

Environment-sensitive fluorescence of COT-fused perylene bisimide based on symmetry-breaking charge separation

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Abstract: Flexible and aromatic photofunctional system (FLAP) is composed of flapping rigid aromatic wings fused with a flexible 8π ring at the center such as cyclooctatetraene (COT). A series of FLAP have been actively studied for the interesting dynamic behaviors. Here, we synthesized a new flapping molecule bearing naphtho-perylenebisimide wings (**NPBI-FLAP**), in which two perylene units are arranged side by side. As a reference compound, we also prepared COT-fused NPBI (**NPBI-COT**) that contains only single perylene unit. In both compounds, inherent strong fluorescence of the NPBI moiety is almost quenched and the FL lifetime becomes much shortened in highly polar solvents (acetone and DMF). Through the analyses of environment-sensitive fluorescence, electrochemical reduction/oxidation, and femto-second transient absorption, the fluorescence quenching behavior was attributed to a rapid symmetry-breaking charge separation (SB-CS) for **NPBI-FLAP** and to an intramolecular charge transfer (ICT) for **NPBI-COT**. Most of the excited species of these compounds decay with the bent geometry, which is in contrast with the excited-state planarization behavior of a previously reported COT-fused peryleneimides with the double-headed arrangement of the perylene moieties. These results indicate that changing the fusion manners between COT and other π skeletons offers new functional molecules with distinct dynamics.

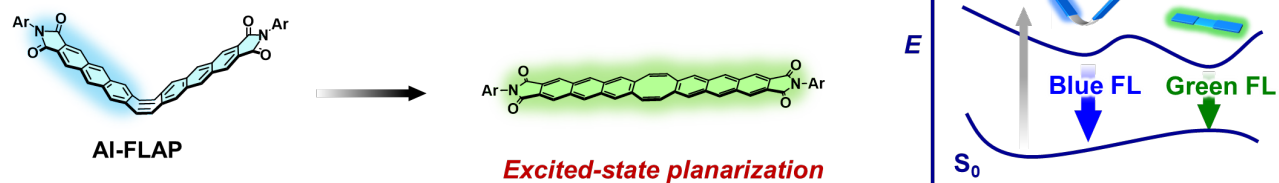
1. Introduction

Flexible and aromatic photofunctional system (FLAP) has been actively studied for the interesting dynamic behaviors^[1]. FLAP is composed of flapping rigid aromatics fused with a flexible 8π ring at the center, such as cyclooctatetraene (COT). A wide variety of applications of FLAP have been demonstrated, such as multi-color fluorescent dyes^[2], highly sensitive viscosity probes^[3], ratiometric force probes (including a flexible mechanophore)^[4], light-melt adhesives^[5], and polymer free-volume probes^[6]. The properties of COT-based FLAP largely depend on the chemical structures of the rigid wings. The energy profile and excited-state dynamics in S_1 are perturbed by changing the structure of the flapping wings. For example, FLAPs bearing anthraceneimide^[3a] and phanazine^[6] wings show a rapid bent-to-planar conformational change in the excited state, emitting a polarity-independent green fluorescence, while the planarization is suppressed in highly viscous environments to show a blue fluorescence. The dual-emission properties are useful for the ratiometric viscosity/tension imaging (Scheme 1a)^[3a, 4a]. In this context, we previously reported a flapping indenoperyleneimide^[3b] (**IPI-FLAP**) as a fluorogenic viscosity probe that increases fluorescence quantum yield and

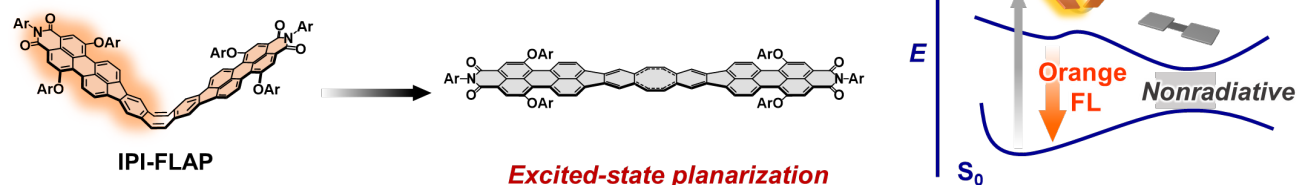
prolongs fluorescence lifetime in extremely low-viscous media even less than 3 cP (Scheme 1b).^[3f]

Here, we synthesized a new flapping molecule bearing naphtho-perylenebisimide wings (**NPBI-FLAP**), in which two perylene units are introduced side by side (Scheme 1c), unlike the double-headed arrangement in **IPI-FLAP**. Due to the strong fluorescence, the high photostability, and the facile chemical modification, the perylene bisimide (PBI) unit has been well studied,^[7] and a wide variety of π -expanded PBIs have been also focused in applications of circularly polarized luminescence (CPL), organic light emitting diode (OLED), and organic photovoltaics (OPV)^[8]. Moreover, several PBI dimer and trimer have attracted much attention due to the symmetry-breaking charge separation (SB-CS) in the photoexcited state^[9]. With this background, it is interesting to study the excited-state dynamics of **NPBI-FLAP** because the characteristics of FLAP (planarization) and the PBI dimer (SB-CS) would compete in the lowest singlet excited state (S_1), like flapping pentacene with the competitive singlet fission dynamics^[10] and *N,N'*-diphenyldihydrophenazine with the competitive PET and FRET dynamics^[11]. Development of those molecular systems would explore new environment-sensitive/stimuli-responsive mechanisms for creating functional materials.^[12]

(a) *Ratiometric FLAP*



(b) *Fluorogenic FLAP*



(c) *This work*

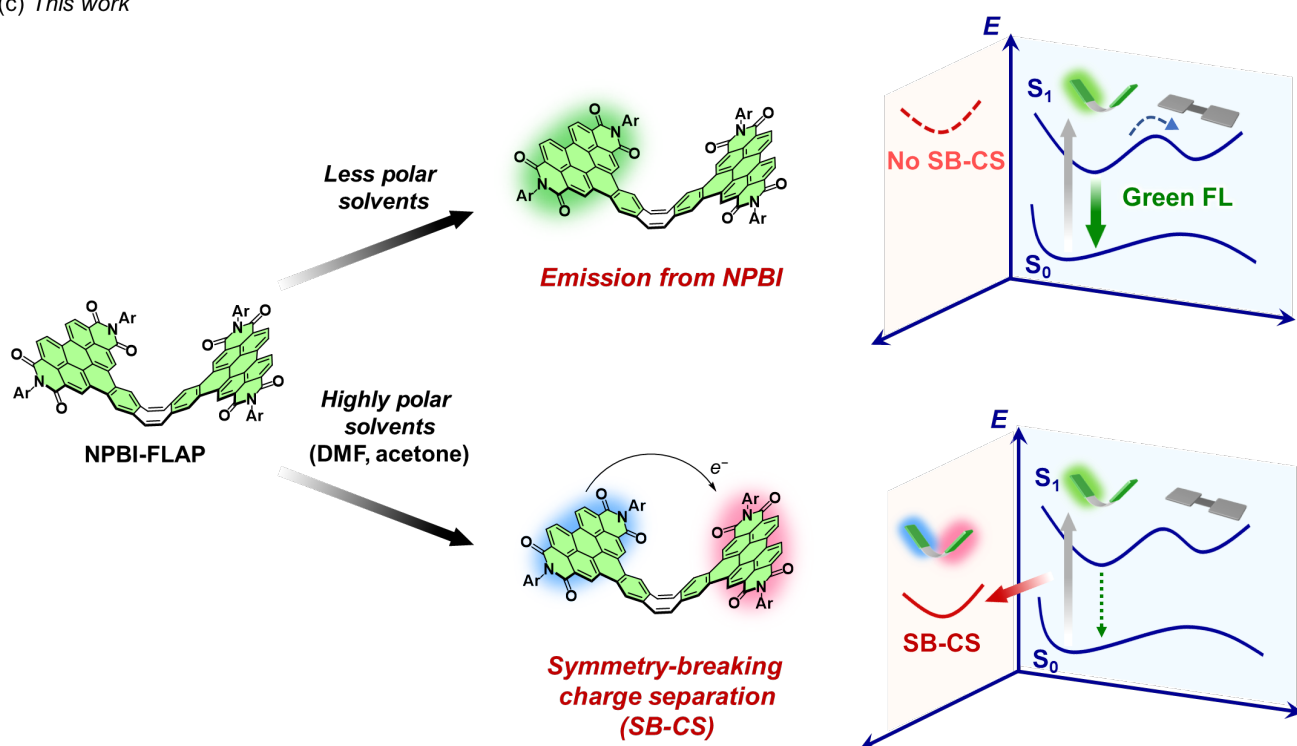


Figure 1. A variety of S_0 and S_1 energy profiles in a series of COT-based flapping molecules (FLAP). (a) FLAP with anthraceneimide wings (**AI-FLAP**), showing a viscosity-dependent dual fluorescence properties. (b) FLAP with indenoperylene-imide wings (**IPI-FLAP**), showing a viscosity-dependent fluorogenic properties. (c) Newly synthesized FLAP with naphthoperylene bisimide wings, **NPBI-FLAP** (This work).

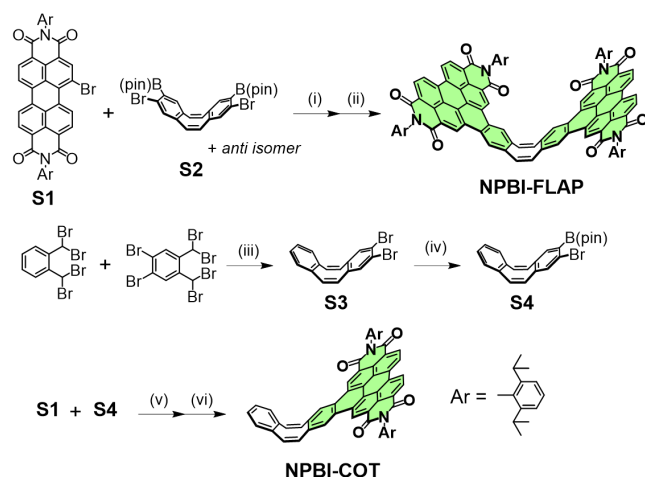
2. Results and discussion

2-1. Synthesis and structural characterization

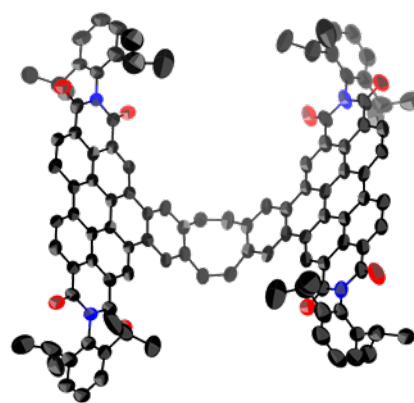
NPBI-FLAP was synthesized using the previously reported diborylated key precursor **S2** as *syn/anti* isomers.^[3b] Suzuki–Miyaura coupling of **S2** with mono-brominated perylenebisimide **S1**^[13] and subsequent Pd-catalyzed intramolecular

C–H arylation under microwave irradiation provided **NPBI-FLAP** in 30% yield in 2 steps (Scheme 1). As a control compound, the NPBI monomer fused with benzo-COT, **NPBI-COT**, was also synthesized in a similar way (SI). 2,3-Dibromodibenzo[*a,e*]COT **S3** was obtained by the combination of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene and $\alpha,\alpha,\alpha',\alpha',4,5$ -hexabromo-*o*-xylene. Borylation of **S3** via the lithiation using n BuLi gave **S4**^[3b, 14]. **NPBI-COT** was synthesized from **S1** and **S4** in 40% yield by the same 2-step annellation protocol.

Single crystals of **NPBI-FLAP** were obtained from a hot toluene solution. The X-ray crystal structure analysis^[15] revealed a bent molecular structure with the COT bending angles,^[16] defined in Figure 8, of $\theta = 38.9^\circ$ and 49.5° . Single-crystals of **NPBI-COT** were also obtained from $\text{CHCl}_3/\text{PrOH}$ co-solvent system, and the COT bending angles were around $39\text{--}41^\circ$. These angles are comparable with the reported COT derivatives (*ca.* 40°),^[2, 3a, 3b, 6] While **NPBI-COT** forms columnar π stacking of the perylene core (Figure S5.2.), **NPBI-FLAP** did not form π stacking due to the bulky 2,6-diisopropylphenyl substituents at the imide moieties (Figure S5.1.).



(a) **NPBI-FLAP**



(b) **NPBI-COT**

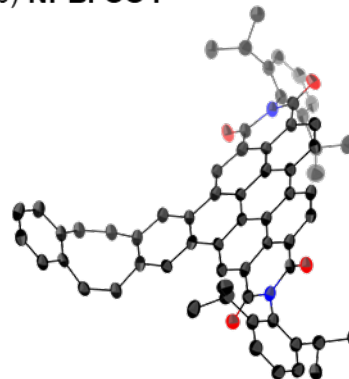


Figure 2. X-ray crystal structures of **NPBI-FLAP** and **NPBI-COT**. Hydrogen atoms were omitted for clarity, and thermal ellipsoids were set to the 30% probability level.

2-2. Steady-state absorption and fluorescence properties

UV/visible absorption and steady-state FL spectra of **NPBI-FLAP**, **NPBI-COT** and parent **NPBI**^[17] in toluene are shown in Figure 2 and Figure S4.1. Absorption spectrum of **NPBI-FLAP** shows characteristic vibronic structures in the visible region (peaked at 518 nm in toluene). Similar vibronic feature was observed in **NPBI-COT** and **NPBI**. In **NPBI-FLAP**, molar absorption coefficient at the peak wavelength was almost doubled ($1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) compared with that of parent **NPBI** ($6.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 510 nm) as well as **NPBI-COT** ($5.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 521 nm), indicating a small electronic interaction between the two wings in S_0 due to the insulated π conjugation at the bent COT joint. **NPBI-FLAP** and **NPBI-COT** showed a bright green fluorescence in toluene (**NPBI-FLAP**: $\lambda_F = 529 \text{ nm}$, $\Phi_F = 0.87$, **NPBI-COT**: $\lambda_F = 532 \text{ nm}$, $\Phi_F = 0.82$, respectively), which was similar to the parent **NPBI** ($\lambda_F = 520 \text{ nm}$, $\Phi_F = 0.96$ in toluene). Stokes shifts were also comparable (400, 380, and 380 cm^{-1} , respectively). This result suggests that the excited-state dynamics in toluene do not largely change by the COT fusion of the two wings, while the FL properties in polar solvents are totally different (*vide infra*).

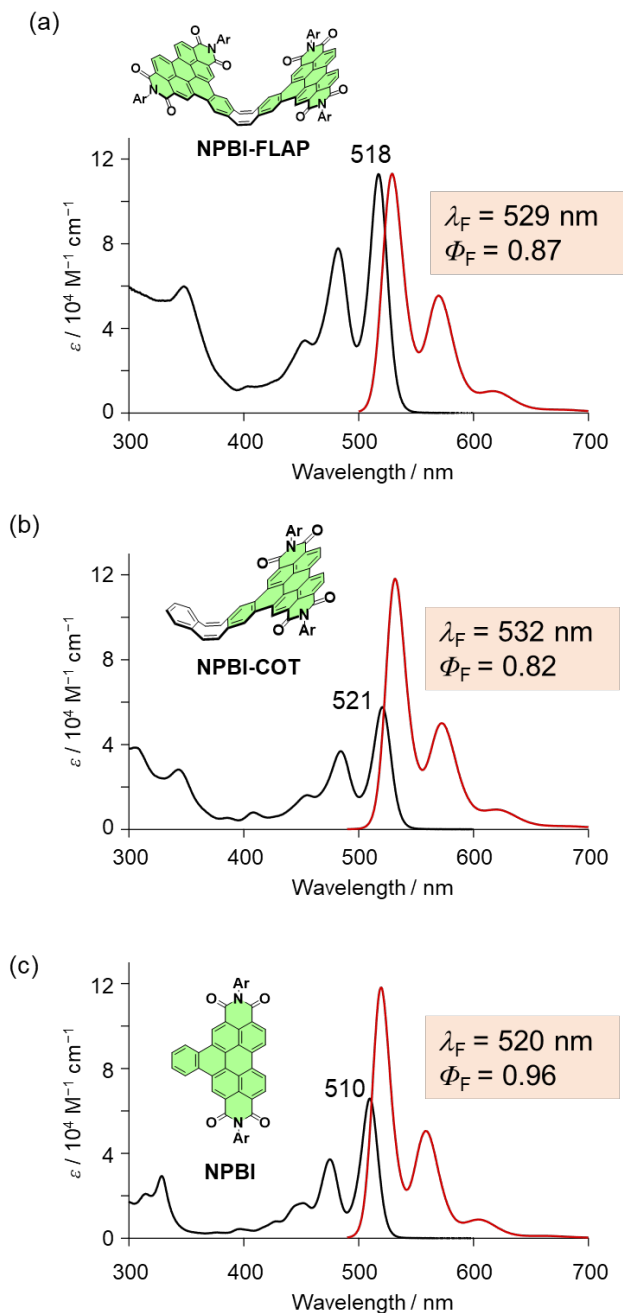


Figure 3. UV/visible absorption and FL spectra of (a) **NPBI-FLAP**, (b) **NPBI-COT**, and (c) **NPBI** in toluene. Φ_F = FL quantum yield. Excitation wavelength: 480 nm (**NPBI-FLAP** and **NPBI-COT**) and 470 nm (**NPBI**).

2-3. Cyclic voltammetry

Cyclic voltammogram (CV) showed reversible two-step reduction waves around -1.1 V and -1.3 V (vs. Fc^+/Fc) in these three compounds, **NPBI-FLAP**, **NPBI-COT**, and **NPBI** (Figure 2 and Figure S7.1.). Since the E_{red}^1 and E_{red}^2 were not largely shifted by the dimerization of the NPBI core, electronic communication through the COT ring is negligible in **NPBI-FLAP**. Namely, two-electron reduction is expected at each reduction potential. On the other hand, an

irreversible oxidation process was observed for **NPBI-FLAP** and **NPBI-COT** (*ca.* $+1.3$ V), while an apparently reversible oxidation was confirmed at the almost same potential in the parent **NPBI**. Therefore, the irreversible oxidation can be attributed to the fusion with COT.

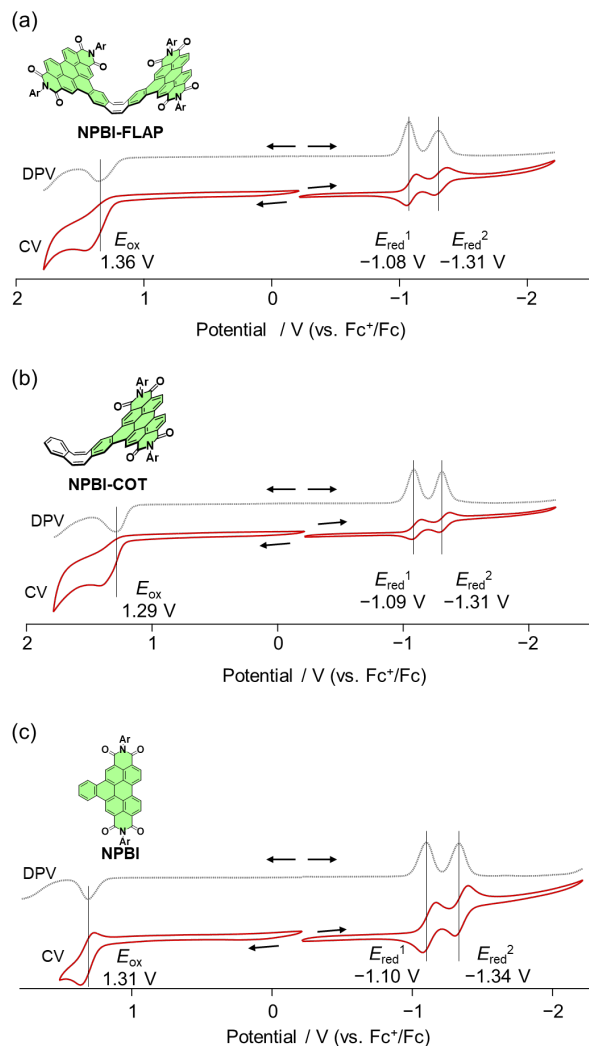


Figure 4. Cyclic voltammogram (CV) and differential pulse voltammograms (DPV) of (a) **NPBI-FLAP**, (b) **NPBI-COT**, and (c) **NPBI**. Conditions: CH_2Cl_2 solvent, 100 mM $n\text{-Bu}_4\text{NPF}_6$ electrolyte, glassy carbon working electrode, Pt counter electrode, and Ag/AgClO_4 reference electrode. Scan rate: 0.05 V/s.

Absorption spectra of the electrically reduced/oxidized species were obtained under application of voltage in the same conditions as the CV measurement (Figure 5). Here, the redox species are generated in the vicinity of a Pt mesh working electrode, and, if these species are stable enough during the steady-state absorption measurement, the corresponding spectrum can be obtained. As the applied voltage slowly shifted, the spectrum of **NPBI-FLAP** gradually changed from -1.1 V (vs. Fc^+/Fc), which corresponds to the first reduction potential, and this tendency continued up to -1.3 V. Eventually, the absorption bands with vibronic features in the range of 420–550 nm, assigned to the neutral

NPBI unit, largely decreased, and new bands arose in the longer wavelength region (600–950 nm) with the peaks of at 698, 779, 836, and 909 nm (Figure 5a). Importantly, very similar spectra were obtained for **NPBI-COT** and **NPBI** at the same voltage, at which each NPBI unit is reduced to the radical anion (Figures 5b and 5c). The spectral feature of the NPBI radical anion is similar to that of PBI.^[18] This analysis clearly indicated no electronic communication between the two NPBI radical anions in **NPBI-FLAP** and small electronic contribution of the benzo-COT unit in reduced **NPBI-COT**. Further application of voltage up to -1.6 V induced a subsequent spectral change in all three compounds, in which the absorption bands in the 650–950 nm region gradually decreased and, concomitantly, a new band appeared at 612 nm (Figures S7.3., S7.4., and S7.5.), which can be attributed to the dianion formation at each NPBI moiety. On the other hand, we also attempted to obtain the absorption spectra of radical cation species by application of voltage ($+1.3$ V to $+1.6$ V). However, degradative behaviors with a small blue shift were observed in **NPBI-FLAP** and **NPBI-COT**. Only in **NPBI**, a small peak appeared at 592 nm upon the electrical oxidation, which could be assigned to an unstable radical cation. Both these results suggest a short lifetime of the NPBI radical cation, as reported for the PBI case^[7a].

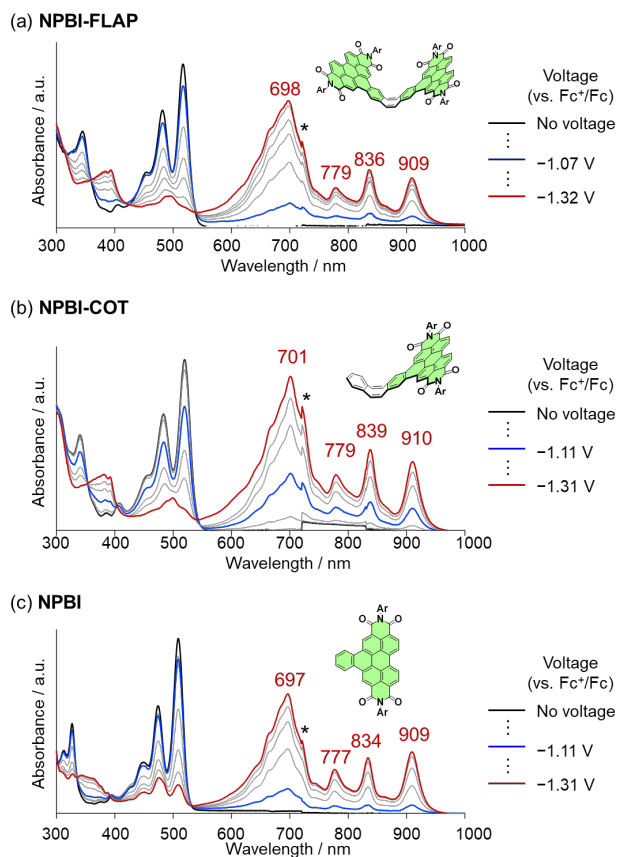


Figure 5. Absorption spectra of (a) **NPBI-FLAP**, (b) **NPBI-COT**, and (c) **NPBI** and their radical anion under voltage. Conditions: CH_2Cl_2 solvent, 100 mM $n\text{-Bu}_4\text{NPF}_6$ electrolyte, Pt mesh working electrode, Pt counter electrode, and Ag/AgClO_4 reference electrode. The applied voltage was

fixed when the absorption spectrum was measured. The asterisk indicates the grating changeover wavelength.

2-4. Environment-dependent fluorescence properties

Solvent effects in the photophysical properties were next investigated. The parent NPBI showed relatively small solvent effects in common organic solvents such as toluene, CHCl_3 , EtOAc, THF, CH_2Cl_2 , acetone, MeOH, and DMF. Smallest energy absorption band was observed in the range of 498–512 nm, while the fluorescence peak of 503–528 nm (Table S4.3.). (In cyclohexane, those bands are significantly blue-shifted.) While the FL quantum yield is very high ($\Phi_F > 0.91$) in these solvents, including acetone ($\Phi_F = 0.94$), MeOH ($\Phi_F = 0.93$), and DMF ($\Phi_F = 0.93$), the FL quantum yield in DMSO is drastically decreased ($\Phi_F = 0.08$). The FL decay curve is well fitted in a single component of the FL lifetime, and the value is also comparable in these solvents ($\tau_F = 3.8$ – 4.8 ns). This value is typical among the reported perylene bisimide derivatives, whereas the short FL lifetime in DMSO ($\tau_F = 0.5$ ns) indicates accelerated nonradiative decay. On the other hand, **NPBI-FLAP** showed a remarkable solvent effect. Although the peak wavelengths in absorption and FL were not largely shifted, the FL quantum yield of **NPBI-FLAP** drastically decreased in polar solvents, particularly in acetone, MeOH, DMF, and DMSO ($\Phi_F = 0.04$ for acetone, and $\Phi_F < 0.01$ for the others). Accordingly, the FL lifetimes became much shorter ($\tau_F = 2.6$ ns for acetone and $\tau_F < 0.1$ ns as a dominant component for the others) (Table S4.1.). Since Φ_F and τ_F in nonpolar solvents were similar to those of the parent **NPBI**, anomalous FL quenching is only expected in acetone, MeOH, and DMF among these solvent systems. A plausible quenching mechanism in the highly polar solvents is symmetry-breaking charge separation (SB-CS), as observed in the reported PBI oligomers.^[9] We compared the FL features with **NPBI-COT**. Interestingly, the FL quenching behavior was confirmed in acetone, MeOH, DMF, and DMSO solutions of **NPBI-COT**. In other solutions, the bright green FL was observed, but the FL quantum yields decreased as the relative permittivity of the solvents increased. Considering that **NPBI-COT** has only single NPBI core, the FL quenching of **NPBI-COT** in acetone, MeOH, and DMF cannot be attributed to SB-CS, unlike **NPBI-FLAP**, and the presence of another non-emissive ICT (intramolecular charge transfer) state provides a plausible interpretation. Namely, the increased population of the non-emissive ICT state in the polar solvents would result in the decrease in the FL quantum yield of **NPBI-COT**.

Viscosity effects on the FL behaviors of **NPBI-FLAP** and **NPBI-COT** were assumed to be small (Figures S4.9. and S4.17.). On the other hand, the FL quantum yields of **NPBI-FLAP** and **NPBI-COT** were drastically improved to $\Phi_F \sim 0.8$ in a rigid polymethyl methacrylate (PMMA) matrix as well as a frozen 2-methyltetrahydrofuran (2-MeTHF) solution (Figures S4.4., S4.7., S4.12. and S4.15.). These results suggest that the emissive pathway from the locally excited NPBI state becomes more significant by the suppression of

fast FL quenching dynamics to the non-emissive states, SB-CS for **NPBI-FLAP** and an ICT state for **NPBI-COT**, respectively. In other words, reorientation of the surrounding

polar solvent molecules plays an important role for the anomalous FL quenching.

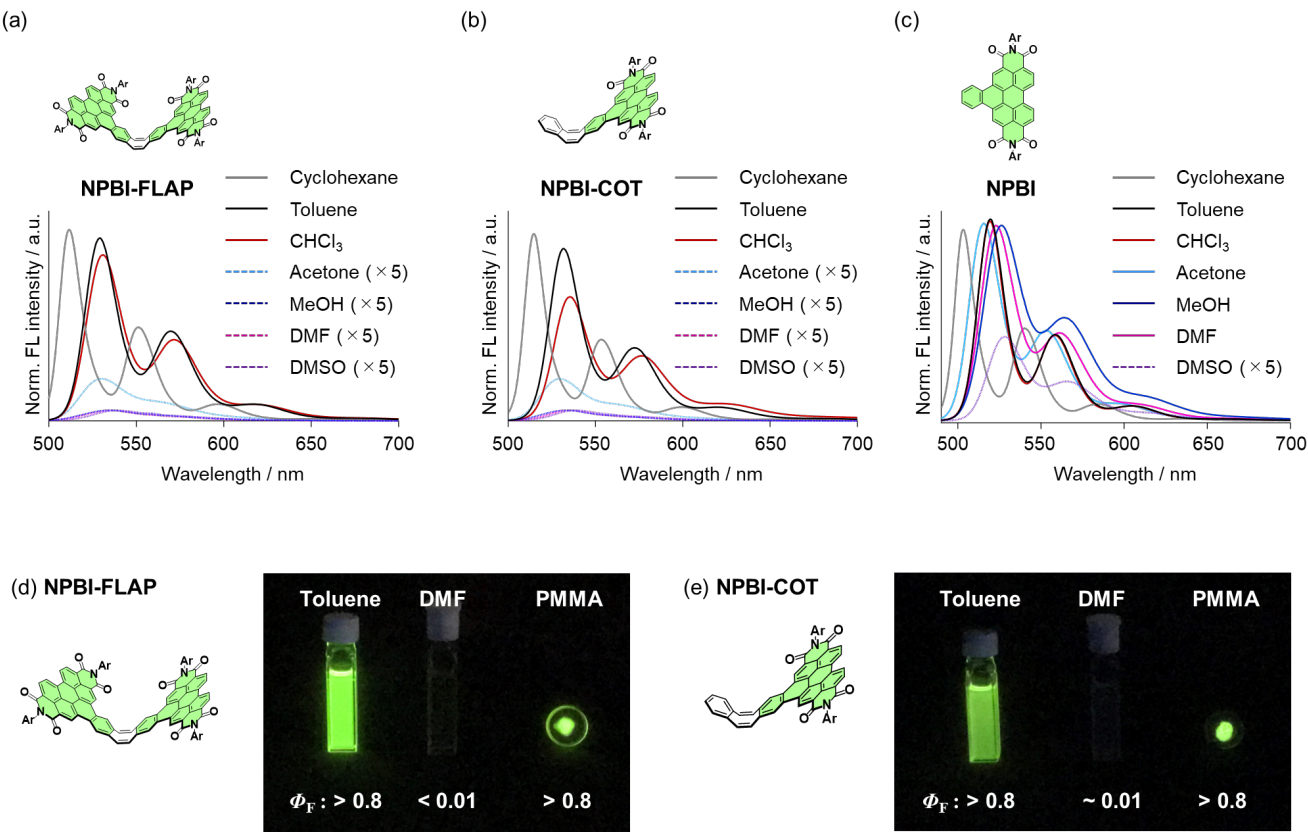


Figure 6. FL responses of **NPBI-FLAP**, **NPBI-COT**, and **NPBI**. (a–c) FL spectra of **NPBI-FLAP**, **NPBI-COT**, and **NPBI** in various solvents. (d,e) Photographs of **NPBI-FLAP** (d) and **NPBI-COT** (e) in toluene, DMF and a PMMA matrix under 365-nm irradiation.

2-5. Ultrafast dynamics in the excited state

To elucidate the mechanism of the anomalous FL quenching of **NPBI-FLAP** and **NPBI-COT** in polar solvents, we examined the excited-state dynamics of **NPBI-FLAP**, **NPBI-COT**, and **NPBI** in CHCl_3 and DMF using femtosecond transient absorption spectroscopy (Figure 7). In the early delay time region (e.g., at 0.1 ps), irrespective of the compound or solvent, all obtained spectra showed similar spectral features with ground-state bleaching (GSB) in the range of 500–550 nm, stimulated emission (SE) in the range of 500–650 nm, and broad excited-state absorption (ESA) in the longer wavelength region (> 600 nm). (Note that the SE significantly overlaps with the GSB and ESA.) The subsequent dynamics were found to be highly dependent on the solvent (and compound). In the nonpolar solvent (CHCl_3), all three compounds showed essentially the same dynamics: The SE band showed a slight spectral shift within 10 ps, which was attributable to structural/vibrational relaxation or solvation in S_1 (Figure 7a–c), followed by a monotonous decay with a time constant longer than 1 ns. In the polar solvent (DMF),

on the other hand, while the dynamics of **NPBI** was essentially the same as in CHCl_3 (Figures 7c, f) with no significant changes, for **NPBI-FLAP**, the ESA signal evolved within 10 ps to a spectrum with characteristic peaks in the 580–850 nm region (Figure 7d). Among them, the peaks at 700, 770, and 840 nm are assigned to the radical anion of the NPBI unit (Figure 5). The other shoulder-like peak at 600 nm can be attributed to the radical cation of the NPBI unit (Figure S7.5.), whose feature is similar to the PBI radical cation.^[7a] These results clearly demonstrate that the highly polar environment promotes electron transfer in **NPBI-FLAP**, leading to the symmetry-breaking charge separation (SB-CS) state. The evolution-associated difference spectra obtained by global analysis indicated that the SB-CS state is formed with a time constant of 9.4 ps and returns to the ground state via charge recombination with a time constant of 860 ps (Figure S9.2.).

For **NPBI-COT**, a rapid spectral change within 10 ps was observed in DMF (Figure 7e), whereas it was absent in CHCl_3 . During this change, the SE feature was quenched, as in the case of **NPBI-FLAP** in DMF. However, the transient

absorption spectrum after 10 ps did not show spectral features characteristic of the radical anion/cation of the NPBI moiety, indicating that electron transfer is not the origin of this change. Based on the insight obtained from Section 2-4, the spectrum after 10 ps, with a peak at 660 nm, can be assigned to the non-emissive ICT state. The ICT state is more stabilized in the polar solvent, resulting in a more pronounced spectral feature of the populated ICT state compared to that in CHCl_3 .

The energy levels of the CS state of **NPBI-FLAP** and **NPBI-COT** in various solvents were estimated based on the Rehm-Weller and Born equations (See SI Section 8)^[19]. In toluene,

the energy level of the CS state (2.86 eV for **NPBI-FLAP** and 2.47 eV for **NPBI-COT**) was higher than that of the S_1 state (~ 2.4 eV). This is consistent with the results that a bright FL derived from NPBI was only observed in less polar solvents. On the other hand, in DMF, the SB-CS or ICT state was more stabilized (~ 2.2 eV for **NPBI-FLAP** and ~ 1.9 eV for **NPBI-COT**) and became lower than the S_1 state. These results support that FL from NPBI was drastically quenched in polar solvents because of rapid SB-CS in **NPBI-FLAP** or ICT from DBCOT to NPBI in **NPBI-COT** (See the discussion in SI Section 8).

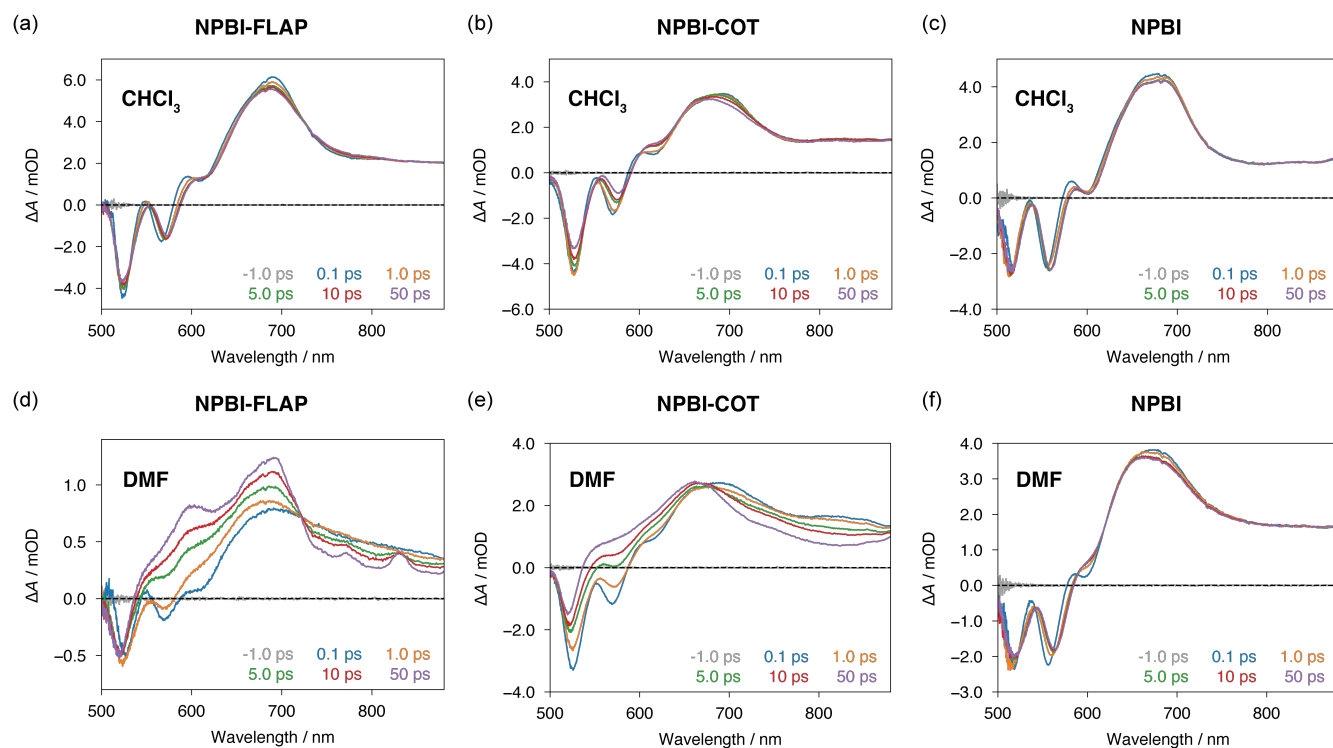


Figure 7. Transient absorption spectra of **NPBI-FLAP**, **NPBI-COT**, and the parent **NPBI** in (a-c) CHCl_3 and (d-f) DMF, obtained after photoexcitation at 530 nm.

2-6. DFT calculations

To interpret the FL behaviors of **NPBI-FLAP** and **NPBI-COT**, (TD-)DFT calculations were performed at the CAM-B3LYP/6-31+G(d) level for the model compound **NPBI-FLAP'** and **NPBI-COT'**, in which the bulky substituents of **NPBI-FLAP** and **NPBI-COT** were replaced by hydrogen atoms. By changing the COT bending angle θ by 5-degree increments, potential energy profiles were delineated in S_1 (Figure 8) as well as S_0 (Figure S6.6.). While geometry optimization in S_0 provided a bent C_{2v} geometry with $\theta = 42.6^\circ$ (Figure S6.13.), two energy minima were obtained in S_1 : a global minimum with a bent C_1 geometry and a local minimum with a planar D_{2h} geometry (Figure S6.12., $\theta = 0^\circ$). These structures have different S_1 electronic configurations: an A_2 state for the planar local minimum and an A state for the bent local minimum located close to another A_2 state of the bent C_{2v} structure. Furthermore, the S_0 – S_1 transition is forbidden ($f = 0$) in the planar A_2 state, while it is allowed ($f = 0.5$) in the bent A state. These calculations suggest that photoexcitation of **NPBI-FLAP** mainly takes place in the bent form, and most of the excited species decay with the bent geometry, emitting the bright FL with the small Stokes shift. In fact, the FL quantum yield is remarkably high in the nonpolar solvent ($\Phi_F = 0.87$ in toluene), indicating small contribution of the equilibrium with the planar local minimum in S_1 (A_2 state, 2.8 kcal/mol higher than the global minimum). In the planarized form of **NPBI-FLAP**, HOMO and LUMO are located on different moieties. Therefore, the energy level of the planar form would be also stabilized in polar solvents, as well as the SB-CS state. However, the supporting experimental evidence was not obtained presumably due to more significant stabilization of the SB-CS state. As a result, planarization dynamics was not observed at least for **NPBI-FLAP** regardless of the solvent polarity.

The calculations of **NPBI-COT'** also support that the bent form is most stable in S_1 as well as S_0 , and the photoexcited species in the nonpolar environment decays without planarization (Figure S6.17.). At the bent geometry in S_1 , both HOMO and LUMO are delocalized over the PBI unit. On the other hand, as the COT ring is planarized in S_1 , an occupied MO on the dibenzocyclooctatetraene (DBCOT) unit is lifted to be HOMO, while the LUMO on the PBI unit remained in the planar geometry (Figure S6.7.). Therefore, the dark ICT state would be induced by the bent-to-planar conformational change in S_1 . The different dynamics of **NPBI-FLAP** and **NPBI-COT** remind us of a simple control of PET and ICT by conjugation/insulation of π systems.^[20]

Finally, we compared the calculation results of **NPBI-FLAP'** with **IPI-FLAP'** to resolve the reason why the different fusion manners of perylene (bis)imide and COT led to the different global-minimum geometries in S_1 , namely, the planarized form of **IPI-FLAP**^[3b] and the bent form of **NPBI-FLAP**. Figure 9 shows the LUMOs of DBCOT and perylene (bis)imide, in which the orbital symmetry of the DBCOT matches with that on the zigzag edge of peryleneimide, whereas it does not match with the bay area of PBI. As a result, an effective conjugation between DBCOT and

two peryleneimide wings is formed in the LUMO of **IPI-FLAP'**, lowering the LUMO level and thus decreasing the S_0 – S_1 transition energy at the planarized geometry (Figure 9a). In sharp contrast, the unmatched phase between the LUMOs of DBCOT and PBI resulted in the isolated unoccupied MOs of the planarized **NPBI-FLAP'** geometry, inhibiting their energy stabilization (Figure 9b). Therefore, the relative energy of the planar S_1 state becomes higher than the bent S_1 state, which led to the different dynamics of **NPBI-FLAP'**, compared with the excited-state planarization of **IPI-FLAP'** (Figure 1).

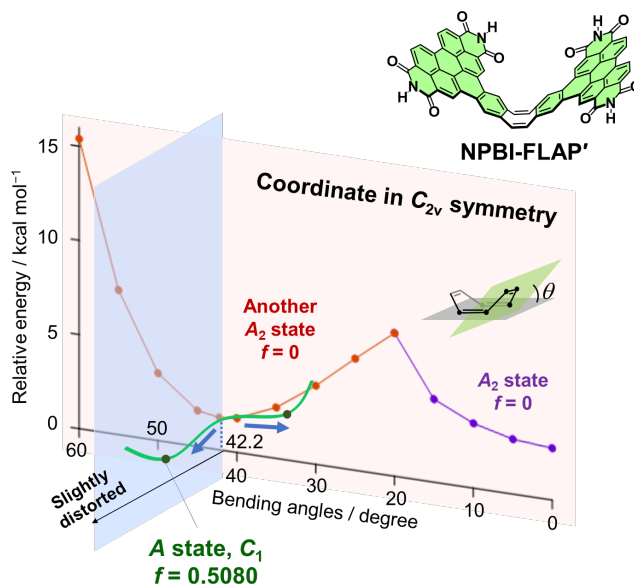
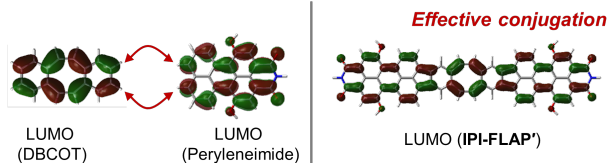


Figure 8. S_1 energy landscape of **NPBI-FLAP'**. Geometry optimization was performed at the TD CAM-B3LYP/6-31+G(d) level. COT bending angle θ was defined by the dihedral angle of the two mean planes shown in the inset.

(a) **IPI-FLAP** (Previous work)



(b) **NPBI-FLAP** (This work)

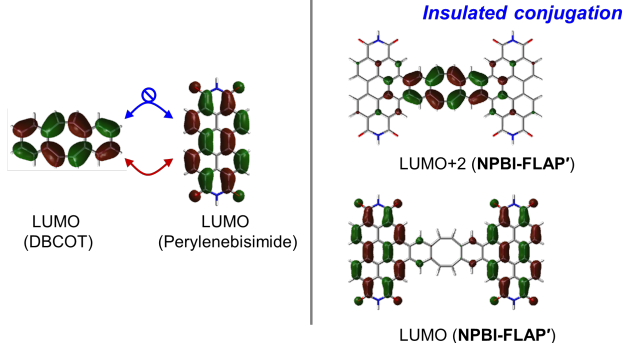


Figure 9. (a) Phase matching between LUMOs of DBCOT and peryleneimide, leading to the effective conjugation in the LUMO of **IPI-FLAP'**. (b) Unmatched LUMOs of DBCOT and PBI led to the isolated unoccupied MOs of **NPBI-FLAP'**. Geometry optimization was performed at the TD CAM-B3LYP/6-31+G(d) level.

3. Conclusion

In summary, we have developed COT-fused flapping naphthoperylene bisimides, **NPBI-FLAP** and **NPBI-COT**, that show an environment-sensitive green FL. These compounds were synthesized from brominated PBI and borylated DBCOT in two steps in 30–40% yield. In both compounds, inherent strong fluorescence of the NPBI moiety was almost quenched and the FL lifetime was much shortened in acetone and DMF. The fluorescence quenching behaviors were attributed to a rapid symmetry-breaking charge separation (SB-CS) for **NPBI-FLAP** and to an intramolecular charge transfer (ICT) for **NPBI-COT**. It is in sharp contrast for **NPBI-FLAP** and **NPBI-COT** to hold bent geometries in S_1 (at least in nonpolar solvents), while the previously reported COT-fused indenoperyleneimide (**IPI-FLAP**) shows an excited-state planarization. Considering the variety of functions in the series of COT-fused flapping molecules (FLAP)^[1–6], the idea of changing the fusion manners between COT^[21] and other π skeletons^[22] would explore new functional molecules with different dynamic behaviors.

ASSOCIATED CONTENT

The Supplementary Information is available free of charge on the Springer Nature website. Crystallographic data are also available free of charge from The Cambridge Crystallographic Data Centre, codes 2268963 and 2268964,

Synthetic protocols, characterization data, photophysical spectra, theoretical calculation (PDF)

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Statements and Declarations

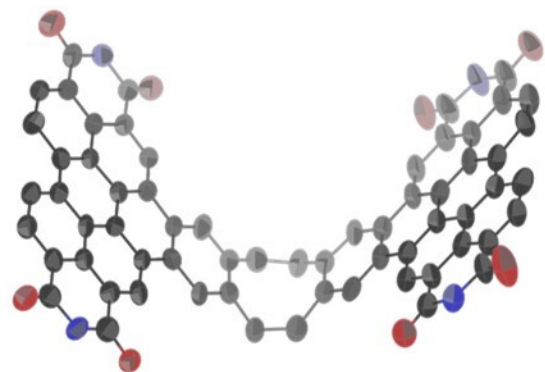
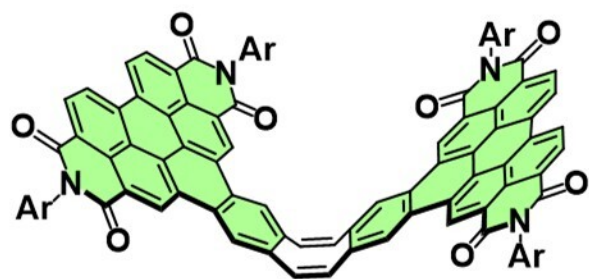
Conflicts of interest: There are no conflicts to declare.

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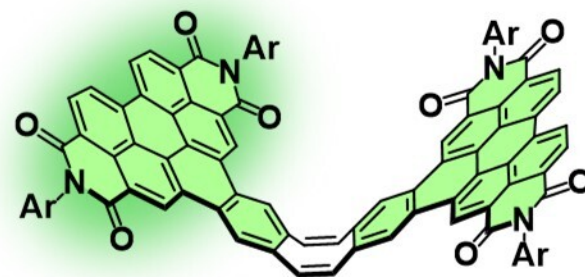
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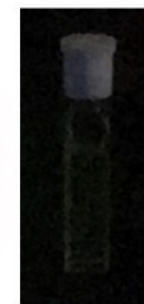
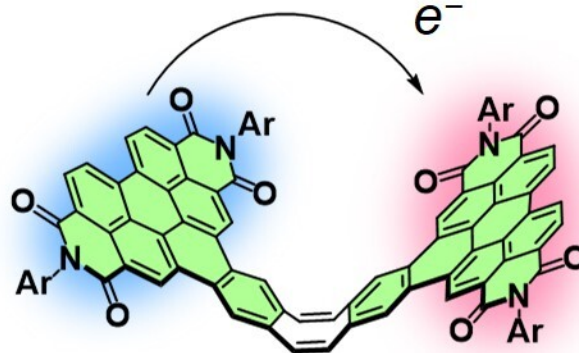
NPBI-FLAP

*Less polar
solvents*

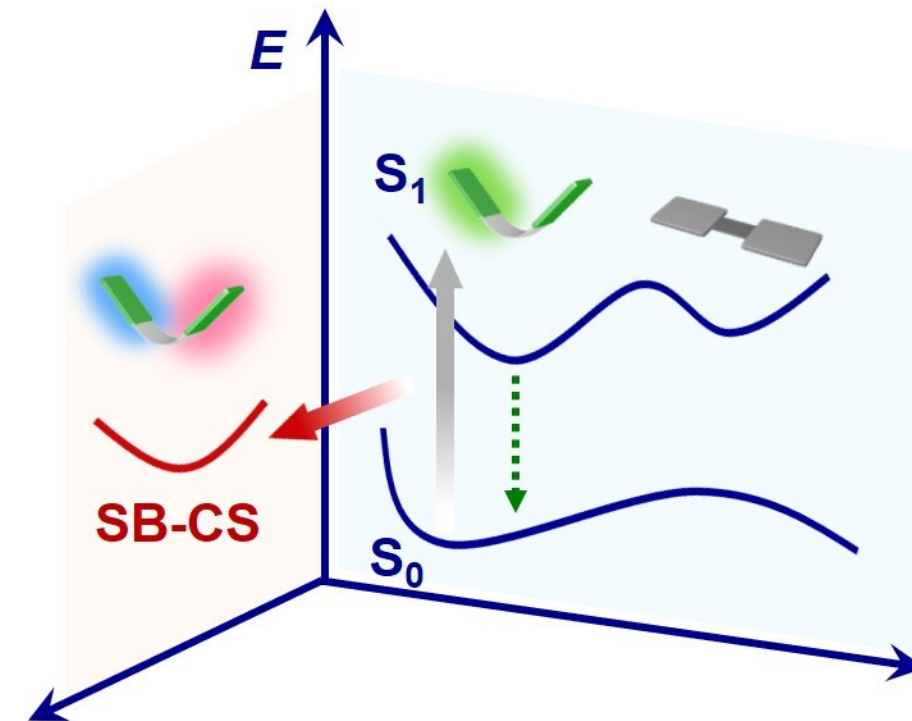
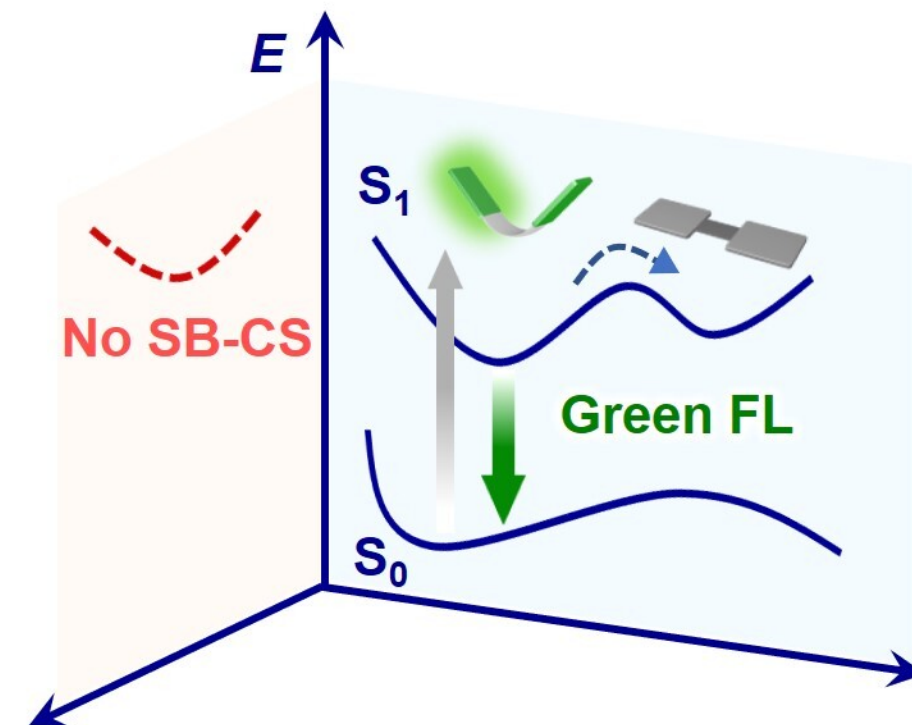


Emission from NPBI

*Highly polar
solvents
(DMF, acetone)*



*Symmetry-breaking
charge separation
(SB-CS)*



Supplementary Information

Environment-sensitive fluorescence of COT-fused perylene bisimide based on symmetry-breaking charge separation

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1. General information

Synthesis

All reagents and solvents were of commercial grade and were used without further purification unless otherwise noted. Tetrahydrofuran (THF) and dioxane were dried using Glass Contour solvent purification system. Microwave-assisted reactions were performed on an Anton Paar Monowave 400 using the “Heat As Fast As Possible” heating method. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F₂₅₄ (Merck). Column chromatography was performed on Wakogel® C-300, C-400, and Wako-Sil®. ¹H and ¹³C NMR spectra were recorded on a JEOL ECA-600 (600 MHz for ¹H and 151 MHz for ¹³C) spectrometer. Chemical shifts were reported in ppm relative to the residual solvents as internal standards (CHCl₃: δ = 7.26 ppm for ¹H, δ = 77.16 ppm for ¹³C, and CDHCl₂: δ = 5.32 ppm for ¹H). High-resolution atmospheric-pressure-chemical-ionization time-of-flight mass spectrometry (HR-APCI-TOF-MS) and high-resolution matrix-assisted-laser-dissociation-ionization time-of-flight mass spectrometry (HR-MALDI-TOF-MS) was recorded on a Shimadzu Axima-CFRplus. Compounds **S1**^[S1], **S2**^[S2] and **NPBI**^[S3] were synthesized according to the reported methods. In the synthesis of new compounds **S3** and **S4**^[S4], the reported synthetic protocols for similar compounds were referenced.

Photophysical measurements

UV-visible absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Steady-state fluorescence and excitation spectra were recorded on a JASCO FP-8500 spectrofluorometer. Absolute fluorescence quantum yields were determined on a HAMAMATSU C9920-02S apparatus. Fluorescence lifetimes were measured on a compact fluorescence lifetime spectrometer Hamamatsu Photonics QuantaTaurusTau C11367. Low temperature measurements were performed using a Unisoku CoolSpeK UV USP-203-B cryostat equipped with the Shimadzu UV-3600 and the JASCO FP-8500. All measurements were conducted using a 10-mm square quartz cell, unless otherwise noted.

X-ray crystallography

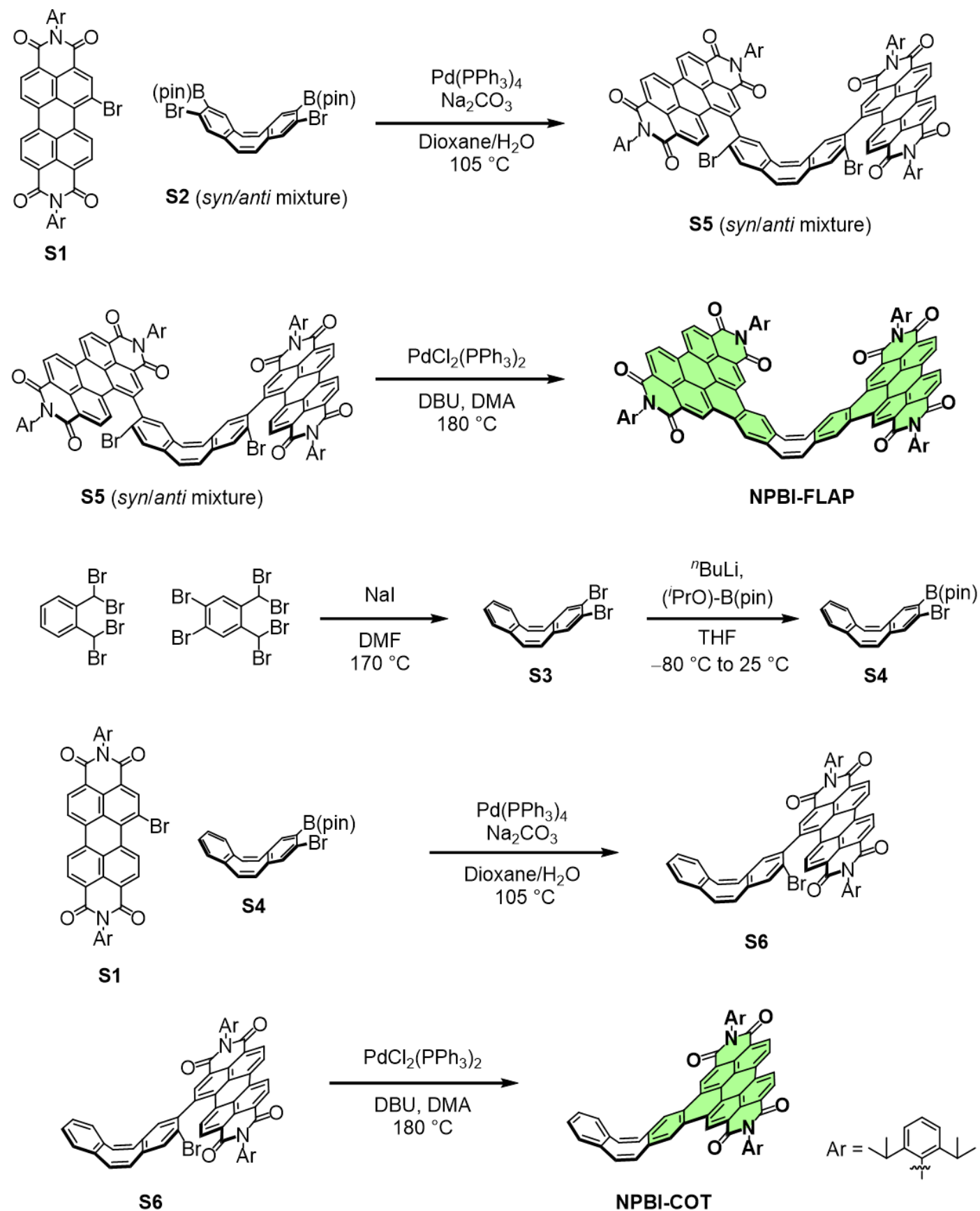
X-ray crystallographic data of **NPBI-FLAP** and **NPBI-COT** were collected at −180 °C with a Rigaku XtaLAB P200 diffractometer equipped with a copper MicroMax007HF generator, VariMax-Cu optics, and a PILATUS 200K two-dimensional detector. The structure was solved by direct method SHELXT^[S5] and refined by SHELXL^[S6] programs. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. Crystallographic data have been deposited in the Cambridge Crystallographic Data Center with the registration numbers of 2268963 (**NPBI-FLAP**) and 2268964 (**NPBI-COT**).

Electrochemical properties

Redox potentials were measured on an ALS electrochemical analyzer model 612E by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Absorption spectra under applied voltage were recorded on a Shimadzu UV-3600 spectrometer using a SEC-C spectroelectrochemical cell (BAS, optical path: 1 mm, 100 mM ⁿBu₄NPF₆ electrolyte, Pt mesh working electrode, Pt counter electrode, and Ag/AgClO₄ reference electrode.)

2. Synthesis of compounds

Scheme S2.1. Synthetic route of NPBI-FLAP and NPBI-COT.

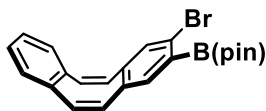


Synthesis of compound S3



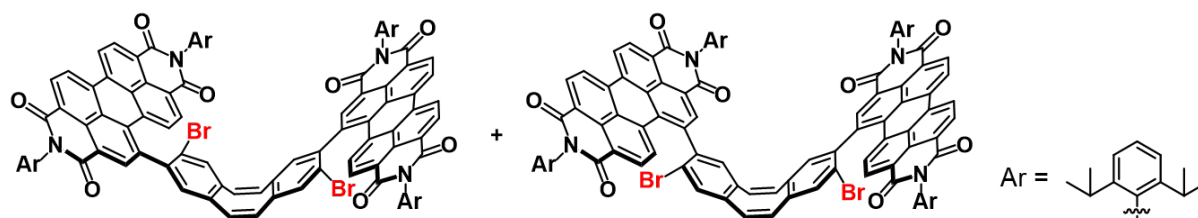
Sodium iodide (18.0 g, 120 mmol) was placed in a two-necked flask, and the flask was purged with argon. Dehydrated *N,N*-dimethylformamide (DMF, 16 mL) was added and the resulting suspension was heated to 170 °C in an oil bath. Then $\alpha,\alpha,\alpha',\alpha',4,5$ -hexabromo-*o*-xylene (3.48 g, 6.0 mmol) and $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (2.53 g, 6.0 mmol) was added to the mixture simultaneously under argon flow with vigorous stirring. The flask was stirred at 170 °C for 4 h, and the reaction mixture was poured into water. To the reaction mixture, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added. The resulting mixture was filtered to afford a brown solid, which was washed with water. The brown solid was dissolved in CH_2Cl_2 and dried with anhydrous Na_2SO_4 . Then, silica gel was added to the CH_2Cl_2 solution, and the resulting slurry was stirred well. CH_2Cl_2 was then evaporated under reduced pressure to form dried light-brown powder of silica gel. This light-brown powder was put on a silica-gel column and eluted with hexane. After the solvent was removed, the residue was purified by a recycling preparative GPC (LaboACE, Japan industry, equipped with 2.5HR and 2HR) using CHCl_3 . Recrystallization from hot hexane afforded **S3** as a white solid (250 mg, 12%). ^1H NMR (CDCl_3 , 600 MHz): δ / ppm 7.31 (s, 2H), 7.20–7.18 (m, 2H), 7.07–7.05 (m, 2H), 6.79 (d, J = 11.9 Hz, 2H), and 6.60 (d, J = 11.9 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ / ppm 138.16, 136.45, 134.93, 133.85, 131.05, 129.19, 127.37, and 123.19; HR-APCI-TOF-MS (m/z) found 359.9135, calcd for $\text{C}_{16}\text{H}_{10}^{79}\text{Br}_2$: 359.9144 [M] $^+$.

Synthesis of compound S4



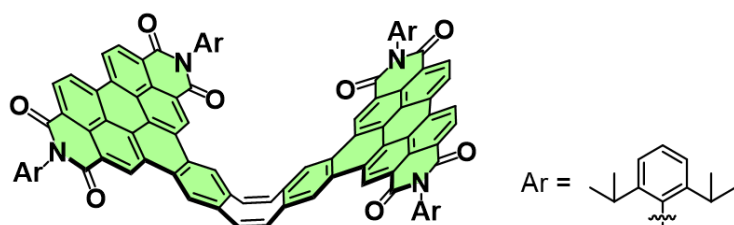
Compound **S3** (202 mg, 0.56 mmol) was placed in a Schlenk flask, and the flask was purged with argon. Anhydrous THF (20 mL) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.25 mL, 1.2 mmol) was added to the flask, and the solution was cooled down to –80 °C. After an *n*-butyllithium solution (1.35 M in hexane, 0.83 mL, 1.1 mmol) was added slowly, the reaction mixture was stirred for 4 h. The mixture was gradually warmed up to room temperature for 10.5 h. Then, the reaction was quenched by addition of water, and the reaction mixture was extracted with CH_2Cl_2 . The organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by a recycling preparative GPC (LaboACE, Japan industry, equipped with 2.5HR and 2HR) using CHCl_3 , providing the compound **S4** as a white solid (132 mg, 58%). ^1H NMR (CDCl_3 , 600 MHz): δ / ppm 7.33 (s, 1H), 7.25 (s, 1H), 7.17–7.14 (m, 2H), 7.05–7.01 (m, 2H), 6.77 (t, J = 12.8 Hz, 2H), 6.67 (d, J = 6.4 Hz, 1H), 6.65 (d, J = 6.4 Hz, 1H), 1.34 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz) δ / ppm 141.36, 137.44, 136.81, 136.65, 135.52, 134.73, 133.88, 132.96, 132.31, 131.88, 129.19, 129.17, 127.18, 127.12, 126.42, 84.39, and 24.92 (Note: 17 peaks were observed for the 18 unique carbons, in which 1 peak was not detected due to broadening.); HR-APCI-TOF-MS (m/z) found 408.0901, calcd for $\text{C}_{22}\text{H}_{22}^{11}\text{B}^{79}\text{BrO}_2$: 408.0895 [M] $^+$

Synthesis of the *syn/anti* isomers of S5



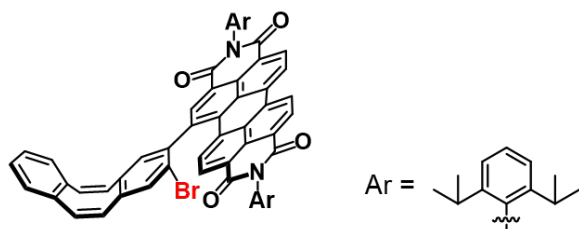
Compound **S2** (60 mg, 98 μmol), compound **S1** (137 mg, 173 μmol), $\text{Pd}(\text{PPh}_3)_4$ (27 mg, 23 μmol), dioxane (3 mL), and an aqueous solution of Na_2CO_3 (1.30 M, 0.60 mL, 780 μmol) were placed in a microwave reactor (30 mL). The solution was degassed by N_2 bubbling for 5 min, and then stirred at 105 $^\circ\text{C}$ for 6 h under microwave irradiation. The mixture was cooled down to room temperature, diluted with CH_2Cl_2 , and dried with anhydrous Na_2SO_4 . After the solvents were evaporated under reduced pressure, the residue was passed through silica-gel column (ethyl acetate/ CH_2Cl_2 = 0/1 to 1/40, v/v), providing *syn/anti* isomers of compound **S5** (141 mg) as a red solid with impurities, which was used without further purification.

Synthesis of NPBI-FLAP



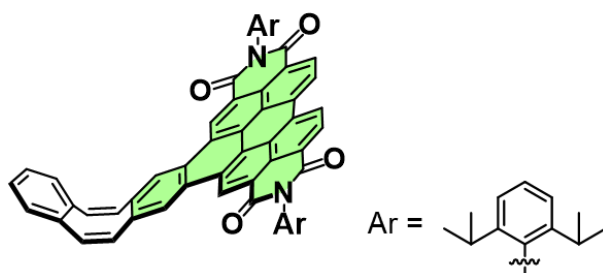
The *syn/anti* isomers of **S5** (58.3 mg, *ca.* 33 μmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (6.3 mg, 9.0 μmol), DMA (4 mL), and DBU (60 μL) were placed in a microwave reactor (10 mL). The solution was degassed by N_2 bubbling for 5 min, and then stirred at 180 $^\circ\text{C}$ for 10 min under microwave irradiation. After cooling down to room temperature, the reaction was quenched by addition of water. The mixture was extracted with organic solvents (ethyl acetate/hexane, 5/1, v/v). The organic layer was washed with water and brine, then dried with anhydrous Na_2SO_4 . After removing the solvents under reduced pressure, the residue was passed through silica-gel column (ethyl acetate/ CH_2Cl_2 , 1/40, v/v), providing **NPBI-FLAP** as a bright orange solid (19.7 mg, 30% in two steps based on **S3**). The product was further purified by recrystallization from a mixed solvent of CHCl_3 /toluene/methanol for optical measurements. ^1H NMR (CDCl_3 , 600 MHz): δ / ppm 10.23 (s, 4H), 9.29 (d, J = 8.7 Hz, 4H), 9.20 (s, 4H), 9.09 (d, J = 7.8 Hz, 4H), 7.58 (s, 4H), 7.56 (t, J = 6.8 Hz, 4H), 7.40 (d, J = 8.3 Hz, 8H), 2.85–2.80 (m, 8H), and 1.19 (m, 48H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ / ppm 164.15, 164.06, 145.86, 138.11, 134.47, 130.79, 130.40, 129.95, 129.21, 128.48, 128.17, 125.49, 125.39, 125.12, 124.34, 123.57, 123.12, 122.70, 29.42, 24.21, and 24.16 (Note: 21 peaks were observed for the 22 unique carbons, in which 1 peak was overlapped.); MALDI-TOF-MS (m/z) found 1617.66, $\text{C}_{112}\text{H}_{89}\text{N}_4\text{O}_8$: 1617.67 [$M + \text{H}$] $^+$; UV-visible absorption (toluene): λ_{max} ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 348 (6.0×10^4), 453 (3.4×10^4), 482 (7.8×10^4), and 516 nm (1.1×10^5); Fluorescence (toluene, λ_{ex} = 480 nm): λ_{F} = 529 and 570 nm; Φ_{F} = 0.87, τ_{F} = 5.3 ns.

Synthesis of compound S6



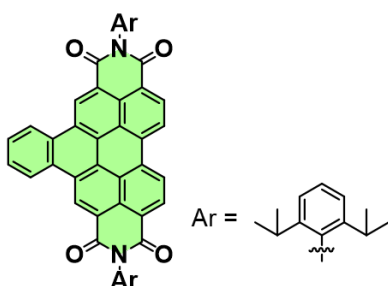
Compound **S4** (40.5 mg, 99 μmol), Compound **S1** (84.5 mg, 107 μmol), $\text{Pd}(\text{PPh}_3)_4$ (34 mg, 30 μmol), dioxane (3 mL), and an aqueous solution of Na_2CO_3 (1.33 M, 0.30 mL, 0.40 mmol) were placed in a microwave reactor (10 mL). The solution was degassed by N_2 bubbling for 5 min, and then stirred at 105 $^\circ\text{C}$ for 3 h under microwave irradiation. The mixture was cooled down to room temperature and dried with anhydrous Na_2SO_4 . After the solvents were evaporated under reduced pressure, the residue was passed through silica-gel column (CH_2Cl_2), providing **S6** (74.2 mg, 76%) as a red solid, which was used without further purification.

Synthesis of NPBI-COT



Compound **S6** (52.7 mg, 53 μmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (15 mg, 21 μmol), DMA (3 mL), and DBU (30 μL) were placed in a microwave reactor (10 mL). The solution was degassed by N_2 bubbling for 5 min, and then stirred at 180 $^\circ\text{C}$ for 10 min under microwave irradiation. The mixture was cooled down to room temperature and poured into water. The brown precipitate was filtrated, and washed with water and MeOH. Then, the solid was dissolved in CH_2Cl_2 and dried with anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography (CH_2Cl_2 /hexane, 5/1, v/v). Recrystallization from CHCl_3 /methanol afforded **NPBI-COT** as a bright orange solid (25.7 mg, 53%). ^1H NMR (CD_2Cl_2 , 600 MHz): δ / ppm 10.24 (s, 2H), 9.38 (d, $J = 8.3$ Hz, 2H), 9.14 (s, 2H), 9.10 (d, $J = 8.3$ Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 8.3$ Hz, 4H), 7.30 (d, $J = 11.9$ Hz, 2H), 7.18 (s, 4H), 7.09 (d, $J = 12.4$ Hz, 2H), 2.89–2.84 (m, 4H), 1.19 (m, 24H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ / ppm 164.34, 164.13, 145.92, 138.92, 136.59, 135.50, 134.53, 132.35, 130.87, 130.34, 129.91, 129.36, 129.31, 128.62, 128.36, 128.17, 127.41, 125.47, 125.41, 124.88, 124.34, 123.56, 123.01, 122.69, 29.45, 24.25, and 24.18; HR-APCI-TOF-MS (m/z) found 910.3744, $\text{C}_{64}\text{H}_{50}\text{N}_2\text{O}_4$: 910.3765 $[M]^+$; UV-visible absorption (toluene): λ_{max} ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 343 (2.8×10^4), 455 (1.8×10^4), 485 (3.7×10^4) and 521 nm (5.8×10^4); Fluorescence (toluene, $\lambda_{\text{ex}} = 480$ nm): $\lambda_{\text{F}} = 532$ and 572 nm; $\Phi_{\text{F}} = 0.82$, $\tau_{\text{F}} = 5.0$ ns.

Synthesis of NPBI



NPBI was synthesized according to the previously reported method and all characterization data matched with those previously reported^[S3]. The product was purified by recrystallization from CHCl₃/methanol for twice. UV-visible absorption (toluene): λ_{max} ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 314 (2.1×10^4), 328 (2.9×10^4), 452 (1.7×10^4), 475 (3.7×10^4) and 510 nm (6.6×10^4); Fluorescence (toluene, $\lambda_{\text{ex}} = 470 \text{ nm}$): $\lambda_{\text{F}} = 520$ and 558 nm; $\Phi_{\text{F}} = 0.96$, $\tau_{\text{F}} = 4.2 \text{ ns}$.

3. Characterization of new compounds

3.1. ¹H and ¹³C NMR spectroscopy

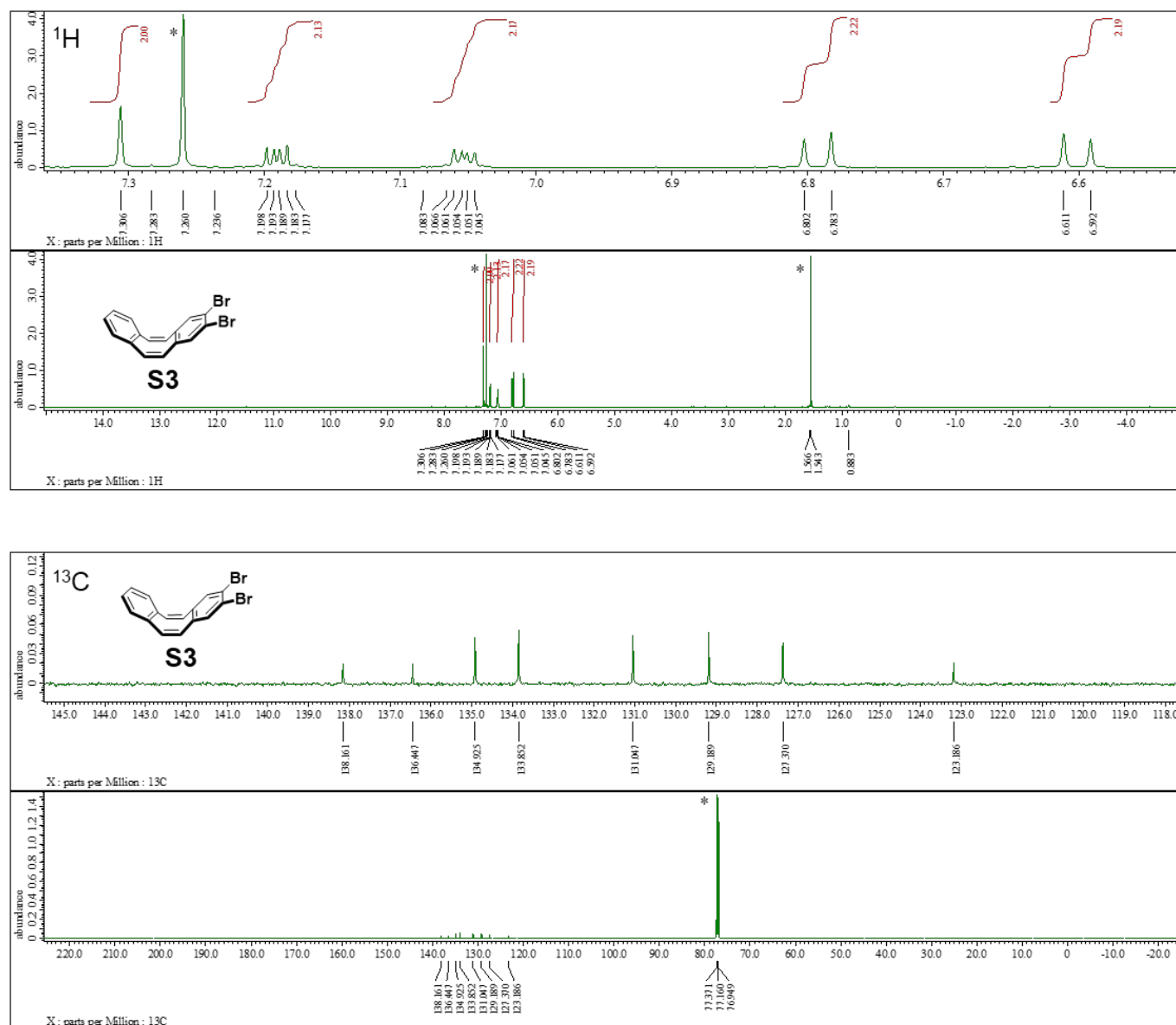


Figure S3.1. ¹H NMR (top) and ¹³C NMR (bottom) spectra of S3 in CDCl₃. Signals marked with an asterisk (*) indicate residual solvents.

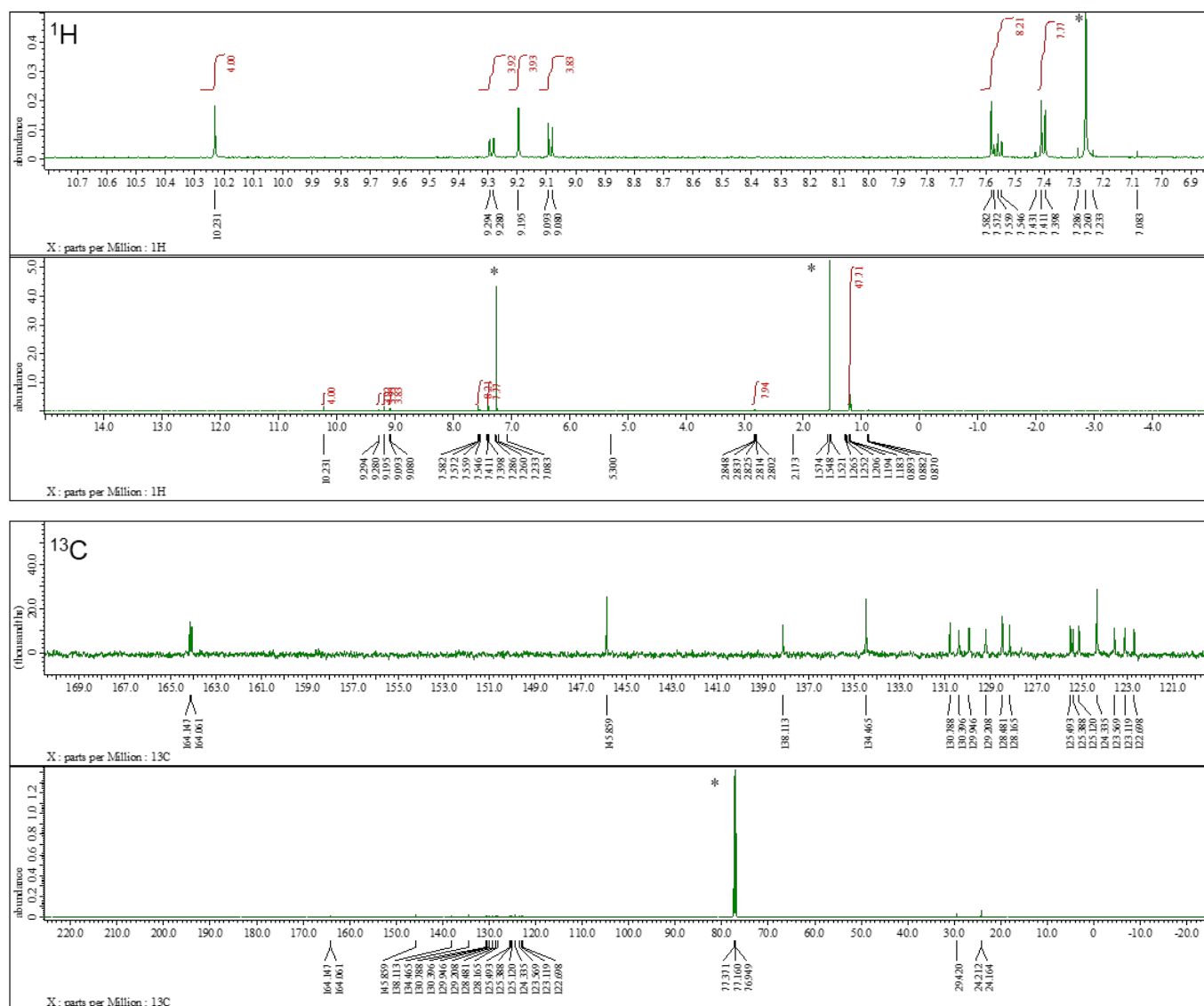
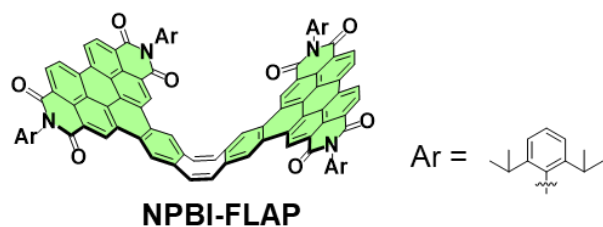


Figure S3.3. ¹H NMR (top) and ¹³C NMR (bottom) spectra of NPBI-FLAP in CDCl₃. Signals marked with an asterisk (*) indicate residual solvents.

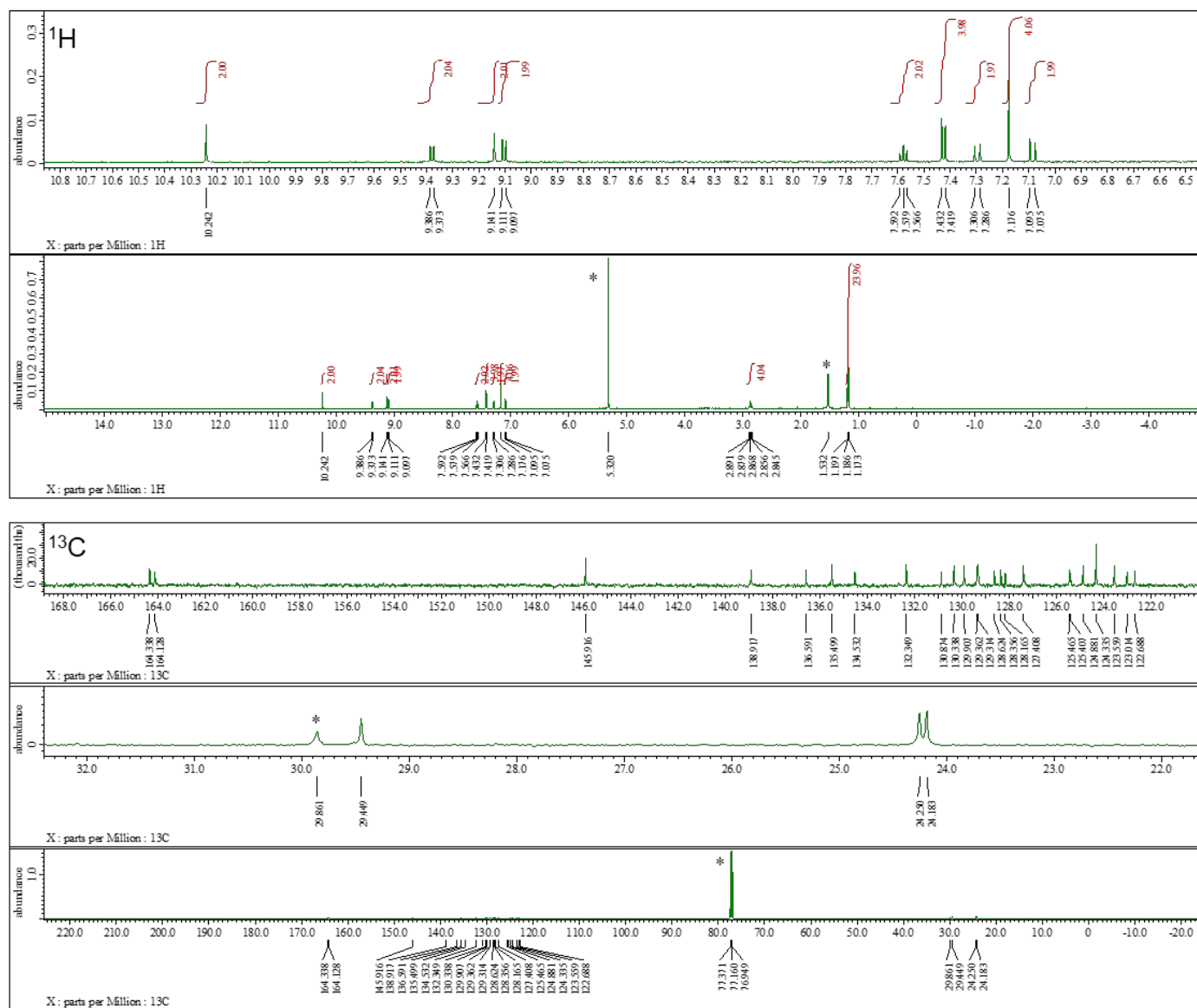
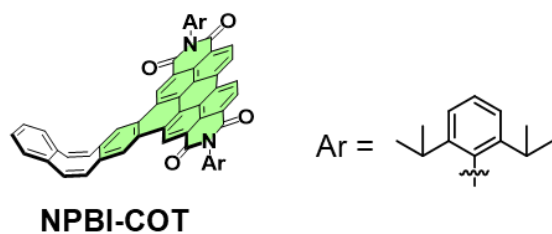


Figure S3.4. ^1H NMR (top) in CD_2Cl_2 and ^{13}C NMR (bottom) spectra of **NPBI-COT** in CDCl_3 . Signals marked with asterisks (*) indicate residual solvents or silicone grease.

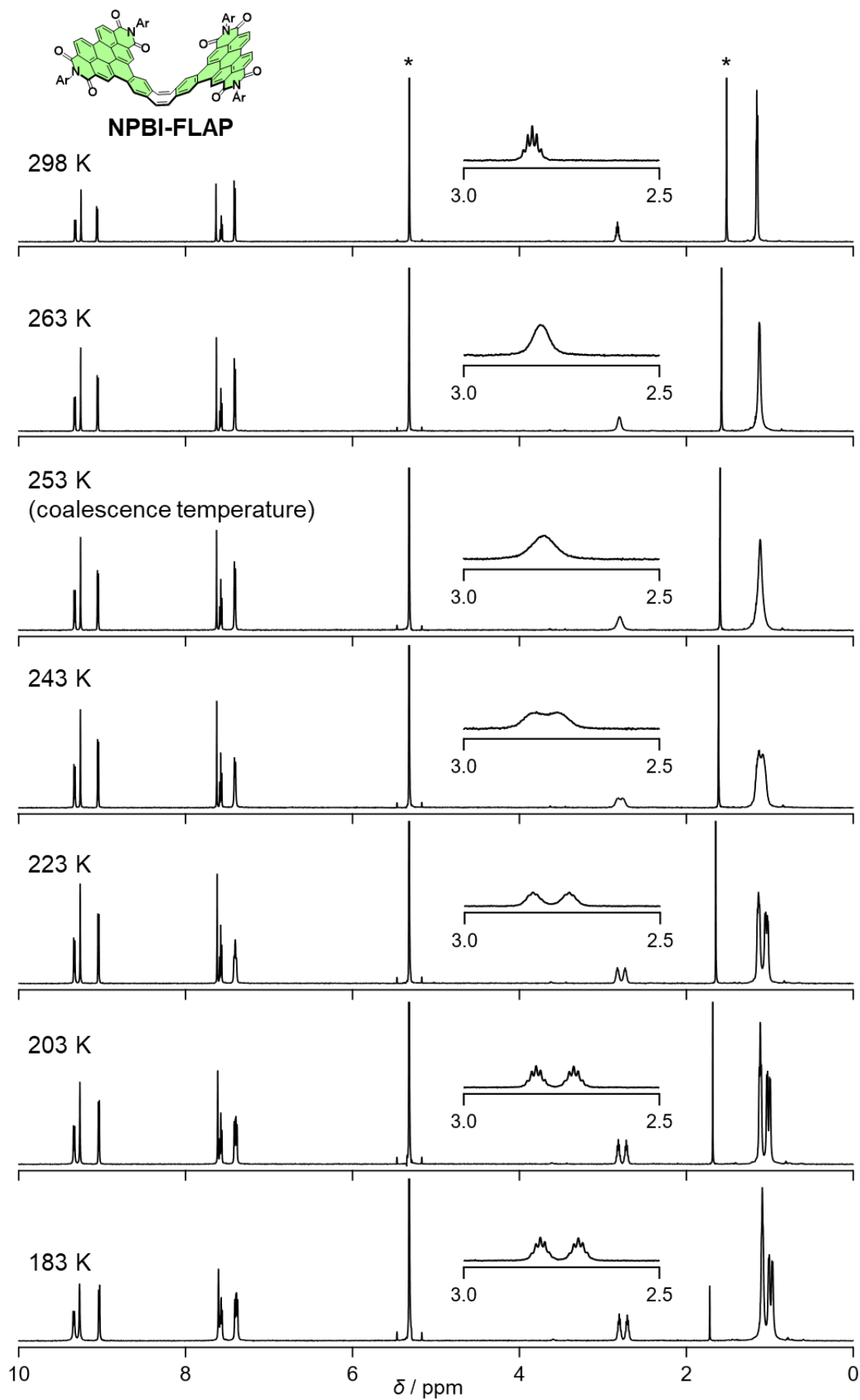


Figure S3.5. Low temperature ^1H NMR spectra of **NPBI-FLAP** in CD_2Cl_2 . Signals marked with an asterisk (*) indicate residual solvents. Magnetic environments of the protons at the isopropyl groups (see inset) were averaged in the NMR time scale of 298 K, while the corresponding signals became split at lower temperatures than 253 K. The result indicates a fast flapping motion of **NPBI-FLAP** at 298 K.

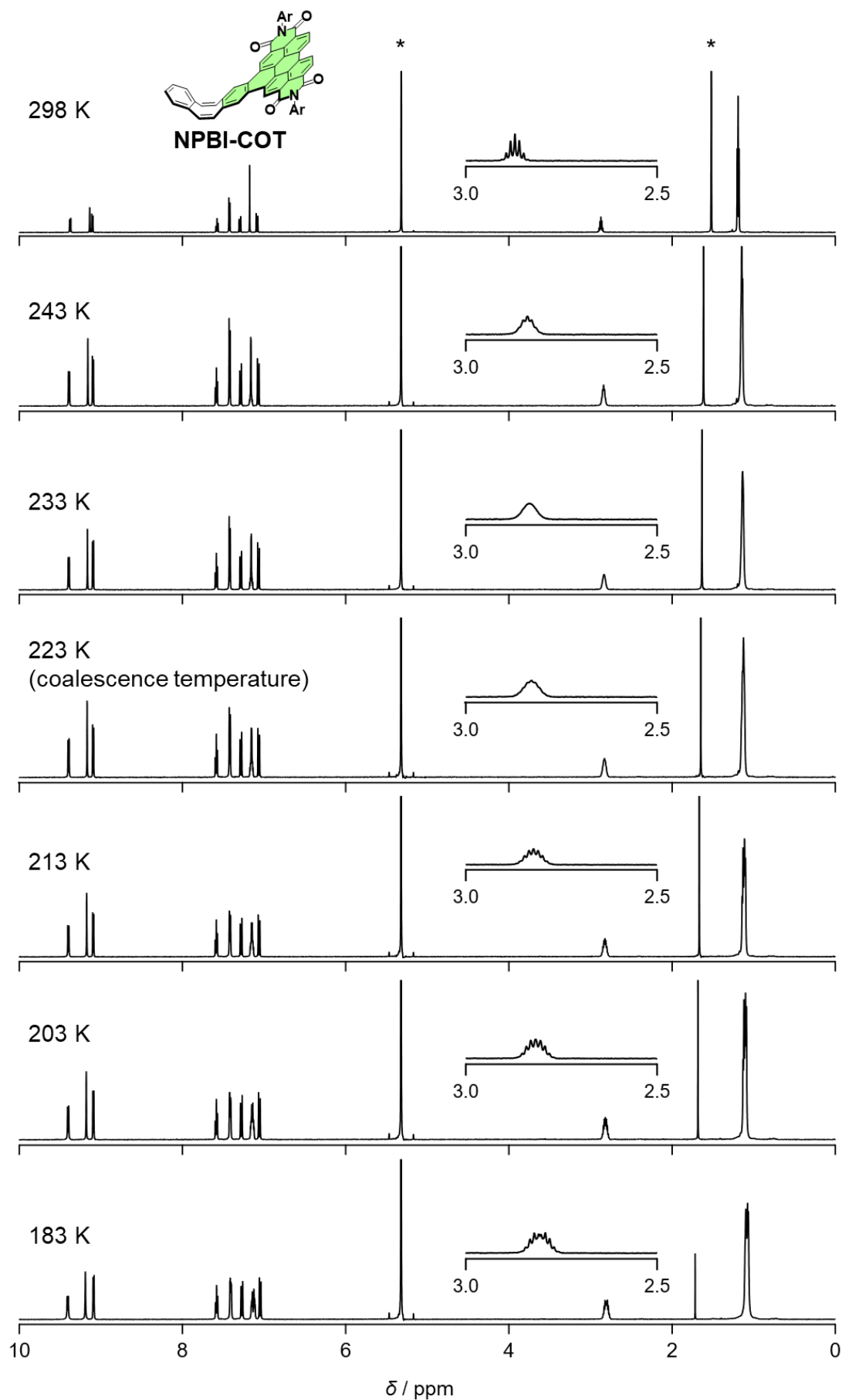


Figure S3.6. Low temperature ^1H NMR spectra of **NPBI-COT** in CD_2Cl_2 . Signals marked with an asterisk (*) indicate residual solvents. Magnetic environments of the protons at the isopropyl groups (see inset) were averaged in the NMR time scale of 298 K, while the corresponding signals became split at lower temperatures than 223 K. The result indicates a fast flapping motion of **NPBI-COT** at 298 K.

3.2. High resolution mass spectrometry

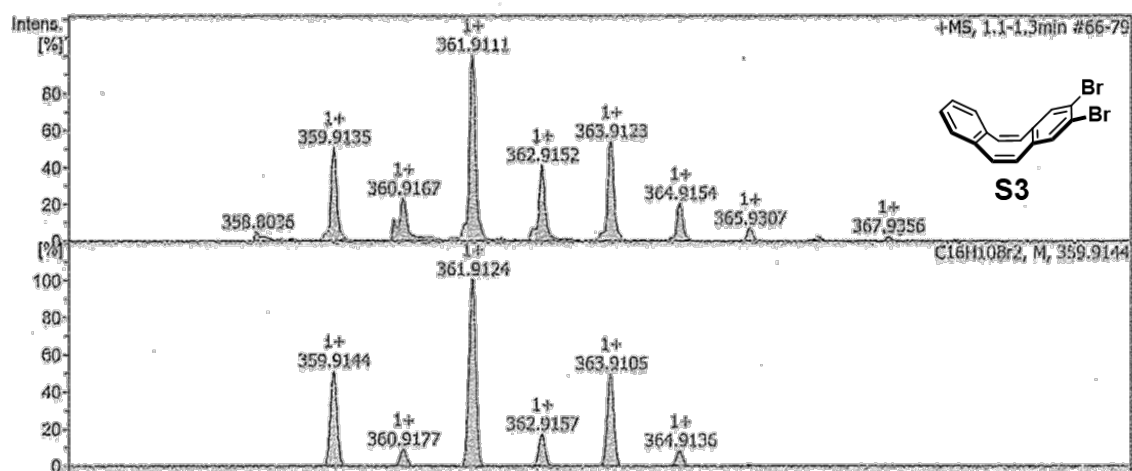


Figure S3.7. HR-APCI-TOF-MS (positive mode) of **S3** (top: observed, bottom: simulated).

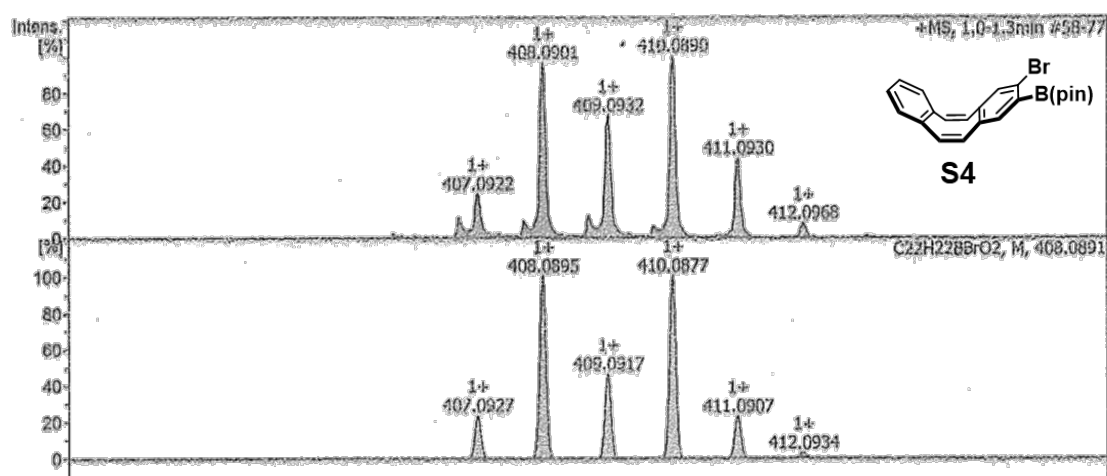


Figure S3.8. HR-APCI-TOF-MS (positive mode) of **S4** (top: observed, bottom: simulated).

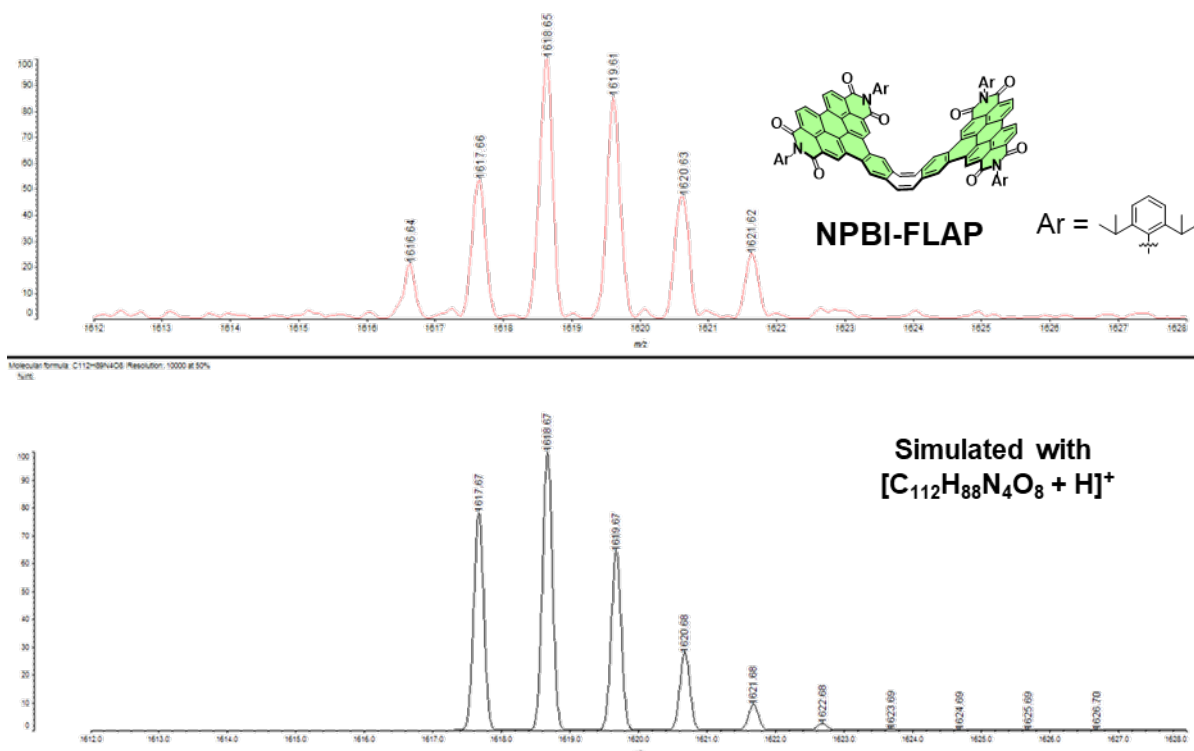
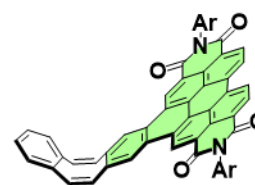
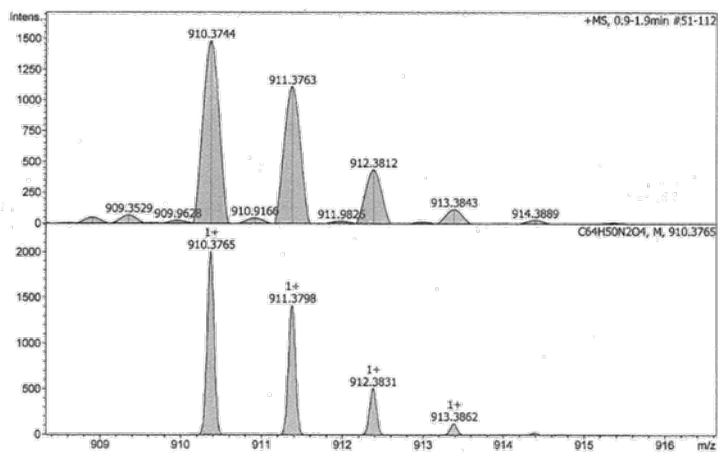


Figure S3.9. MALDI-TOF-MS (positive mode) of **NPBI-FLAP** (top: observed, bottom: simulated).



NPBI-COT

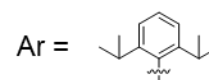


Figure S3.10. HR-APCI-TOF-MS (positive mode) of NPBI-COT (top: observed, bottom: simulated).

4. Photophysical properties

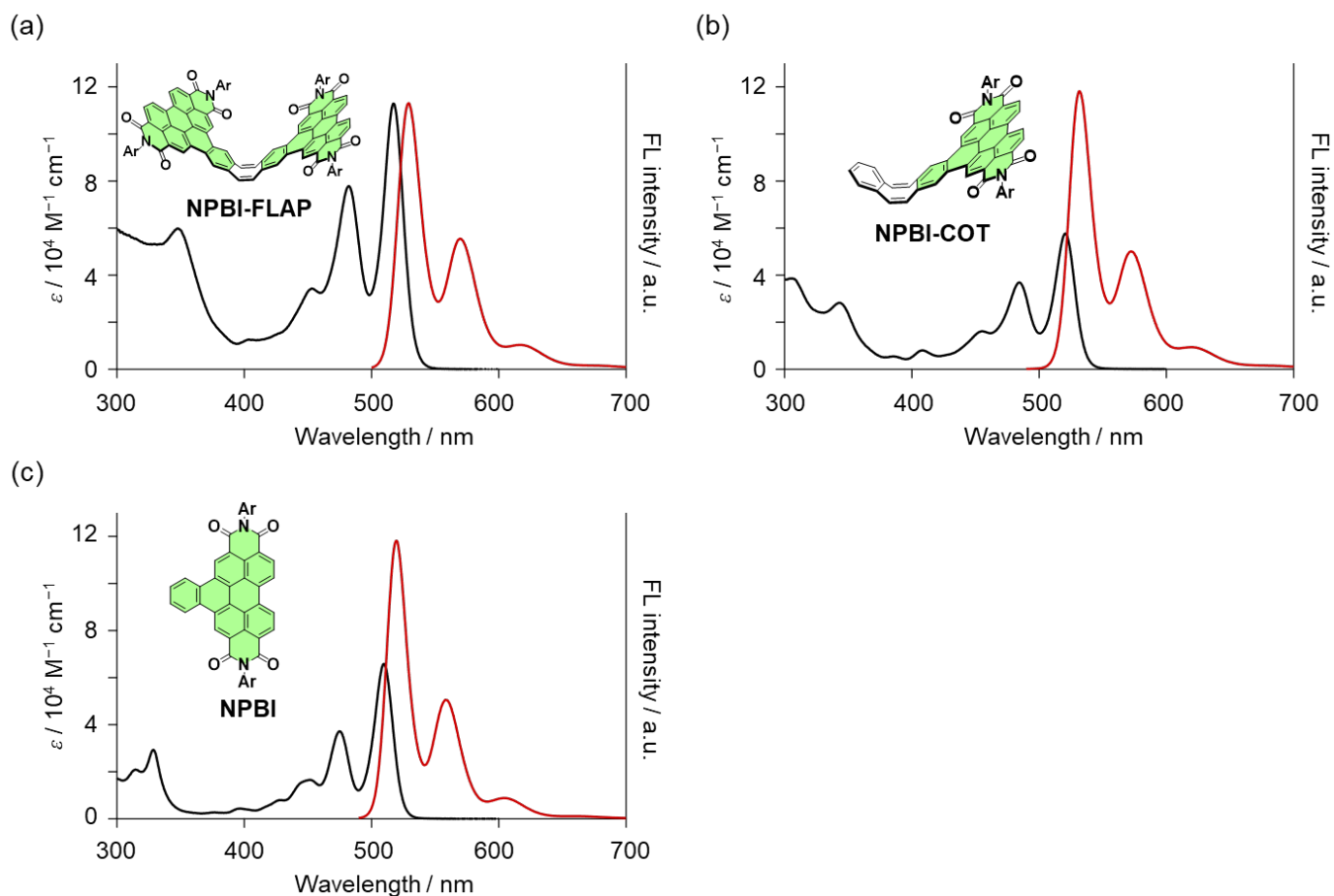


Figure S4.1. UV-visible absorption (black line) and fluorescence (red line) spectra of (a) NPBI-FLAP, (b) NPBI-COT, and (c) NPBI in toluene.

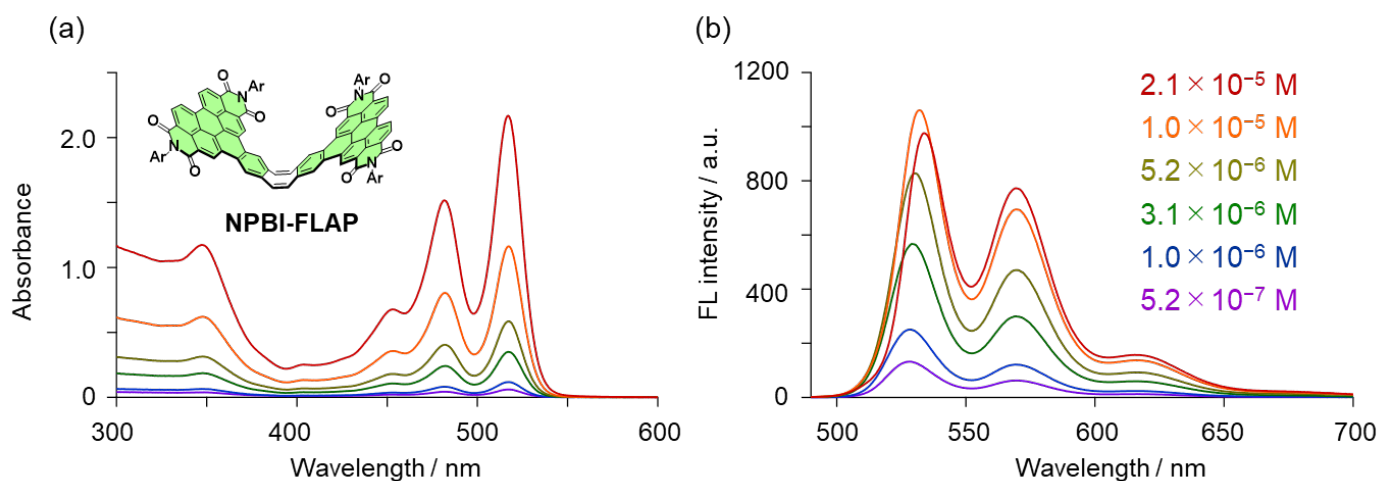


Figure S4.2. Photophysical properties of NPBI-FLAP in toluene. (a) Concentration dependence of the absorption spectra and (b) concentration dependence of the fluorescence spectra (excited at 480 nm).

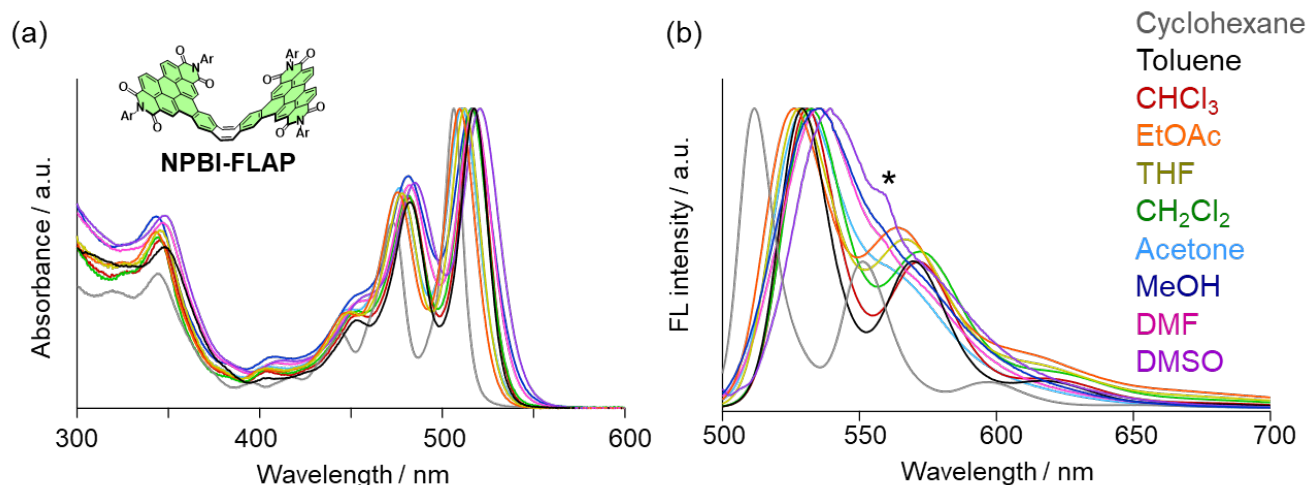


Figure S4.3. (a) UV-visible absorption spectra of **NPBI-FLAP** in various solvents. (b) Fluorescence spectra of **NPBI-FLAP** in various solvents. (Excitation wavelength: 470 nm in cyclohexane, 480 nm in the other solvents) A peak marked with an asterisk (*) indicates the Raman peak derived from DMSO.

Note: Fluorescence spectra in acetone, MeOH, DMF, and DMSO were not treated with the correction function due to the faint fluorescence.

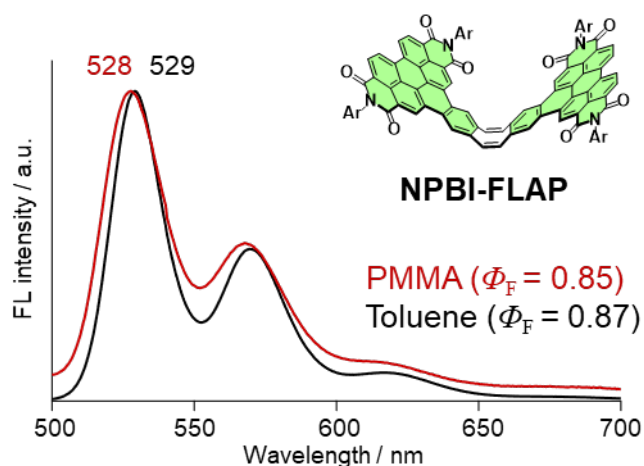


Figure S4.4. Fluorescence spectra of **NPBI-FLAP** in toluene and a PMMA film. (Excitation wavelength: 480 nm in toluene and 450 nm in the PMMA film). The PMMA film was prepared by the following method: **NPBI-FLAP** (~30 μg , 0.01 wt%) and PMMA (300 mg, typical $M_w = 15000$, Aldrich) were dissolved in chloroform (2 mL), and this solution was dropped onto a quartz plate and dried under vacuum for 1 h.

Table S4.1. Optical properties of **NPBI-FLAP** measured in various solvents and a PMMA film

Solvents	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{FL}} / \text{nm}$	Stokes shift / cm^{-1}	Φ_{F}	$\tau_{\text{F}} (A)$	χ^2
Cyclohexane	506	512	230	0.91	4.9 ns	1.53
Toluene	518	529	400	0.87	5.3 ns	1.45
CHCl_3	517	531	510	0.79	5.1 ns	1.47
EtOAc	510	526	600	0.59	5.6 ns	1.40
THF	512	528	590	0.68	6.1 ns	1.40
CH_2Cl_2	516	532	580	0.69	5.2 ns	1.58
Acetone	511	531	740	0.04	2.6 ns	2.01
MeOH	516	536	720	< 0.01	$< 0.1 \text{ ns (17447)}$ 3.1 ns (43)	1.74
DMF	517	534	630	< 0.01	$< 0.1 \text{ ns (10616)}$ 0.80 ns (436) 4.5 ns (31)	1.17
DMSO	521	540	660	< 0.01	$< 0.1 \text{ ns (10851)}$ 0.69 ns (341) 6.4 ns (2.7)	1.80
PMMA	---	528	---	0.85	5.2 ns	1.58

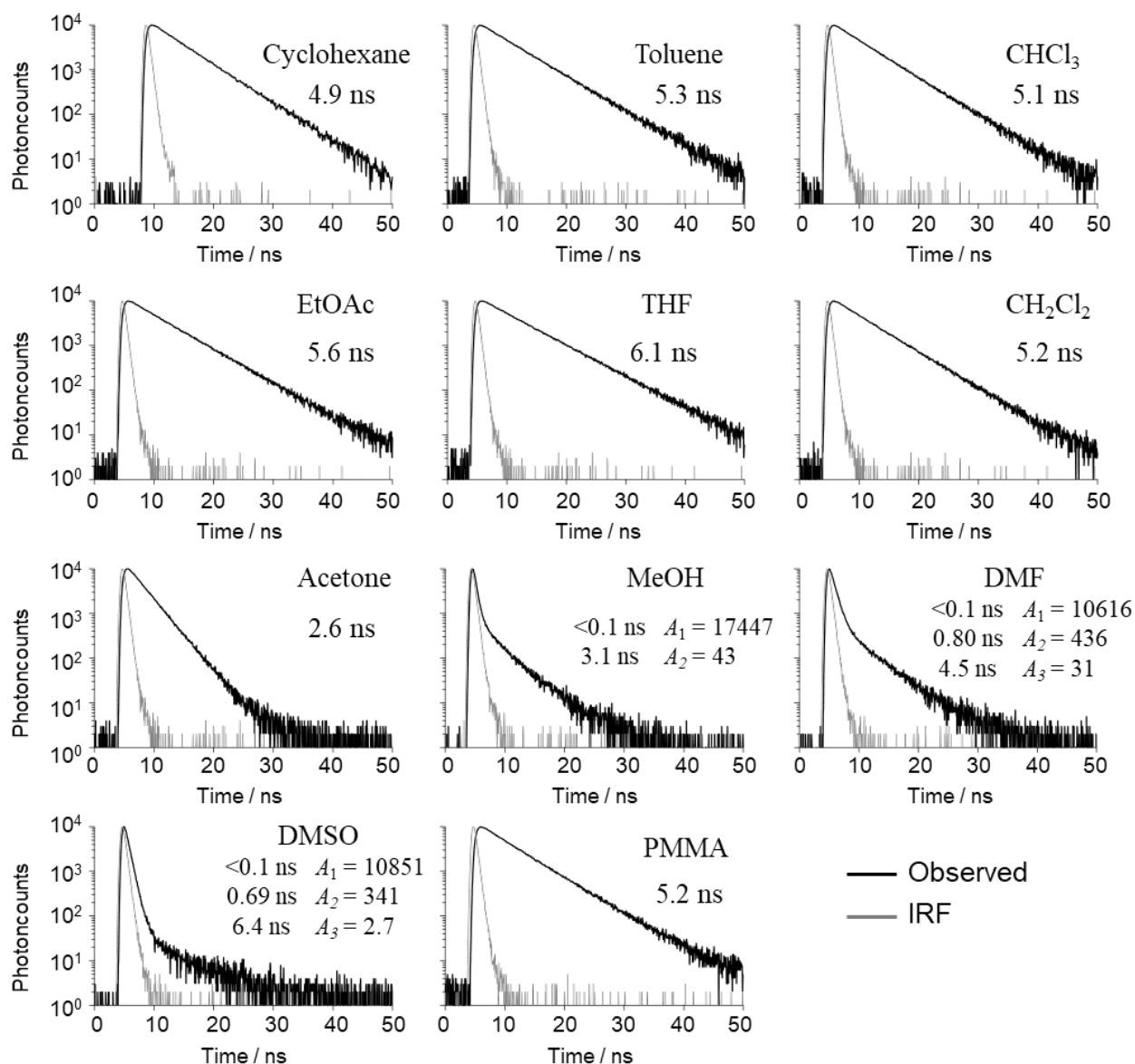


Figure S4.5. Fluorescence decay profiles of **NPBI-FLAP** in various solvents. IRF: Instrument response function.

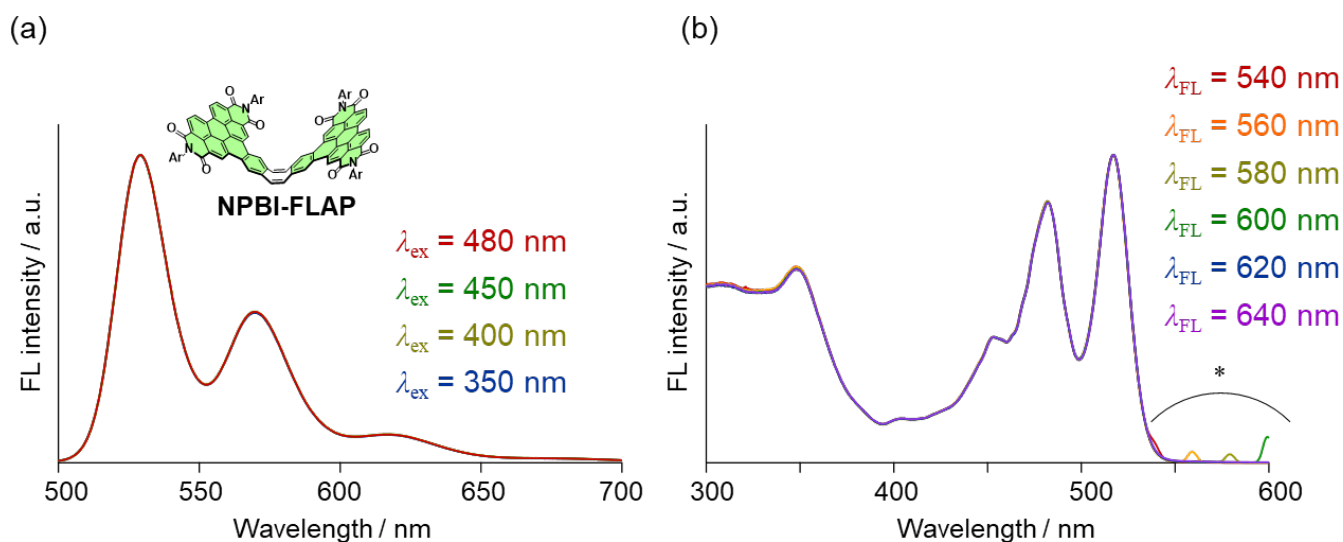


Figure S4.6. (a) Fluorescence spectra of **NPBI-FLAP** obtained with different excitation energies. (b) Fluorescence excitation spectra of **NPBI-FLAP** monitored at different emission wavelengths. Peaks marked with an asterisk (*) are due to the scattered excitation light.

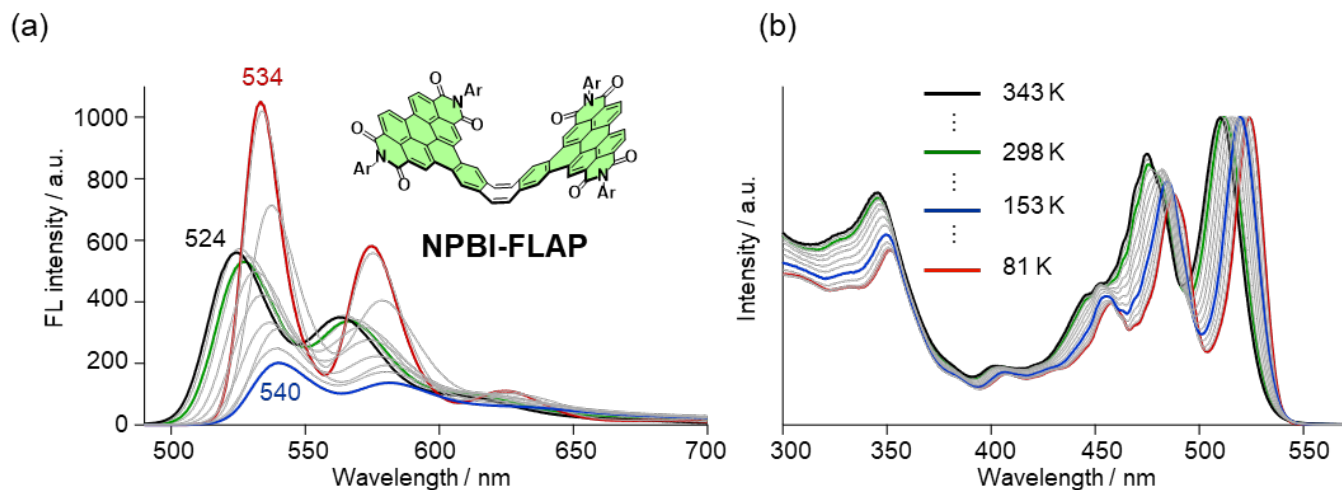


Figure S4.7. (a) Temperature dependence of the fluorescence spectra of **NPBI-FLAP** in 2MeTHF ($\lambda_{\text{ex}} = 480$ nm) and (b) excitation spectra of **NPBI-FLAP** ($\lambda_{\text{FL}} = 580$ nm).

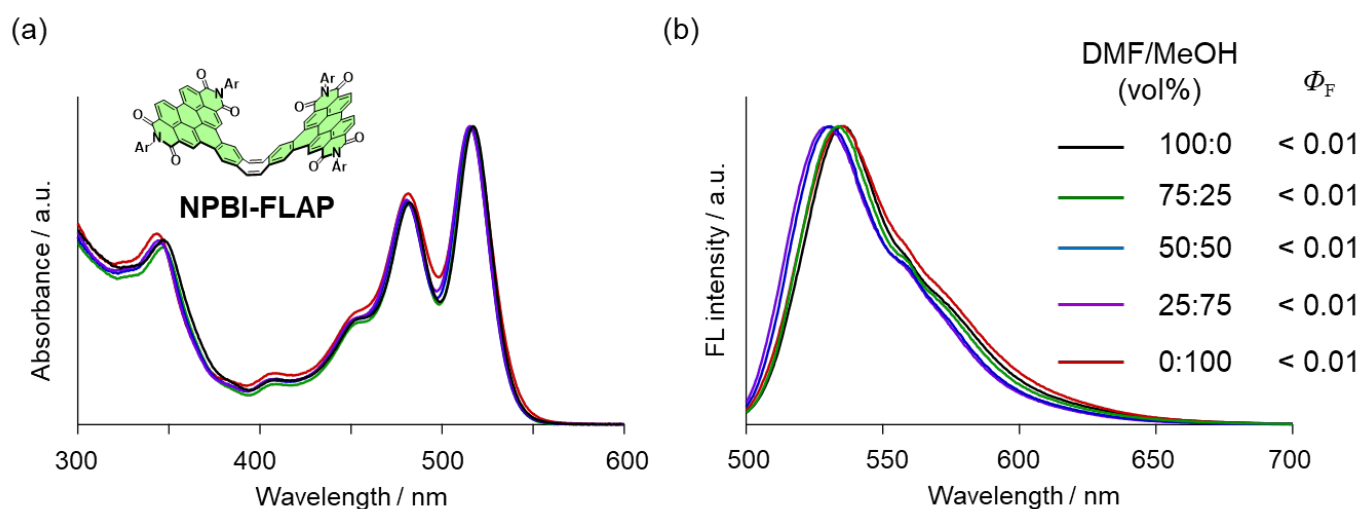


Figure S4.8. (a) Absorption spectra of **NPBI-FLAP** in DMF/MeOH mixed solvents with different ratio and (b) fluorescence spectra of **NPBI-FLAP** ($\lambda_{\text{ex}} = 480$ nm). Note: Fluorescence spectra were not treated with the correction function due to the faint fluorescence.

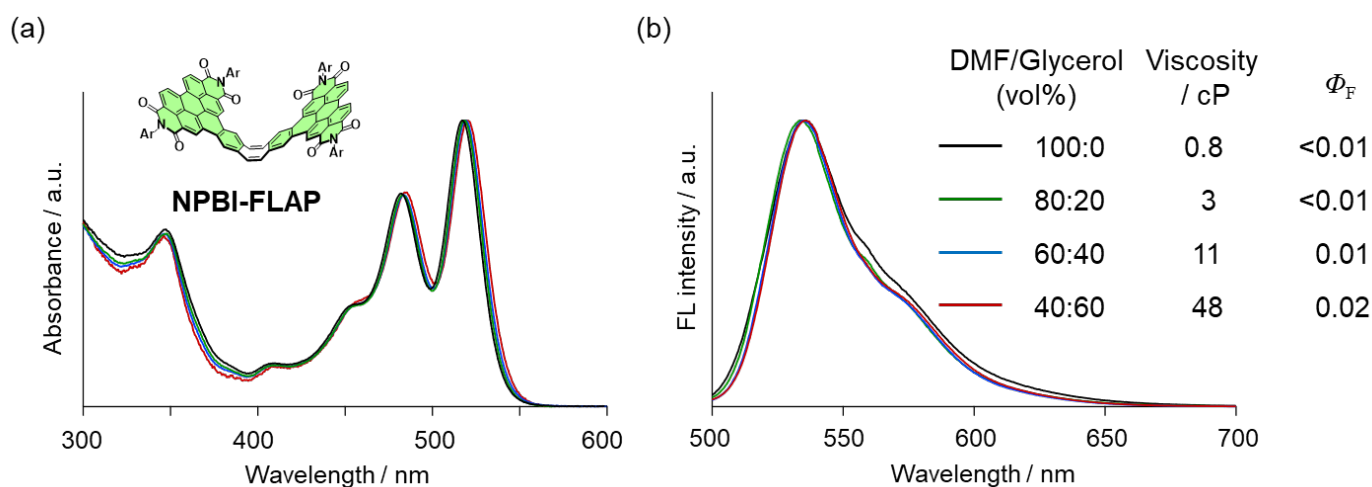


Figure S4.9. (a) Absorption spectra of **NPBI-FLAP** in DMF/glycerol mixed solvents with different ratio and (b) fluorescence spectra of **NPBI-FLAP** ($\lambda_{\text{ex}} = 480$ nm). Note: Fluorescence spectra were not treated with the correction function due to the faint fluorescence.

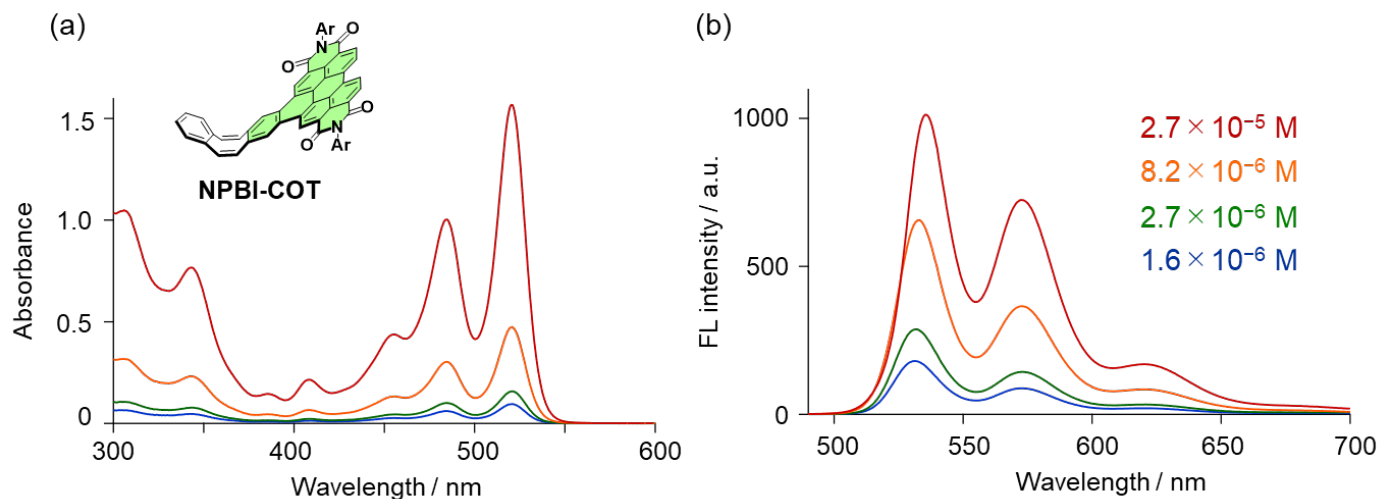


Figure S4.10. Photophysical properties of NPBI-COT in toluene. (a) Concentration dependence of the absorption spectra and (b) Concentration dependence of the fluorescence spectra (Excited at 480 nm).

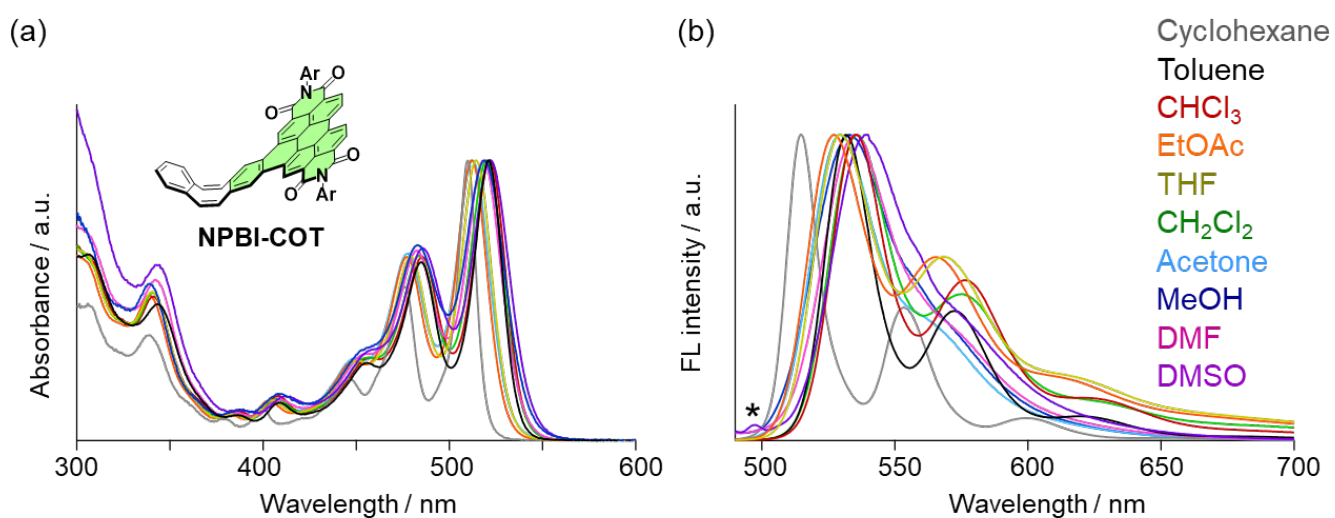


Figure S4.11. (a) UV-visible absorption spectra of NPBI-COT in various solvents. (b) Fluorescence spectra of NPBI-COT in various solvents. (Excitation wavelength: 480 nm). A peak marked with an asterisk (*) indicates the Raman peak derived from DMSO. Note: Fluorescence spectra in acetone, MeOH, DMF and DMSO were not treated with the correction function due to the faint fluorescence.

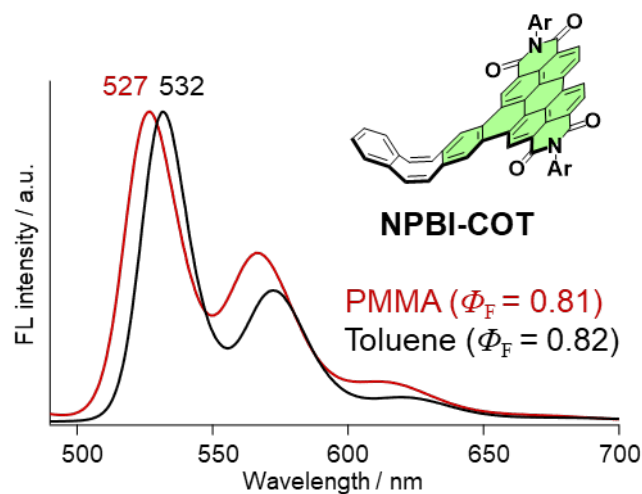


Figure S4.12. Fluorescence spectra of **NPBI-COT** in toluene and a PMMA film. (Excitation wavelength: 480 nm in toluene and 450 nm in the PMMA film). The PMMA film was prepared by the following method: **NPBI-COT** (~25 μg , 0.01 wt%) and PMMA (250 mg, typical $M_w = 15000$, Aldrich) were dissolved in chloroform (2 mL), and this solution was dropped onto a quartz plate and dried under vacuum for 1 h.

Table S4.2. Optical properties of **NPBI-COT** measured in various solvents and a PMMA film

Solvents	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{FL}} / \text{nm}$	Stokes shift / cm^{-1}	Φ_F	$\tau_F (A)$	χ^2
Cyclohexane	510	514	170	0.89	4.5 ns	1.42
Toluene	521	532	380	0.82	5.0 ns	1.75
CHCl_3	522	536	520	0.59	4.1 ns	1.62
EtOAc	512	527	560	0.28	2.9 ns	1.63
THF	514	530	550	0.26	2.8 ns	1.24
CH_2Cl_2	520	536	560	0.32	3.1 ns	1.85
Acetone	512	530	630	0.04	0.67 ns (1196) 5.0 ns (5)	1.10
MeOH	519	533	510	< 0.01	< 0.1 ns (19335) 4.4 ns (51)	1.37
DMF	518	536	650	0.01	0.21 ns (2617) 4.1 ns (13)	1.89
DMSO	522	540	620	< 0.01	< 0.1 ns (11319) 0.47 ns (158) 5.1 ns (8)	1.40
PMMA	---	527	---	0.81	5.0 ns	1.11

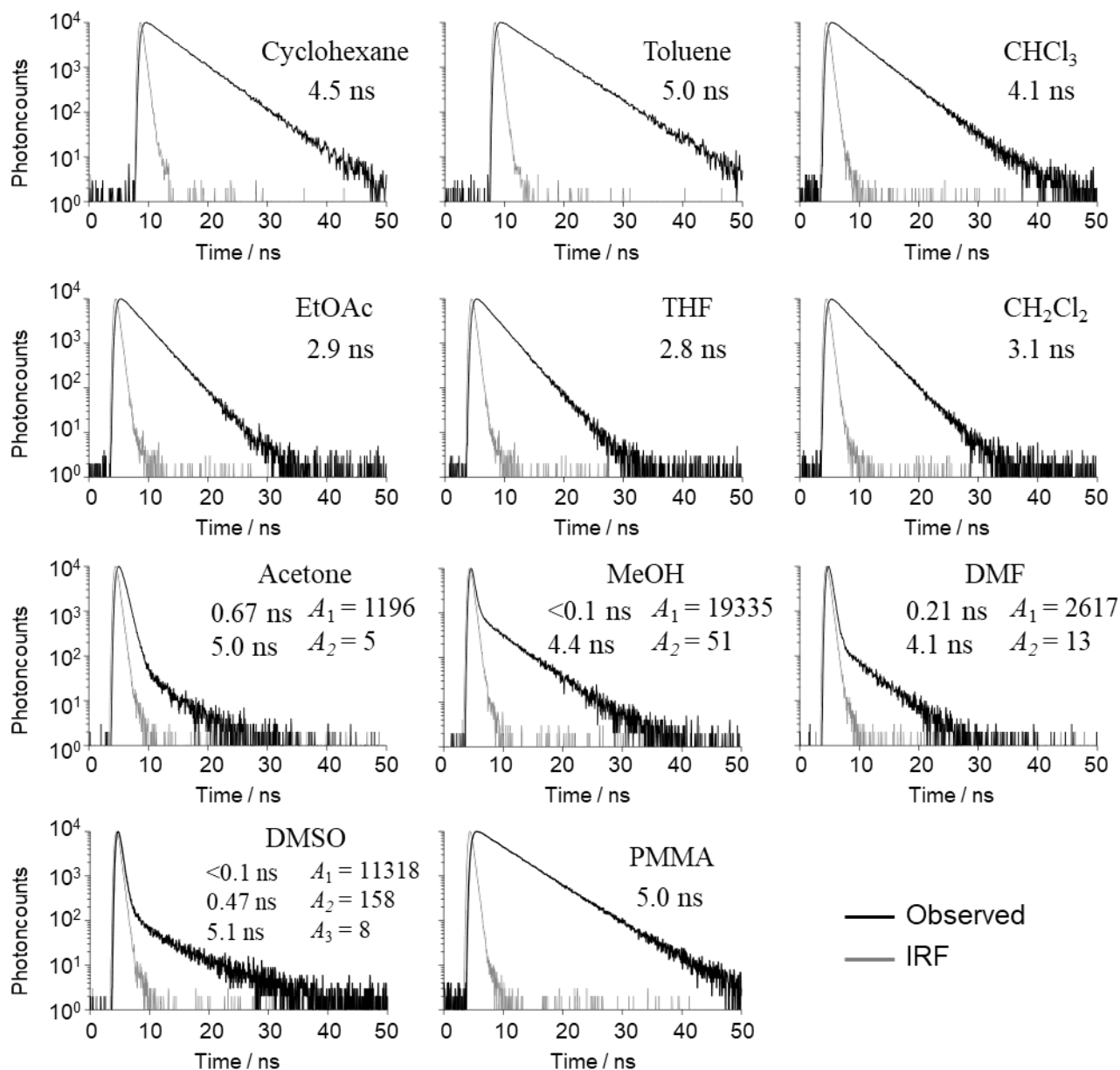


Figure S4.13. Fluorescence decay profiles of NPBI-COT in various solvents. IRF: Instrument response function.

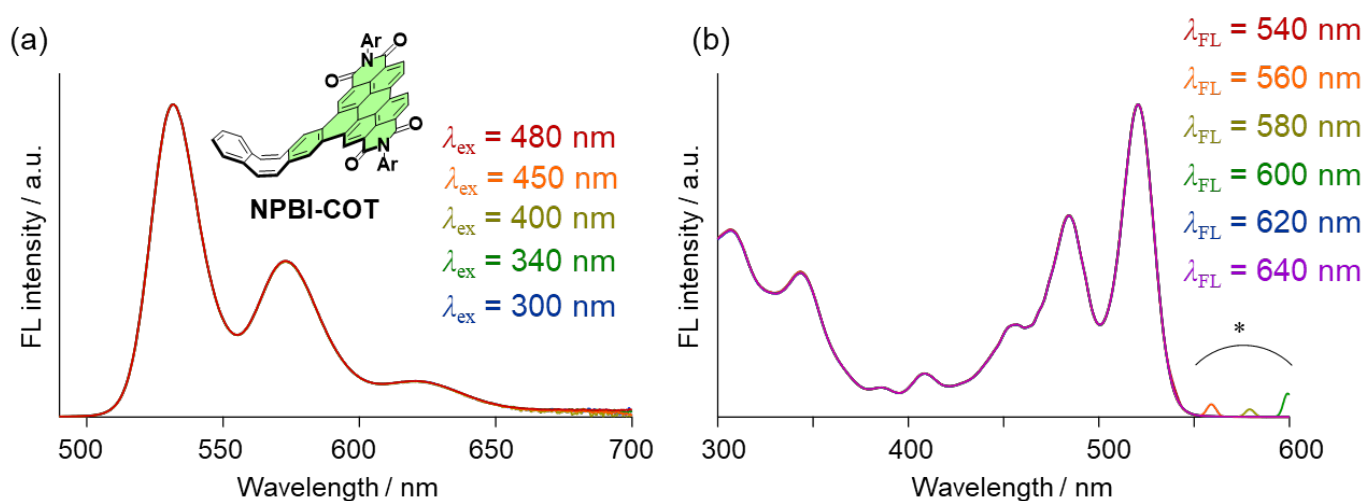


Figure S4.14. (a) Fluorescence spectra of NPBI-COT observed with different excitation energies. (b) Fluorescence excitation spectra of NPBI-COT monitored at different emission wavelengths. Peaks marked with an asterisk (*) are due to scattered excitation light.

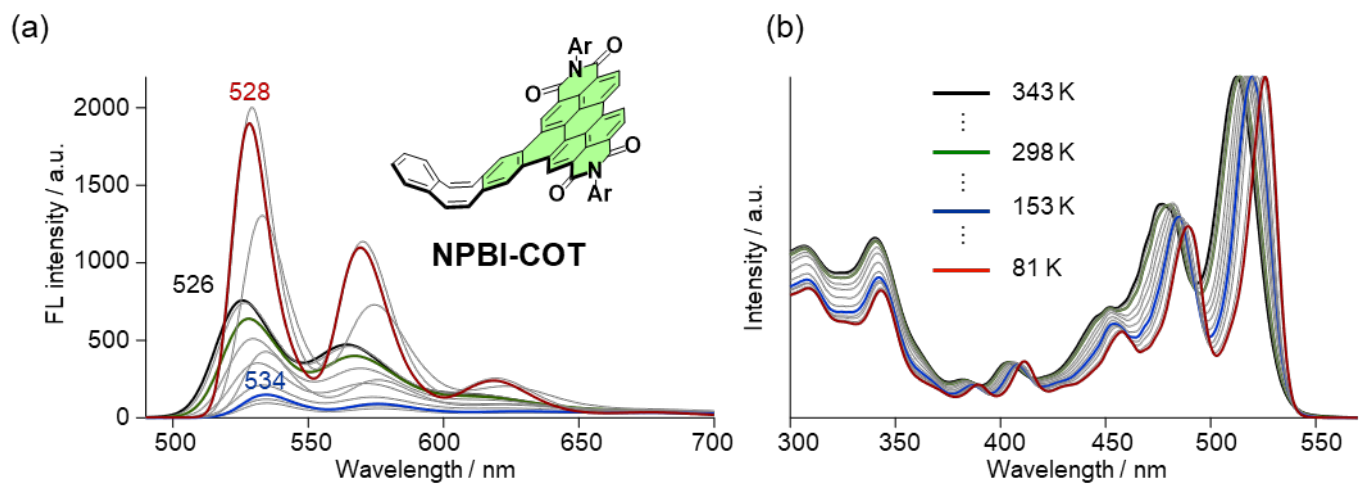


Figure S4.15. (a) Temperature dependence of fluorescence spectra of NPBI-COT in 2MeTHF ($\lambda_{\text{ex}} = 480$ nm) and (b) fluorescence spectra of FLAP2 ($\lambda_{\text{FL}} = 580$ nm).

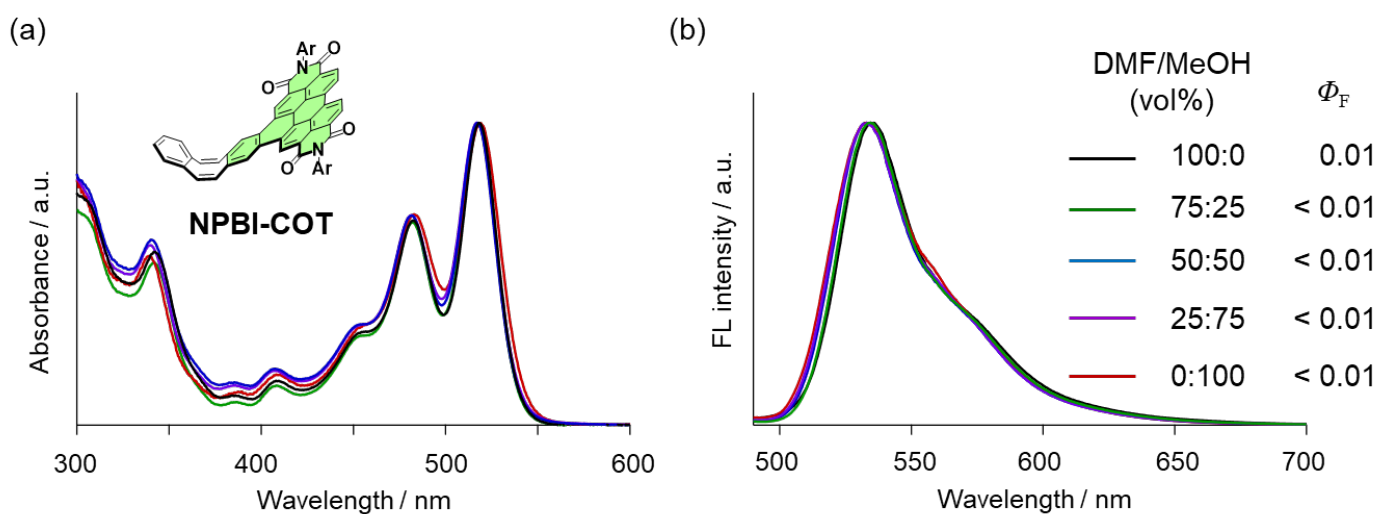


Figure S4.16. (a) Absorption spectra of NPBI-COT in DMF/MeOH mixed solvents with different ratio and (b) fluorescence spectra of NPBI-COT ($\lambda_{\text{ex}} = 480$ nm). Note: Fluorescence spectra were not treated with the correction function due to the faint fluorescence.

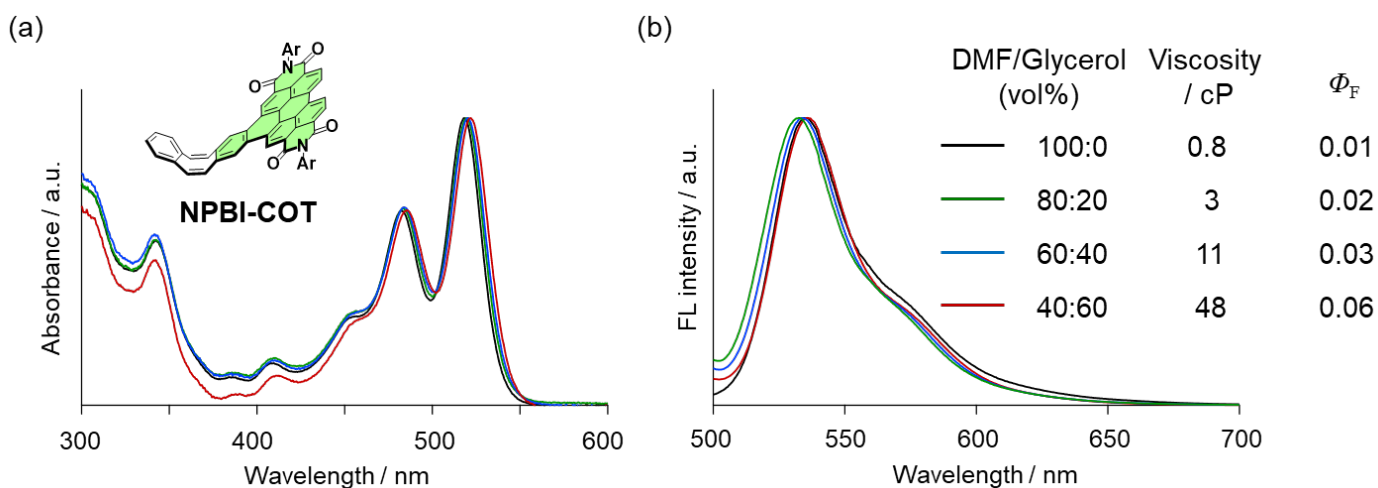


Figure S4.17. (a) Absorption spectra of **NPBI-COT** in DMF/glycerol mixed solvents with different ratio and (b) fluorescence spectra of **NPBI-COT** ($\lambda_{\text{ex}} = 480$ nm). Note: Fluorescence spectra were not treated with the correction function due to the faint fluorescence.

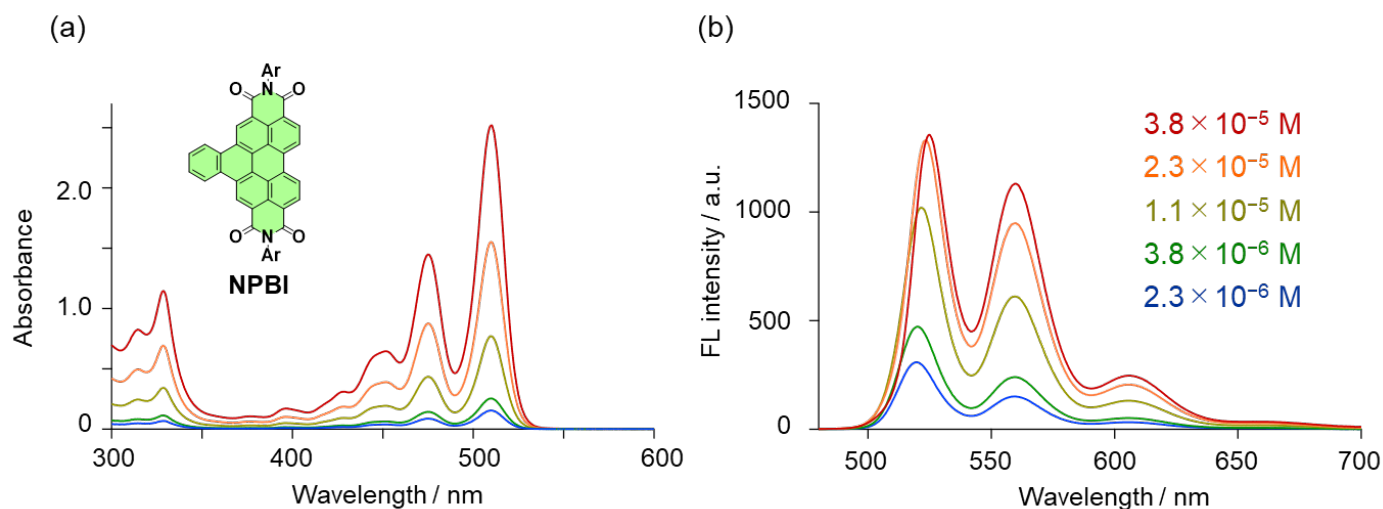


Figure S4.18. Photophysical properties of **NPBI** in toluene. (a) Concentration dependence of the absorption spectra and (b) concentration dependence of the fluorescence spectra (excited at 470 nm).

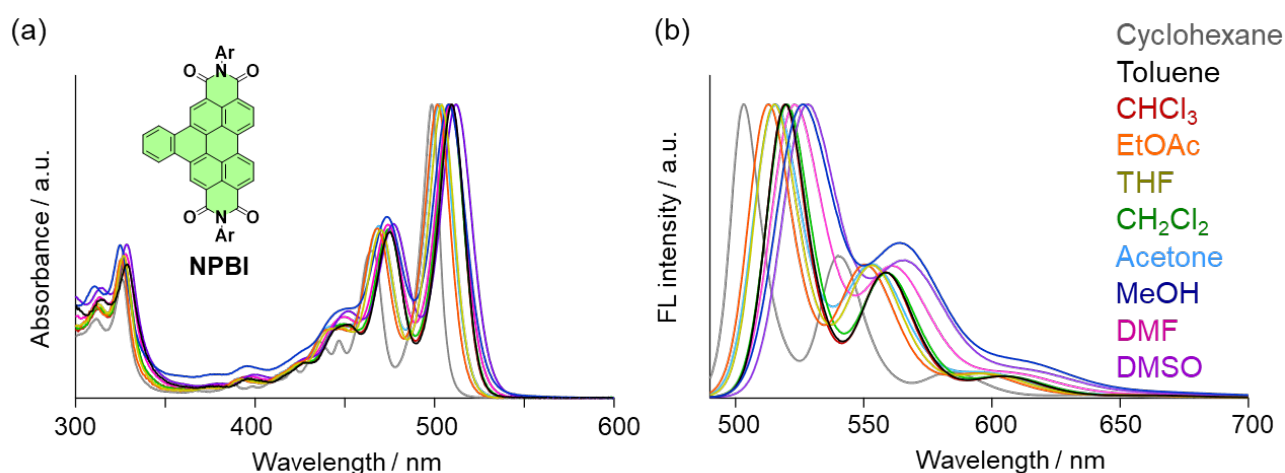


Figure S4.19. (a) UV-visible absorption spectra of **NPBI** in various solvents. (b) Fluorescence spectra of **NPBI** in various solvents. (Excitation wavelength: 470 nm)

Table S4.3. Optical properties of **NPBI** measured in various solvents

Solvents	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{FL}} / \text{nm}$	Stokes shift / cm^{-1}	Φ_{F}	τ_{F}	χ^2
Cyclohexane	498	503	200	0.91	3.8 ns	1.38
Toluene	510	520	380	0.96	4.2 ns	1.58
CHCl_3	510	520	380	0.95	4.1 ns	1.39
EtOAc	502	513	430	0.93	4.4 ns	1.32
THF	504	515	420	0.95	4.3 ns	1.30
CH_2Cl_2	508	520	450	0.96	4.2 ns	1.24
Acetone	503	516	500	0.94	4.5 ns	1.14
MeOH	508	526	670	0.93	4.8 ns	1.29
DMF	508	523	560	0.93	4.4 ns	1.29
DMSO	512	528	590	0.08	0.46 ns	1.77

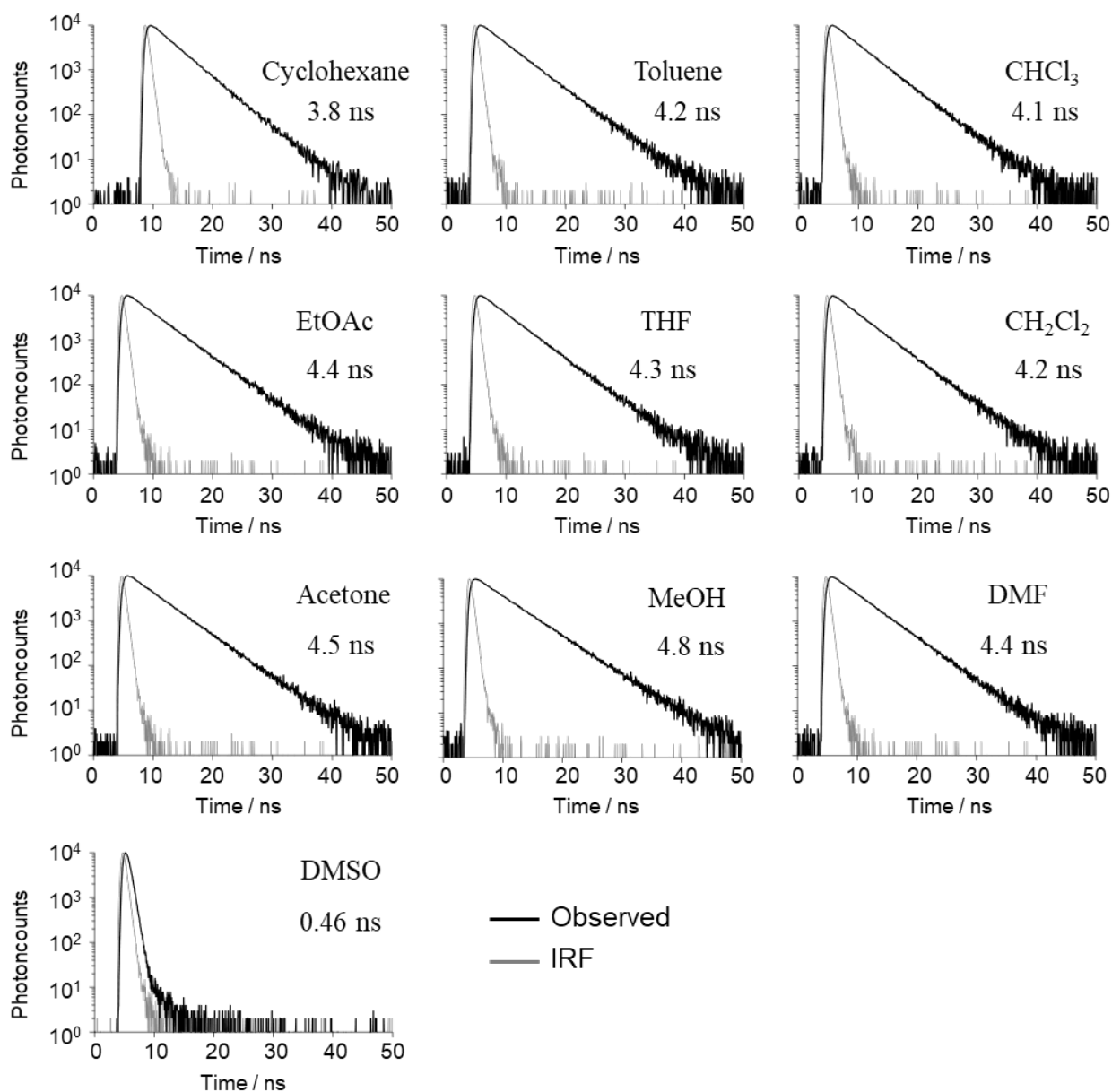


Figure S4.20. Fluorescence decay profiles of NPBI in various solvents. IRF: Instrument response function.

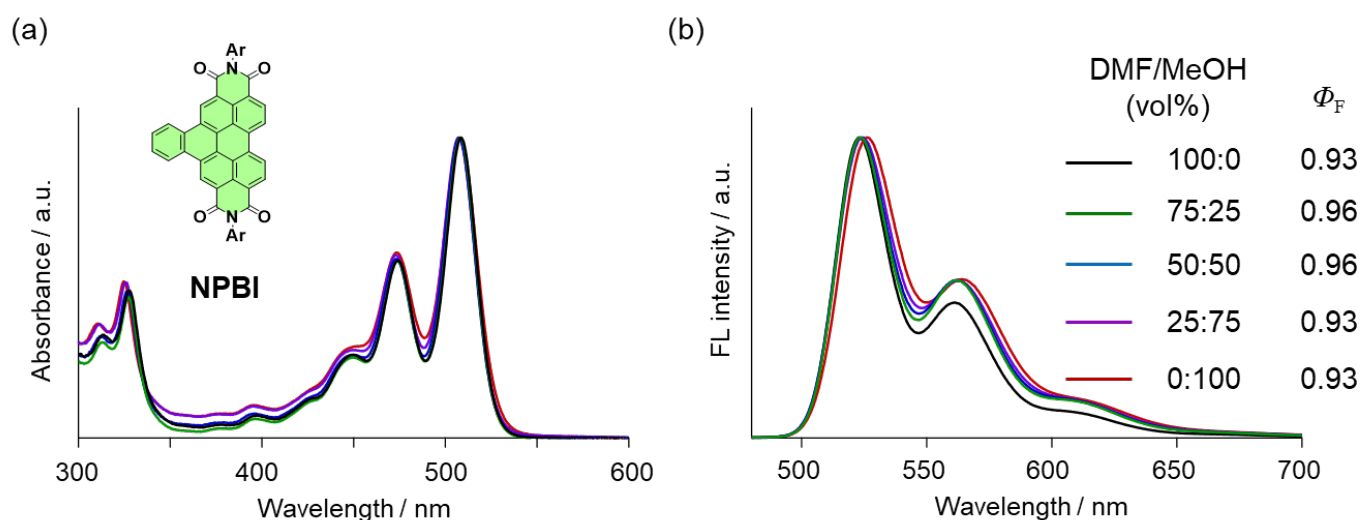


Figure S4.21. (a) Absorption spectra of NPBI-FLAP in DMF/MeOH mixed solvents with different ratio and (b) fluorescence spectra of NPBI-FLAP ($\lambda_{ex} = 470$ nm).

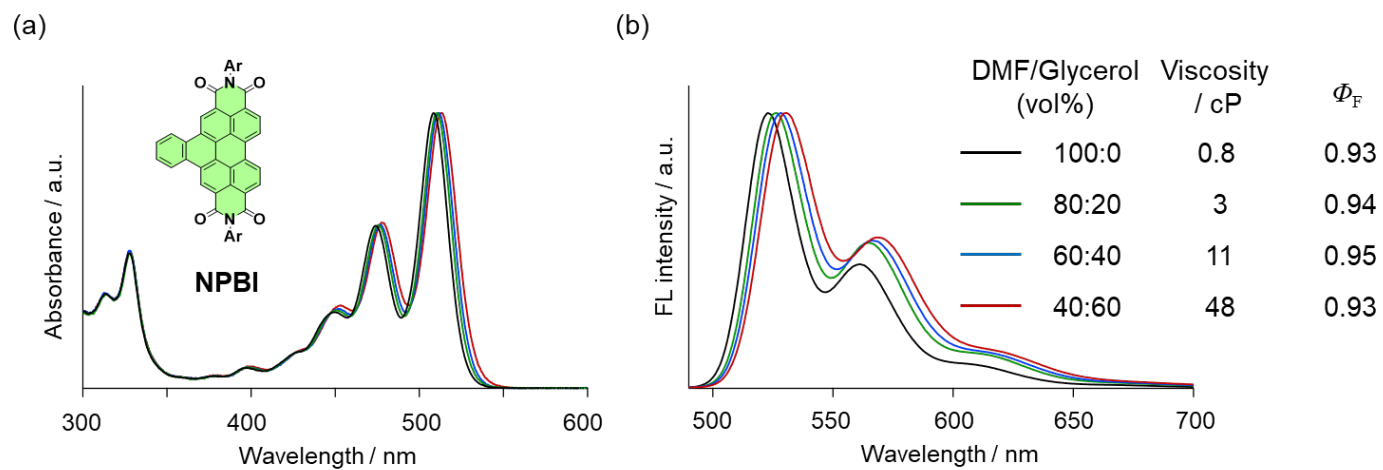
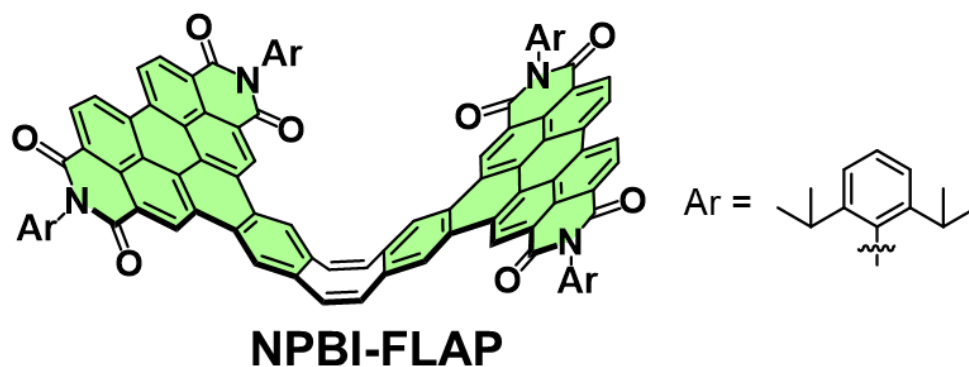
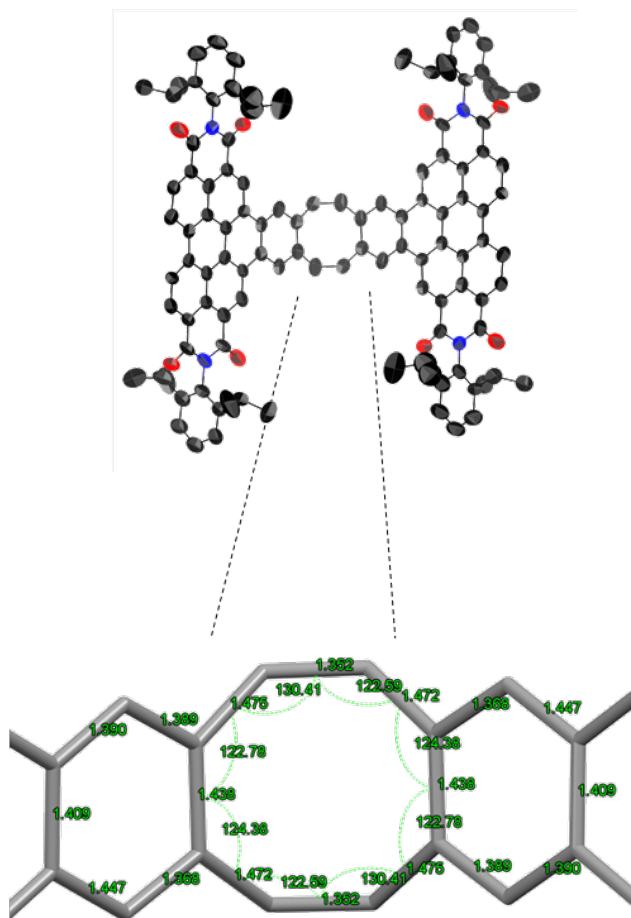


Figure S4.22. (a) Absorption spectra of **NPBI** in different DMF/glycerol ratio and (b) fluorescence spectra of **NPBI** ($\lambda_{\text{ex}} = 470$ nm).

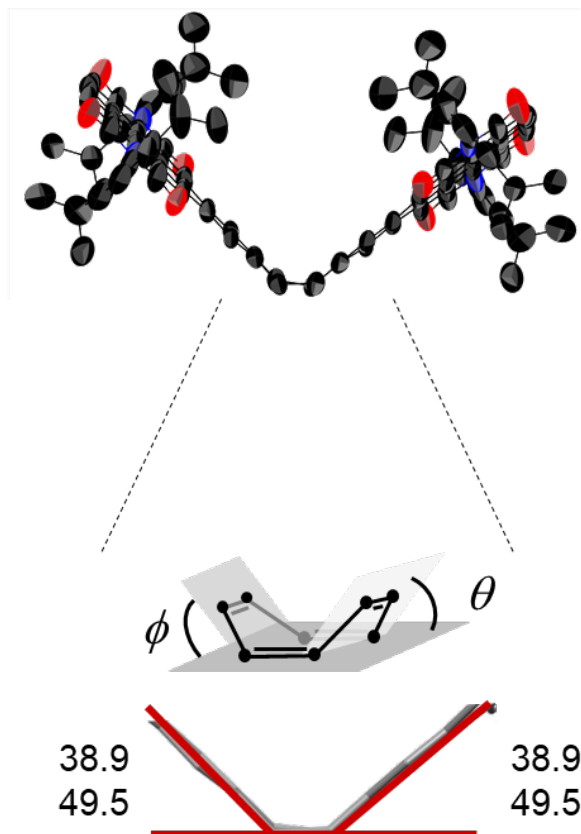
5. X-ray crystallographic analysis



(a)



(b)



(c)

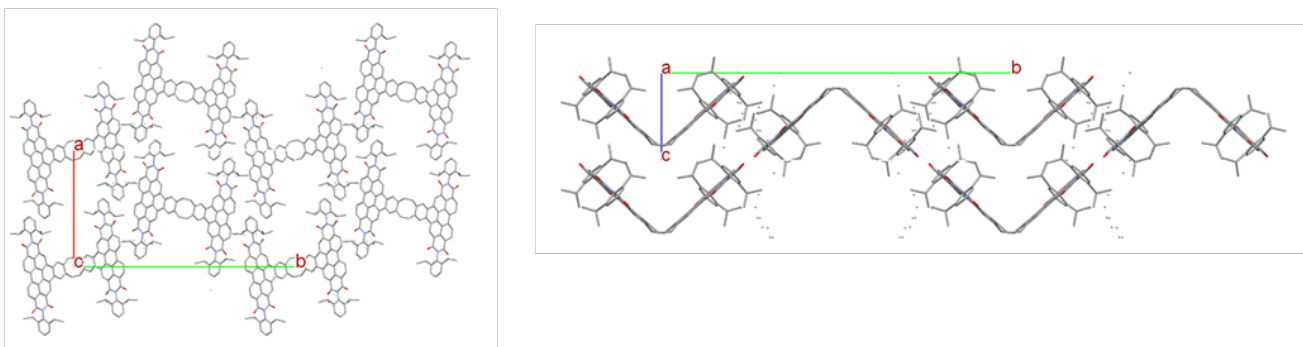


Figure S5.1. Crystal structure of **NPBI-FLAP** viewed from (a) top and (b) side, and (c) the packing structure. The COT bending angles (see Figure S6.2. for the definition) are shown in (b). Hydrogen atoms and disordered groups with low occupancy are omitted for clarity. Thermal ellipsoids are scaled to 30% probability.

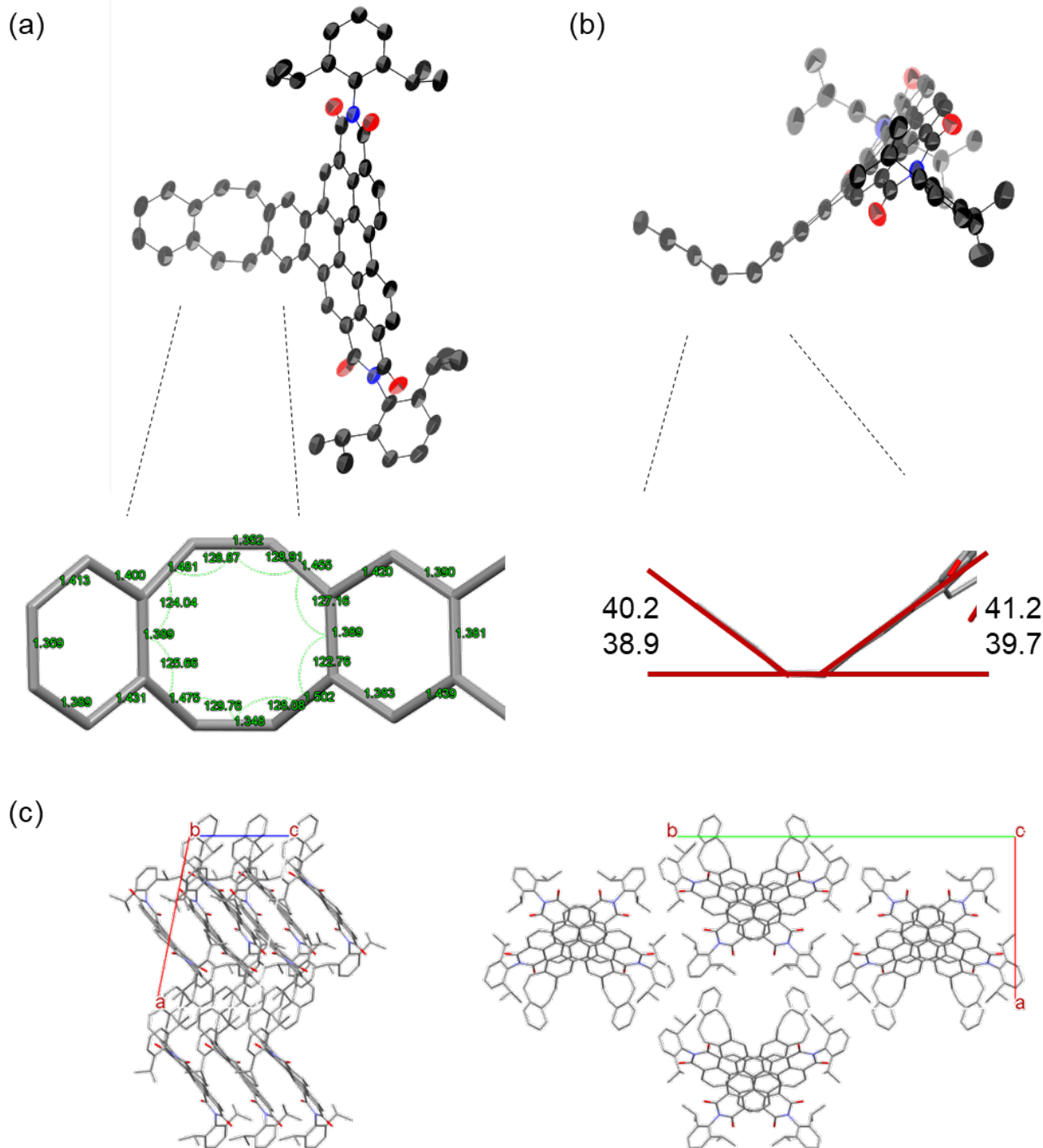
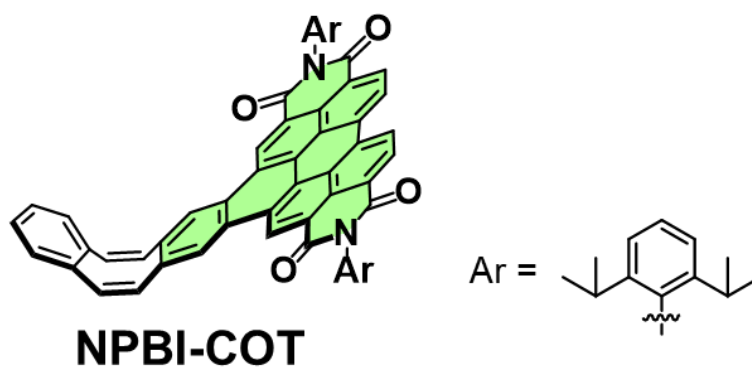


Figure S5.2. Crystal structure of NPBI-COT viewed from (a) top and (b) side, and (c) packing structure. The COT bending angles (see Figure S6.2. for the definition) are shown in (b). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are scaled to 50% probability.

Table S5.1. Crystal data of NPBI-FLAP and NPBI-COT

	NPBI-FLAP ^[a]	NPBI-COT ^[a]
Formula	C ₁₁₂ H ₈₈ N ₄ O ₈	C ₆₄ H ₅₀ N ₂ O ₄
FW	1617.86	911.06
Crystal system	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	19.0361(4)	16.4230(7)
<i>b</i> / Å	36.1483(9)	32.7487(16)
<i>c</i> / Å	9.0588(3)	9.4104(5)
<i>α</i> / °	90	90
<i>β</i> / °	90	101.107(5)
<i>γ</i> / °	90	90
<i>V</i> / Å ³	6233.6(3)	4966.4(4)
<i>Z</i>	2	4
<i>T</i> / K	93	93
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0870	0.1211
w <i>R</i> ₂ (all data)	0.3054	0.3410
Completeness	0.99	0.99
Goodness-of-fit	1.098	1.094
Solvents system	Toluene	CHCl ₃ / ^t PrOH
CCDC No. ^[b]	2268963	2268964

[a] Electron densities of severely disordered solvent molecules were removed by the *SQUEEZE* program in the PLATON software package.^[S7] [b] The crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

6. Theoretical calculations

DFT calculations of the isolated molecules were performed using the Gaussian 16 program^[S8]. Model structures **NPBI-FLAP'**, **NPBI-COT'** and **NPBI'** were calculated, which have hydrogen atoms in place of the 2,6-diisopropylphenyl groups of the corresponding molecules (Figure S6.1). The COT bending angle was defined as the dihedral angle between the C1–C2–C3 and C2–C3–C4 planes in Figure S6.2. Constrained geometry optimization was performed with the fixed COT bending angles using the ModRedundant keyword.

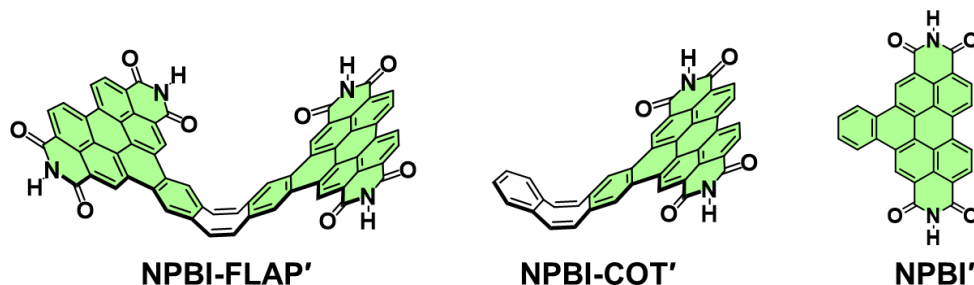


Figure S6.1. The model compounds **NPBI-FLAP'**, **NPBI-COT'** and **NPBI'** for the DFT calculations.

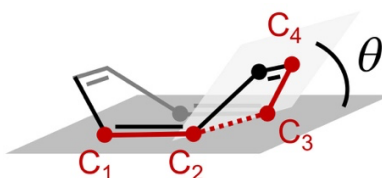


Figure S6.2. Definition of the COT bending angle.

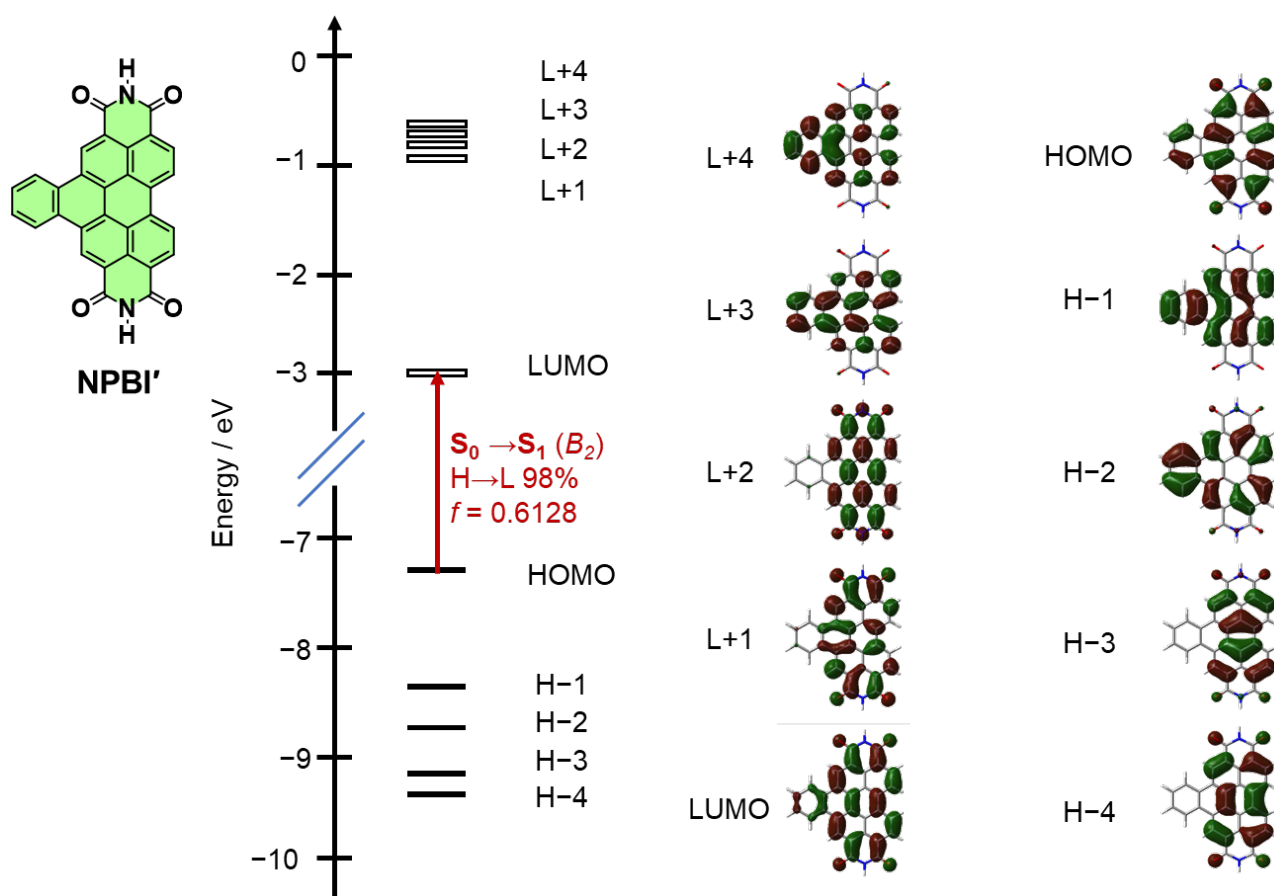


Figure S6.3. Kohn-Sham molecular orbitals and their energy levels of **NPBI'** in S_1 . Constrained geometry optimization in S_1 was conducted with C_{2v} symmetry at the TD CAM-B3LYP/6-31+G(d) level.

6.1. Molecular orbitals of optimized geometries in S_1 and S_0

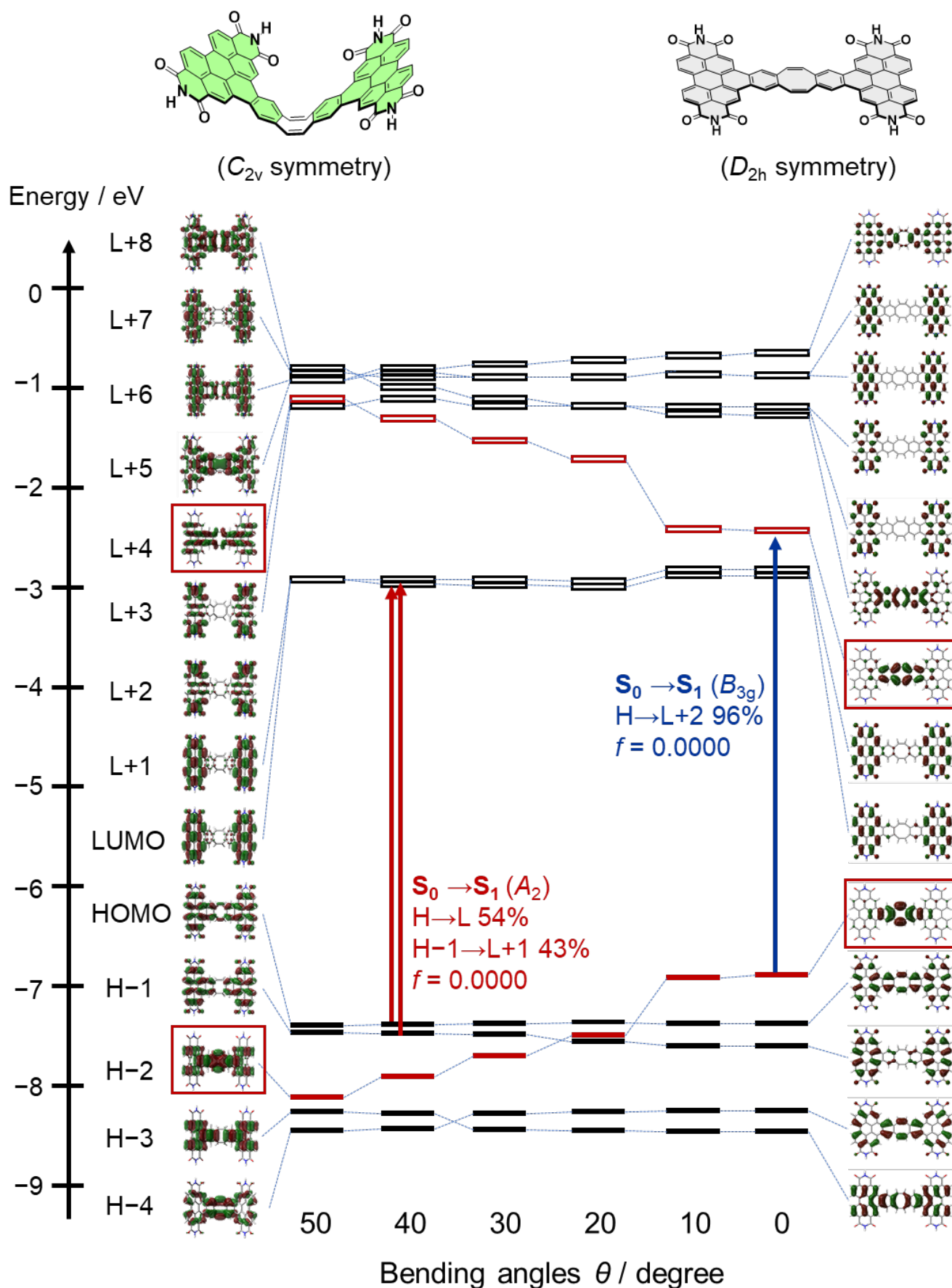


Figure S6.4. Kohn-Sham molecular orbitals and their energy levels of NPBI-FLAP' with different bending angles. Constrained geometry optimization in S_1 was conducted with C_{2v} symmetry at the TD CAM-B3LYP/6-31+G(d) level.

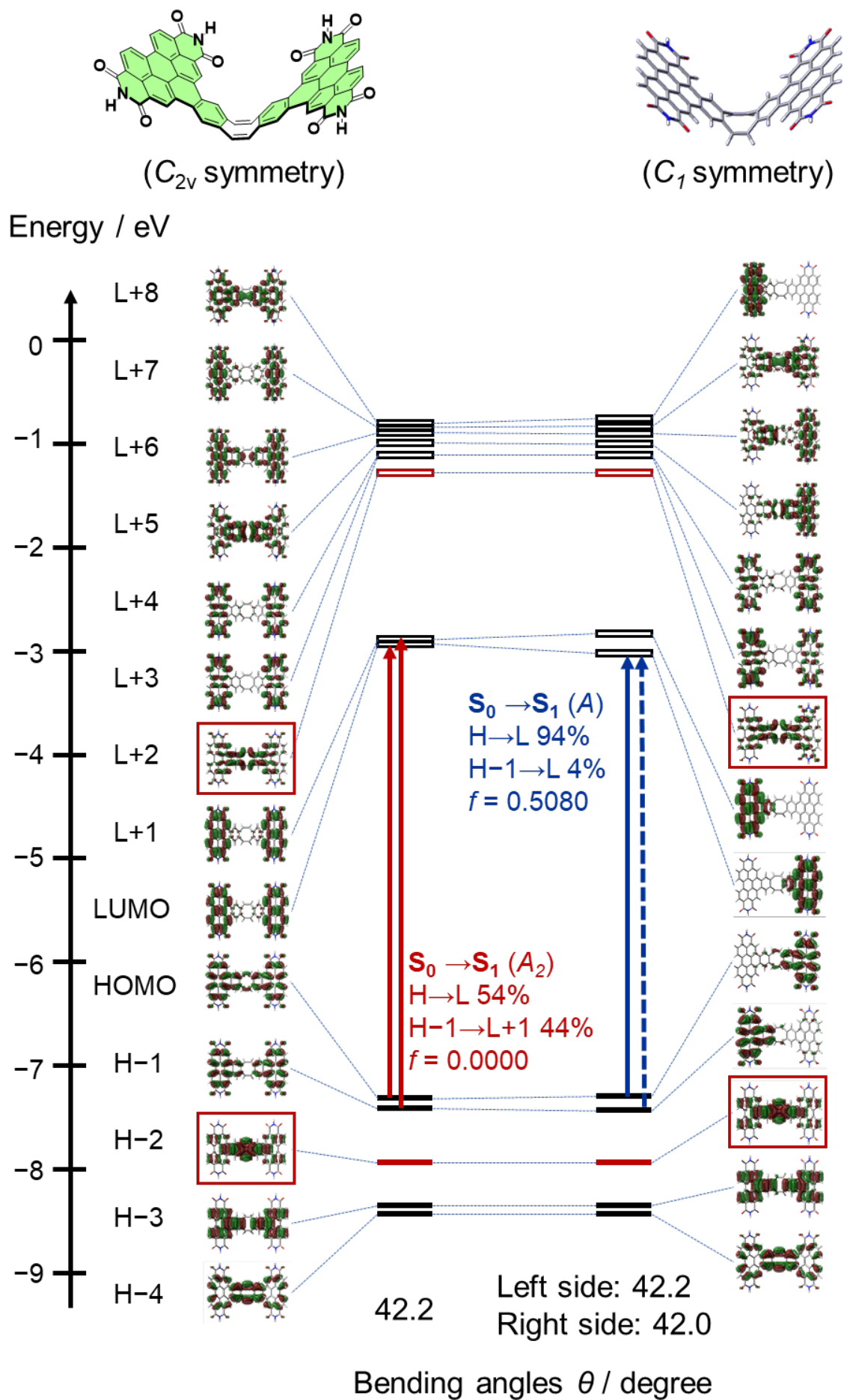


Figure S6.5. Kohn-Sham molecular orbitals and their energy levels of **NPBI-FLAP'** with C_{2v} symmetry (left) and with C_1 symmetry (right, global minimum). Structural optimization in S_1 was conducted at the TD CAM-B3LYP/6-31+G(d) level.

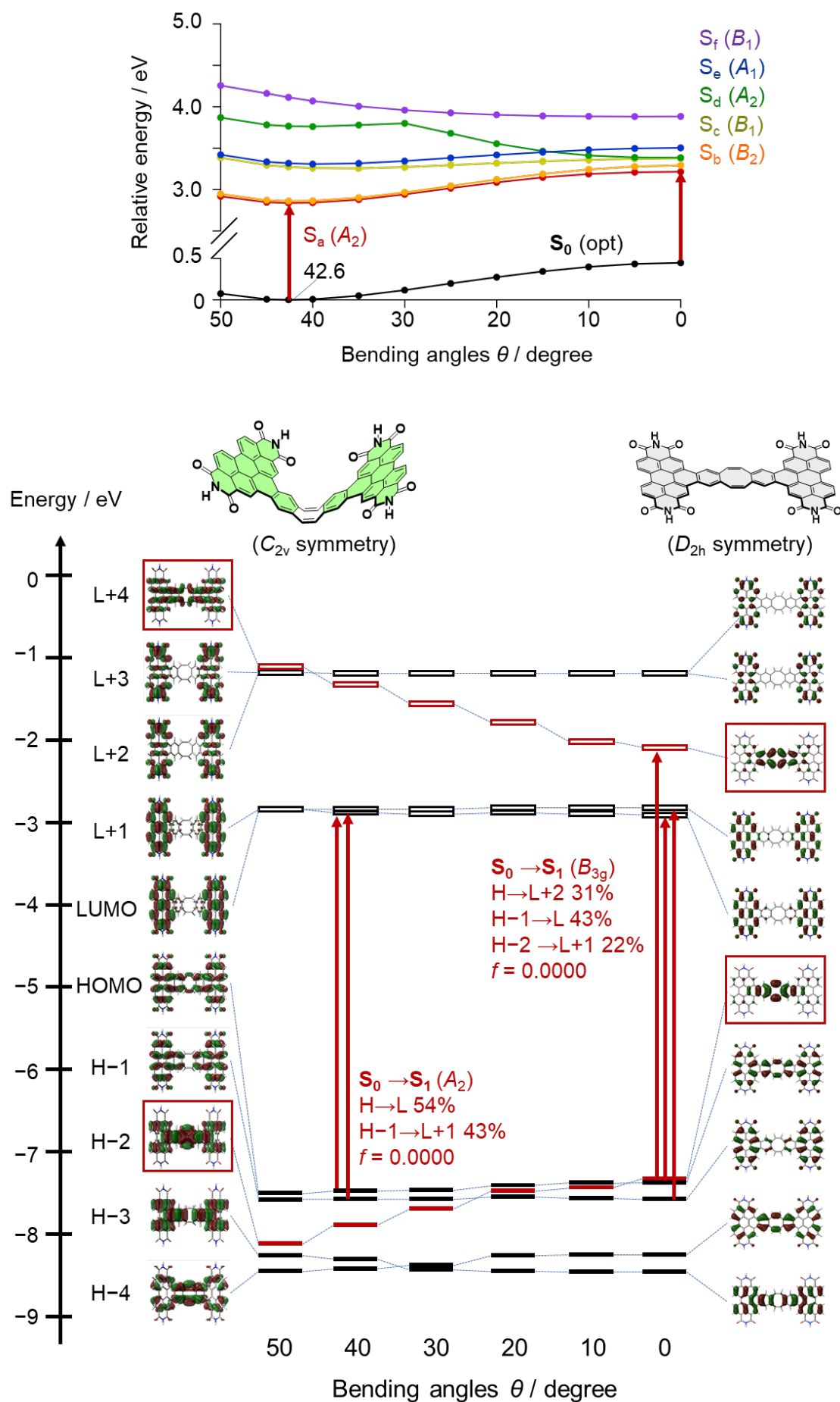


Figure S6.6. Kohn-Sham molecular orbitals and their energy levels of NPBI-FLAP' with different bending angles. DFT optimized geometries with C_{2v} symmetry at the CAM-B3LYP/6-31+G(d) level in S_0 were used for the TD-DFT calculations at the same level.

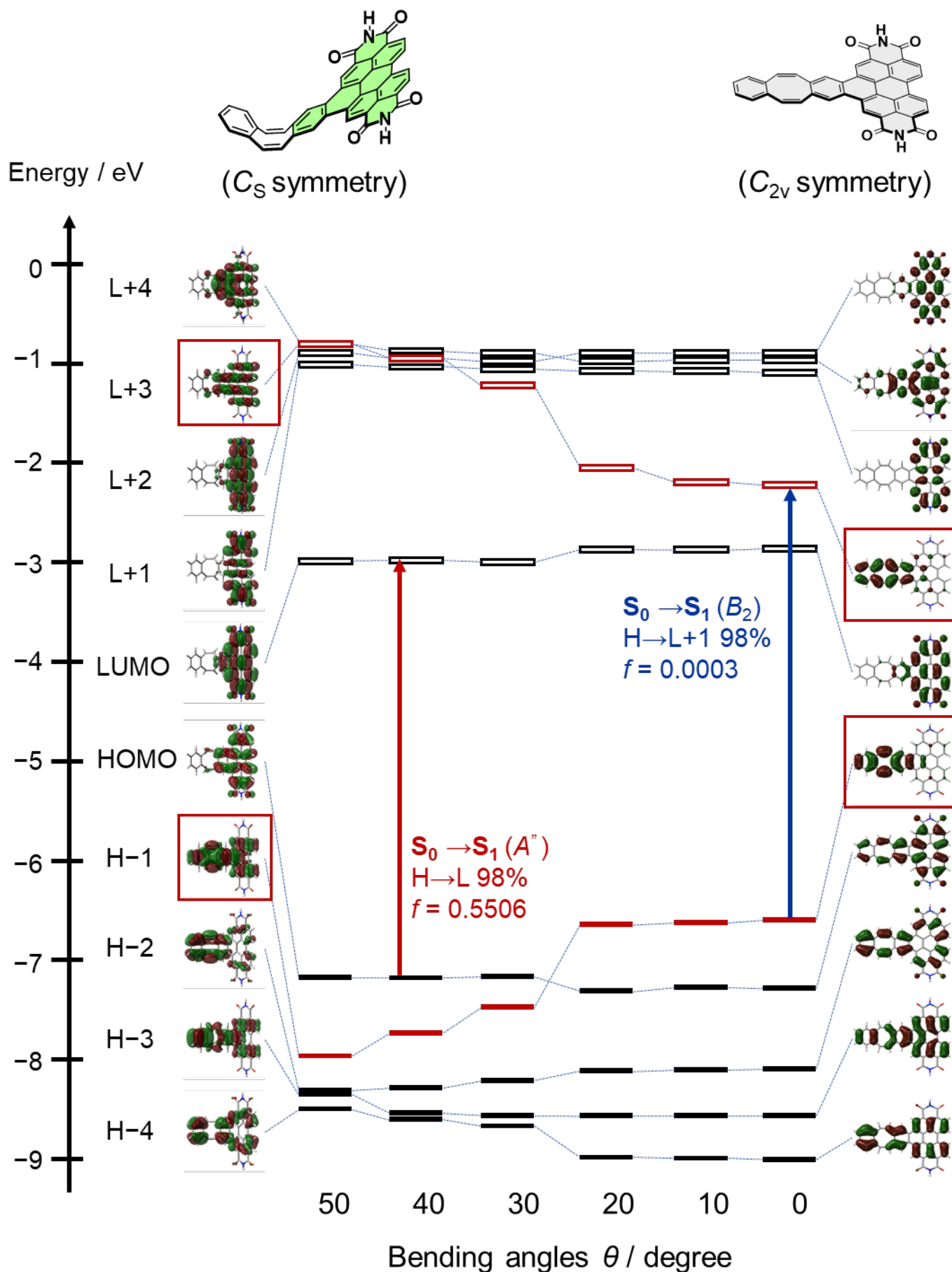


Figure S6.7. Kohn-Sham molecular orbitals and their energy levels of NPBI-COT' with different bending angles. Constrained geometry optimization in S_1 was conducted with C_{2v} symmetry at the TD CAM-B3LYP/6-31+G(d) level.

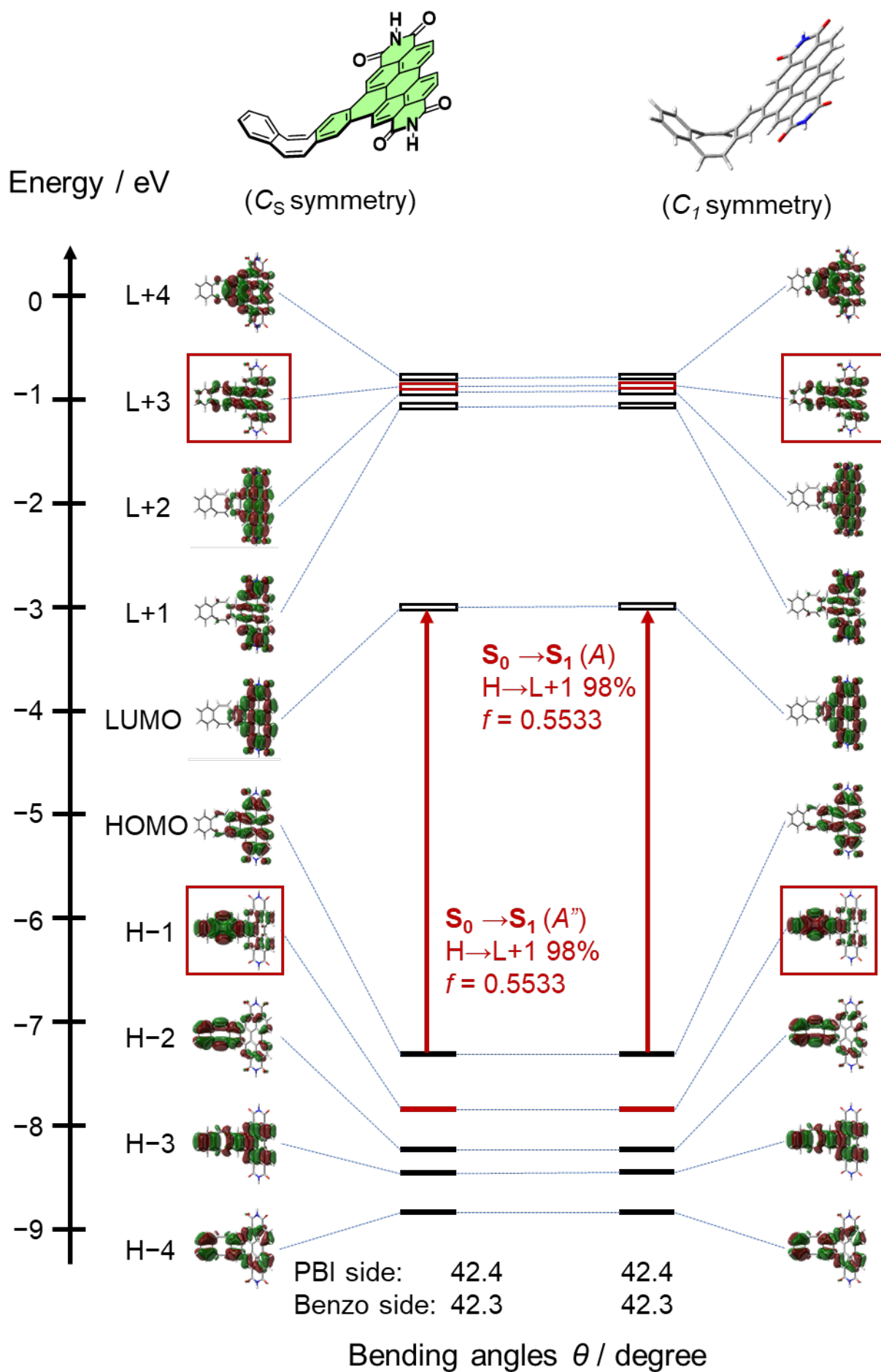


Figure S6.8. Kohn-Sham molecular orbitals and their energy levels of **NPBI-COT'** with C_s symmetry (left) and with C_1 symmetry (right, global minimum). Structural optimization in S_1 was conducted at the TD CAM-B3LYP/6-31+G(d) level.

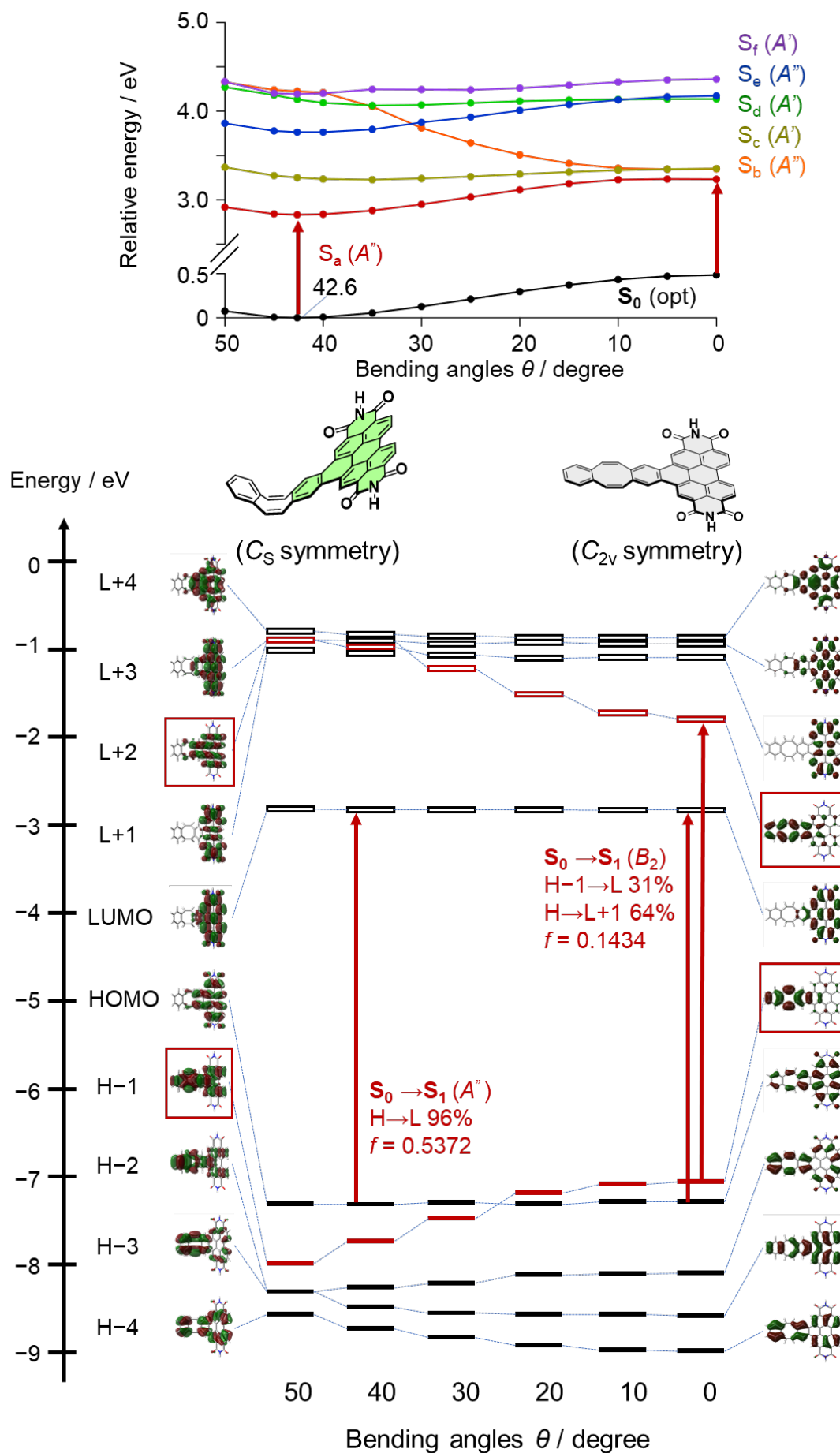
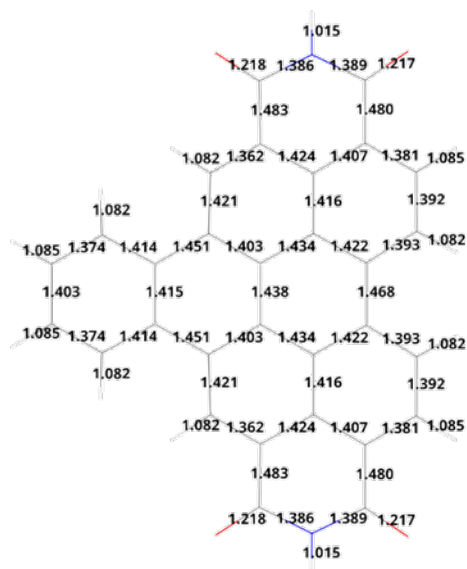


Figure S6.9. Kohn-Sham molecular orbitals and their energy levels of **NPBI-COT'** with different bending angles. DFT optimized geometries with C_{2v} symmetry at the CAM-B3LYP/6-31+G(d) level in S_0 were used for the TD-DFT calculations at the same level.

6.2. Calculated geometries and structural parameters in S_0 and S_1

S_0 (C_{2v} symmetry)



S_1 (C_{2v} symmetry)

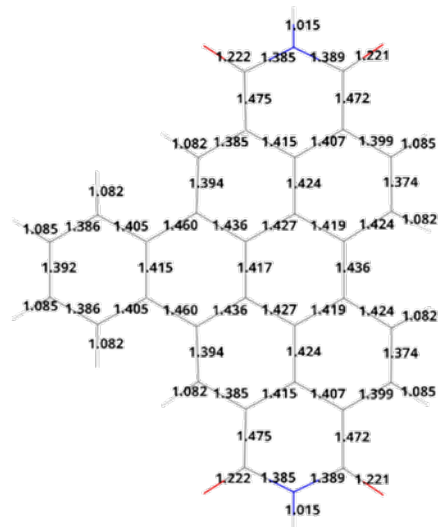


Figure S6.10. Bond lengths (Å) of NPBI' based on the S_0 (left) and S_1 (right) optimized geometries calculated at the (TD) CAM-B3LYP/6-31+G(d) level.

S_1 (V-shaped: C_1 symmetry)

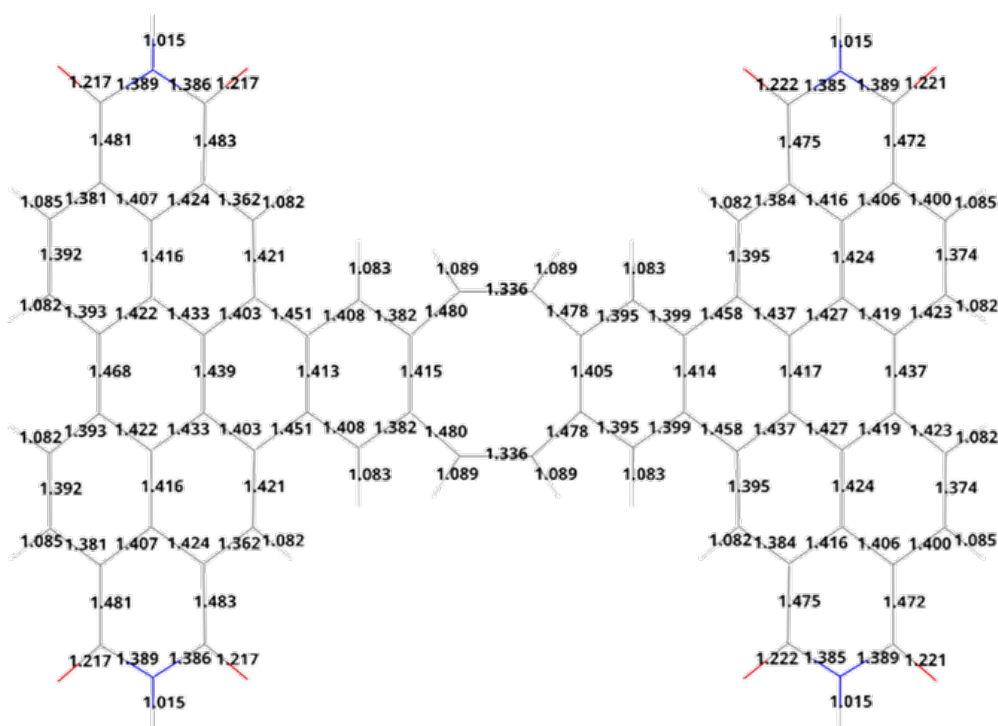


Figure S6.11. Bond lengths (Å) of NPBI-FLAP' based on the S_1 optimized geometry ($\theta = 42.2^\circ$ and 42.0°) calculated at the TD CAM-B3LYP/6-31+G(d) level.

S_1 (Planar: D_{2h} symmetry)

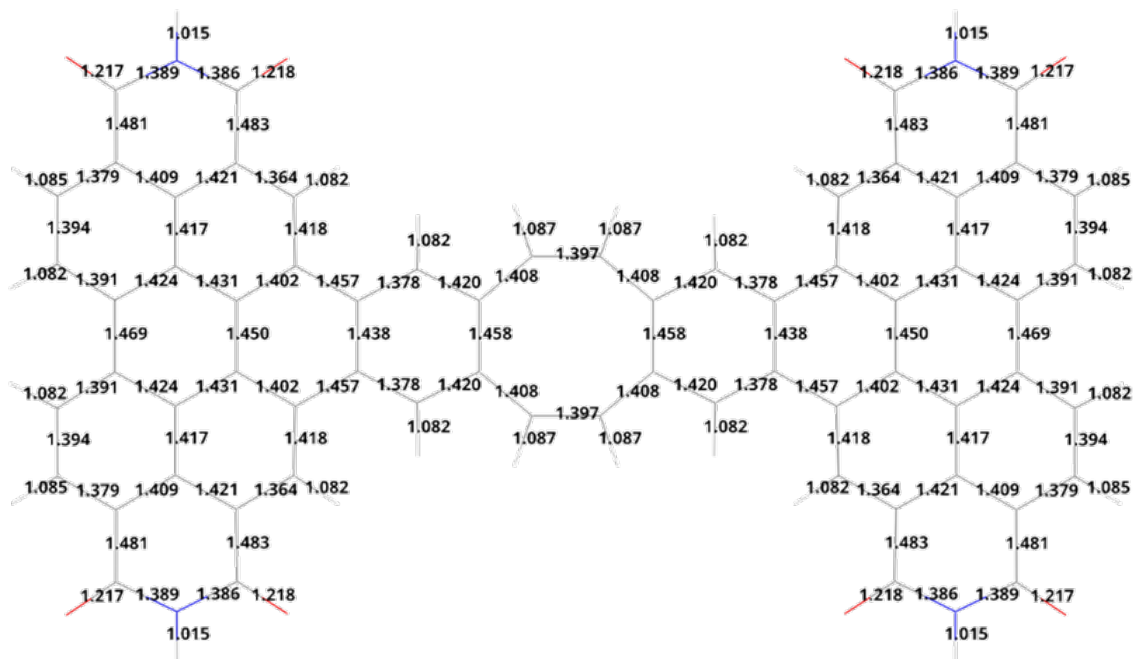


Figure S6.12. Bond lengths (Å) of NPBI-FLAP' based on the S_1 optimized geometry ($\theta = 0^\circ$) calculated at the TD CAM-B3LYP/6-31+G(d) level.

S_0 (V-shaped: C_{2v} symmetry)

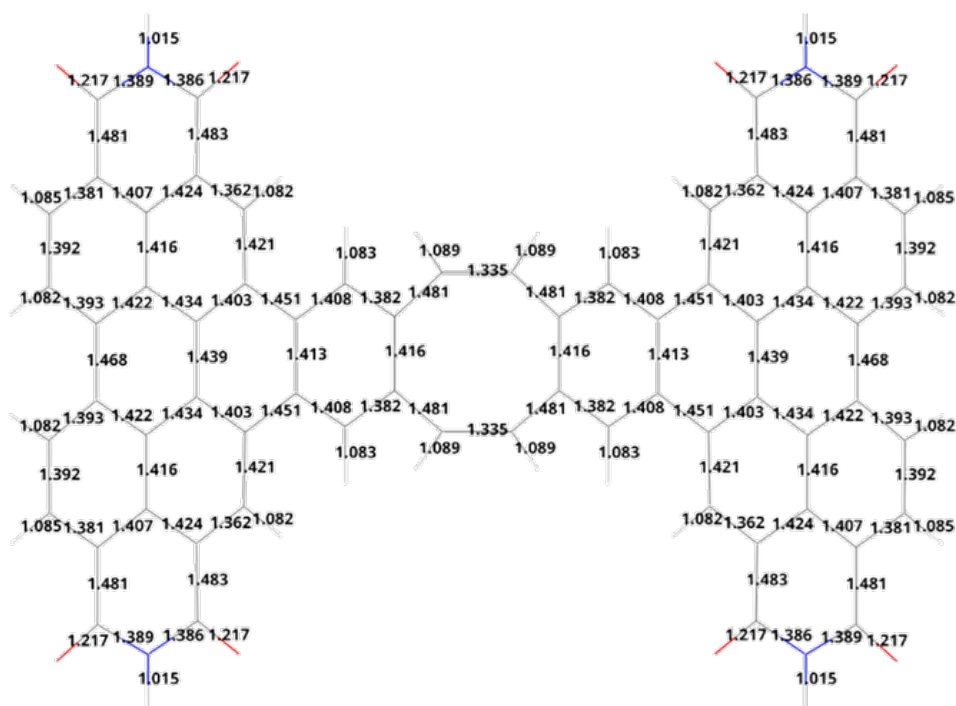


Figure S6.13. Bond lengths (Å) of NPBI-FLAP' based on the S_0 optimized geometry ($\theta = 42.6^\circ$) calculated at the CAM-B3LYP/6-31+G(d) level.

S_1 (V-shaped: C_1 symmetry)

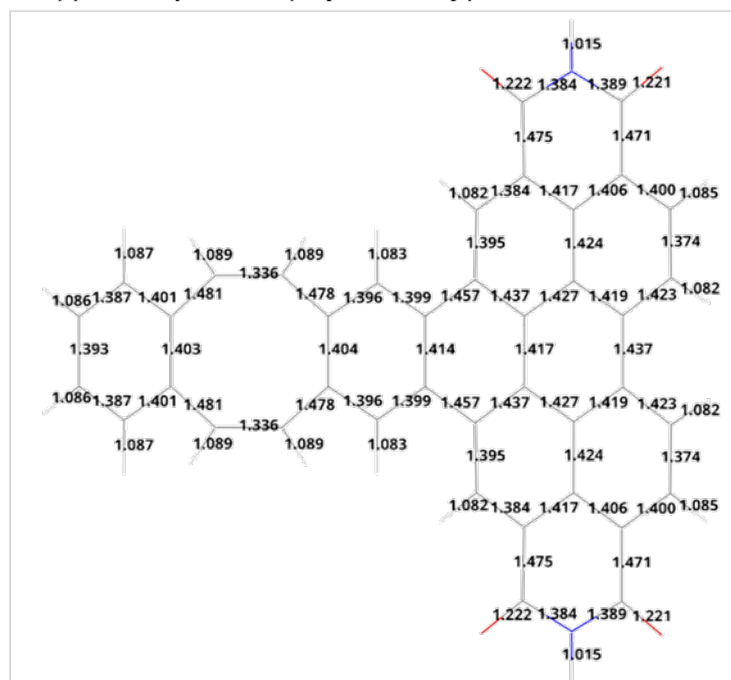


Figure S6.14. Bond lengths (Å) of NPBI-COT' based on the S_1 optimized geometry (NPBI side: $\theta = 42.4^\circ$ Benzo-fusion side: $\theta = 42.3^\circ$) calculated at the TD CAM-B3LYP/6-31+G(d) level.

S_1 (Planar: C_{2v} symmetry)

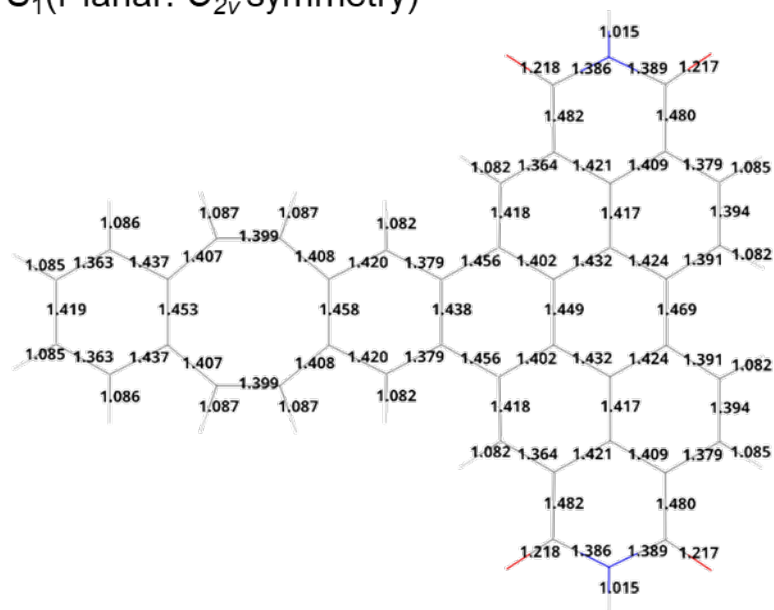


Figure S6.15. Bond lengths (Å) of NPBI-COT' based on the S_1 optimized geometry ($\theta = 0^\circ$) calculated at the TD CAM-B3LYP/6-31+G(d) level.

S_0 (V-shaped: C_s symmetry)

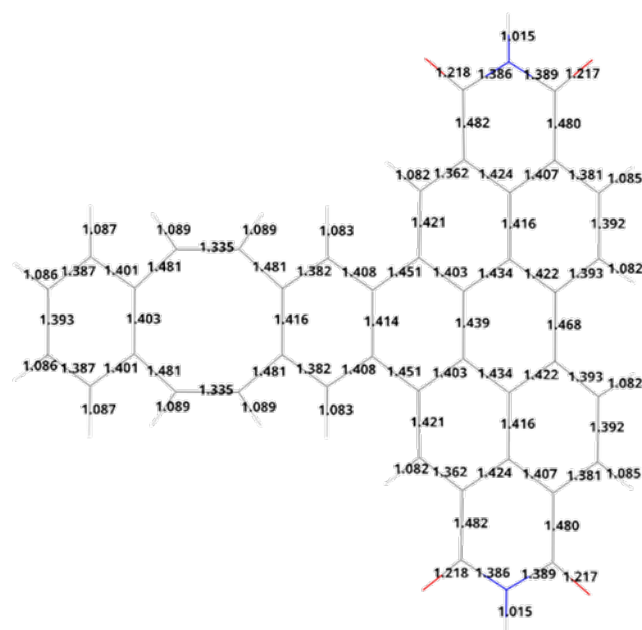


Figure S6.16. Bond lengths (Å) of **NPBI-COT'** based on the S_1 optimized geometry (Benzo-fusion side: $\theta = 42.5^\circ$, and NPBI side: 42.9°) calculated at the TD CAM-B3LYP/6-31+G(d) level.

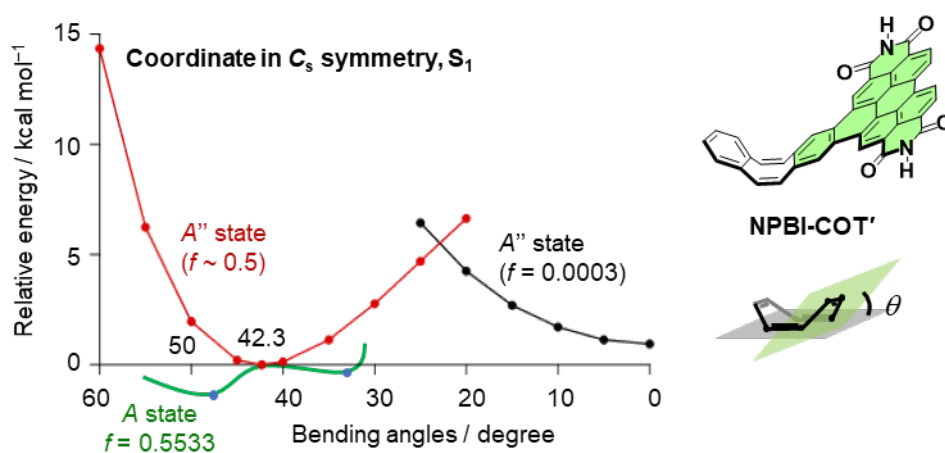


Figure S6.17. S_1 energy landscape of **NPBI-COT'**. Geometry optimization was performed at the TD CAM-B3LYP/6-31+G(d) level. COT bending angle θ was defined by the dihedral angle of the two mean planes shown in the inset figure.

7. Electrochemical analysis

Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were obtained under the following conditions; solvent: CH₂Cl₂ (Figure S7.1.) or DMF (Figure S7.2.), electrolyte: 100 mM ⁿBu₄NPF₆, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgClO₄, scan rate: 0.05 V/s.

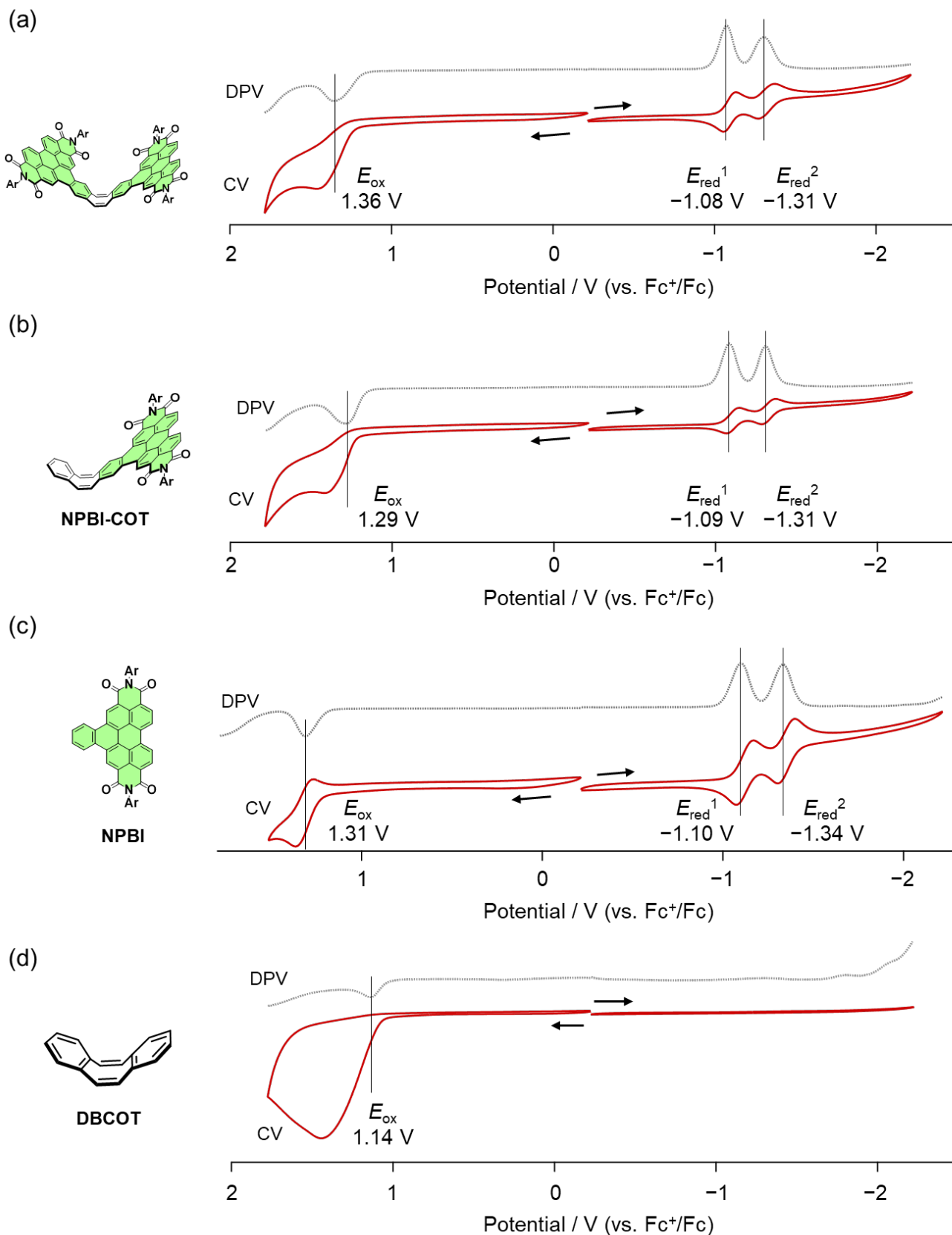


Figure S7.1. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of (a) **NPBI-FLAP**, (b) **NPBI-COT**, (c) **NPBI** and (d) **DBCOT** in CH₂Cl₂.

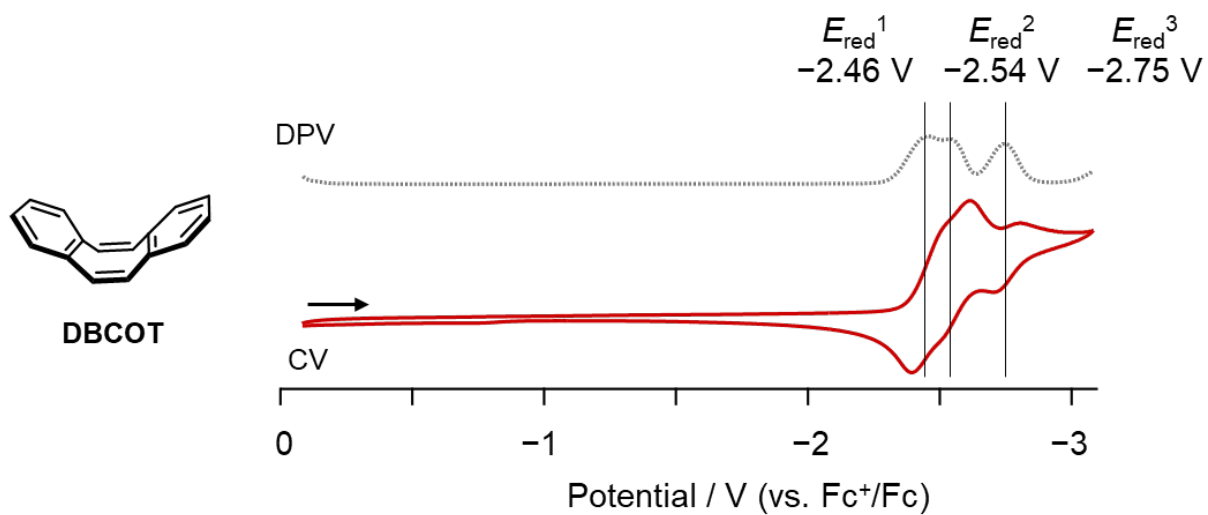
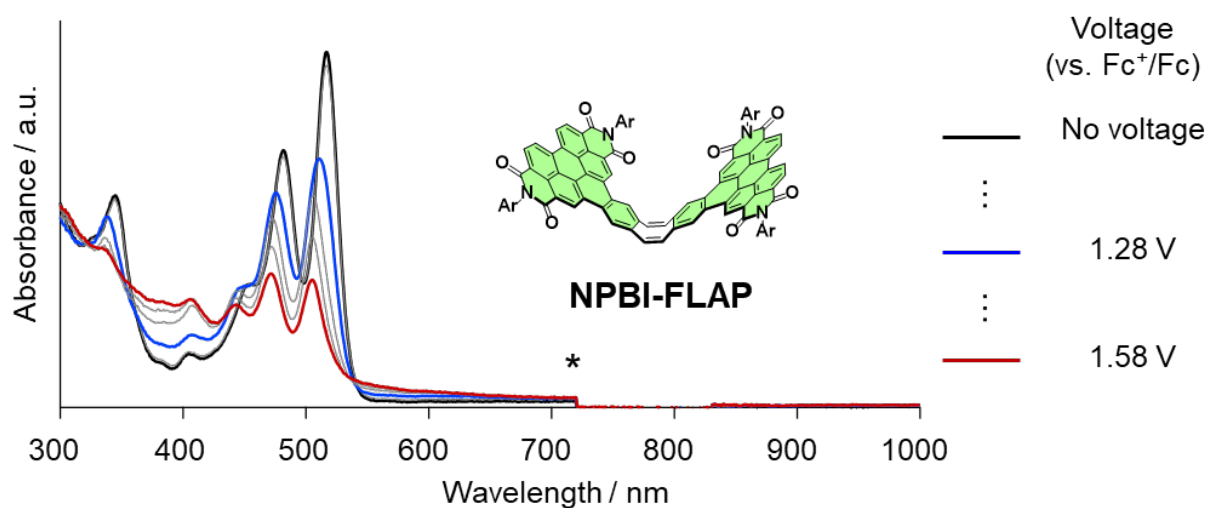


Figure S7.2. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of DBCOT in DMF.

(a) Electrical oxidation



(b) Electrical reduction

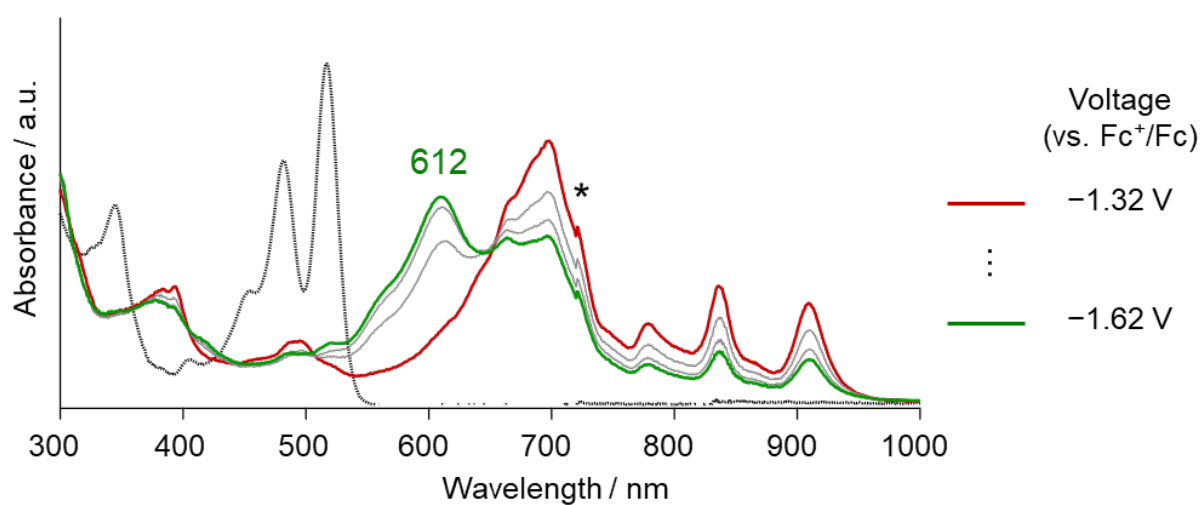
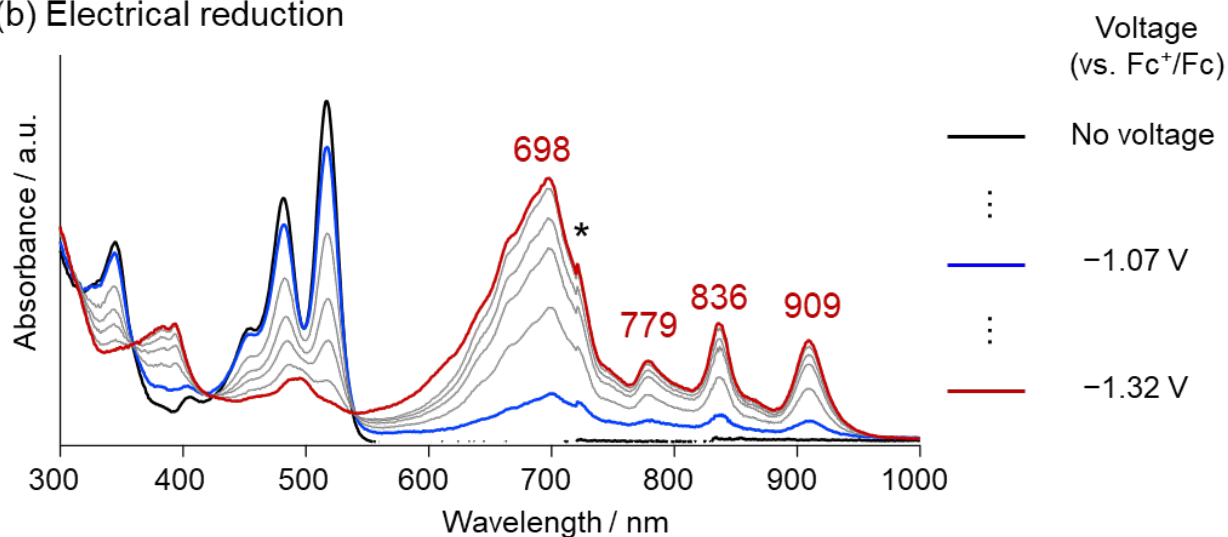
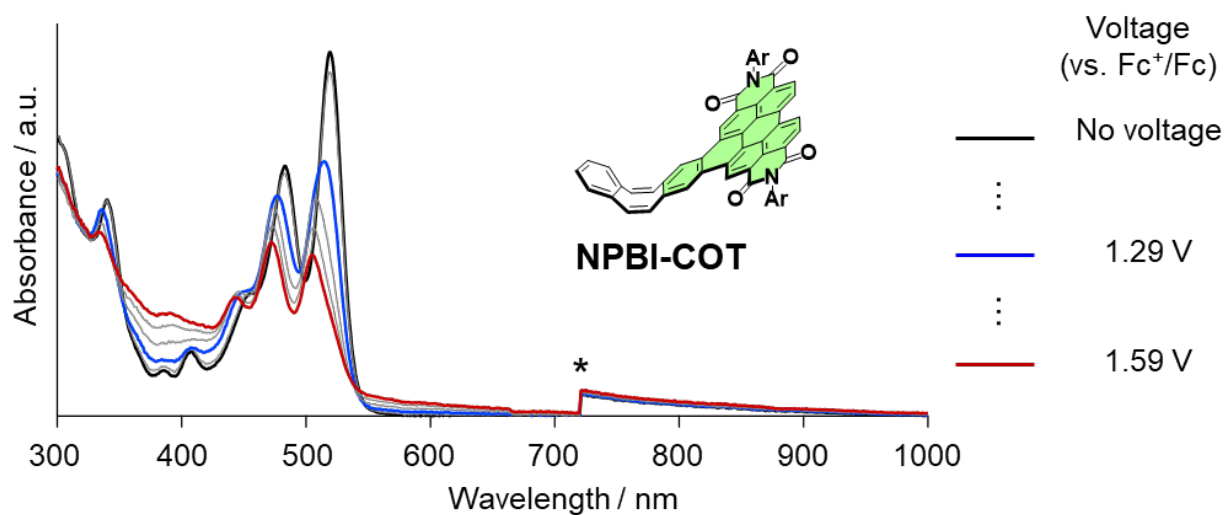


Figure S7.3. Absorption spectral change of NPBI-FLAP under (a) electrical oxidation and (b) electrical reduction. The asterisk indicates the grating changeover wavelength. Conditions; solvent: CH_2Cl_2 , scan rate: 0.001 V/s. The other condition was shown in General information. No clear signal for radical cation species was observed, which may be due to the instability of the radical cation.

(a) Electrical oxidation



(b) Electrical reduction

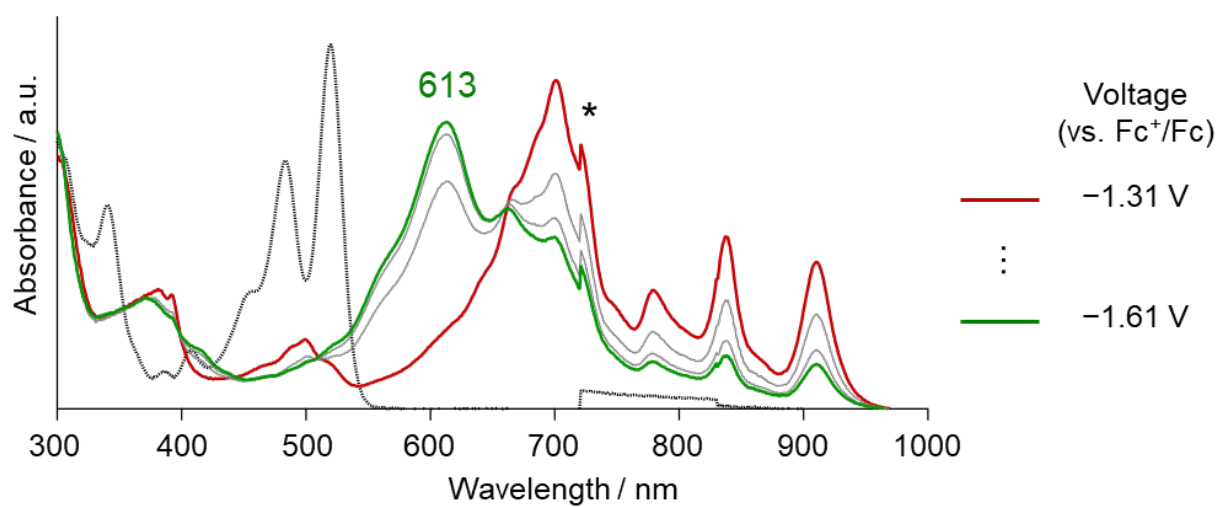
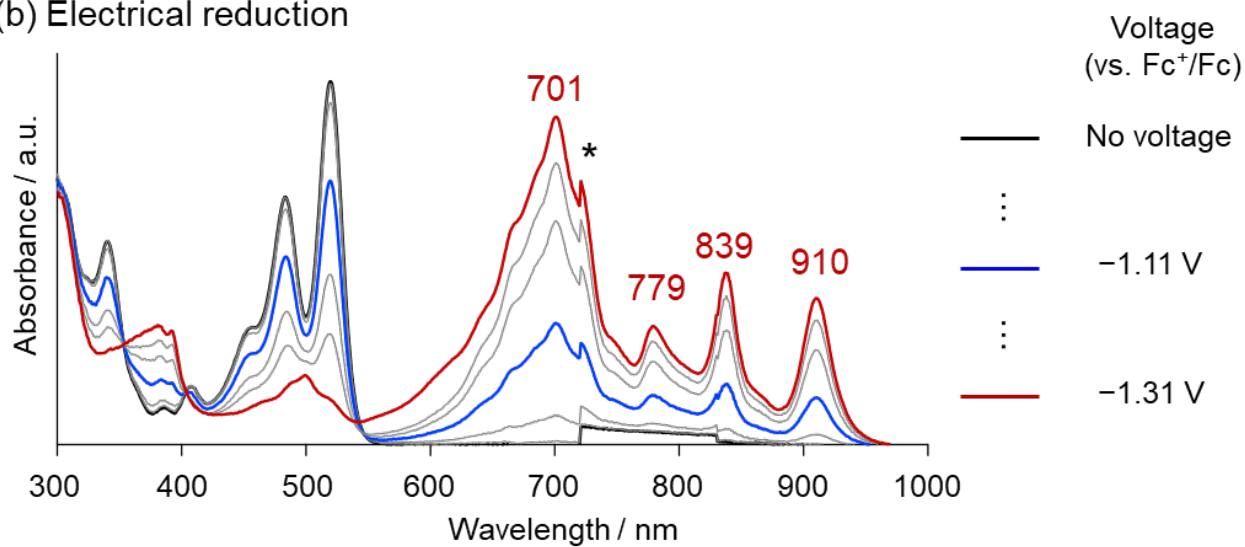
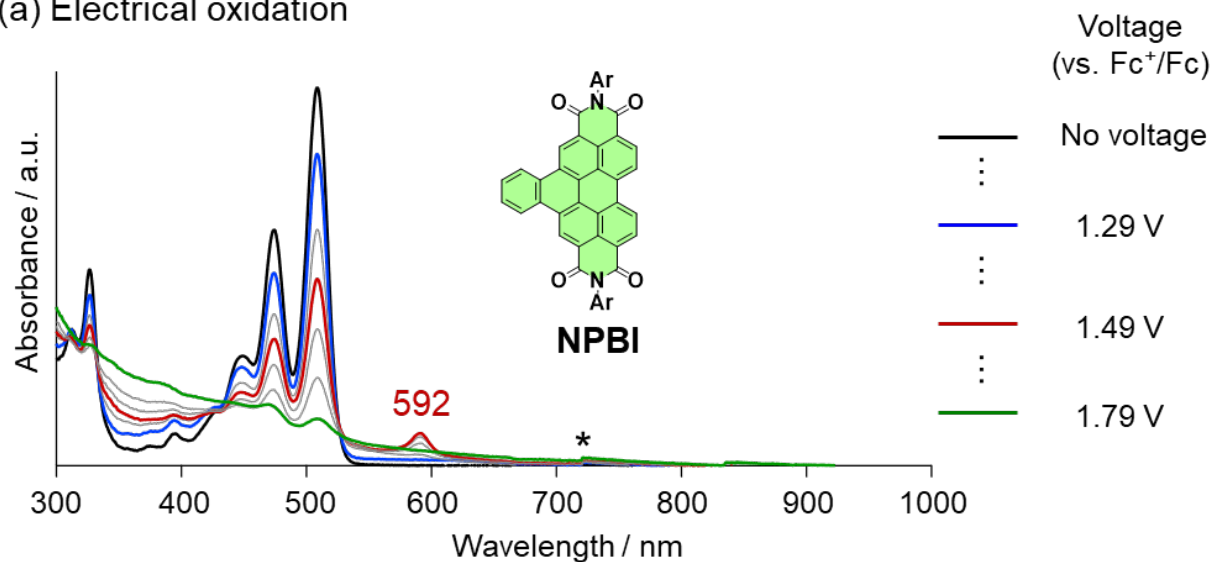


Figure S7.4. Absorption spectral change of NPBI-COT under (a) electrical oxidation and (b) electrical reduction. The asterisk indicates the grating changeover wavelength. Conditions; solvent: CH₂Cl₂, scan rate: 0.001 V/s. The other condition was shown in General information. No clear signal for radical cation was observed, which may be due to the instability of the radical cation.

(a) Electrical oxidation



(b) Electrical reduction

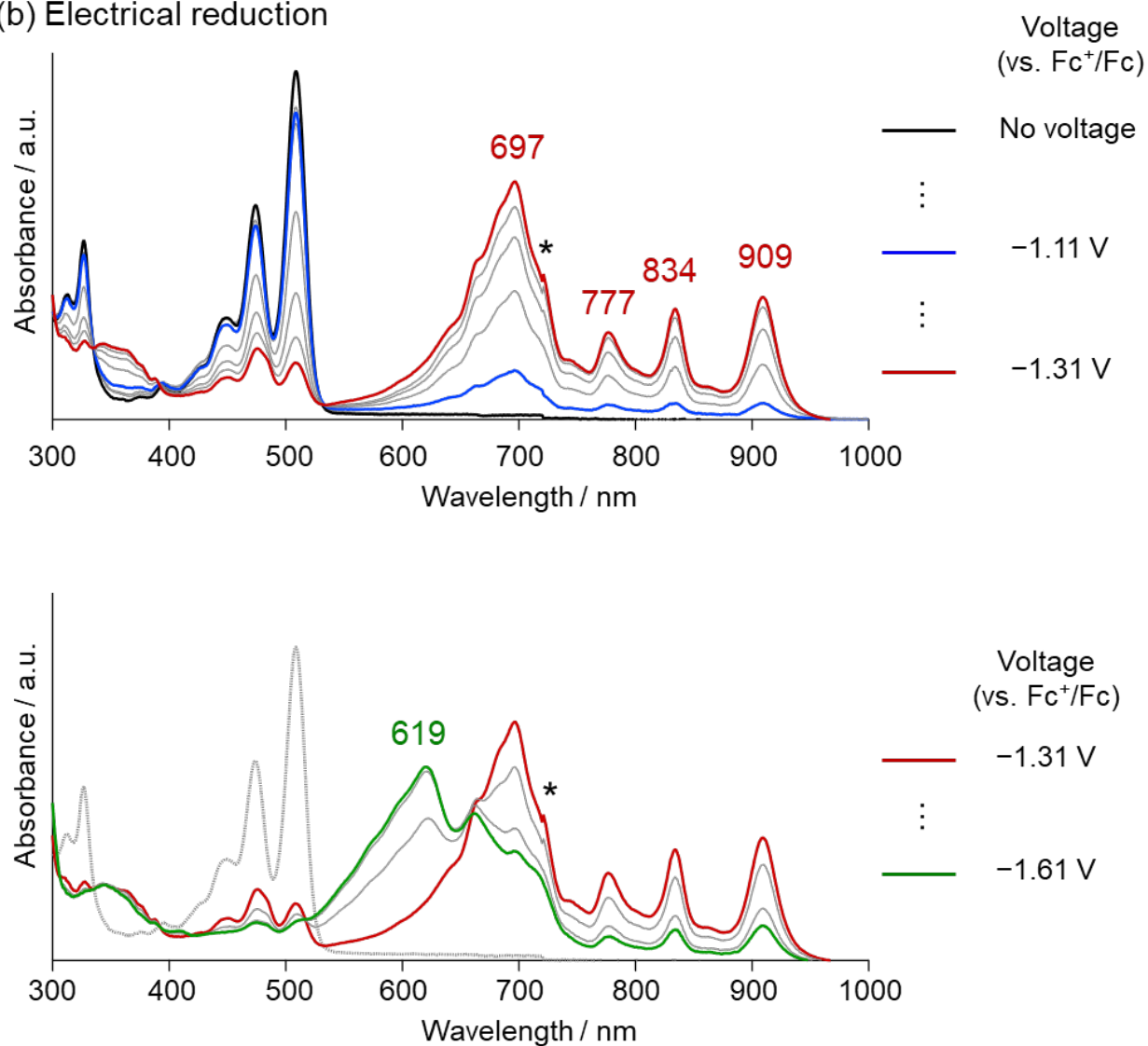


Figure S7.5. Absorption spectral change of **NPBI** under (a) electrical oxidation and (b) electrical reduction. The asterisk indicates the grating changeover wavelength. Conditions; solvent: CH_2Cl_2 , scan rate: 0.001 V/s. The other condition was shown in General information. A small peak at 592 nm was assigned to radical cation of **NPBI**.

8. Estimation of the CS energy level for NPBI-FLAP and NPBI-COT

The energy level of the CS state in CH₂Cl₂ for **NPBI-FLAP** and **NPBI-COT** was estimated by the following equation^[S9, 10]:

$$E_{CS,CH_2Cl_2} = E_{ox,CH_2Cl_2} - E_{red,CH_2Cl_2} - \frac{e^2}{4\pi\epsilon_{CH_2Cl_2}\epsilon_0 r_{CS}}$$

E_{ox,CH_2Cl_2} and E_{red,CH_2Cl_2} are the oxidation and reduction potentials for electron donor and acceptor molecules. For **NPBI-FLAP**, E_{ox,CH_2Cl_2} and E_{red,CH_2Cl_2} were determined from the cyclic voltammograms in CH₂Cl₂ (Figure S7.1.(a)). For **NPBI-COT**, the oxidation potential of DBCOT (Figure S7.1.(d)) was used for E_{ox,CH_2Cl_2} and the reduction potential of **NPBI-COT** (Figure S7.1.(b)) was used for E_{red,CH_2Cl_2} . The interionic distance, r_{CS} , was determined to be 1.3 nm for **NPBI-FLAP** and 0.8 nm for **NPBI-COT** as a center-to-center distance between the two moieties (NPBI and NPBI for **NPBI-FLAP**, DBCOT and NPBI for **NPBI-COT**). e , ϵ_0 , and $\epsilon_{CH_2Cl_2}$ are the elementary charge, dielectric constant of vacuum, and the relative dielectric constant of CH₂Cl₂ (8.93), respectively.

The reduction and oxidation potentials measured in CH₂Cl₂ were corrected for various solvents by using the Born equation,^[S11] and E_{CS} are defined by the following equations:

$$\begin{aligned} E_{CS,sol} &= E_{ox,CH_2Cl_2} - E_{red,CH_2Cl_2} + \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{R^+} + \frac{1}{R^-} \right) \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{CH_2Cl_2}} \right) - \frac{e^2}{4\pi\epsilon\epsilon_0 r_{CS}} \\ &= E_{ox,CH_2Cl_2} - E_{red,CH_2Cl_2} + \Delta E_{sol} - E_{IPS} \end{aligned}$$

R^+ and R^- are the radius of the cation and that of the anion, respectively. For **NPBI-FLAP**, both R^+ and R^- values were determined to be 0.5 nm (NPBI). For **NPBI-COT**, the R^+ and R^- values were determined to be 0.4 nm (DBCOT) and 0.5 nm (NPBI), respectively. ϵ is the relative dielectric constant of the solvent to be estimated.

The reduction potential of DBCOT was obtained in DMF (Figure S7.2.). In this case, ΔE_{sol} and $E_{CS,sol}$ were estimated by the following equation^[S11]: (ϵ_{DMF} is the relative dielectric constant of DMF (36.7)).

$$\begin{aligned} \Delta E_{sol} &= \frac{e^2}{8\pi\epsilon_0 R^+} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{CH_2Cl_2}} \right) + \frac{e^2}{8\pi\epsilon_0 R^-} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{DMF}} \right) \\ E_{CS,sol} &= E_{ox,CH_2Cl_2} - E_{red,DMF} + \Delta E_{sol} - E_{IPS} \end{aligned}$$

The energy levels of the CS and S₁ states were summarized in Table S8.1. (**NPBI-FLAP**), Table S8.2., and Table S8.3. (**NPBI-COT**). For **NPBI-FLAP**, the S₁ energy level is lower than that of the CS state in toluene, which is consistent with the high FL quantum yield. On the other hand, in acetone and DMF, the CS state is more stable, supporting the FL quenching due to CS. For **NPBI-COT**, the S₁ energy is lower than that of the CS (DBCOT to NPBI) state in toluene, which is consistent with the results of the steady-state FL, while the energy level of the CS (NPBI to DBCOT) state is always higher than that of the S₁ state. These results indicate that rapid ICT occurs from DBCOT to NPBI.

Table S8.1. The estimated energy levels of the BS-CS and S₁ states of **NPBI-FLAP**. $E_{\text{ox,CH}_2\text{Cl}_2} - E_{\text{red,CH}_2\text{Cl}_2} = 2.44$ eV

Solvents	ε	$\Delta E_{\text{sol}} / \text{eV}$	$E_{\text{IPS}} / \text{eV}$	$E_{\text{CS}} / \text{eV}$	$S_1 / \text{eV}^{[a]}$	Φ_{F}
Toluene	2.38	0.89	0.47	2.86	2.37	0.87
CHCl ₃	4.81	0.28	0.23	2.49	2.37	0.79
CH ₂ Cl ₂	8.93	0	0.12	2.32	2.37	0.69
Acetone	21.0	−0.19	0.05	2.20	2.38	0.04
DMF	36.7	−0.24	0.03	2.17	2.36	< 0.01

[a] The energy level of the S₁ state was calculated as the average of the 0–0 transition energies of the absorption and fluorescence bands (See Table 4.1.).

Table S8.2. The estimated energy levels of the CS (DBCOT to NPBI) and S₁ states of **NPBI-COT**.

$$E_{\text{ox,CH}_2\text{Cl}_2} - E_{\text{red,CH}_2\text{Cl}_2} = 2.23 \text{ eV}$$

Solvents	ε	$\Delta E_{\text{sol}} / \text{eV}$	$E_{\text{IPS}} / \text{eV}$	$E_{\text{CS}} / \text{eV}$	$S_1 / \text{eV}^{[a]}$	Φ_{F}
Toluene	2.38	1.00	0.76	2.47	2.36	0.82
CHCl ₃	4.81	0.31	0.37	2.17	2.35	0.59
CH ₂ Cl ₂	8.93	0	0.20	2.03	2.35	0.32
Acetone	21.0	−0.21	0.09	1.94	2.38	0.04
DMF	36.7	−0.27	0.05	1.91	2.35	0.01

[a] The energy level of the S₁ state was calculated as the average of the 0–0 transition energies of the absorption and fluorescence bands (See Table 4.2.).

Table S8.3. The estimated energy levels of the CS (NPBI to DBCOT) and S₁ states of **NPBI-COT**.

$$E_{\text{ox,CH}_2\text{Cl}_2} - E_{\text{red,DMF}} = 3.75 \text{ eV}$$

Solvents	ε	$\Delta E_{\text{sol}} / \text{eV}$	$E_{\text{IPS}} / \text{eV}$	$E_{\text{CS}} / \text{eV}$	$S_1 / \text{eV}^{[a]}$	Φ_{F}
Toluene	2.38	1.15	0.76	4.14	2.36	0.82
CHCl ₃	4.81	0.46	0.37	3.84	2.35	0.59
CH ₂ Cl ₂	8.93	0.15	0.20	3.70	2.35	0.32
Acetone	21.0	−0.06	0.09	3.61	2.38	0.04
DMF	36.7	−0.12	0.05	3.58	2.35	0.01

[a] The energy level of the S₁ state was calculated as the average of the 0–0 transition energies of the absorption and fluorescence bands (See Table 4.2.).

9. Time-resolved spectroscopy

9.1. Experimental setup

Details of the femtosecond time-resolved absorption setup will be reported elsewhere. Briefly, the setup is based on a Yb:KGW regenerative amplifier (PHAROS-SP, Light Conversion, 1028 nm, 170 fs, 1 mJ, 6 kHz). A portion of the regenerative amplifier output was used to pump a home-built noncollinear optical parametric amplifier (NOPA) to generate the pump pulse centered at 530 nm. Another small portion of the regenerative amplifier output was focused onto a sapphire crystal to generate a white-light continuum, which was divided into two, and they were used as the probe and reference pulses. The pump and probe pulses were focused into a 300- μm -thick static sample cuvette in a non-collinear geometry. The spectral intensities of the probe, after passing through the sample, and reference pulses were detected by a pair of CMOS cameras through prism spectrographs. The time-resolved absorption data was corrected for the temporal chirp of the white-light probe, which was evaluated by measuring a coherent artifact signal of the pure solvent. The pulse duration of the pump pulse was evaluated by a second-harmonic generation frequency-resolved optical gating (SHG-FROG) measurement, and it was ~ 10 fs. All the measurements were carried out with the pump polarization set at the magic angle (54.7°) with respect to the probe, and the pump pulse energy was set to ~ 4 nJ. Global analysis was performed using Glotaran software.^[S12, 13]

9.2. Additional transient absorption data

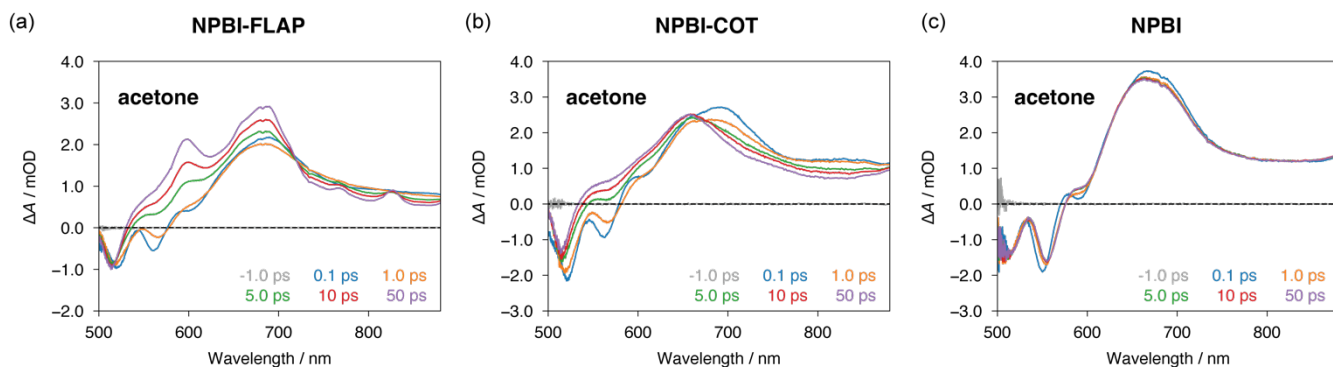


Figure S9.1. Transient absorption spectra of NPBI-FLAP, NPBI-COT, and parent NPBI in acetone.

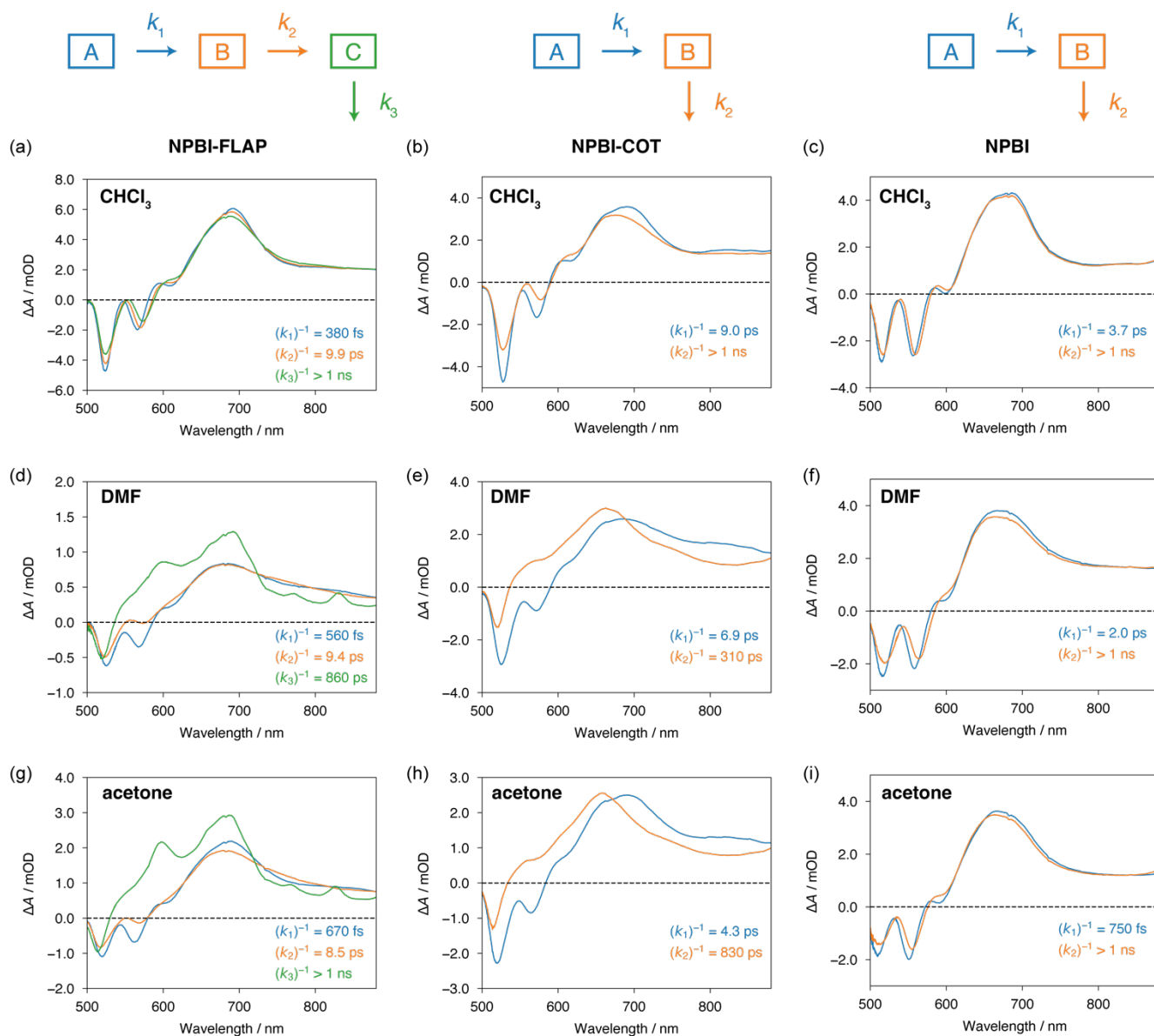


Figure S9.2. Evolution-associated difference spectra of NPBI-FLAP, NPBI-COT, and parent NPBI in CHCl_3 , DMF, and acetone obtained by global fitting of the transient absorption data based on a sequential model.^[S14] For NPBI-FLAP in DMF and in acetone, 9.4 and 8.5 ps components can be assigned to SB-CS because the subsequent (green) spectra show characteristic spectral features of the NPBI radical anion and cation. The kinetic models used in the analysis for each compound are shown at the top.

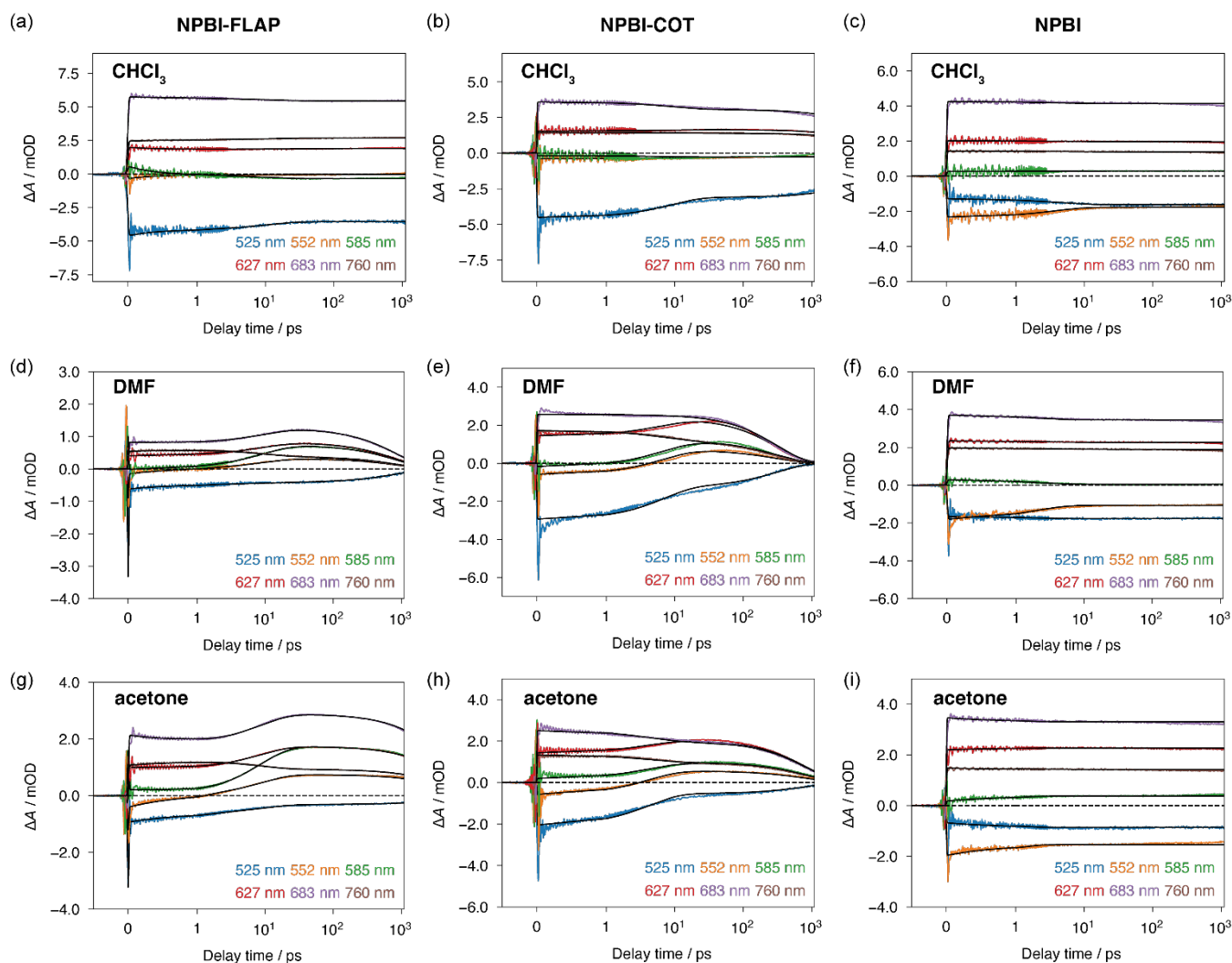


Figure S9.3. Time traces of the transient absorbance of NPBI-FLAP, NPBI-COT, and parent NPBI in CHCl_3 , DMF, and acetone at the selected wavelengths. The solid black curves are the best fit for the data. Note that the time axis is linear in the -0.5 to 1 ps range and switched to a logarithmic scale for later delay times.

10. Supplementary references

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