Ratiometric Flapping Force Probe That Works in Polymer Gels

Takuya Yamakado, and Shohei Saito*

Graduate School of Science, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan.

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ABSTRACT: A ratiometric flapping force probe that can evaluate the nanoscale stress concentration in the polymer chain network of common organogels has been developed. Stress-dependent dual-fluorescence properties of the chemically doped flapping force probe has been demonstrated even when the probe is solvated in the wet materials (Figure 1). The fluorescence ratiometric analysis is robust against the local concentration change induced by the macroscopic polymer deformation. While the force-responsive FRET dyads, widely used in mechanobiology, are sensitive to the distance and orientation of the two chromophores, the flapping fluorophore works as a single-component flexible force probe regardless of the FRET efficiency. Realtime and reversible spectral response to the mechanical stress is observed with a low threshold on the order of sub-MPa compression due to its conformational flexibility. The previously reported flapping probe only shows a negligible response in the solvated environments because the undesired spontaneous planarization occurs in the S_1 excited state, even without mechanical force. The excited-state engineering by changing the flapping wings from the anthraceneimide units to the pyreneimide units endows this molecule with the force probe function in the wet conditions. The structurally modified force probe also has an advantage in terms of a wide dynamic range of the fluorescence response in solvent-free elastomers, which enabled the ratiometric fluorescence imaging of the molecular-level stress concentration during the crack growth in a stretched polyurethane film. The percentage of the stressed force probes has been experimentally estimated to be approximately 30–40% before the fracture of the elastomers. The flapping force probe is useful for elucidating the toughening mechanism of recently focused unique topological gels and elastomers at molecular level.

INTRODUCTION

Polymer gels are composed of polymer chain network swollen with solvents. Hydrogels have been widely used for drug delivery systems¹ and biocompatible materials² due to their high solvent retention properties and flexibility. In addition to these classical applications, functional gels attract increasing attention in wearable electronics,³ actuators,⁴ and soft robotics.⁵

Polymer gels have an inherent problem in fragility because of the low volume fraction of polymer chains and inhomogeneous network structure.⁶ To make tough polymer gels, many strategies have been proposed in these decades,^{7,8} leading to the development of tough hydrogels incorporating a double network structure,^{9–12} non-covalent sacrificial bonds,^{13–16} nanoparticles,^{18–21} and a crystal structure.^{22,23} These materials are designed to dissipate the energy of the mechanical stress concentrated on the specific polymer chains,²⁴ as it has also been reported for elastomers.^{25–29} Furthermore, to overcome the heterogeneity of polymer networks, unique polymer networks have been studied based on 1) multi-arm macromers with uniform chain length^{31–34} and 2) polymer gels with rotaxane-based slidable cross-links.^{23,35–37} These nanoscopic polymer designs are intrinsically important to create polymer gels with remarkable mechanical properties. However, it remains challenging to directly elucidate the toughening mechanism at the nanoscale.³⁸

Figure 1. Schematic illustration of the compression-induced fluorescence change of a common organogel chemically doped with the flapping force probe (FLAP). λ_{FL} : Fluorescence wavelength.

On the other hand, polymer mechanochemistry has been rapidly developed as a related area.^{39,40} A variety of mechanophores exhibit color changes^{41–52} and/or luminescence responses^{25,53–60} when a relatively weak covalent bond undergoes the intramolecular cleavage by mechanical stimuli, as represented by spiropyran. While these mechanophores are widely used for developing mechanoresponsive materials,^{61–64} they could also be used as "force probes" to evaluate molecular-level forces transmitted in the polymer chain network, as long as the chemical doping of the mechanophore does not have a significant influence in the intrinsic mechanical properties of host polymers.^{65,66} Recently, several examples have been reported to demonstrate quantitative mapping of the local stress distribution in multi-network elastomers during the crack propagation.^{67–70} In these reports, the important role of the sacrificial bonds

in the toughening mechanism of the topological polymers has been demonstrated. Mechanoresponsive system with a reversible response is more useful,^{71–78} which allows us to investigate local force distribution in the elastic polymer deformation. To evaluate the stress applied to fragile polymer gels, flexible force probes are more suitable, which should have a lower force threshold than that required for the covalent bond scission (> 200 pN). FRET dyads would be an alternative to probe such the small forces.^{79–82} Supramolecular structural changes,^{83–87} such as the unravelling of the DNA linker,^{88,89} induce a fluorescence

(FL) response with the perturbation of the FRET efficiency. The force threshold to cleave hydrogen bonds of DNA/proteins has been estimated as tens of piconewtons, which is one or two orders of magnitude lower than that of conventional mechanophores,^{79–82} although the FRET efficiency is sensitive to multiple parameters such as the distance and the relative orientation of the two chromophores.⁸³

Figure 2. (a) Synthesis of segmented polyurethane elastomer with chemically doped **FLAP0** as a force probe. (b) The S_0 and S_1 energy profiles of **FLAP0** in the presence of solvent molecules. A photograph of the **FLAP0**-doped organogel is shown in the inset. (c) The patterns of the FL spectral change of **FLAP0** and **FLAP1** by stretching films of the solvent-free elastomers. (d) The excited-state engineering of the S_1 energy profile in the wet conditions by changing the molecular structure from **FLAP0** into **FLAP1**.

Flapping molecule (FLAP) provide another category of the conformationally flexible force probe,⁹⁰ which is unique due to its single-component dual FL properties originating from the interchangeable bent and planar conformations.^{91,92} FLAP is a promising ratiometric force probe to obtain the high signal-to-noise ratio in a simple experimental setup by canceling out the effects of the local probe concentration, excitation source variation, and light scattering by the sample. We recently reported a flapping force probe **FLAP0** bearing the anthraceneimide wings (Figure 2a and 2c).⁹⁰ In the narrow free volume of the solvent-free elastomers, **FLAP0** was surrounded by the polymer chains, suppressing the spontaneous planarization in the S_1 excited state. As a result, only the short λ_{FL} band of the bent form was observed in the steady-state FL spectrum of **FLAP0**-doped unstretched film, while the compulsory planarization in the S_0 ground state was induced by stretching the film, accompanied by the enhancement of the long λ_{FL} band (Figure 2a and 2c). In the previous report, the ratiometric FL analysis of the **FLAP0**-doped polyurethanes revealed that the local stress concentration is twice as biased at crosslinkers than at main chains of the polymer network, particularly in a strain-hardening region.⁹⁰ With these results in hand, we hypothesized that the flapping force probes would also be useful for quantifying local stress concentration in gels, which are more fragile than elastomers (Figure 1). However, **FLAP0** only showed negligible FL response to the mechanical stress in organogels, because the solvated **FLAP0** molecule underwent the spontaneous conformational planarization in the S_1 excited state, emitting the long λ_{FL} band even without mechanical stress (Figure 2b). To solve this problem, the molecular design of the FLAP force probe has been modified from the flapping anthraceneimide (**FLAP0**) to the flapping pyreneimide (**FLAP1**). Tuning the excited-state energy profile with a higher S_1 barrier partially suppressed the S_1 planarization, and realized the mechanical response in polymer gels (Figure 2d). Namely, the distribution of the planar S_1 species of **FLAP1** became more populated only when the mechanical stress was applied. The excited-state engineering by changing **FLAP0** into **FLAP1** also resulted in the improvement of the dynamic range of the stress-induced FL spectral change in the stretched elastomers (Figure 2c).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Force Probes

Molecular design was conceived based on the previously obtained insight. In a series of flapping acene dimers, we have reported that π -extension of the rigid wings of FLAP suppresses the spontaneous excited-state planarization.^{93,94} Since this suppression is necessary for designing the force probe working in gels, we here selected a flapping wing with a large π -conjugated system. Since the condensation reaction of pyrene dione and aromatic amines is reliable to construct large aromatic wings,⁹⁵ we adopted the synthetic approach toward "pyrazaacenes"⁹⁶ for the scheme.

Synthesis of a pyrene dione derivative **1** was performed with a bulky 2,6-diisopropylphenyl group on the nitrogen atom (Figure 3), according to the previous study.⁹⁷ The 2,6-diisopropylphenyl group was introduced to prevent the aggregation of the fluorophore in solution or polymers. Reactions of the rigid wings, a pyrene dione derivative **3**, with the flexible COT joint, tetramine of dibenzo[*a,e*]cyclooctatetraene **4**⁹⁸ was conducted in a mixed solvent of chloroform and acetic acid under heating, providing **FLAP1-H** as a model compound of the force

probe in 72% yield. **FLAP1-OH** was synthesized from **9**, in which the hydroxy groups were introduced at the R^1 position as a reactive group for polymerization. Note that mesityl groups (Mes) were attached to the R^2 position to improve solubility. **Wing1-H** and **Wing1-OH** (see Figure 4b and Section 2 in SI) were synthesized as reference compounds by the reaction of *o*-phenylenediamine with **1** or **2**.

Structural characterization of the flapping force probe was conducted by single-crystal X-ray crystallography. While **Wing1-OH** readily gave crystals suitable for single-crystal X-ray structure analysis (Figure S3.2), the crystals of **FLAP1-OH** and **FLAP1-BC** (capped with the butylcarbamoyloxy groups at the probe termini) were not suitable for the measurement. We finally obtained the single-crystal X-ray structure of **FLAP1-OH'** with a 3,5-di-*tert*-butylphenyl group instead of mesityl groups. As shown in Figure 3b, **FLAP1-OH'** has a V-shaped structure in crystals, and the bending angles of the central cyclooctatetraene (COT), defined by the inset of Figure 5a, are 44.2° and 45°, which are comparable to those of the previously reported flapping molecules.^{93,99}

Figure 3. (a) Synthesis of the flapping pyreneimides. Mes: mesityl groups. Conditions: (i) HOAc, 135 °C; (ii) BBr₃, CH₂Cl₂, -78 °C to r.t.; (iii) Ag₂O, CH₂Cl₂, r.t.; (iv) [Ir(μ-OMe)(cod)]₂, 4,4'-di-*tert*-butyl-2,2'-bipyridyl, B₂(pin)₂, *tert*-butyl methyl ether/mesitylene, 70 °C; (v) mesityl bromide, SPhos Pd G2, methyltriocetylammmonium chloride, toluene/K₂CO₃ aq., 100 °C; (vi) 1-bromo-3,5-di-*tert*-butylbenzene, SPhos Pd G2, methyltriocetylammmonium chloride, toluene/K₂CO₃ aq., 100 °C; (vii) CHCl₃/HOAc, 75 °C; (viii) butyl isocyanate, Et₃N, toluene, 110 °C. (b) Single crystal X-ray structure analysis of **FLAP1-OH'**. Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms except for OH groups and 3,5-di-*tert*-butylphenyl groups were omitted for clarity.

Dual Fluorescence in Solution

Optical properties of **FLAP1-H** were measured in toluene to confirm whether the excited-state planarization of the new force probe was properly suppressed. As shown in Figure 4a, the absorption spectrum showed a maximum at 447 nm, and the peak of the FL spectrum was around 479 nm with a small Stokes shift (1720 cm^{-1}). On the other hand, the conventional anthracene-based force probe (**FLAP0-H**) showed the spontaneous planarization in toluene and gave the FL spectrum peaked at 525 nm with a large Stokes shift (4800 cm^{-1}) (Figure 5a, inset).⁹² This result suggests that **FLAP1-H** emits FL mainly from the bent form due to the effective suppression of the excited-state planarization as expected. The FL quantum yield of **FLAP1-H** was 0.44 in toluene. More importantly, **FLAP1-H** showed a small FL peak at 523 nm in addition to the maximum around 460 nm, and the spectral shape at the longer wavelength region was similar to that of **FLAP0-H**. When the FL spectrum of **FLAP1-H** was measured in a rigid PMMA matrix, in which the conformation planarization of FLAP is not allowed due to the confined space with small free volume,¹⁰⁰ the peak at 523 nm disappeared, as shown by the blue dotted line. Such spectral change was not observed in **Wing1-H** (Figure 4b), indicating the long-wavelength FL of **FLAP1-H** was emitted from a partially populated planar form in the excited state. This assignment was supported by the fact that the FL lifetime of **FLAP1-H** can be fitted by two components (SI, Section 4.3).

Variable-temperature FL spectra of **FLAP1-H** were measured in toluene to gain insight into the equilibrium between the bent and planar forms in the S_1 excited state. Relative FL intensity of the long-wavelength component got decreased as the temperature became lower or higher than 233 K (Figures 4c and 4d). On the other hand, such behavior was not observed in **Wing1-H** (Figure S4.5). Since there was no concentration dependence in the shape of the absorption and FL spectra (Figure S4.1), and no significant changes were observed in the variable-temperature excitation spectra of **FLAP1-H** (Figure S4.4), the possibility of the presence of impurities or any structural changes in the ground state was excluded. The variable-temperature FL spectra in Figure 4c and 4d are typical to the dual FL system based on the equilibrium in the excited state (Figure 4f),^{101,102} and the parameters related to this equilibrium (E_a and ΔH in S_1) can be calculated by Stevens–Ban plot^{101,103} based on the area ratio of the two FL bands and the measurement temperature. Assuming that the FL spectral shape of the planar **FLAP1-H** was similar to that of flapping anthracene, the activation energy E_a was estimated to be 4.3 kcal/mol, and the enthalpy change ΔH was around -0.6 kcal/mol in S_1 (Figure 4e). The activation barrier of **FLAP1-H** for the S_1 planarization is larger than the energy difference between the bent and planar forms, which is in stark contrast to the flapping anthracene (**FLAP0-H**) showing fast planarization dynamics in S_1 .⁹²

Figure 4. Optical properties of the pyreneimide-based force probe in toluene. (a) Absorption and FL spectra of **FLAP1-H**, compared with those of the reference compound (**Wing1-H**). (c, d) Variable temperature FL spectra of **FLAP1-H**. (e) Stevens–Ban plot of the FL quantum yield ratio of the V-shaped and planar forms of **FLAP1-H**. (See Section 4.2 in SI for details on spectral decomposition.) (f) Energy profile that accounts for the dual FL of **FLAP1-H**.

Interpretation of the Dual Fluorescence by Calculations

DFT calculations were performed to explain why the excited state planarization of **FLAP1-H** was suppressed in the solution. Model compounds **FLAP0'**, **FLAP1'**, and **Wing1'** were treated, in which the 2,6-diisopropylphenyl groups of the original compounds were replaced by hydrogen atoms. Although the calculated results were sensitive to the level of theory, we adopted the PBE0/6-31+G(d)/PCM(toluene) level because the calculated absorption wavelength of **Wing1'** is close to the experimental results, and the shape of the S_1 energy diagram of **FLAP1'** is qualitatively in agreement with the Stevens–Ban plot (SI, Section 5.3). Figures 5a and 5b show the energy profiles of **FLAP0'** and **FLAP1'** in the S_0 and S_1 states delineated by changing the COT bending angle by 2.5° . In S_0 , the bent forms ($\theta \sim 40^\circ$) are the most stable for both FLAPs due to the ring strain of COT, and the conformational relaxation in S_1 occurs from these structures. Interestingly, the energy diagram of the S_1 state is quite different between **FLAP0'** and **FLAP1'**, where **FLAP0'** partially flattens to a shallow V-shaped form ($\theta = 29.5^\circ$) followed by a complete planarization with a very small energy barrier (~ 0.2 kcal/mol), consistent with the observed green FL (inset of Figure 5a) and previously reported ultrafast dynamics in the excited state. On the other hand, **FLAP1'** showed a larger energy barrier (~ 1.3 kcal/mol) between the bent and planar forms than **FLAP0'**. Although these results are qualitative, the difference in the planarization behavior can be interpreted from the viewpoint of molecular orbital distribution. In **FLAP0'**, the frontier orbitals are delocalized over the whole molecular frame including the central COT ring, in which the orbital phase is favorable for planarization (Figure 5c). On the other hand, LUMO of **FLAP1'** is localized on the electron-withdrawing imide moiety without the contribution of the COT moiety (Figure 5d), suggesting that planarization is less prone to occur. This difference in the orbital distribution is also consistent with the charge-transfer (CT) nature of the FL from the bent form of **FLAP1-H**, experimentally evaluated by Lippert–Mataga plot (SI, Section 4.4).^{104,105} Note that the FL derived from the planar form, peaked at 523 nm in toluene, showed less solvent dependence (Figure S4.13), consistent with the similarly delocalized HOMO and LUMO over the planar molecular frame ($\theta = 0^\circ$) of **FLAP1'**. The excited-state engineering based

on the molecular orbitals (de)localization is useful for designing dual-fluorescence molecules with desired optical properties.

Figure 5. S_0 and S_1 energy profiles of (a) **FLAP0'** and (b) **FLAP1'**. COT bending angle θ was defined by the dihedral angle shown in the inset of (b). (c, d) Kohn–Sham orbitals of **FLAP0'** and **FLAP1'** displaying the distinct S_1 electronic character at the S_0 -optimized bent geometries. The inset of (a) shows FL spectra of **FLAP0-H** measured in toluene for comparison with **FLAP1-H**. Geometry optimizations were performed at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure 6. (a) Synthesis of segmented polyurethane elastomer (SPU) chemically doped with **FLAP1-OH** as a force probe. (b) Stress–strain curves of the SPUs. (c) FL spectral change of **SPU1** during the tensile test. Photographs of the specimen under UV light are shown beside. (d) FL intensity ratio plotted against nominal stress in the tensile test. I_{533nm}/I_{472nm} was used as the ratio for **SPU1** and **SPU1-BC**, and I_{525nm}/I_{474nm} was used for **SPU0**. (e) Photographs (RGB) and stress mapping (FL ratio) of the notched **SPU1** film. The images were recorded using a hyperspectral camera, and the photographs were reconstructed from RGB channels (R = 700 nm, G = 545 nm, B = 480 nm). (f) FL spectra averaged over the regions A–C shown in the left panel (bandwidth: 5 nm), and the estimated local stress based on the panel (d). (g) Energy profile of **FLAP1'** obtained by constrained geometry optimization, in which the distance between terminal hydrogen atoms (x) was fixed to the given extension distance (Δx). The elongation distance was calculated by taking the S_0 optimized structure ($x = 23.1$ Å) as the initial geometry. The calculation was conducted on the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Improved Dynamic Range of the FL Ratio Change

Since the photophysical properties of **FLAP1-H** in solution have been clarified, the FL response of **FLAP1-OH** as a force probe was demonstrated in the stretched elastomers. Since the FL spectrum of **FLAP1-BC** (bearing the butylcarbamoyloxy groups at the termini) in toluene was similar to that of **FLAP1-H** (Figure S4.3), the mesityl groups and urethane moiety would not affect the photophysical properties of the force probe introduced into polyurethane. First, **FLAP1-OH** was incorporated into segmented polyurethane (SPU) composed of poly(tetrahydrofuran) (PTHF), methylenediphenyl 4,4'-diisocyanate (MDI), and 1,4-butanediol (BDO). This is a widely used polymer for introducing various mechanophores,³⁹ and 0.1–0.2 mm thick dumbbell-shaped specimens were prepared (Figure 6a). In the same way, the following three polymers, 1) **SPU0** chemically doped (covalently incorporated) with **FLAP0-OH**, 2) **SPU1-BC** physically (non-covalently) doped with **FLAP1-BC**, and 3) **SPU2** without any force probe were prepared as control experiments (Figure S6.1). The synthesized polyurethanes were

characterized by ^1H NMR spectra, and the ratio of soft segments to hard segments was confirmed to be 1:2.3, the same as the preparation ratio (Figures S6.2–S6.5). On the contrary, the ^1H NMR signal of the incorporated force probe was not observed due to the minimal amount of addition. Besides, the thermal properties of the synthesized SPUs measured by differential scanning calorimetry (DSC) were comparable to previously reported similar polyurethanes (Figure S6.7).⁸⁴

The stress–strain curves obtained from tensile tests of the prepared specimens are shown in Figure 6b. Stress was calculated as nominal stress. The mechanical properties of the synthesized SPUs were comparable regardless of the presence of the probe, indicating that the addition of the flapping force probe has little effect on the mechanical properties. The FL spectrum of **SPU1** was monitored during the tensile tests (Figure 6c). The relative intensity of the FL band at 472 nm, emitted from the bent form of FLAP, became decreased, and the FL peak at 533 nm concomitantly increased with a characteristic vibrational band at 575 nm, assigned to the FL emitted from the

planarized form of FLAP. The distinct blue-to-green FL color change occurred rapidly and reversibly, which can be clearly recognized by the naked eye (Supporting Movie 1). Note that the average distance between the fluorescent probes was approximately 20 nm, estimated from the concentration of FLAP in the specimen (SI, Section 6.1). Since the distance is much farther than that for FRET (< 10 nm), the FRET-induced FL perturbation can be ignored.

The FL intensity ratio at 533 nm and 472 nm (I_{533}/I_{472}) was plotted against stress. The FL intensity ratio monotonically increased from about 0.3 up to ≈ 11 (Figure 6d). In contrast, when the same measurement was performed for **SPU0** incorporating **FLAP0**, the FL intensity ratio only reached up to ≈ 2 (Figure S6.10). The wider dynamic range in the FL ratio of **FLAP1** is an important advantage of the new flapping force probe. The FL spectra of the negative control specimen **SPU1-BC** showed little response by stretching, as expected. However, only when the film was strongly stretched with over 40 MPa stress, a small spectral change was observed, which might be related to the strain-induced crystallization of the polymer chains (Figure S6.9–S6.12). Therefore, we only discuss the response of **SPU1** below 40 MPa. The ratiometric FL imaging of the notched **SPU1** specimen was performed with a hyperspectral camera (Figure 6e). As shown Supporting Movie 2, the FL intensity ratio increases in the crack front region just before the crack propagation, while it returns to a small ratio after the crack propagation completed at the corresponding region. From the relationship between the stress and the FL ratio in Figure 6d, the average stress was estimated in each of the three regions A–C (Figure 6e, right). As a result, the local stress distribution in the range of 12–27 MPa were visualized with the submillimeter spatial resolution. The ratiometric FL imaging enables sensitive and reversible stress mapping due to the conformational flexibility of the flapping force probe.

Synthesis of Crosslinked Polyurethanes and Preparation of the Organogels

To demonstrate the efficacy of the force probe **FLAP1** in wet materials, crosslinked polyurethanes (PU) were synthesized (Figure 7a). Poly(tetrahydrofuran) (PTHF) and hexamethylene diisocyanate (HDI) were selected as the main chain components, while triethanolamine (TEA) was used as the crosslinker.⁹⁰ The crosslinking density, defined as the molar fraction of TEA to all monomers, was set to 8.7%. A trace amount of **FLAP1-OH** (0.01 mol% to HDI) was added to the solution of the mixture of the monomers, and the polymerization was initiated by a tin catalyst (DBTDL). The resulting solution was poured into a poly(tetrafluoroethylene) (PTFE) mold to prepare a dry cylindrical specimen of **PU1**. Organogels were prepared by swelling the crosslinked polyurethane **PU1** with organic solvents. By using cyclopentyl methyl ether (CPME) as a less volatile solvent (Figure 7b), the FL spectra of the bent and planar forms of **FLAP1-H** were well separated. The cylindrical specimens of **PU0** and **PU1** were prepared using a custom-made PTFE mold and immersed in CPME for more than 48 hours to reach the equilibrium swelling (Figure S8.1), designated as **Gel0** and **Gel1**, respectively. The swelling ratio V/V_0 , defined as the volume ratio before and after swelling, was approximately 4.3. Figures 7d and 7e show the spectral change in absorption before and after swelling. As seen in the photographs, the blue FL of **PU1** was preserved even after swelling, while **PU0** showed a significant FL change by swelling. Since the intrinsic sensitivities of the force probes **FLAP0** and **FLAP1** would be

comparable (SI, Section 7.5), the planarization of **FLAP0** should not be caused by swelling pressure, unlike the example of the mechanophores activated by swelling glassy PMMA.^{106,107} Rather, **FLAP0** in **Gel0** would undergo the spontaneous S_1 planarization when surrounded by solvent molecules. On the other hand, the undesired S_1 planarization was almost completely suppressed for **FLAP1** in **Gel1**.

Figure 7. (a) Synthesis of the crosslinked polyurethane elastomer (**PU1**) chemically doped with **FLAP1-OH** as a force probe. Cylindrical specimens of (b) **Gel0** and (c) **Gel1** prepared by swelling the corresponding crosslinked PU elastomers with cyclopentyl methyl ether (CPME). FL spectra of (d) **Gel0** and (e) **Gel1** compared to those before swelling.

Fluorescence Response by Compressing the Organogels

Compression tests of the cylindrical gel specimens were successfully conducted (Figure 8a and Supporting Movie 3), while the tensile tests using the dumbbell specimens were difficult due to the fragility of the gel materials. Although the fracture strain was considerably dependent on the individual samples, **Gel0** and **Gel1** showed the similar stress–strain curves in Figure 8b. In contrast, the FL spectra of **Gel0** and **Gel1** showed distinct behaviors upon the compression (Figures 8c and 8d), where the bottom surface of the cylindrical specimen was observed using the same experimental setup shown in Figure 9a. The ratio of FL intensity at 480 nm and 523 nm was monitored during the compression test, whose values were plotted against the nominal (engineering) strain, stress, and strain energy density in Figures 8e, 8f, and 8g, respectively. While the dynamic range of the FL response of **Gel1** was limited due to its fragility compared to the solvent-free **PU1**, the quantitative analysis was well performed with the sufficient signal-to-noise ratio. The control material, **Gel0**, gave the negative results in the spectroscopic analysis (Figure S9.3).

Figure 8. (a) Photographs of the compression process of a cylindrical specimen of **Gel1** under UV light (365 nm). (b) Nominal stress-strain curves of the gels. FL spectral change of (c) **Gel0** and (d) **Gel1** during the compression test. FL intensity ratio plotted against (e) strain, (f) stress, and (g) strain energy density in the compression test. (h) Reversible response of the FL ratio during ten cycles of compression and release processes.

Interestingly, the FL response of **Gel1** was different from that of the corresponding solvent-free elastomer in the low-stress region (<1 MPa) (Figure 8f and S7.7), where **PU1** did not show the change in the FL intensity ratio. The FL ratio showed an excellent linear relationship when the strain energy density, defined as the area under the stress-strain curve, was taken as the abscissa (Figure 8g). These results suggested that the polymer chains were pre-stretched by swelling before compression, although the degree was not remarkable. The FL response of **Gel1** was reversible, and the cycling test with a strain rate of 0.14 s^{-1} (Figures S9.4) showed that the FL intensity ratio can follow the strain or stress quickly (Figure 8h).

Real-time Stress Mapping of the Compressed Organogels by Ratiometric Fluorescence Imaging

Visualization of the non-uniform stress distribution on the gel was demonstrated. We applied pressure to the plate-shaped **Gel1** with metal stamps using the experimental setup shown in Figure 9a–c. With the naked eye, it was difficult to distinguish the degree of the mechanical stress applied under each alphabetical stamp. However, the ratiometric FL imaging showed that the local stress was more applied under the "L" and "P" metal stamps rather than "F" and "A" (Figure 9d and Supporting

Movie 4), which probably originates from the slightly different thicknesses of these metal stamps. Since the bottom area of the cylindrical specimen in Figure 8 largely changed upon compression, a calibration curve was obtained to estimate the true stress from the observed FL intensity ratio, by tracking and correcting the bottom area change (Figure 9e and S9.5). According to this estimation, true compression stresses applied on the regions A–C of **Gel1** were quantitatively evaluated in the range of 0–1 MPa with the submillimeter spatial resolution (Figure 9d and 9f).

Figure 9. (a) Experimental setup for the cyclic compression test of **Gel1** using metal stamps. Photographs of (b) metal stamps placed on **Gel1**. (c) The bottom of the gel was observed with a hyperspectral camera through the prism. (d) Photographs (RGB) and stress mapping (FL ratio) of **Gel1** compressed by metal stamps. The images were obtained in the same protocol as Figure 6. (e) Calibration curve for estimating true stress from the observed FL ratio of **Gel1**, obtained from Figure 8f with the consideration of the change in the bottom area of the gels. (f) FL spectra averaged over the regions A–C shown in the panel (d) (bandwidth: 5nm), and the local true stress estimated from the calibration curve in the panel (e).

ASSOCIATED CONTENT

Supporting Information

Experimental and theoretical details (PDF)
Movie 1 showing the reversible FL response of the **SPU1** film (MP4)

Movie 2 showing the ratiometric imaging of the stress applied to the notched **SPU1** film (MP4)
 Movie 3 showing compression of the cylindrical **Gel1** specimen (MP4)
 Movie 4 showing the ratiometric imaging of the stress applied to **Gel1** by the metal stamps (MP4)

Accession Codes

CCDC 2122594 and 2122595 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Shohei Saito: saito.shohei.4c@kyoto-u.ac.jp

Author

Takuya Yamakado

Notes

The authors declare no competing financial interest.

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Supporting Information

Ratiometric Flapping Force Probe That Works in Polymer Gels

*Takuya Yamakado, and Shohei Saito**

Graduate School of Science, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan.

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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. 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 or C-400. 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 and δ = 77.16 ppm for ¹³C. Tetrachloroethane-*d*₂: δ = 6.00 ppm for ¹H and δ = 73.78 ppm for ¹³C. THF-*d*₈: δ = 3.58 ppm for ¹H). High-resolution atmospheric-pressure-chemical-ionization time-of-flight mass spectrometry (HR-APCI-TOF-MS) was recorded on a Bruker micrOTOF spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (HR-MALDI-TOF-MS) was conducted with a Bruker Autoflex III spectrometer. Compounds **1**^[S1] and **4**^[S2] were synthesized according to the reported methods. **FLAP0-OH** and **FLAP0-H** were prepared following the previous reports.^[S3]

Photophysical measurements

UV-visible absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Steady-state fluorescence (FL) and excitation spectra were recorded on a JASCO FP-8500 spectrofluorometer. Absolute fluorescence quantum yields were determined on a Hamamatsu Photonics C9920-02S. FL lifetimes were measured on a Hamamatsu Photonics QuantaTaurus-Tau C11367. Variable temperature measurements were performed using a Unisoku CoolSpeK UV USP-203-B cryostat. All measurements of solution samples were conducted using a 10-mm square quartz cell unless otherwise noted. FL spectra plotted in wavenumber units were calculated considering the Jacobian factor ($|d\lambda/d\tilde{\nu}| = \tilde{\nu}^{-2}$). Curve fitting was performed by using (non-)linear least square algorithms in the Igor Pro 8.04 software.

Single-crystal X-ray diffractometry

X-ray crystallographic data was 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^[S4] and refined by SHELXL^[S5] 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 CCDC numbers of 2122594 (**Wing1-OH**) and 2122595 (**FLAP1-OH'**).

Measurements of the polymer samples

Tensile tests were carried out using a Shimadzu Autograph AGS-X with a 1-kN load cell at crosshead. Differential scanning calorimetry (DSC) was conducted on a Hitachi High-Tech Science DSC7000X. Real-time FL measurements of PU specimens were performed using an Otsuka Electronics Multichannel Photodetector MCPD-6800. FL imaging was conducted by a EBA JAPAN hyperspectral camera NH-8. The FL spectra of each pixel of the hyperspectral camera was corrected according to Figure S1.1.

Figure S1.1. Spectra of the standard halogen lamp acquired by the spectrofluorometer and the hyperspectral camera. From these spectra, the spectral correction factor for the hyperspectral camera was obtained.

Uniaxial tensile tests were conducted on dumbbell-shaped specimens prepared in Section 6.1 and 7.1 in SI. Stress–stress curves are displayed as nominal stress (σ_N) versus nominal strain (ε_N) defined as below:

$$\sigma_N = \frac{f}{S_0}, \quad \varepsilon_N = \frac{\Delta L}{L_0},$$

where f is an applied force, S_0 is an initial cross-sectional area, L_0 is an initial gauge length (10 mm), and ΔL is an elongation. Toughness was calculated as the integrated area under a stress–strain curve. Young’s modulus is defined as the slope of stress–strain curves at 0–5% strain. Tensile velocity was fixed at 100 mm min^{−1}, corresponding to strain rate of 0.17 s^{−1}, unless otherwise noted.

Experimental setup for real-time collection of FL/absorption spectra during tensile tests

Real-time FL/absorption measurements of PU specimens during the tensile tests were performed according to the previous study^[S3] with a modified setup, where the light source and the detector follow the center of the stretched polymer by using linear guides and pulleys (Figure S1.2 and S1.3). The FL spectra were recorded with a two-second exposure time, and the specimens were excited with a UV LED ($\lambda_{\text{ex}} \sim 365$ nm). For the measurements of absorption spectra, an exposure time was set to 0.8 second.

Figure S1.2. (a,b) Photographs and (c,d) schematic illustration of the experimental setup for real-time collection of FL spectra.

Figure S1.3. (a) Photographs and (c) schematic illustration of the experimental setup for real-time collection of absorption spectra.

2. Synthesis of the force probes

Figure S2.1. Synthesis of the flapping pyreneimide (**FLAP1-H**) and the reference compound (**Wing1-H**).

N-(2,6-Diisopropylphenyl)-9,10-dimethoxy-4,5-dicarboximide (**2**):

Compound **1** (1.47 g, 4.42 mmol), acetic acid (50 mL), and 2,6-diisopropylaniline (2.0 mL, 11 mmol) were placed in a Schlenk flask. The reaction mixture was stirred for 16 h at 135 °C, and then the solvent was evaporated under reduced pressure. The resultant solid was dissolved into dichloromethane, and washed with water and aqueous NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: hexane/dichloromethane, 1:1) to give **2** (2.09 g, 4.25 mmol, 96%) as an orange solid.

¹H NMR (CDCl₃, r.t., 600 MHz): δ / ppm = 9.42 (d, J = 7.2 Hz, 2H), 8.72 (d, J = 6.6 Hz, 2H), 8.24 (t, J = 8.1 Hz, 2H), 7.51 (t, J = 8.1 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 4.26 (s, 6H), 2.96 (sept, J = 6.9 Hz, 2H), and 1.23 (d, J = 6.6 Hz, 12H); ¹³C{¹H} NMR (CDCl₃, r.t., 151 MHz): δ / ppm = 170.0, 147.9, 144.8, 130.3, 128.9, 128.4, 127.8, 127.2, 125.5, 124.6, 124.2, 123.8, 122.7, 61.4, 29.6, and 24.2. HRMS (APCI/TOF) m/z : [M]⁺ Calcd for C₃₂H₂₉NO₄ 491.2091; Found 491.2088.

***N*-(2,6-Diisopropylphenyl)-9,10-dioxo-9,10-dihydropyrene-4,5-dicarboximide (**3**):**

Compound **2** (2.08 g, 4.23 mmol) was placed in a three-neck flask, and the flask was purged with argon. Anhydrous dichloromethane (180 mL) was added to the flask, and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. Then, 1.0 M boron tribromide solution in dichloromethane (17 mL, 17 mmol) was added dropwise, and the mixture was allowed to warm to room temperature with stirring. After 9 h, the reaction was quenched with water at $0\text{ }^{\circ}\text{C}$, and the mixture was extracted with dichloromethane. To the organic layer was added silver(I) oxide (3.52 g, 15.2 mmol), and the reaction mixture was sonicated for 10 min at room temperature. The resultant mixture was filtered through a Celite pad, and the filtrate was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: dichloromethane) to obtain **3** (1.25 g, 2.72 mmol, 64%) as an orange solid.

^1H NMR (CDCl_3 , r.t., 600 MHz): δ / ppm = 9.50 (dd, $J_1 = 8.4\text{ Hz}$, $J_2 = 1.2\text{ Hz}$, 2H) 8.71 (dd, $J_1 = 7.5\text{ Hz}$, $J_2 = 1.5\text{ Hz}$, 2H), 8.00 (t, $J = 7.8\text{ Hz}$, 2H), 7.52 (t, $J = 7.8\text{ Hz}$, 1H), 7.52 (d, $J = 7.8\text{ Hz}$, 2H), 2.86 (sept, $J = 6.9\text{ Hz}$, 2H), and 1.22 (d, $J = 7.2\text{ Hz}$, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , r.t., 151 MHz): δ / ppm = 179.5, 168.8, 147.7, 134.4, 133.1, 131.7, 130.6, 130.4, 130.1, 128.0, 126.5, 126.0, 124.3, 29.7, and 24.2. HRMS (APCI/TOF) m/z : $[M+H]^+$ Calcd for $\text{C}_{30}\text{H}_{24}\text{NO}_4$ 462.1700; Found 462.1702.

***N*-(2,6-Diisopropylphenyl)phenanthro[4,5-*abc*]phenazine-4,5-dicarboximide (Wing1-H):**

Compound **3** (152 mg, 0.330 mmol) and *o*-phenylenediamine (36 mg, 0.33 mmol) were placed in a two-neck flask, and the flask was purged with argon. Then, chloroform (8.6 mL) and acetic acid (5.2 mL) were added to the flask and the mixture was stirred at $85\text{ }^{\circ}\text{C}$. After 1 h, the solvent was evaporated under reduced pressure, and the crude product was purified by recrystallization from the mixture of diethyl ether and acetic acid to afford **Wing1-H** (194 mg, quant.) as a yellow solid.

^1H NMR (tetrachloroethane- d_2 , $120\text{ }^{\circ}\text{C}$, 600 MHz): δ / ppm = 9.89 (d, $J = 7.8\text{ Hz}$, 2H), 9.59 (d, $J = 7.8\text{ Hz}$, 2H), 8.48 (m, 2H), 8.33 (t, $J = 7.8\text{ Hz}$, 2H), 7.99 (m, 2H), 7.56 (t, $J = 7.8\text{ Hz}$, 1H), 7.40 (d, $J = 7.8\text{ Hz}$, 2H), 3.04 (sept, $J = 6.9\text{ Hz}$, 2H), and 1.31 (d, $J = 7.2\text{ Hz}$, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (tetrachloroethane- d_2 , $120\text{ }^{\circ}\text{C}$, 151 MHz): δ / ppm = 169.2, 147.8, 142.6, 142.1, 130.2, 130.0, 129.9, 129.5, 128.7, 128.4, 128.1, 127.5, 127.1, 126.9,

124.8, 123.8, 29.4, and 23.8. HRMS (APCI/TOF) m/z : $[M]^+$ Calcd for $C_{36}H_{27}N_3O_2$ 533.2098; Found 533.2094. UV-visible absorption (in CH_2Cl_2): λ_{max} ($\epsilon / M^{-1} cm^{-1}$) = 279 (6.6×10^4) and 415 nm (5.3×10^4). Fluorescence (in CH_2Cl_2 , λ_{ex} = 365 nm): λ_{max} = 518 and 555 nm; Φ_F = 0.42; τ_F = 2.4 ns (λ_{obs} = 518 nm).

COT-fused *N*-(2,6-diisopropylphenyl)phenanthro[4,5-*abc*]phenazine-4,5-dicarboximide dimer (FLAP1-H):

Compound **3** (92 mg, 0.20 mmol) and **4** (41 mg, 0.10 mmol) was placed in a Schlenk flask, and the flask was purged with argon. Then, chloroform (2.6 mL) and acetic acid (1.6 mL) were added to the flask and the mixture was stirred at 75 °C. After 17.5 h, the mixture was diluted with chloroform and extracted with aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 , and concentrated under reduced pressure. The crude mixture was purified by recrystallization from hot chlorobenzene to furnish **FLAP1-H** (80 mg, 7.2 mmol, 72%) as a yellow solid.

1H NMR (tetrachloroethane- d_2 , 120°C, 600 MHz): δ / ppm = 9.77 (d, J = 7.8 Hz, 4H), 9.53 (d, J = 7.8 Hz, 4H), 8.30 (s, 4H), 8.25 (t, J = 8.1 Hz, 4H), 7.54 (t, J = 7.8 Hz, 2H), 7.47 (s, 4H), 7.38 (d, J = 7.8 Hz, 4H), 3.01 (sept, J = 6.6 Hz, 4H), and 1.29 (d, J = 6.6 Hz, 24H); $^{13}C\{^1H\}$ NMR ($CDCl_3$ /trichloroacetic acid, r.t., 151 MHz): δ / ppm = 169.7, 147.7, 143.1, 140.8, 137.3, 134.0, 131.2, 131.0, 130.0, 129.2, 128.8, 128.4, 126.3, 126.0, 125.4, 125.3, 124.5, 29.7, and 24.2 (Note: due to the low solubility of **FLAP1-H**, trichloroacetic acid was added to dissolve it as a protonated species). HRMS (APCI/TOF) m/z : $[M]^+$ Calcd for $C_{76}H_{54}N_6O_4$ 1114.4212; Found 1114.4169. UV-visible absorption (in CH_2Cl_2): λ_{max} ($\epsilon / M^{-1} cm^{-1}$) = 279 (6.6×10^4) and 415 nm (5.3×10^4). Fluorescence (in CH_2Cl_2 , λ_{ex} = 365 nm): λ_{max} = 518 and 555 nm; Φ_F = 0.42; τ_F = 2.4 ns (λ_{obs} = 518 nm).

Figure S2.2. Synthesis of the precursors (**5–10**), the compounds for X-ray crystallography (**Wing1-OH**, **FLAP1-OH'**), the force probe (**FLAP1-OH**), and the dopant for control experiments (**FLAP1-BC**).

***N*-(2,6-Diisopropyl-4-methoxyphenyl)-9,10-dimethoxy-4,5-dicarboximide (5):**

Compound **1** (4.98 g, 15.0 mmol), acetic acid (170 mL), and 2,6-diisopropyl-4-methoxyaniline (3.42 g, 16.5 mmol) were placed in a Schlenk flask. The reaction mixture was stirred for 101 h at 135 °C, and then the solvent was evaporated under reduced pressure. The resultant solid was dissolved into dichloromethane, and washed with water and aqueous HCl solution. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: hexane/dichloromethane, 1:1) to give **5** (5.67 g, 10.9 mmol, 72%) as an orange solid.

¹H NMR (CDCl₃, r.t., 600 MHz): δ / ppm = 9.42 (d, J = 7.8 Hz, 2H), 8.71 (d, J = 7.8 Hz, 2H), 8.23 (t, J = 7.5 Hz, 2H), 6.87 (s, 2H), 4.25 (s, 6H), 3.91 (s, 3H), 2.92 (sept, J = 6.6 Hz, 2H), and 1.22 (d, J = 6.6 Hz, 12H); ¹³C{¹H} NMR (CDCl₃, r.t., 151 MHz): δ / ppm = 170.3, 160.9, 149.4, 144.8, 128.9, 128.4, 127.8, 125.5, 124.6, 123.8, 122.7, 119.8, 109.7, 61.4, 55.5, 29.8, and 24.2. HRMS (APCI/TOF) m/z : [M]⁺ Calcd for C₃₃H₃₁NO₅ 521.2197; Found 521.2191.

***N*-(2,6-Diisopropyl-4-methoxyphenyl)-9,10-dimethoxy-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene-4,5-dicarboximide (6):**

In a two-neck flask were placed compound **5** (5.62 g, 10.8 mmol), bis(pinacolato)diboron (6.02 g, 23.7 mmol), (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (179 mg, 0.270 mmol), and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (DTBPY, 145 mg, 0.540 mmol), and the flask was purged with argon. Then, methyl *tert*-butyl ether (MTBE, 162 mL) and mesitylene (54 mL) were added, and the mixture was stirred at 70 °C. After 14.5 h, methanol (220 mL) was added, and the precipitate was collected by filtration and washed with methanol. The product was dried under reduced pressure at 150 °C to remove mesitylene, giving **6** (8.15 g, 10.5 mmol, 97%) as an orange solid.

¹H NMR (CDCl₃, r.t., 600 MHz): δ / ppm = 9.78 (s, 2H), 9.10 (s, 2H), 6.85 (s, 2H), 4.26 (s, 6H), 3.91 (s, 3H), 2.90 (sept, J = 6.9 Hz, 2H), 1.45 (s, 24H), and 1.21 (d, J = 7.2 Hz, 12H); ¹³C{¹H} NMR (CDCl₃, r.t., 151 MHz): δ / ppm = 170.1, 160.8, 149.5, 144.9, 129.8, 128.7, 128.60, 128.57, 126.8, 124.3, 120.0, 109.5, 84.6,

61.4, 55.5, 29.7, 25.2, and 24.2 (Note: 18 peaks were observed for the 19 unique carbons, in which 1 peak was not observed due to broadening). HRMS (APCI/TOF) m/z : $[M]^-$ Calcd for $C_{45}H_{53}^{10}B_2NO_9$ 771.3985; Found 771.3962.

***N*-(2,6-Diisopropyl-4-methoxyphenyl)-2,7-dimesityl-9,10-dimethoxypyrene-4,5-dicarboximide (7):**

Compound **6** (3.00 g, 3.88 mmol) and SPhos Pd G2 (140 mg, 0.194 mmol) were placed in a three-neck flask, and the flask was purged with argon. Here, SPhos Pd G2 is a commercially available 2nd generation SPhos precatalyst, that is, chloro(2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II). Then, to the mixture were added anhydrous toluene (78 mL), mesityl bromide (1.74 mL, 11.6 mmol), aqueous K_2CO_3 solution (2.0 M, 39 mL), and methyltrioctylammonium chloride (0.16 g, 0.39 mmol). The reaction mixture was stirred at 100 °C for 1.5 h and then diluted with dichloromethane. After washing with water, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: hexane/dichloromethane, 1:1) to obtain **7** (2.77 g, 3.65 mmol, 94%) as an orange solid.

1H NMR ($CDCl_3$, r.t., 600 MHz): δ / ppm = 9.24 (s, 2H), 8.55 (s, 2H), 7.07 (s, 4H), 6.86 (s, 2H), 4.23 (s, 6H), 3.91 (s, 3H), 2.94 (sept, J = 6.6 Hz, 2H), 2.42 (s, 6H), 2.10 (s, 12H), and 1.22 (d, J = 6.6 Hz, 12H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t., 151 MHz): δ / ppm = 170.1, 160.8, 149.4, 145.0, 141.1, 138.7, 137.3, 136.1, 128.9, 128.6, 128.5, 124.9, 124.7, 124.4, 124.0, 119.9, 109.6, 61.5, 55.4, 29.7, 24.2, 21.31, and 21.26. HRMS (APCI/TOF) m/z : $[M]^+$ Calcd for $C_{51}H_{51}NO_5$ 757.3762; Found 757.3757.

2,7-Bis(3,5-di-*tert*-butylphenyl)-*N*-(2,6-diisopropyl-4-methoxyphenyl)-9,10-dimethoxypyrene-4,5-dicarboximide (8):

Compound **6** (155 mg, 0.200 mmol) and SPhos Pd G2 (7.2 mg, 0.010 mmol), and 1-bromo-3,5-di-*tert*-butylbenzene (162 mg, 0.600 mmol) were placed in a three-neck flask, and the flask was purged with argon. Then, to the mixture were added anhydrous toluene (4.0 mL), aqueous K₂CO₃ solution (2.0 M, 2.0 mL), and methyltriocetylammmonium chloride (1 drop). The reaction mixture was stirred at 100 °C for 3 h and then diluted with dichloromethane. After washing with water, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: hexane/dichloromethane, 2:1) to obtain **8** (152 mg, 0.170 mmol, 85%) as an orange solid.

¹H NMR (CDCl₃, r.t., 600 MHz): δ / ppm = 9.81 (d, *J* = 1.8 Hz, 2H), 9.06 (d, *J* = 1.8 Hz, 2H), 7.93 (d, *J* = 1.2 Hz, 4H), 7.70 (t, *J* = 1.5 Hz, 2H), 6.99 (s, 2H), 4.42 (s, 6H), 3.99 (s, 3H), 3.10 (sept, *J* = 6.9 Hz, 2H), 1.58 (s, 36H), and 1.36 (d, *J* = 6.6 Hz, 12H); ¹³C{¹H} NMR (CDCl₃, r.t., 151 MHz): δ / ppm = 170.4, 161.0, 151.8, 149.4, 145.3, 142.2, 140.6, 129.1, 128.7, 125.0, 124.5, 123.0, 122.3, 121.7, 119.8, 109.9, 61.5, 55.5, 35.3, 31.8, 29.8, and 24.2 (Note: 22 peaks were observed for the 23 unique carbons, in which 2 peaks were overlapped). HRMS (APCI/TOF) *m/z*: [*M*][−] Calcd for C₆₁H₇₁NO₅ 897.5338; Found 897.5321.

***N*-(4-Hydroxy-2,6-diisopropylphenyl)-2,7-dimesityl-9,10-dioxo-9,10-dihydropyrene-4,5-dicarboximide (**9**):**

Compound **7** (2.74 g, 3.62 mmol) was placed in a three-neck flask, and the flask was purged with argon. Anhydrous dichloromethane (160 mL) was added to the flask, and the solution was cooled to −78 °C. Then, 1.0 M boron tribromide solution in dichloromethane (20 mL, 20 mmol) was added dropwise, and the mixture was allowed to warm to room temperature with stirring. After 15 h, the reaction was quenched with water at 0 °C, and the mixture was extracted with dichloromethane. To the organic layer was added silver(I) oxide (3.02 g, 13.0 mmol), and the reaction mixture was sonicated for 10 min at room temperature. The resultant mixture was filtered through a Celite pad, and the filtrate was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: dichloromethane) to obtain **9** (1.91 g, 2.67 mmol, 74%) as an orange solid.

¹H NMR (CDCl₃, r.t., 600 MHz): δ / ppm = 9.29 (d, *J* = 1.2 Hz, 2H), 8.55 (d, *J* = 1.8 Hz, 2H), 7.02 (s, 4H), 6.77 (s, 2H), 5.18 (s, 1H), 2.81 (sept, *J* = 6.9 Hz, 2H), 2.37 (s, 6H), 2.10 (s, 12H), and 1.17 (d, *J* = 6.6 Hz, 12H); ¹³C{¹H} NMR (CDCl₃, r.t., 151 MHz): δ / ppm = 179.8, 169.0, 157.2, 149.6, 143.7, 138.1, 136.1, 135.6, 134.9, 134.4, 130.5, 130.4, 128.8, 128.2, 126.3, 119.2, 111.4, 29.6, 24.1, 21.2, and 21.1. HRMS (APCI/TOF) *m/z*: [*M*]⁺ Calcd for C₄₈H₄₃NO₅ 713.3136; Found 713.3132.

2,7-Bis(3,5-di-*tert*-butylphenyl)-*N*-(4-hydroxy-2,6-diisopropylphenyl)-9,10-dioxo-9,10-dihydropyrene-4,5-dicarboximide (10**):**

Compound **8** (152 mg, 0.169 mmol) was placed in a three-neck flask, and the flask was purged with argon. Anhydrous dichloromethane (8.5 mL) was added to the flask, and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. Then, 1.0 M boron tribromide solution in dichloromethane (0.93 mL, 0.93 mmol) was added dropwise, and the mixture was allowed to warm to room temperature with stirring. After 6 h, the reaction was quenched with water at $0\text{ }^{\circ}\text{C}$, and the mixture was extracted with dichloromethane. To the organic layer was added silver(I) oxide (141 mg, 0.608 mmol), and the reaction mixture was sonicated for 10 min at room temperature. The resultant mixture was filtered through a Celite pad, and the filtrate was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (eluent: dichloromethane) to obtain **10** (91 mg, 0.11 mmol, 63%) as an orange solid.

^1H NMR (CDCl_3 , r.t., 600 MHz): δ / ppm = 9.73 (d, J = 1.8 Hz, 2H), 8.98 (d, J = 2.4 Hz, 2H), 7.69 (d, J = 1.8 Hz, 4H), 7.60 (t, J = 1.5 Hz, 2H), 6.83 (s, 2H), 5.27 (s, 1H), 2.87 (sept, J = 6.9 Hz, 2H), 1.45 (s, 36H), and 1.23 (d, J = 7.2 Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , r.t., 151 MHz): δ / ppm = 179.9, 169.3, 157.4, 152.2, 149.6, 144.1, 137.9, 132.4, 131.9, 130.5, 130.4, 128.3, 126.5, 123.4, 122.0, 119.0, 111.5, 35.3, 31.7, 29.7, and 24.2. HRMS (APCI/TOF) m/z : $[M]^-$ Calcd for $\text{C}_{58}\text{H}_{63}\text{NO}_5$ 853.4712; Found 853.4722.

***N*-(4-Hydroxy-2,6-diisopropylphenyl)-2,7-dimesitylphenanthro[4,5-*abc*]phenazine-4,5-dicarboximide (Wing1-OH):**

Compound **9** (128 mg, 0.180 mmol) and *o*-phenylenediamine (20 mg, 0.18 mmol) were placed in a Schlenk flask, and the flask was purged with argon. Then, chloroform (4.7 mL) and acetic acid (2.8 mL) were added to the flask and the mixture was stirred at $70\text{ }^{\circ}\text{C}$. After 12 h, the solvent was evaporated under reduced pressure, and the crude product was purified by silica-gel column chromatography (eluent: chloroform) to afford

Wing1-OH (115 mg, 81%) as a yellow solid. Slow evaporation of CDCl_3 solution of **Wing1-OH** gave yellow crystals suitable for the single crystal X-ray diffractometry.

^1H NMR (CDCl_3 , 60°C , 600 MHz): δ / ppm = 9.72 (d, J = 1.8 Hz, 2H), 9.41 (d, J = 1.2 Hz, 2H), 8.34 (m, 2H), 7.89 (m, 2H), 7.08 (s, 4H), 6.78 (s, 2H), 4.82 (s, 1H), 2.94 (sept, J = 6.9 Hz, 2H), 2.43 (s, 6H), 2.16 (s, 12H), and 1.21 (d, J = 7.2 Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 60°C , 151 MHz): δ / ppm = 169.9, 157.1, 150.0, 143.0, 142.9, 142.3, 138.4, 137.5, 136.2, 130.5, 130.4, 129.9, 129.0, 128.69, 128.64, 127.9, 125.5, 120.2, 111.3, 29.7, 24.1, 21.29, and 21.25 (Note: 23 peaks were observed for the 24 unique carbons, in which 2 peaks were overlapped). HRMS (APCI/TOF) m/z : $[M]^-$ Calcd for $\text{C}_{54}\text{H}_{47}\text{N}_3\text{O}_3$ 785.3623; Found 785.3650.

COT-fused *N*-(4-hydroxy-2,6-diisopropylphenyl)-2,7-dimesitylphenanthro[4,5-*abc*]phenazine-4,5-dicarboximide dimer (FLAP1-OH):

Compound **9** (1.53 g, 2.14 mmol) and **4** (440 mg, 1.07 mmol) was placed in a three-neck flask, and the flask was purged with argon. Then, 1,2-dichloroethane (DCE, 15 mL) and acetic acid (9 mL) were added to the flask and the mixture was stirred at 95°C . After 22 h, the solvent was evaporated under reduced pressure, and the resultant solid was washed with dichloromethane. The crude product was purified by reprecipitation from the mixture of chloroform and hexane for three times to afford **FLAP1-OH** (1.21 g, 0.747 mmol, 70%) as a yellow solid.

^1H NMR (CDCl_3 , 60°C , 600 MHz): δ / ppm = 9.66 (s, 4H), 9.33 (d, J = 1.2 Hz, 4H), 8.12 (s, 4H), 7.33 (s, 4H), 6.99 (s, 8H), 6.74 (s, 4H), 4.71 (d, J = 1.8 Hz, 2H), 2.88 (sept, J = 6.6 Hz, 4H), 2.40 (s, 12H), 2.06 (s, 24H), and 1.17 (d, J = 7.2 Hz, 24H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 /trichloroacetic acid, r.t., 151 MHz): δ / ppm = 170.0, 156.8, 149.9, 143.1, 141.8, 141.7, 138.8, 137.9, 137.1, 135.8, 133.8, 130.5, 129.9, 128.6, 128.5, 128.0, 127.2, 127.1, 125.6, 119.3, 111.6, 29.7, 25.1, 21.3 and 21.2 (Note: due to the low solubility of **FLAP1-OH**, trichloroacetic acid was added to dissolve it as a protonated species). HRMS (MALDI/TOF) m/z : $[M]^+$ Calcd for $\text{C}_{112}\text{H}_{94}\text{N}_6\text{O}_6$ 1618.7229; Found 1618.727. UV-visible absorption (in CH_2Cl_2): λ_{max} (ϵ / $\text{M}^{-1} \text{cm}^{-1}$) = 279 (6.6×10^4) and 415 nm (5.3×10^4). Fluorescence (in CH_2Cl_2 , λ_{ex} = 365 nm): λ_{max} = 518 and 555 nm; Φ_{F} = 0.42; τ_{F} = 2.4 ns (λ_{obs} = 518 nm).

COT-fused 2,7-bis(3,5-di-*tert*-butylphenyl)-*N*-(4-hydroxy-2,6-diisopropylphenyl)phenanthro[4,5-*abc*]phenazine-4,5-dicarboximide dimer (FLAP1-OH'):

Compound **10** (91 mg, 0.11 mmol) and **4** (22 mg, 0.053 mmol) was placed in a three-neck flask, and the flask was purged with argon. Then, 1,2-dichloroethane (DCE, 2.8 mL) and acetic acid (1.6 mL) were added to the flask and the mixture was stirred at 95 °C. After 23.5 h, the solvent was evaporated under reduced pressure, and the resultant solid was dissolved into dichloromethane and washed with aqueous NaHCO₃ solution. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (eluent: chloroform/ethyl acetate, 50:1) to obtain **FLAP1-OH'** (61 mg, 0.032 mmol, 60%) as a yellow solid. Slow diffusion of *n*-octane into a benzonitrile solution of **FLAP1-OH'** gave yellow crystals suitable for the single crystal X-ray diffractometry.

¹H NMR (CDCl₃, r.t., 600 MHz): δ / ppm = 10.00 (d, *J* = 1.8 Hz, 4H), 9.77 (d, *J* = 1.8 Hz, 4H), 8.25 (s, 4H), 8.74 (d, *J* = 1.8 Hz, 8H), 7.60 (t, *J* = 1.8 Hz, 4H), 7.41 (s, 4H), 6.78 (s, 4H), 4.93 (s, 2H), 2.92 (sept, 6.6 Hz, 4H), 1.49 (s, 72H), and 1.20 (d, *J* = 6.6 Hz, 24H); ¹³C{¹H} NMR (CDCl₃, r.t., 151 MHz): δ / ppm = 170.1, 157.1, 151.9, 149.8, 143.2, 142.9, 141.6, 139.9, 139.7, 133.6, 130.2, 129.2, 128.5, 127.9, 126.5, 126.3, 125.5, 122.8, 122.5, 119.7, 111.4, 35.3, 31.8, 29.7, and 24.1. HRMS (MALDI/TOF) *m/z*: [*M*+H]⁺ Calcd for C₁₃₂H₁₃₅N₆O₆ 1900.0438; Found 1900.052.

COT-fused *N*-(4-butylcarbamoyloxy-2,6-diisopropylphenyl)-2,7-dimesitylphenanthro[4,5-*abc*]phenazine-4,5-dicarboximide dimer (FLAP1-BC):

FLAP1-OH (130 mg, 0.080 mmol) was placed in a Schlenk flask, and the flask was purged with argon. Then, anhydrous toluene (8.0 mL), butyl isocyanate (0.45 mL, 4.0 mmol), and triethylamine (0.56 mL, 4.0 mmol) were added, and the mixture was stirred at 110 °C for 9 h. The solvent was evaporated under reduced pressure, and the residue was purified by silica-gel column chromatography (eluent: chloroform/ethyl acetate, 100:1) to give **FLAP1-BC** (116 mg, 0.064 mmol, 80%) as a yellow solid.

^1H NMR (tetrachloroethane- d_2 , 100 °C, 600 MHz): δ / ppm = 9.66 (s, 4H), 9.37 (s, 4H), 8.21 (s, 4H), 7.38 (s, 4H), 7.13 (s, 4H), 7.11 (s, 8H), 4.96 (s, 2H), 3.35 (m, 4H), 2.97 (sept, J = 6.9 Hz, 4H), 2.47 (s, 12H), 2.18 (s, 24H), 1.65 (m, 4H), 1.49 (m, 4H), 1.23 (d, J = 7.2 Hz, 24H), and 1.03 (t, J = 7.2 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (tetrachloroethane- d_2 , 50 °C, 151 MHz): δ / ppm = 169.1, 153.9, 152.3, 149.1, 142.6, 141.7, 141.3, 139.3, 137.7, 137.3, 135.7, 133.2, 129.9, 128.8, 128.6, 128.4, 128.2, 128.1, 127.3, 125.0, 123.5, 116.8, 40.9, 31.7, 29.4, 23.8, 21.1, 21.0, 19.8, and 13.6. HRMS (MALDI/TOF) m/z : $[M+H]^+$ Calcd for $\text{C}_{112}\text{H}_{113}\text{N}_8\text{O}_8$ 1817.8676; Found 1817.867.

Figure S2.3. (a) ^1H NMR and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** in CDCl_3 at room temperature. Peaks marked with asterisks indicate residual solvents.

Figure S2.5. (a) ^1H NMR and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **Wing1-H** in tetrachloroethane- d_2 at 120 °C. Peaks marked with asterisks indicate residual solvents or impurities.

Figure S2.6. (a) ^1H NMR spectra of **FLAP1-H** in tetrachloroethane- d_2 at 120 °C and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **FLAP1-H** in CDCl_3 /trichloroacetic acid at room temperature. Peaks marked with asterisks indicate residual solvents or impurities, and red circles correspond to peaks derived from trichloroacetic acid.

Figure S2.8. (a) ^1H NMR and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **6** in CDCl_3 at room temperature. Peaks marked with asterisks indicate residual solvents.

Figure S2.10. (a) ^1H NMR and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **8** in CDCl_3 at room temperature. Peaks marked with asterisks indicate residual solvents or impurities.

Figure S2.13. (a) ¹H NMR and (b) ¹³C{¹H} NMR spectra of **Wing1-OH** in CDCl₃ at 60 °C. Peaks marked with asterisks indicate residual solvents or impurities.

Figure S2.14. (a) ^1H NMR spectra of **FLAP1-OH** in CDCl_3 at 60 °C and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **FLAP1-OH** in $\text{CDCl}_3/\text{trichloroacetic acid}$ at room temperature. Peaks marked with asterisks indicate residual solvents or impurities, and red circles correspond to peaks derived from trichloroacetic acid.

Figure S2.15. (a) ^1H NMR and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **FLAP1-OH'** in CDCl_3 at room temperature. Peaks marked with asterisks indicate residual solvents or impurities.

Figure S2.16. (a) ¹H NMR spectra of FLAP1-BC in tetrachloroethane-*d*₂ at 100 °C and (b) ¹³C{¹H} NMR spectra of FLAP1-BC in tetrachloroethane-*d*₂ at 50 °C. Peaks marked with asterisks indicate residual solvents or impurities.

Figure S2.17. HR-APCI-TOF mass spectra of **2** (top: observed, bottom: simulated).

Figure S2.18. HR-APCI-TOF mass spectra of **3** (top: observed, bottom: simulated).

Figure S2.19. HR-APCI-TOF mass spectra of **Wing1-H** (top: observed, bottom: simulated).

Figure S2.20. HR-APCI-TOF mass spectra of **FLAP1-H** (top: observed, bottom: simulated).

Figure S2.21. HR-APCI-TOF mass spectra of **5** (top: observed, bottom: simulated).

Figure S2.22. HR-APCI-TOF mass spectra of **6** (top: observed, bottom: simulated).

Figure S2.23. HR-APCI-TOF mass spectra of **7** (top: observed, bottom: simulated).

Figure S2.24. HR-APCI-TOF mass spectra of **8** (top: observed, bottom: simulated).

Figure S2.25. HR-APCI-TOF mass spectra of **9** (top: observed, bottom: simulated).

Figure S2.26. HR-APCI-TOF mass spectra of **10** (top: observed, bottom: simulated).

Figure S2.28. HR-MALDI-TOF mass spectra of **FLAP1-OH** (top: observed, bottom: simulated).

Figure S2.29. HR-MALDI-TOF mass spectra of FLAP1-OH' (top: observed, bottom: simulated).

Figure S2.30. HR-MALDI-TOF mass spectra of FLAP1-BC (top: observed, bottom: simulated).

3. X-ray crystallographic analysis

Figure S3.1. Crystal structure of **FLAP1-OH'** viewed from different directions. The COT bending angles (see Figure S5.2 for the definition) are shown in (b). Hydrogen atoms except for OH groups and disordered groups with low occupancy are omitted for clarity. Thermal ellipsoids are scaled to 50% probability.

Figure S3.2. Crystal structure of **Wing1-OH** viewed from different directions. Hydrogen atoms except for OH groups and disordered solvent molecules with low occupancy are omitted for clarity. Thermal ellipsoids are scaled to 50% probability.

Table S3.1. Crystal data of **Wing1-OH** and **FLAP1-OH'**.

	Wing1-OH	FLAP1-OH' ^[a]
Formula	C ₅₄ H ₄₇ N ₃ O ₃ · 3(CHCl ₃)	C ₁₃₂ H ₁₃₄ N ₆ O ₆
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
<i>a</i> /Å	13.2643(5)	15.4670(5)
<i>b</i> /Å	14.5232(4)	20.2490(7)
<i>c</i> /Å	15.8069 (4)	27.4203(9)
α /°	80.507(2)	87.637(3)
β /°	86.172 (3)	87.0623)
γ /°	64.941(3)	80.183(3)
<i>V</i> /Å ³	2720.63(16)	8446.3(5)
<i>Z</i>	2	2
<i>T</i> /K	93	93
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0942	0.0985
<i>wR</i> ₂ (all data)	0.2679	0.3328
Completeness	0.971	0.980
GOF	1.068	1.015
CCDC No.	2122594	2122595

[a] Contributions to the scattering arising from the presence of disordered solvent molecules were removed by the SQUEEZE program in the PLATON software package.^[S6]

4. Photophysical properties of the force probe in solution

4.1 Absorption, fluorescence (FL) spectra at room temperature

Figure S4.1. Photophysical properties of **FLAP1-H** in solution. (a) Concentration dependence of the absorption spectra in toluene. (b) Concentration dependence of the FL spectra in toluene ($\lambda_{\text{ex}} = 389 \text{ nm}$).

Figure S4.2. Photophysical properties of **Wing1-H** in solution. (a) Concentration dependence of the absorption spectra in toluene. (b) Concentration dependence of the FL spectra in toluene ($\lambda_{\text{ex}} = 378 \text{ nm}$).

Figure S4.3. Absorption and FL spectra of **FLAP1-BC** in toluene and PMMA.

4.2 Variable temperature FL/excitation spectra and details of the Stevens–Ban plot

Figure S4.4. Variable temperature excitation spectra of **FLAP1-H** monitored at different FL wavelength in toluene.

Figure S4.5. (a) Variable temperature FL spectra ($\lambda_{\text{ex}} = 389 \text{ nm}$) and (b) variable temperature excitation spectra ($\lambda_{\text{FL}} = 467 \text{ nm}$) of **Wing1-H** monitored at different FL wavelength in toluene.

Details of the Stevens–Ban plot

Figure S4.6. A kinetic model of the excited-state planarization of the flapping molecules.

The simple kinetic analysis in the steady-state approximation based on Figure S4.6 affords the relationship between the ratio of the FL quantum yield and the rate constants (Eq. 1).^[S7]

$$\frac{\Phi_P}{\Phi_V} = \frac{k_r^P}{k_r^V} \cdot \frac{k_1}{k_{-1} + k_r^P + k_{nr}^P} \quad (1)$$

The temperature dependence of the planarization dynamics can be described as follows:

$$K_{eq} = \frac{k_1}{k_{-1}} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (2)$$

$$k_1 = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

By assuming only the planarization dynamics depends on temperature, Eq. 1 can be transformed into

$$\ln \frac{\Phi_P}{\Phi_V} = \ln \frac{k_r^P}{k_r^V} - \ln \left[\exp\left(\frac{\Delta G}{RT}\right) + (k_r^P + k_{nr}^P) A \exp\left(\frac{E_a}{RT}\right) \right] \quad (4)$$

When the temperature-independent terms are written as constants (a and b), Eq. 4 is described as below:

$$\ln \frac{\Phi_P}{\Phi_V} = -\ln \left[a \exp\left(\frac{\Delta H}{R} \cdot \frac{1}{T}\right) + b \exp\left(\frac{E_a}{R} \cdot \frac{1}{T}\right) \right] \quad (5)$$

The left-hand side contains the ratio of the FL quantum yields of the V-shaped and the planar form of **FLAP1-H**, but since the shape of FL spectra of both species are different and overlapped, the quantum yield ratio cannot be directly calculated. Therefore, we performed the FL spectral decomposition using the spectral shape of the anthracene-based FLAP (**FLAP**) as a reference.

Figure S4.7 Chemical structure of **FLAP** and FL spectrum of **FLAP** in CH_2Cl_2 fitted with Lorentz functions.

Figure S4.7 shows the fluorescence spectrum of **FLAP** in CH_2Cl_2 , which almost completely planarizes in the S_1 and exhibits the characteristic FL spectrum from the planar conformation.^[S8] Since this FL spectrum can be well described as a sum of Lorentz functions (Eq. 6), we assumed that Lorentz functions could also represent the contribution of the planar form of **FLAP1-H**. This assumption can be rationalized because a characteristic FL spectrum similar to that of **FLAP** is observed when **SPU1** is stretched (Figure 6c in the main text). Then, the remaining V-shaped contributions of **FLAP1-H** were approximated by a sum of log-normal distribution functions (Eq. 7) according to the literature.^[S9] Finally, the obtained FL spectra of **FLAP1-H** were approximated by Eq. 8, and the FL quantum yield ratio was estimated by the area ratio of each function. Figure S4.9 demonstrates the fitting results at the representative temperatures in the Stevens–Ban plot.

$$f_i(\tilde{\nu}) = I_i \cdot \frac{w_i^2}{4(\tilde{\nu} - \tilde{\nu}_{0i})^2 + w_i^2} \quad (6)$$

$$g_i(\tilde{\nu}) = I_i \exp \left\{ -\ln 2 \left[a_i^{-1} \ln \left(\frac{2(\tilde{\nu} - \tilde{\nu}_{0i}) \sinh a_i}{w_i} + 1 \right) \right]^2 \right\} \quad (7)$$

$$F(\tilde{\nu}) = \sum_{i=1}^3 f_i(\tilde{\nu}) + \sum_{j=1}^2 g_j(\tilde{\nu}) \quad (8)$$

Figure S4.8 Parameters that characterize the shape of fitting functions: I_i = intensity, w_i = full width at half maximum, $\tilde{\nu}_{0i}$ = peak wavenumber, a_i = asymmetry parameter ($a_i = -0.5$ was selected in the figure as an example. For larger $|a_i|$, the function becomes more asymmetric).

Figure S4.9. Stevens–Ban plot of FLAP1-H constructed from FL spectra measured in toluene, and the fitting results by Eq. 8 at the representative temperatures (a–f).

4.3 Fluorescence lifetime analysis

The fluorescence lifetime of **FLAP1-H** and **Wing1-H** was measured by fitting FL decay profiles ($\lambda_{\text{ex}} = 405 \text{ nm}$) with single- or double-exponential functions. The goodness of fit was evaluated by χ^2 , and a double-exponential model provided better results for **FLAP1-H** (Table S4.1) than a single-exponential function (Table S4.2). Short-lived components ($\tau_1 \sim 0.1\text{--}0.2 \text{ ns}$) may originate from planarization dynamics in the excited state. The amplitude A_1 of the short-lifetime component ($\tau_1 \sim 0.1\text{--}0.2 \text{ ns}$) was obtained as negative values at the longer fluorescence wavelengths. This negative amplitude would correspond to the rise of the long-wavelength FL signals, which suggests that it takes around $0.1\text{--}0.2 \text{ ns}$ for the excited bent **FLAP1-H** molecule to planarize in S_1 and start to emit the long-wavelength fluorescence. After reaching the equilibrium in S_1 , population of the both V-shaped and planar form decreased in the lifetime of 2.3 ns (τ_2).

Table S4.1. FL lifetime of **FLAP1-H** in toluene fitted with a double-exponential function^[a]

$\lambda_{\text{FL}} / \text{nm}$	χ^2	τ_1 / ns	τ_2 / ns	A_1	A_2
460	0.98	0.19	2.3	530	1440
480	1.13	0.09	2.3	−2080	1590
500	1.08	0.14	2.3	−1970	1640
520	1.04	0.18	2.3	−2130	1740
540	0.98	0.15	2.3	−1590	1650
560	1.12	0.16	2.3	−1690	1660

[a] $f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$

Table S4.2. FL lifetime of **FLAP1-H** and **Wing1-H** in toluene fitted with a single-exponential function

	$\lambda_{\text{FL}} / \text{nm}$	χ^2	τ / ns
FLAP1-H	460	3.02	2.2
	480	2.15	2.3
	500	2.21	2.3
	520	1.68	2.3
	540	2.60	2.4
	560	3.92	2.3
Wing1-H	467	1.20	9.5

Figure S4.10. FL decay profiles of (a) **FLAP1-H** and (b) **Wing1-H** in toluene.

4.4 Solvent dependence of absorption/FL spectra and details of the Lippert–Mataga plot

Figure S4.11. (a) Absorption and (b) FL spectra of **FLAP1-H** measured in different solvents. Figure (c) and (d) are the corresponding absorption and FL spectra plotted in wavenumber units.

Figure S4.12. (a) Absorption and (b) FL spectra of **Wing1-H** measured in different solvents. Figure (c) and (d) are the corresponding absorption and FL spectra plotted in wavenumber units.

Table S4.3. Optical properties of **FLAP1-H** measured in different solvents

	Φ_{FL}	$\lambda_{\text{abs}} / \text{nm}$ ($\tilde{\nu}_{\text{abs}} / \text{cm}^{-1}$)	$\lambda_{\text{FL,V}} / \text{nm}^{[\text{a}]}$ ($\tilde{\nu}_{\text{FL,V}} / \text{cm}^{-1}$)	Stokes shift $\Delta\tilde{\nu}_V / \text{cm}^{-1}$	$\lambda_{\text{FL,P}} / \text{nm}^{[\text{b}]}$ ($\tilde{\nu}_{\text{FL,P}} / \text{cm}^{-1}$)	Stokes shift $\Delta\tilde{\nu}_P / \text{cm}^{-1}$
Cyclohexane	0.38	443 (22600)	454 (22000)	600	518 (19320)	3280
Toluene	0.44	447 (22360)	479 (20640)	1720	523 (19100)	3260
Bu ₂ O	0.41	444 (22550)	460 (20900)	1650	519 (19270)	3280
CPME	0.41	444 (22520)	463 (20810)	1710	521 (19180)	3340
CHCl ₃	0.40	445 (22420)	482 (20490)	1930	525 (19050)	3370
THF	0.43	444 (22510)	486 (20400) ^[c]	2110	524 (19070)	3440
CH ₂ Cl ₂	0.40	445 (22470)	484 (20450)	2020	525 (19100)	3370
Acetone	0.16	443 (22570)	478 (20510)	2060	521 (19160)	3410
DMF	0.42	446 (22410)	493 (20010) ^[c]	2400	527 (18940)	3470
DMSO	0.08	450 (22250)	505 (19690) ^[c]	2560	531 (18780)	3470

[a] FL maxima around 450–500 nm attributed to the FL from the V-shaped form. [b] FL maxima around 525 nm assigned to the FL from the planar structure. [c] FL maxima of the shoulder peaks were estimated using Eq. 8.

Table S4.4. Optical properties of **Wing1-H** measured in different solvents

	Φ_{FL}	$\lambda_{\text{abs}} / \text{nm}$ ($\tilde{\nu}_{\text{abs}} / \text{cm}^{-1}$)	$\lambda_{\text{FL}} / \text{nm}$ ($\tilde{\nu}_{\text{FL}} / \text{cm}^{-1}$)	Stokes shift $\Delta\tilde{\nu} / \text{cm}^{-1}$
Cyclohexane	0.18	428 (23390)	456 (21930)	1460
Toluene	0.36	431 (23230)	468 (21120)	2110
Bu ₂ O	0.23	428 (23390)	458 (21810)	1580
CPME	0.27	428 (23360)	460 (21650)	1710
CHCl ₃	0.37	430 (23260)	492 (19980)	3280
THF	0.30	428 (23360)	473 (20920)	2440
CH ₂ Cl ₂	0.37	429 (23310)	493 (19980)	3330
Acetone	0.31	427 (23450)	481 (20530)	2920
DMF	0.41	429 (23310)	492 (19940)	3370
DMSO	0.03	430 (23230)	506 (19570)	3660

Details of the Lippert–Mataga plot

The solvent polarity effect on the absorption/FL spectra of **FLAP1-H** and **Wing1-H** was quantitatively estimated by Lippert–Mataga plots (Figure S4.13), in which Stokes shifts $\Delta\tilde{\nu}$ were plotted against the solvent polarity parameter Δf defined as follows:

$$\Delta f = \frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad (9)$$

where ϵ_r is relative permittivity, and n is refractive index of the solvents. From the well-known Lippert–Mataga equation (Eq. 10),^[S10] the difference in dipole moments between the ground state (μ_g) and the excited state (μ_e) was calculated for **Wing1-H** and the V-shaped form of **FLAP1-H**.

$$\Delta\tilde{\nu} = \frac{1}{hc} \cdot \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 a^3} \cdot \Delta f + \text{const.} \quad (10)$$

The parameter a is the Onsager's cavity radius, which was estimated to be 5.55 Å for **Wing1-H** and 7.02 Å for **FLAP1-H** by DFT calculations (S_0 , PBE0/6-31+G(d)/PCM(toluene)). Since the coefficient of Δf in Eq. 10 corresponds to the slope b in Figure S4.13, the difference in dipole moments ($\mu_e - \mu_g$) was calculated to be 10 Debye for **Wing1-H** and 12 Debye for the V-shaped form of **FLAP1-H**, suggesting the similar excited-state electronic character bearing a large excited-state dipole moment.

Figure S4.13. Lippert–Mataga plots of **Wing1-H** (gray triangles) and **FLAP1-H** (blue circles for the V-shaped form, and green squares for the planar form) fitted with a linear function $y = a + bx$.

5. Density functional theory (DFT) calculations

DFT calculations of the isolated molecules were performed using the Gaussian 16 program,^[S11] and Kohn–Sham orbitals are displayed by the Avogadro program.^[S12] Model structures **FLAP1'** and **Wing1'** were calculated, which have hydrogen atoms in place of the 2,6-diisopropylphenyl groups of the corresponding molecules (Figure S5.1). The COT bending angle was defined as the dihedral angle between the C1–C2–C3 and C2–C3–C4 planes in Figure S5.2. Constrained geometry optimization was performed with the fixed COT bending angles using the ModRedundant keyword.

Figure S5.1. Structures of **FLAP1'** and **Wing1'**.

Figure S5.2. Definition of the COT bending angle θ used in the constrained geometry optimization.

5.1. Assignment of the absorption spectra in toluene

In Section 4.4, we confirmed the solvent dependence of the Stokes shifts of **FLAP1-H** and **Wing1-H**, and we will subsequently discuss the reasons for this dependence by DFT calculations. The calculation conditions were selected based on the experimental absorption spectra and excited-state behaviors (See details in Section 5.5 of SI). For **Wing1-H**, the transition energies and oscillator strengths calculated by TD-DFT calculations well reproduced the absorption spectrum (Figure S5.3a). In particular, the absorption maximum with the longest wavelength can be well described by the HOMO–LUMO transition from HOMO mainly distributed on the pyrene moiety (PYR) to LUMO localized on the five-membered imide ring (IMD). The transitions with higher energies involve the HOMO–1 and LUMO+1 localized on the phenazine moiety (PZH) (Figure S5.3c, left side). Furthermore, although the agreement of transition energies and oscillator strengths is not as perfect as **Wing1-H**, the longest wavelength absorption of **FLAP1-H** is similarly described by the transition from the pyrene-distributed orbital to the imide-localized orbital.

Figure S5.3. Calculated oscillator strength (bars) and observed UV-visible absorption spectra (line) of (a) **Wing1'** and (b) **FLAP1'** in toluene. (c) Kohn-Sham molecular orbitals of **Wing1'** and **FLAP1'** in the S_0 optimized geometries and selected transition characters with non-zero oscillator strengths, calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level. H = HOMO, L = LUMO.

Table S5.1. Excitation energies and oscillator strengths of the $S_0 \rightarrow S_n$ ($n \leq 5$) transitions for the S_0 optimized **Wing1'** calculated at the TD-PBE0/6-31+G(d)/PCM(toluene) level

Transition	Excitation energy	Configurations	f
$S_0 \rightarrow S_1 (B_2)$	2.88 eV (431 nm)	HOMO $\rightarrow$ LUMO (96%)	0.1216
$S_0 \rightarrow S_2 (A_1)$	3.12 eV (397 nm)	HOMO $\rightarrow$ LUMO+1 (60%) HOMO-1 $\rightarrow$ LUMO (35%)	0.0661
$S_0 \rightarrow S_3 (A_1)$	3.27 eV (380 nm)	HOMO-1 $\rightarrow$ LUMO (57%) HOMO $\rightarrow$ LUMO+1 (38%)	0.4382
$S_0 \rightarrow S_4 (B_1)$	3.38 eV (367 nm)	HOMO-3 $\rightarrow$ LUMO+2 (98%)	0.0018
$S_0 \rightarrow S_5 (B_2)$	3.47 eV (357 nm)	HOMO-1 $\rightarrow$ LUMO+1 (96%)	0.0226

Table S5.2. Excitation energies and oscillator strengths of the $S_0 \rightarrow S_n$ ($n \leq 5$) transitions for the S_0 optimized **FLAP1'** calculated at the TD-PBE0/6-31+G(d)/PCM(toluene) level

Transition	Excitation energy	Configurations	f
$S_0 \rightarrow S_1 (A_2)$	2.85 eV (434 nm)	HOMO $\rightarrow$ LUMO (58%) HOMO-1 $\rightarrow$ LUMO+1 (37%)	0
$S_0 \rightarrow S_2 (B_1)$	2.86 eV (434 nm)	HOMO $\rightarrow$ LUMO+1 (58%) HOMO-1 $\rightarrow$ LUMO (36%)	0.2205
$S_0 \rightarrow S_3 (B_2)$	2.92 eV (425 nm)	HOMO $\rightarrow$ LUMO+2 (79%) HOMO-1 $\rightarrow$ LUMO+3 (16%)	0.8369
$S_0 \rightarrow S_4 (A_1)$	3.03 eV (409 nm)	HOMO $\rightarrow$ LUMO+3 (38%) HOMO-1 $\rightarrow$ LUMO+2 (29%) HOMO-2 $\rightarrow$ LUMO+1 (19%)	0.0930
$S_0 \rightarrow S_5 (B_2)$	3.12 eV (397 nm)	HOMO-2 $\rightarrow$ LUMO (67%) HOMO-3 $\rightarrow$ LUMO+1 (22%)	0.3814

Figure S5.4. (a) Energy profiles of S_0 and vertically excited states (S_a – S_f) of **FLAP1'** calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level. Geometries are optimized in S_0 with the fixed COT bending angle. (b) Change in transition characters during the ground-state planarization. H = HOMO, L = LUMO.

5.2. Calculated geometries and structural parameters in S_0 and S_1

Figure S5.5. Bond lengths (Å) of **FLAP1'** based on the S_0 optimized geometry ($\theta = 41.9^\circ$) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure S5.6. Bond lengths (Å) of **FLAP1'** based on the S_1 optimized geometry (A'' state, $\theta = 39.5^\circ$ and 39.3°) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure S5.7. Bond lengths (Å) of FLAP1' based on the S_1 optimized geometry (A_2 state, $\theta = 0^\circ$) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure S5.8. Bond lengths (Å) of FLAP1' based on the S_1 optimized geometry (B_2 state, $\theta = 0^\circ$) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure S5.9. Bond lengths (Å) of **FLAP0'** based on the S_0 optimized geometry ($\theta = 41.0^\circ$) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure S5.10. Bond lengths (Å) of **FLAP0'** based on the S_1 optimized geometry ($\theta = 29.5^\circ$) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

Figure S5.11. Bond lengths (Å) of **FLAP0'** based on the S_1 optimized geometry ($\theta = 0^\circ$) calculated at the (TD-)PBE0/6-31+G(d)/PCM(toluene) level.

5.3. Selection of a calculation level for the interpretation of the observed FL spectra

To explain the dual FL behavior of **FLAP1-H** from a theoretical point of view, we considered the proper conditions for DFT calculations. First, we compared the S_1 energy profiles of the model compound **FLAP1'** under several calculation conditions (Figure S5.12 and S5.14). First, the TD-PBE0/6-31+G(d) level employed in previous calculations of anthracene-based FLAP^[S8] resulted in a double-well potential energy curve (Figure S5.12). However, under these conditions, the global energy minimum becomes a non-luminescent A_2 state ($f = 0$), and the oscillator strength does not agree with the experimental results. On the other hand, the bright B_2 state ($f \sim 0.8$), which reasonably explains the dual FL in the solution, was found at a higher energy level than that of the A_2 state. Therefore, we focused on the energy difference between the B_2 and A_2 states and the transition energy of the B_2 state to further examine the calculation conditions (Table S5.3).

Figure S5.13 summarizes the correlation between the calculation results and the fraction of Hartree–Fock (HF) exchange in the functional. As for the FL wavelengths, PBE0 was in the best agreement with the experimental results ($\lambda_{\text{FL}} = 523$ nm in toluene), while CAM-B3LYP underestimated the FL wavelength and the other functionals overestimated them (Figure S5.13a). Although the energy of the B_2 state approaches that of the A_2 state as the fraction of HF exchange decreases, no conditions were found under which the bright B_2 state is the most stable in the planar form. In the case of TPSSh, which reproduces the experimental results of the reported phenazine-based FLAP, the B_2 and A_2 states have almost the same energy. However, the energy barrier between the V-shaped and planar structures disappears, which is qualitatively incompatible with the experimental results (Figure S5.14c).

Since TD-DFT calculations sometimes give incorrect state orderings in $\pi\pi^*$ states even for the simple heteroaromatic systems, higher levels of theory such as double hybrid functionals, CC2, or ADC(2) are preferred.^[S13] In the case of **FLAP1'**, we tried to use the B2PLYP functional by the ORCA program,^[S14] but the S_1 calculations were difficult due to the computational cost. Therefore, we determined the calculation conditions by giving more importance to the agreement with the absorption spectra and the shape of the potential energy curves, regardless of the oscillator strength of the planar form. Finally, the TD-PBE0/6-31+G(d) level, together with the polarizable continuum model (PCM) for considering the solvent effect, reproduced the absorption spectrum of **Wing1-H** (Figure S5.3a) and the double-well S_1 potential of **FLAP1-H** (Figure S5.14d).

Figure S5.12. S_1 energy profiles of **FLAP1'** calculated at the TD-PBE0/6-31+G(d) level. See Figure S5.14e for details of the electronic configuration of each excited state.

Table S5.3. Attempted DFT calculations of **FLAP1'** for selecting optimal calculation conditions

Functional	HF exchange	Basis set	Additional conditions	$\Delta E = E(B_2) - E(A_2)$	$\lambda_{FL} (S_0 \rightarrow S_1(B_2))$
PBE0	25%	6-31+G(d)	—	3.6 kcal/mol	534 nm
		6-31+G(d)	D3BJ	3.6 kcal/mol	535 nm
		6-31+G(d)	PCM(toluene)	2.5 kcal/mol	547 nm
		def2-SVP	—	4.1 kcal/mol	528 nm
		D95+(d)	—	3.6 kcal/mol	536 nm
		Others ^[a]	—	SCF convergence failure	
M06	27%	6-31+G(d)	—	4.2 kcal/mol	539 nm
HSE06	25%	6-31+G(d)	—	2.4 kcal/mol	560 nm
X3LYP	21%	6-31+G(d)	—	3.1 kcal/mol	555 nm
B3LYP	20%	6-31+G(d)	—	2.8 kcal/mol	565 nm
		6-31+G(d)	PCM(toluene)	1.7 kcal/mol	579 nm
tHCTHhyb	15%	6-31+G(d)	—	1.8 kcal/mol	595 nm
O3LYP	11.61%	6-31+G(d)	—	1.2 kcal/mol	610 nm
TPSSh	10%	6-31+G(d)	—	0.7 kcal/mol	610 nm
CAM-B3LYP	19–65%	6-31+G(d)	—	9.0 kcal/mol	434 nm
Others ^[b]		6-31+G(d)	—	B_2 state was not found.	

[a] def2-SVPD, aug-cc-pVDZ, jul-cc-pVDZ, jun-cc-pVDZ. [b] TPSS, M06-L, M06-2X, BMK, BHandHLYP, ω B97X-D, LC- ω HPBE

Figure S5.13. Calculation results of **FLAP1'** in the planar form ($\theta = 0^\circ$) in relation to the fraction of HF exchange in the functionals: (a) the error of the estimated transition energy of the bright B_2 state from the observed fluorescence (523 nm) of **FLAP1-H** in the planar form in toluene, (b) the energy difference between the A_2 and B_2 states $\Delta E = E(B_2) - E(A_2)$.

Figure S5.14. (a–d) S₁ energy profiles of FLAP1' using different functionals. (e) Kohn–Sham orbitals and their energy levels of the V-shaped and planar form of FLAP1' (TD-PBE0/6-31+G(d)/PCM(toluene)). The B_{1u} and B_{3g} states in D_{2h} symmetry correspond to the B₂ and A₂ states in C_{2v} symmetry, and the orbital shapes of the B_{1u} state are almost the same as that of the B_{3g} state.

6. Synthesis and properties of the segmented polyurethanes (SPUs)

6.1. Synthesis and preparation of the SPU films

Figure S6.1. (a) Chemical structures of the FLAP dopants. (b) Synthesis of SPUs and photographs of the SPU films for stretching. (c) Chemical structure of the representative SPU (**SPU1**).

Synthesis of the segmented polyurethanes (SPUs) was performed according to the reported procedure.^[S15] Poly(tetrahydrofuran) (PTHF, $M_n \approx 1000$, 3.00 g, 3.00 mmol) was placed in a two-neck flask, which was dried under vacuum at 100 °C for 2 h. After cooling to room temperature, anhydrous THF (60 mL), the FLAP dopants (**FLAP0-OH** or **FLAP1-OH**, 1.5 μ mol), methylenediphenyl 4,4'-diisocyanate (MDI, 10.5 mmol, 2.63 g), and dibutyltin dilaurate (DBTDL, 6 drops) were added. The reaction mixture was stirred at room temperature for 3 h, and then a solution of 1,4-butanediol (BDO, 7.0 mmol, 0.63 mL) in anhydrous THF (20 mL) was added. After stirring 48 h at room temperature, the reaction was quenched by adding methanol (4 mL), and the mixture was further stirred for 30 min. The mixture was poured into ethanol (500 mL) to precipitate the polymer, which was collected by filtration. The obtained precipitates were dissolved into THF (300 mL) and filtrated. The filtrate was concentrated by evaporating half of the solvent and poured into hexane (400 mL) to reprecipitate the polymer. The precipitates were dried under vacuum to afford SPUs (**SPU0** or **SPU1**) as a very pale yellow solid. **SPU2** was synthesized without adding FLAP dopants.

Preparation of the films

The synthesized SPUs (5.0 g) was dissolved into anhydrous THF (50 mL) and casted into a stainless steel tray. **SPU1-BC** was prepared by adding **FLAP1-BC** (0.05 mol%) to the solution of **SPU2** before casting. After evaporation of THF under ambient conditions, the film was further dried under vacuum. Transparent specimens for the tensile tests were made by punching the SPU sheets with a dumbbell-shaped die cutter.

Average distance between the FLAP molecules in SPUs

The concentration of FLAP in SPUs calculated from the feed ratio is 0.24 $\mu\text{mol/g}$, which is equal to 0.22 $\mu\text{mol/cm}^3$ (density of SPUs: 1.1 g/cm^3). By converting this molar concentration to number density and then taking the reciprocal, the average volume occupied by a single FLAP molecule was calculated to be $7.5 \times 10^{-24} \text{ m}^3$. Therefore, by taking the cube root, the average distance between the FLAP molecules was determined to be 20 nm.

Figure S6.2. ^1H NMR spectrum of **SPU0** in $\text{THF-}d_8$ at room temperature. Peaks marked with asterisks indicate impurities.

Figure S6.3. ^1H NMR spectrum of **SPU1** in $\text{THF-}d_8$ at room temperature. Peaks marked with asterisks indicate impurities.

Figure S6.4. ^1H NMR spectrum of **SPU1-BC** in $\text{THF-}d_8$ at room temperature. Peaks marked with asterisks indicate impurities.

Figure S6.5. ^1H NMR spectrum of **SPU2** in $\text{THF-}d_8$ at room temperature. Peaks marked with asterisks indicate impurities.

6.2. Differential scanning calorimetry (DSC) analysis of the SPUs

DSC measurements of the SPU specimens were performed under N₂ atmosphere at a flow rate of 30 mL mm⁻¹. Programmed heating and cooling cycles are shown in Figure S6.6. DSC profiles are displayed in Figure S6.7 for the 2nd cooling (E→F) and heating (G→H) cycles. Each SPU sample was placed into an aluminum pan, covered with an aluminum cover, and then pressed with a designated tool. As a reference sample, a vacant pan was also pressed with the cover.

Figure S6.6. Programmed heating and cooling cycles in the DSC measurements of the SPUs.

Figure S6.7. DSC profiles of the segmented polyurethanes (SPUs).

6.3. Mechanical and optical properties of the SPUs during stretching

Figure S6.8. Stress–strain curves of the SPUs.

Table S6.1. Mechanical properties of the SPUs in the uniaxial tensile testing^[a]

	Rupture strain / %	Rupture stress / MPa	Toughness / MJ m ⁻³	Young's modulus / MPa
SPU0	512 ± 18	69 ± 3	134 ± 8	47 ± 6
SPU1	497 ± 27	65 ± 1	126 ± 5	59 ± 2
SPU1-BC	561 ± 12	68 ± 5	166 ± 13	71 ± 10
SPU2	534 ± 28	62 ± 8	149 ± 22	78 ± 3

[a] Values of average ± standard deviation of three specimens were shown.

Figure S6.9. FL spectral change during the tensile tests of the SPUs. FL spectra are normalized at each maximum.

Figure S6.10. FL ratiometric analysis of the SPUs plotted against strain and stress in the tensile tests. The results of the three measurements are superimposed.

Figure S6.11. FL spectral change during the tensile tests of **SPU0** before normalization. The red arrow indicates the increase of the scattered excitation light intensity during stretching.

Figure S6.12. Scattered excitation light intensity plotted against (a) stress and (b) strain. (c) A photograph of **SPU0** with cloudy white center at 500% strain under an ambient light.

7. Synthesis and properties of the crosslinked polyurethanes (PUs) before swelling

7.1. Synthesis and preparation of the crosslinked PU films

Figure S7.1. (a) Synthesis of PUs and photographs of the PU films for stretching. (b) Chemical structure of the representative PU (PU1).

Synthesis of the crosslinked polyurethanes (PUs) was performed according to the previous report.^[S3] Poly(tetrahydrofuran) (PTHF, $M_n \approx 650$, 5.95 g, 9.15 mmol) was placed in a two-neck flask, which was dried under vacuum at 100 °C for 2 h. After cooling to room temperature, anhydrous DMF (16 mL), the FLAP dopants (**FLAP0-OH** or **FLAP1-OH**, 1.5 μ mol), hexamethylene diisocyanate (HDI, 1.96 mL, 12.2 mmol), and triethanolamine (TEA, 0.27 mL, 2.0 mmol) were added. The mixture was stirred at 27 °C for 10 min, and then a 0.2 M solution of dibutyltin dilaurate in anhydrous THF (0.35 mL, 0.07 mmol) was added. After stirring at 27 °C for 2 min, the reaction mixture was poured into a custom-made mold of poly(tetrafluoroethylene) (PTFE) and polymerized under N_2 atmosphere at room temperature for 48 h. Next, the PU specimens were soaked in acetone for 4 hours and then in fresh acetone for 12 hours to remove DMF. The acetone-containing specimens were dried under vacuum for 8 h at 50 °C to obtain transparent PU specimens (**PU0** and **PU1**). **PU2** was synthesized without adding FLAP dopants.

Average distance between the FLAP molecules in PU0 and PU1

The concentration of FLAP in PUs calculated from the feed ratio is $0.15 \mu\text{mol/g}$, which is equal to $0.15 \mu\text{mol/cm}^3$ (density of PUs: 1.0 g/cm^3). By converting this molar concentration to number density and taking the reciprocal, the average volume occupied by a single FLAP molecule was calculated to be $1.1 \times 10^{-23} \text{ m}^3$. Thus, by taking the cube root, the average distance between the FLAP molecules was determined to be 23 nm.

Preparation of PU1-BC

PU1-BC was prepared by soaking the swollen specimens into a solution of **FLAP1-BC** in acetone after removing DMF. Namely, **FLAP1-BC** (2.9 mg, $1.3 \mu\text{mol}$) was dissolved into acetone (50 mL), and then acetone-swollen **PU2** specimens (6 pieces, $V_{\text{total}} \sim 17 \text{ cm}^3$) were soaked into the solution. After 48 h, the surface of specimens was washed with acetone and dried under vacuum for 8 h at 50°C to obtain **PU1-BC** samples. The concentration of **PU1-BC** was estimated as follows: assuming that **FLAP1-BC** is dispersed throughout the system, the concentration in the swollen specimen is $1.9 \times 10^{-5} \text{ M}$. Because the swelling ratio of PU in acetone is 3.7 (see Section 8 in SI), the concentration of **FLAP1-BC** in the dry specimen is estimated to be $7 \times 10^{-5} \text{ M}$. Since the concentration of FLAP in **PU0** and **PU1** is $1.5 \times 10^{-4} \text{ M}$ (see above), the concentration of FLAP is slightly lower in **PU1-BC**, but it does not affect the discussion of the FL measurements.

Preparation of PUs with a fluorescent internal standard (rhodamine)

Rhodamine 640 perchlorate was employed as a fluorescent internal standard. Rhodamine 640 perchlorate (0.74 mg, $1.3 \mu\text{mol}$) was dissolved into acetone (250 mL), then acetone-swollen PU specimens (**PU0**, **PU1**, and **PU2**) were soaked into the solution. After 48 h, the specimens were dried under vacuum for 8 h at 50°C to obtain rhodamine-doped PU specimens (**PU0-Rho**, **PU1-Rho**, and **PU2-Rho**). The concentration of rhodamine was similarly estimated to be $5 \times 10^{-6} \text{ M}$, which is lower than that of the FLAP dopants.

Figure S7.2. Preparation of PUs with the fluorescent internal standard.

7.2. Differential scanning calorimetry (DSC) analysis of the crosslinked PUs

DSC measurements of the PU specimens were performed under N₂ atmosphere at a flow rate of 30 mL mm⁻¹. Programmed heating and cooling cycles are shown in Figure S7.3. DSC profiles are displayed in Figure S7.4 for the 2nd cooling (E→F) and heating (G→H) cycles. Each PU sample was placed into an aluminum pan, covered with an aluminum cover, and then pressed with a designated tool. As a reference sample, a vacant pan was also pressed with the cover.

Figure S7.3. Programmed heating and cooling cycles in the DSC measurements of the PUs.

Table S7.1. DSC parameters of the PU films.

	$T_g^{[a]} / ^\circ\text{C}$	$T_{r \rightarrow c}^{[b]} / ^\circ\text{C}$	$\Delta H_{r \rightarrow c}^{[c]} / \text{J g}^{-1}$	$T_{c \rightarrow r}^{[d]} / ^\circ\text{C}$	$\Delta H_{c \rightarrow r}^{[e]} / \text{J g}^{-1}$
PU0	-58	-10	-21	31	22
PU1	-57	1	-22	33	21
PU1-BC	-58	-3	-23	34	20
PU2	-58	-8	-23	31	20
PU0-Rho	-57	-8	-25	34	24
PU1-Rho	-57	-7	-20	32	22
PU2-Rho	-57	-4	-26	34	23

[a] Glass transition temperature determined by the 2nd heating profile.

[b] Rubbery-to-semicrystalline transition temperature determined by the 2nd cooling profile.

[c] Enthalpy change in the rubbery-to-semicrystalline transition determined by the DSC signal area.

[d] Semicrystalline-to-rubbery transition temperature determined by the 2nd heating profile.

[e] Enthalpy change in the semicrystalline-to-rubbery transition determined by the DSC signal area.

Figure S7.4. DSC profiles of the crosslinked polyurethanes (PUs).

7.3. Mechanical and optical properties of the PUs during stretching before swelling

Figure S7.5. Stress-strain curves of the crosslinked polyurethanes (PUs).

Table S7.2. Mechanical properties of the crosslinked PUs in the uniaxial tensile testing^[a]

	Rupture strain / %	Rupture stress / MPa	Toughness / MJ m ⁻³	Young's modulus / MPa
PU0	713 ± 35	9.9 ± 2.1	15.7 ± 3.5	1.4 ± 0.1
PU1	713 ± 8	10.2 ± 0.5	16.8 ± 0.7	1.5 ± 0.1
PU1-BC	722 ± 20	10.8 ± 0.7	18.0 ± 1.2	1.6 ± 0.1
PU2	724 ± 15	10.1 ± 1.1	16.7 ± 2.0	1.5 ± 0.1
PU0-Rho	721 ± 7	10.3 ± 0.2	16.3 ± 0.1	1.4 ± 0.1
PU1-Rho	721 ± 25	11.3 ± 1.3	18.1 ± 2.2	1.6 ± 0.3
PU2-Rho	726 ± 20	10.4 ± 0.9	16.9 ± 1.0	1.5 ± 0.1

[a] Values of average ± standard deviation of three specimens were shown.

Figure S7.6. FL spectral change during the tensile tests of the crosslinked PUs before swelling. FL spectra are normalized at each maximum.

Figure S7.7. FL ratiometric analysis of the crosslinked PUs before swelling plotted against strain and stress in the tensile tests. The results of the three measurements are superimposed.

7.4. Measurements of the absorption spectrum of PU1

The absorption spectra $A(\lambda, \Delta x)$ were obtained from the following equation: $A(\lambda, \Delta x) = -\log[I(\lambda, \Delta x)/I_0(\lambda)]$, where $I_0(\lambda)$ is the spectrum of the incident tungsten light, and $I(\lambda, \Delta x)$ is a spectrum of the tungsten light transmitted through a specimen with the distance between grips is Δx in the tensile test. Here, nominal strain (ε_N) was not measured to avoid light reflection by the strain gauge. When we measured the absorption spectrum of **PU1** based on this method, the contribution of light scattering by the sample was observed on the long-wavelength side (Figure S7.8a). Therefore, the absorption spectrum of **PU2** without FLAP was measured as a baseline in the same way (Figure S7.8b). Since the difference in the degree of scattering due to individual specimens was unavoidable, the baseline was employed after normalization so that the value at 600 nm is the same as that of the uncorrected absorption spectrum of **PU1**. Namely, the corrected absorption spectrum of **PU1** $A_{\text{PU1}}(\lambda, \Delta x)$ was obtained by the following equation:

$$A_{\text{PU1}}(\lambda, \Delta x) = A_{\text{PU1}}^{\text{uncorrected}}(\lambda, \Delta x) - A_{\text{PU2}}(\lambda, \Delta x) \cdot \frac{A_{\text{PU1}}^{\text{uncorrected}}(600 \text{ nm}, \Delta x)}{A_{\text{PU2}}(600 \text{ nm}, \Delta x)}.$$

Figure S7.8. (a) Absorption spectrum of **PU1** before baseline correction. (b) Absorption spectrum of **PU0** employed as baseline. (c) Absorption spectrum of **PU1** after baseline correction.

7.5. Discussion on the FL response of FLAP-doped PU before swelling

Since the concentration of the force probes is minimal, the occurrence of FRET can be ignored, and the stress–strain curves (Figure S7.9a) and DSC profiles (Figure S7.4) of the dry elastomers are almost identical regardless of the presence of the probes. The FL spectral changes during tensile testing of the dry elastomer **PU1** are qualitatively similar to the behavior of SPUs in that **PU1** showed a more pronounced response than **PU0** (Figures S7.9b and S7.9c), but the threshold for the FL response (~ 1 MPa) was lower than SPUs (Figure S7.9c). Since no FL response was observed in the stretched **PU1-BC** specimen, the FL response of **PU1** is indeed due to the force transmitted through the covalent bond (Figure S7.9c). In addition, measurement of absorption spectra of **PU1** by a modified experimental setup (Figure S1.3) showed that the threshold for the FL response is smaller than that of the absorption response (around 3–6 MPa) (Figures S7.9e). This result supports the hypothesis in previous studies that the flapping force probe spontaneously planarizes in S_1 to emit FL prior to the complete planarization in S_0 .^[S3]

Figure S7.9. (a) Stress–strain curves of the PUs. (b) FL spectral change of **PU1** during the tensile test. (c) FL intensity ratio (filled) and absorbance ratio (empty) plotted against stress in the tensile test. (d) Absorption spectra of **PU1** recorded in the tensile test.

7.5. Estimation of the activation ratio of the flapping force probes in PUs before swelling

The activation ratio of the force probes while stretching the PU specimens was calculated from the degree of decrease in FL intensity derived from the V-shaped form ($\lambda_{\text{FL}} = 475 \text{ nm}$). The change in the amount of the force probes in the region of detection due to the deformation of the specimen was taken into account by adding Rhodamine 640 perchlorate as a fluorescent internal standard, as shown in Figure S7.2. It should be noted that the FL spectral shape of Rhodamine 640 does not change during the tensile test, which was confirmed by stretching **PU2-Rho** (Figure S7.10). In addition, since the concentration of FLAP and Rhodamine 640 is very low, the possibility of FRET (Förster resonant energy transfer) between fluorophores can be ignored. Indeed, the intermolecular distance of fluorophores in **PU1-Rho** is estimated to be 22 nm based on the discussion on page S69, much farther than the typical distance allowed for FRET ($< 10 \text{ nm}$). Furthermore, as shown in Figure S7.11, Rhodamine 640 does not have significant absorption at around 475 nm, and thus the effect of fluorescence reabsorption in the specimen is also negligible.

Figure S7.10 FL spectra recorded during the tensile test of **PU2-Rho**. FL spectra are normalized at each maximum.

Figure S7.11 Absorption spectrum of Rhodamine 640 perchlorate in CH_2Cl_2 and fluorescence spectrum of **PU1** before stretching.

Figure S7.12 (a) FL spectral change during the tensile tests of **PU1-Rho**. FL intensity are corrected by normalization at 650 nm, where only the internal standard shows FL. (b,c) FL intensity of the V-shaped form and FL intensity ratio plotted against (b) strain and (c) stress in the three tensile tests.

Figure S7.13 (a) FL spectral change during the tensile tests of **PU0-Rho**. FL intensity are corrected by normalization at 650 nm, where only the internal standard shows FL. (b,c) FL intensity of the V-shaped form and FL intensity ratio plotted against (b) strain and (c) stress in the two tensile tests.

The percentage of the stressed force probe in stretched polyurethanes was evaluated to gain insight into the intrinsic properties of **FLAP0** and **FLAP1** as force probes. Since the flapping force probes are dual-fluorescent, the ratio of the stressed force probes can be experimentally estimated by the decrease in the FL intensity of the V-shaped form. The change in FL intensity due to deformation of the specimen was corrected by doping rhodamine 640 perchlorate as a fluorescent internal standard. It should be noted that the properties of the cross-linked polyurethanes were not affected by the addition of rhodamine (Figures S7.4 and S7.5), and the FL spectral shape of the rhodamine was not affected by stretching (Figure S7.10). Figure S7.12a displays the FL spectrum of **PU1-Rho**, which was prepared by doping **PU1** with the rhodamine.

Interestingly, the FL intensity of the V-shaped form of **FLAP1** first increased with a slight peak shift (475 nm) and then decreased with a critical stress of 1–2 MPa (Figure S7.12c). Since this threshold is comparable to that of the fluorescence intensity ratio (I_{533}/I_{472}), the FL intensity of the V-shaped form initially increased with keeping the spectral shape, and then the V-shaped form was stretched into the planar form. Although we cannot identify the reason for the increase in FL intensity at this stage, it is meaningful to relate it to the reported rigidochromic molecules in that the non-radiative decay of the V-shaped form might be suppressed.^[S16] Assuming that there is no change in the FL quantum yield in the decreasing region of the FL intensity at 475 nm, the ratio of the stressed FLAP can be calculated by the percentage decrease in the FL intensity from the maximum value. The results show that the ratio of stressed probes at 10 MPa is $37 \pm 4\%$ for **FLAP0** and $31 \pm 3\%$ for **FLAP1**, which are comparable (Figures S7.14). From Figure S7.9c, the FL intensity ratio (I_{525}/I_{474}) in **PU0** at 10 MPa is estimated to be about 1.4. On the other hand, the percentage of the stressed probe reported based on the theoretically estimated molar absorption coefficients is around 17% at the same I_{525}/I_{474} value,^[S3] which is slightly different but of the same order as the experimental results.

Figure S7.14. Ratio of the stressed FLAP calculated from the decrease in FL intensity of the V-shaped probe. The solid line represents the mean of the linear fit to the results of 2–3 experiments, and the shade represents the 95% prediction interval of the fitting.

8. Swelling behavior of the crosslinked polyurethanes (PUs)

Figure S8.1 Volume change of cylindrical **PU1** specimens when swollen with CPME, showing the mean (red line) and standard deviation (shading) measured for three specimens. The cylindrical specimens that reached the equilibrium swelling state after 48 hours were used as **GelI** for the compression tests.

9. Mechanical and photophysical properties of the polyurethanes gels

Figure S9.1. Stress–strain curves of the polyurethane gels swollen with CPME.

Table S9.1. Mechanical properties of the polyurethane gels swollen with CPME in the compression test^[a]

	Rupture strain / %	Rupture stress / MPa	Toughness / MJ m ⁻³	Young's modulus / MPa
Gel0	76 ± 1	2.6 ± 0.1	0.410 ± 0.02	0.12 ± 0.05
Gel1	81 ± 6	3.5 ± 1.7	0.52 ± 0.18	0.13 ± 0.07

[a] Values of average ± standard deviation of 3–4 specimens were shown.

Figure S9.2. FL ratiometric analysis of the polyurethane gels swollen with CPME (**Gel1**) plotted against strain, stress, and strain energy density in the compression. The results of the four measurements are superimposed.

Figure S9.3. FL ratiometric analysis of the polyurethane gels swollen with CPME (**Gel0**) plotted against strain, stress, and strain energy density in the compression. The results of the three measurements are superimposed.

Figure S9.4. (a) Strain–time profile and (b) stress–strain curve for the repeated compression test of **Gel1** (See Figure 10h in the main text).

Figure S9.5. Calculation of the change in the bottom area of the cylindrical specimen during compression to estimate true stress applied to **Gel1**. (a) Evaluation of the relative bottom area of a cylindrical specimen using the ImageJ software. (b) Calibration curve (red) for calculating true stress from nominal stress. The calibration curve was obtained by fitting the discrete data from ImageJ (black dots) with the quartic function $y = K_0 + K_1x + K_2x^2 + K_3x^3 + K_4x^4$.

10. Supporting references

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