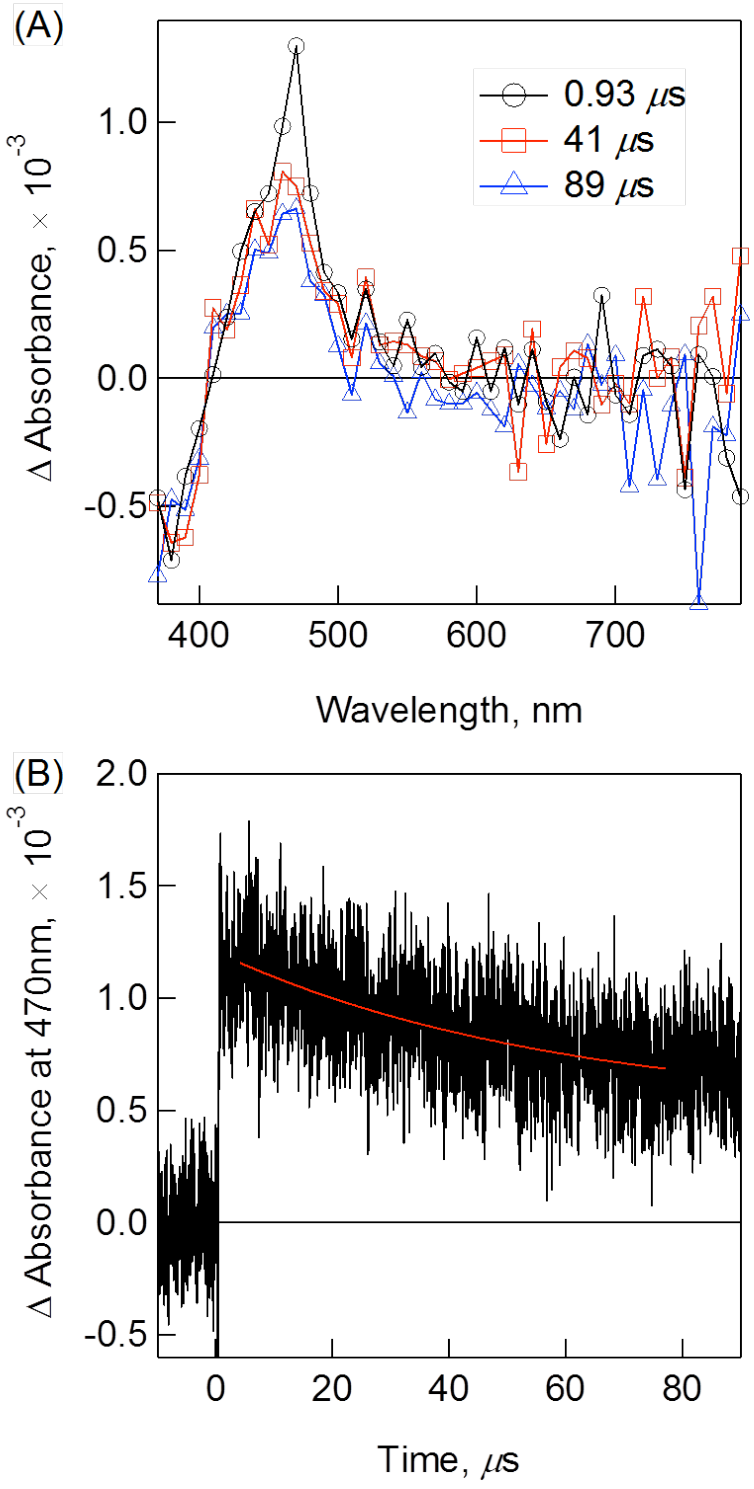


Fig. S15 (A) Nanosecond transient absorption spectra of 100 μM DABP in DMF. (B) The time profile of absorbance at λ = 470 nm. The lifetime is 58 μs.

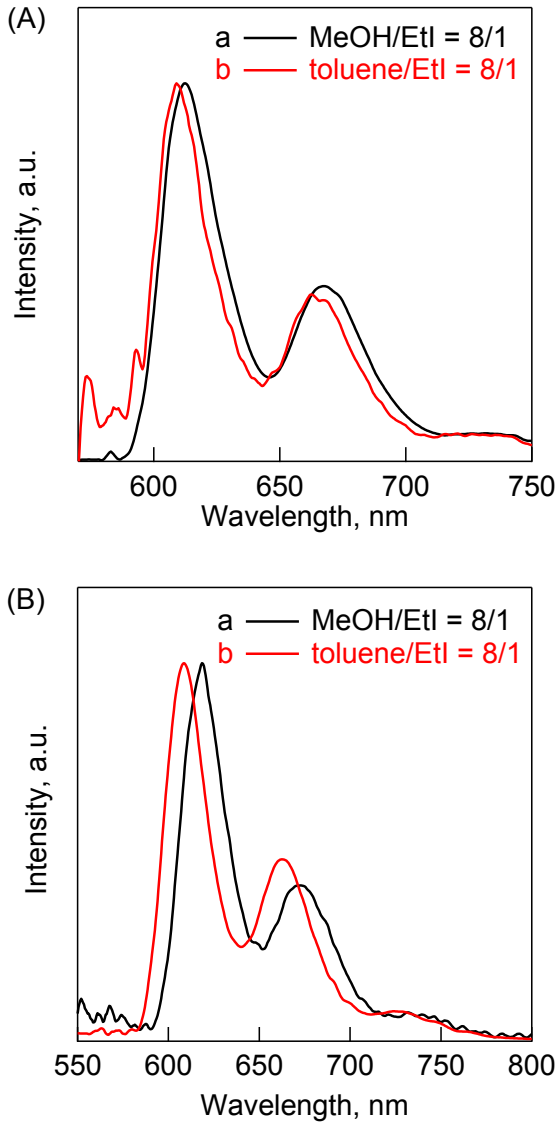


Fig. S16 Phosphorescence emission spectra of (A) DABP and (B) DABPIm in frozen mixed solvent [MeOH/ethyl iodide = 8/1 (v/v)] and [toluene/ethyl iodide = 8/1 (v/v)] (77 K). Excitation wavelengths: 390 nm for DABP and 335 nm for DABPIm.

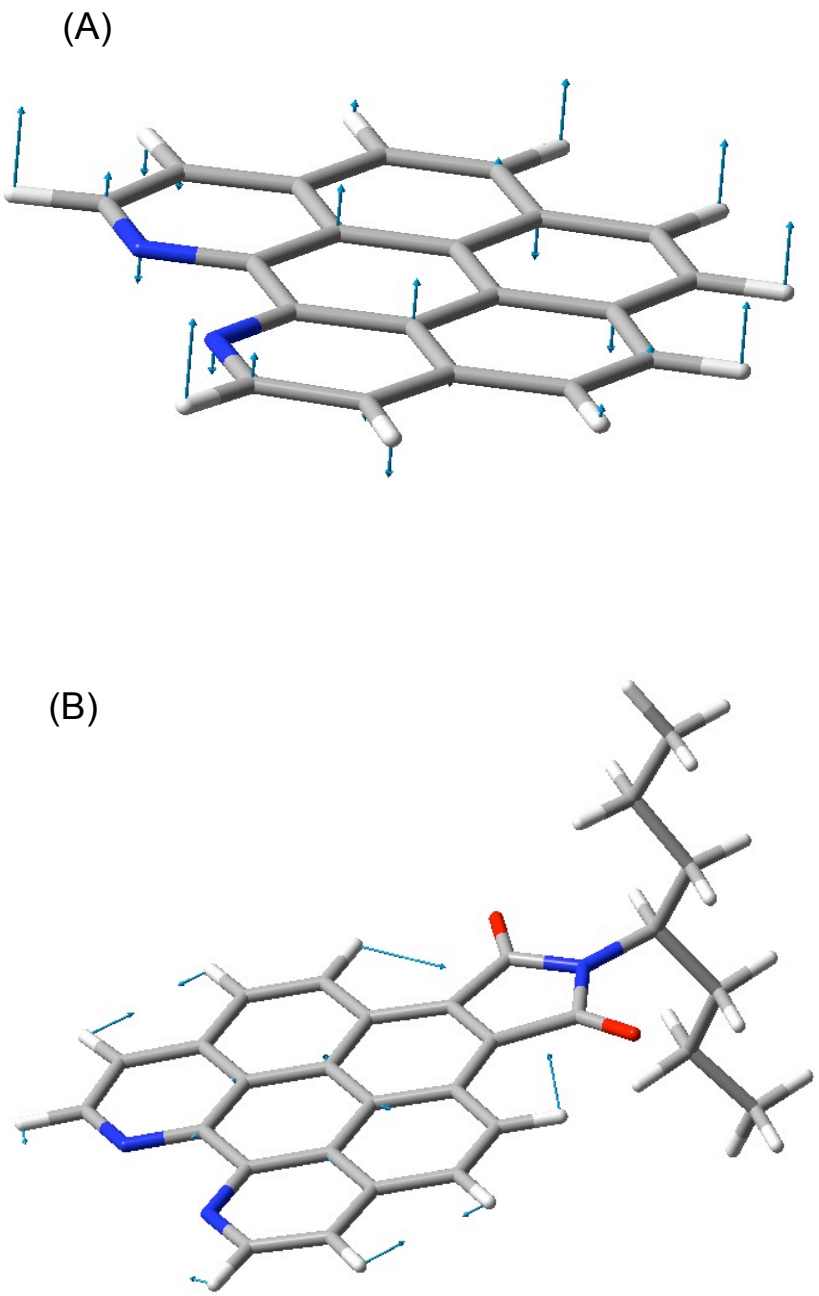


Fig. S17 Displacement vectors of molecular vibrations calculated in B3LYP/6-31+G(d) level of 1,12-diazabenzo[*ghi*]perylene (DABP) derivatives. (A) Out-of-plane C–C Vibration of DABP (541 cm^{-1}). (B) In-plane C–H vibration of DABPIm (1247 cm^{-1}).