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Complete List of Authors:	Kawajiri, Ikumi; University of Hyogo, Graduate School of Applied Chemistry Nagahara, Masaya; University of Hyogo, Graduate School of Applied Chemistry Ishikawa, Hiroyuki; University of Hyogo, Graduate School of Applied Chemistry Yamamoto, Yuma; University of Hyogo, Graduate School of Applied Chemistry Nishida, Jun-ichi; University of Hyogo, Graduate School of Applied Chemistry Kitamura, Chitoshi; The University of Shiga Prefecture, School of Engineering Kawase, Takeshi; University of Hyogo, Graduate School of Applied Chemistry
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π -Extended Fluoranthene Imide Derivatives: Synthesis, Structures, and Electronic and Optical Properties

Ikumi Kawajiri,¹ Masaya Nagahara,¹ Hiroyuki Ishikawa,¹ Yuma Yamamoto,¹ Jun-ichi Nishida,¹

Chitoshi Kitamura,² and Takeshi Kawase*¹

¹ *Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan*

² *School of Engineering, The University of Shiga Prefecture, 2500, Hassaka-cho, Hikone, Shiga 522-8533, Japan*

Corresponding author email: kawase@eng.u-hyogo.ac.jp tel. +81-79-267-4889, fax +81-79-267-4889

Draft

Abstract

Diels-Alder reactions of acenaphthylene-5,6-dicarboximide (**AI**) derivatives with the corresponding dienes afforded some derivatives of π -extended fluoranthene imide, namely *N*-(2-ethylhexyl)-7,10-diphenylfluoranthene imide (**DPFI**) and *N*-(2-ethylhexyl)-7,8,9,10-tetraphenylfluoranthene imide (**TPFI**), *N*-(*n*-octyl)-benzo[*k*]fluoranthene imide (**BFI**), and *N*-(*n*-octyl)-naphtho[*k*]fluoranthene imide (**NFI**). Molecular structures of **TPFI** and **BFI** reveal that the core π -skeletons have a highly planar structure, and the molecules form a dimeric structure in the crystals. The absorption spectra exhibit bathochromic shift with π -extension of the core π -skeletons. On the other hand, **DPFI** and **TPFI** show the long-wavelength emission related to **BFI**, probably due to π -extension toward the phenyl substituents in the excited states. **BFI** and **NFI** exhibited an interesting concentration-dependent $^1\text{H-NMR}$ behavior in CDCl_3 , suggesting self-aggregation formation. Moreover, **BFI** and **NFI** show moderate and remarkable solvatofluorochromism in solutions (**BFI** for $\Delta\lambda_{\text{EM}} = 67$ nm, **NFI** for $\Delta\lambda_{\text{EM}} = 116$ nm), respectively, while **DPFI** and **TPFI** show weak solvatofluorochromism. The density functional theory calculations demonstrate that the considerable spatial separation between the HOMO and LUMO coefficients in the **NFI** molecule. The result indicates that the ground-to-excited state transition of **NFI** should have intramolecular charge transfer (ICT) character.

Key words: imides, π -extended fluoranthene, fluorophore, self-aggregation, solvatochromism, crystal structure

Introduction

Fluorophores have received considerable attention as sensors owing in part to their extreme sensitivity to subtle environmental changes that are signaled by changes in either their fluorescence intensities or wavelengths.^[1] One

sub-class of sensors called solvatochromic fluorophores usually possesses “push–pull” structures bearing opposed electron-donating and -withdrawing groups.^[2] In general, theoretical calculations of these fluorophores indicate the existence of excited state intramolecular charge transfer (ICT) between the electron-donating and -withdrawing groups.^[3] Polycyclic aromatic hydrocarbon (PAH) possessing an imide group would be promising model compounds having a “push–pull” structure,^[1d,4] because the imide group can be act as an electron-withdrawing group and the PAH moiety with high HOMO energy level should act as an electron-donating group. Imide derivatives involving a fluoranthene moiety, namely fluoranthene imides (FI), have recently emerged as an important class of compounds exhibiting intense fluorescence and n-type of semiconducting properties.^[5] However, to the best of our knowledge, no FI derivatives have been known to exhibit a solvatofluorochromic property. Acenaphthene-5,6-dicarboximides (AI) **1** would be a versatile synthon for construction of the FI derivatives, because the AI possesses a highly reactive C–C double bond ascribed to the ring strain of the fused cyclopentene ring. Thus, the Diels–Alder reactions of **1** with appropriate dienes should produce the variety of the FI derivatives. However, only a few studies have been performed to date.^[6] To elucidate the insight into the relationship between the structural and optical properties, we synthesized π -extended FI derivatives, namely *N*-(2-ethylhexyl)-7,10-diphenylfluoranthene 3,4-dicarboximide (DPFI: **2a**) and *N*-(2-ethylhexyl)-7,8,9,10-tetraphenylfluoranthene 3,4-dicarboximide (TPFI: **3a**), and *N*-(*n*-octyl)-benzo[*k*]fluoranthene 3,4-dicarboximide (BFI: **4b**) and *N*-(*n*-octyl)-naphtho[*k*]fluoranthene 3,4-dicarboximide (NFI: **5b**), from the corresponding AI derivatives (**1a** and **1b**) (Scheme 1), respectively. We found that **4b** and **5b** exhibit moderate and large solvatofluorochromism in organic solvents and formed self-aggregates in CDCl₃. It has been known that diimide derivatives bearing a PAH moiety construct various

supramolecular architectures by self-aggregation in solution.^[7] On the other hand, few monoimide derivatives bearing a simple *N*-alkyl group cause self-aggregation in organic solvents. We recently reported as a rare example that *N*-(*n*-octyl)acenaphtho[1,2-*j*]fluoranthene imide (**6b**) exhibits self-aggregation behavior in CDCl₃.^[8] We here describes the structural, electronic, optical and supramolecular properties of the π -extended FI derivatives together with density functional theory (DFT) calculations^[9] as helpful information.

<Scheme 1>

Results and Discussion

Synthesis of π -extended fluoranthene imides

The acenaphthene imides **1a** and **1b** were prepared from acenaphthene-5,6-dicarboxylic anhydride (**7**) via the corresponding acenaphthene imides **8a** and **8b** (Scheme 2).^[10] The Diels–Alder reactions of **1a** with 2,5-diphenylthiophene 1,1-dioxide (**9**)^[11] and tetracyclone **10** were examined; the reaction mixtures of **1a** and the dienes in *o*-xylene were heated at reflux for 24 h. Under the reaction conditions, subsequent aromatization occurred to form **2a** and **3a** as yellow crystals in 10% and 22% yields, respectively (Scheme 3a). The reaction of **1b** with α,α' -dibromo-*o*-xylylene^[12] generated by reductive debromination of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylylene **11** with potassium iodide produced **4b** as stable orange crystals in 25% yield.^[13] The reaction using 2,3-bis(dibromomethyl)naphthalene **12**^[14] also afforded **4b** as stable orange crystals in 5% yield (Scheme 3b). The relatively low yields of the products would be ascribed to the thermal lability of the AIs as the starting materials, because thermal treatment at around the melting points readily converted the AIs into insoluble polymeric materials. Actually, after the reactions, **1a** and **1b** disappeared completely.

<Schemes 2 and 3>

X-ray crystallographic analysis of 3a and 4b

Good single crystals of **3a** and **4b** for the X-ray analysis were collected from toluene/hexane solutions. Both the compounds crystallize with triclinic and belong to a $P\bar{1}$ space group. The molecular structures and molecular packing modes of **3a** and **4b** are disclosed in Figures 1 and 2, respectively. The FI skeleton of **3a** possesses high planarity. Four phenyl groups are highly twisted from the FI plane with 67.2, 63.6, 71.1 and 86.7°, respectively (Figures 1a and 1b). Thus, the conjugation between the FI unit and each phenyl group would be highly retarded in the ground state. The molecules stack with a head-to-tail manner to form a dimer structure (Figure 1c), in which the closed π - π distance was 3.54 Å. The dimers form a one-dimensional slipped- π -stack columnar structure. The π -skeleton of **4b** possesses high planarity despite slightly curved with 8.17° (Figures 2a and 2b). The molecules stack with a head-to-tail manner and form a one-dimensional slipped- π -stack columnar structure. The convex surfaces of the molecules are almost perfectly overlapped each other with 3.30 Å of the closed π - π distance between stacked BFI planes. On the other hand, the concave surfaces are slipped and stacked with the naphthalimide units.

<Figures 1 and 2>

UV/Vis and fluorescence spectra

UV/Vis and fluorescence spectra of **1a**, **2a**, **3a**, **4b**, and **5b** in CH_2Cl_2 were shown in Figure 3. The spectral data are summarized in Table 1. The absorption maxima (λ_{ABS}) of these compounds cause bathochromic shift with the extension of core π -systems. Actually, the λ_{ABS} of **1a** (374 nm) is the shortest and **5b** (511 nm) is the longest among these compounds. In the case of **2a** and **3a**, the presence of the two or four phenyl groups cause little difference in the absorption spectra (both λ_{ABS} values are 422 nm). Their short-wavelength-absorptions around

370–460 nm should be due to retardation of the π -conjugations by highly twisting structures of the molecules, as it was expected from the molecular structure of **3a**. On the other hand, the fluorescence maxima (λ_{EM}) of these compounds in CH_2Cl_2 show the different order from the λ_{ABS} values; the λ_{EM} values of **2a** and **3a** are longer than that of **4b**. Thus, the Stokes shift of **2a** (4100 cm^{-1}) and **3a** (5080 cm^{-1}) are considerably larger than those of **4b** (1500 cm^{-1}) and **5b** (2100 cm^{-1}). Moreover, the fluorescence quantum yields (Φ_{SL}) of **2a** and **3a** in CH_2Cl_2 are remarkably low (0.01–0.02). These results suggest that π -conjugation of **2a** and **3a** in the excited states would be partially extended toward their phenyl groups by relaxation of the highly twisted structures. Moreover, the rotatory motion of the phenyl groups would accelerate a non-radiative process in the excited states, because the known FI derivatives with phenyl substituents at 7 and 10 positions show low Φ_{SL} values.^[5] On the other hand, the small Stokes shifts and the relatively large Φ_{SL} values of **4b** and **5b** indicate the rigid conformation of π -systems of these compounds.

<Figure 3>

<Table 1>

Self-aggregation behavior of 4b and 5b

It became evident during routine characterization of **4b** and **5b** with ^1H -NMR spectroscopy in CDCl_3 that their aromatic chemical shifts were dependent on the concentration. As increasing the concentration, the chemical shifts of the aromatic protons of **4b** and **5b** undergo a pronounced high-field shift (Figures 4a and S1 in the Supporting Information). These observations suggest that **4b** and **5b** self-associate in CDCl_3 with π - π stacking, and the up-field shift of aromatic protons would be attributed to the influence of the ring current from the neighboring molecule. Because of the large high-field shift ($>1\text{ ppm}$), it's probably fair to say that indefinite self-association is actually the more appropriate interpretation. Assuming a monomer–oligomer equilibrium,^[15] the association

constants (K_a) of **4b** and **5b** at 20 °C were determined to be 11.8 ± 36.5 and $13.1 \pm 3.2 \text{ M}^{-1}$ (Figures S2–S4).

Under high concentration, however, fluorescence of **4b** and **5b** was almost quenched. Thus, the

aggregation-induced-quenching occurred in these compounds (Figure S5).

<Figure 4>

Solvatofluorochromism

The compounds **4b** and **5b** also display moderate and remarkable solvatofluorochromism in various solvents

under dilution conditions (ca. 10^{-5} M), although the fluorescence colors of **2a** and **3a** are almost independent upon

the solvent polarities. The λ_{ABS} values of **4b** and **5b** are only slightly affected by solvent polarity ($\Delta\lambda_{\text{ABS}} < 10 \text{ nm}$,

Figure S6). The λ_{EM} of **4b** is 452 nm in cyclohexane, 495 nm in CH_2Cl_2 and 518 nm in CH_3OH (**4b**: $\Delta\lambda_{\text{EM}} = 67 \text{ nm}$,

Figure S7). From the images shown in Figure 5, the fluorescence colors of **5b** cover blue-green to red range ($\Delta\lambda_{\text{EM}}$

= 116 nm). Specifically, the λ_{EM} of **5b** is 507 nm in cyclohexane, 535 nm in toluene, 572 nm in CH_2Cl_2 , 593 nm in

CH_3CN , and 623 nm in CH_3OH . Only in cyclohexane does the emission spectrum of **5b** become the mirror image

of its absorption spectrum. The solvation relaxation of the singlet excited state of **5b** does not occur in

cyclohexane while it does occur in other solvents.

<Figure 5>

Further information regarding the solvent sensitivity of the absorption and emission spectra of **4b** and **5b** was

obtained from the Lippert-Mataga plots (Figure 6a).^[16] The Lippert-Mataga equation^[17] can be used to correlate

the energy difference between absorption and emission, also known as Stokes' shift (Δ_{SS}), with solvent polarity

represented by Δf ^[18].

The Lippert-Mataga equation is as follow:

<Equation (1)>

where ν_{abs} and ν_{em} are the wavenumbers (cm^{-1}) corresponding to the absorption and the emission, respectively, h is Planck's constant, c is the speed of light, and a is the Onsager radius of the solvent cavity in which the fluorophore resides. The dipole moment differences between the excited and the ground state ($\Delta\mu$) values were determined to be 10.8 D for **4b**, and 16.0 D for **5b** (see the SI), which reflects a highly polarized excited-state. These values are in the range of those reported for solvatofluorochromic dyes (3 – 20 D).^[19] Moreover, a good linear correlation also exists between the λ_{EM} of **4b** and **5b**, and the solvent polarity parameter $E_{\text{T}}(30)$ (Figures 6b).^[20] These results clearly confirm the ICT nature of the emission of **4b** and **5b**.

<Figure 6>

Electrochemical properties and DFT calculations.

The cyclic voltammograms (CV) of π -extended FI derivatives were measured in CH_2Cl_2 in the presence of $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) as an electrolyte using Fc/Fc^+ as an internal standard (Table 2). Two reversible one-electron reduction waves were observed at -1.01 and -1.41 V for **2a**, -1.10 and -1.51 V for **3a**, -0.97 and -1.38 V for **4b**, and -0.97 and -1.37 V for **5b** (Table 1 and Figure S7), respectively. The high reversibility of each CV indicates the high stability of the corresponding radical anions and dianions of the π -extended FIs. On the other hand, no oxidation potentials of all the imides were observed in the measurable range ($< +1.3$ V). The reduction potentials indicate highly electron-accepting abilities of these imide derivatives. However, these values are little sensitive to π -extension of the compounds.

<Figure 7>

To investigate the relationship between optical and electronic properties, the DFT calculations with the *N*-methyl

π -extended FI derivatives **2c–5c** were performed by using B3LYP/6-31G(d) level of theory embedded in the Gaussian 09 software package.^[11] For simplicity, **2c–5c** were used as models for the calculations. Figure 7 illustrates the HOMO and LUMO coefficients on the optimized conformations of **2c–5c**. The HOMO and LUMO coefficients of **2c** and **3c** extend all the molecules without the carbons of phenyl substituents, owing to large torsion of the phenyl ring planes. The phenyl groups in the calculated geometries of **3c** appear to be substantially more twisted than in the crystal structure of **3a** (Figure 1). The crystal packing forces would cause the somewhat conformational planarization of the molecules. The calculated HOMO and LUMO energies (E_{HOMO} and E_{LUMO}), and calculated and observed energy gaps (ΔE_{cal} and ΔE_{obs}) of the π -extended FI derivatives are shown in Table 2. The E_{LUMO} levels of **2c–5c** are almost constant. The predictions are in good agreement with the synchronized reduction potentials of **2a**, **3a**, **4b** and **5b**. Thus, the variation of ΔE_{cal} and ΔE_{ob} are mainly ascribed to the changes of E_{HOMO} . The E_{HOMO} values increase with the extension of π -conjugation. The HOMO coefficient of **5c** is found to be located on the anthracene moiety, while the LUMO coefficient is mainly located on the naphthalene imide moiety (Figure 7). The high spatial separation between the HOMO and LUMO coefficients in the molecule indicates that the ground-to-excited state transition should have intramolecular charge transfer (ICT) character. Thus, the structural features of **5b**, correctly classified as having a “push–pull” structure,^[2] are consistent with its remarkable solvatochromic emission properties. Moreover, the weak solvatochromic properties of **2a** and **3a** are probably due to poor spatial separation between the HOMO and LUMO in the molecules. Moreover, the calculations indicate that π -extended FI derivatives possess considerably high dipole moments (> 5.2 D). Among them, the dipole moment of **5b** (6.18 D) is the highest. As mentioned before, acenaphtho[1,2-*j*]fluoranthene imide **6b** with relatively high dipole moment (3.0 D) exhibits self-aggregation behavior in CDCl_3 .^[8] According to

crystallographic analysis of **3a** and **4b**, these compounds exist in a head-to-tail dimer form in the solid states.

However, there is no proof that **3a** with high dipole moment (5.76 D) aggregates in CDCl_3 . Owing to the large high-field shift (>1 ppm), we adopted the indefinite self-association model to determine the K_a value of **4d** and **5b** as mentioned above. The large aromatic surfaces of **4d** and **5b** together with **6b** would play an important role in the formation of oligomeric aggregates in CDCl_3 .

<Table 2>

Conclusion

The Diels–Alder reactions of the AI derivatives **1** with some dienes produced a series of π -extended FI derivatives **2a**, **3a**, **4b** and **5b**. An X-ray crystallographic analysis of **3a** reveal that the FI moiety has a planar structure, and the phenyl substituents are highly twisted from the FI plane. The analysis of **4b** reveals that the π -unit has a slightly bent structure. The molecules of **3a** and **4b** stack with a head-to-tail manner, and form a columnar stacking in the crystals. The λ_{ABS} values of π -extended FI derivatives cause a bathochromic shift with the extension of core π -systems, while the λ_{EM} values of **2a** and **3a** are longer than that of **4b**. The presence of two or four phenyl substituents of **2a** and **3a** has little effect on the absorption spectra, due to retardation of the π -conjugations by highly twisting structures of the molecules. The π -conjugation of **2a** and **3a** in the excited states would be fairly extended toward their phenyl substituents by relaxation of the highly twisted structures. On the other hand, the relatively large Φ_{SL} values and the small Stokes shifts of **4b** and **5b** indicate the rigid conformation of these compounds. The fluorophore **4b** and **5b** are found to display both solvatofluorochromism (**4b** for $\Delta\lambda_{\text{EM}} = 67$ nm and **5b** for $\Delta\lambda_{\text{EM}} = 116$ nm) and self-aggregation in CDCl_3 solutions. Their electrochemical measurements

using CV clearly indicate low E_{LUMO} of the FIs and high stability of the anionic species. The electrochemical properties are in good agreement with the results of the DFT calculations. Especially, the DFT calculations with model compounds of **5b** revealed the existence of excited-state ICT between the donor anthracene and acceptor naphthalimide moieties. Further studies on the applicability of π -extended FI derivatives to the design of other π -conjugated systems, as well as their potential use in organic optoelectronic materials, are underway.

Experimental Section

General:

All reactions of air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe. Analytical thin-layer chromatography was performed using glass plates pre-coated with Merck Art. 7730 Kiesel-gel 60 GF-254. Thin layer chromatography plates were visualized by exposure to UV light. Organic solutions were concentrated by using rotary evaporation at ca. 15 Torr obtained with a diaphragm pump. Column chromatography was performed with Merck Kiesel-gel 60. All reagents were commercially available and used without further purification unless otherwise noted. THF was purchased from Wako Chemical Co. and distilled from lithium aluminum hydride at 760 Torr under a nitrogen atmosphere before use. Melting points were recorded on a Yanaco MP-S3 apparatus and reported uncorrected. FAB and high-resolution mass spectra were measured on a JEOL JMS-700. ^1H and ^{13}C NMR spectra were recorded on a Bruker-Biospin DRX-500 spectrometer. ^1H NMR spectral data for the compounds were measured at 20 °C. IR spectra were obtained using a JASCO FTIR-4100 spectrometer. Electronic (UV-Vis) and fluorescence spectra in solution were recorded with a JASCO V650 and a

SHIMADZU RF-5300PC spectrophotometers, respectively. Quantum yields for solution state fluorescence (Φ_{SN}) were determined using 9,10-diphenylanthracene ($\Phi_{\text{SN}} = 0.86$)^[21] in CH_2Cl_2 as an actinometer. DFT calculations were carried out by using the B3LYP/6-31G(d) method with the Gaussian 09 program package.^[9]

Acenaphthene-5,6-dicarboxylic anhydride **7** was prepared from acenaphthene using reported procedure.^[10]

Synthesis

N-(2-Ethylhexyl)-acenaphthene-5,6-dicarboxyimide (**8a**)^[10]

A solution of **7** (3.36 g, 15 mmol) and 2-ethylhexylamine (3.7 mL, 23 mmol) in ethanol (80 mL) was heated at reflux for 12 h. After cooling at rt, the solvent was evaporated under reduced pressure. The resulting solid was recrystallized from hexane to give **8a** as colorless crystals in 80% yield (4.01 g, 12.0 mmol). Mp: 102–104 °C (ref. 10: 142–143 °C); ¹H NMR (500MHz, CDCl_3) δ 0.92 (t, $J = 7.4$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H), 1.29–1.39 (m, 8H), 1.91–1.95 (m, 1H), 3.56 (s, 4H), 4.07–4.16 (m, 2H), 7.55 (d, $J = 7.4$ Hz, 2H), 8.48 (d, $J = 7.4$ Hz, 2H); ¹³C NMR (125 MHz, CDCl_3): δ 10.74, 14.16, 23.12, 24.09, 28.80, 30.79, 31.70, 38.00, 44.01, 119.23, 120.92, 126.44, 132.79, 137.81, 153.71, 164.83.

N-(*n*-Octyl)-acenaphthene-5,6-dicarboxyimide (**8b**)

A solution of acenaphthene-5,6-dicarboxylic anhydride **7** (897 mg, 4.0 mmol) and *n*-octylamine (0.83 mL, 5.0 mmol) in ethanol (70 mL) was heated at reflux for 12 h. After cooling at rt, the solvent was evaporated under reduced pressure. The resulting solid was recrystallized from hexane to give **8b** as colorless crystals in 70% yield (938 mg, 2.8 mmol). Mp: 94–96 °C; ¹H NMR (500 MHz, CDCl_3): δ 0.90 (t, $J = 7.4$ Hz, 3H), 1.27–1.43 (m, 10H), 1.70–1.73 (m, 2H), 3.54 (s, 4H), 4.16 (t, $J = 7.7$ Hz, 2H), 7.52 (d, $J = 7.3$ Hz, 2H), 8.46 (d, $J = 7.3$ Hz, 2H); ¹³C NMR (125 MHz, CDCl_3): δ 14.14, 22.68, 27.22, 28.29, 29.28, 29.42, 31.68, 31.86, 40.38, 119.20, 120.86, 126.33,

132.66, 137.73, 153.71, 164.37; IR (KBr): ν 2952 (m), 2934 (m), 2919 (m), 2856 (m), 1690 (s), 1660 (s), 1628 (m), 1460 (m), 1415 (m), 1341 (m), 1236 (m), 1073 (m), 771 (m) cm^{-1} ; HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{22}\text{H}_{26}\text{NO}_2]$, 335.1965; found: 336.1959.

N-(2-Ethylhexyl)acenaphthylene-5,6-dicarboxyimide (**1a**)

To a solution of **8a** (4.0 g, 12 mmol) and NBS (2.4 g, 13 mmol) in carbon tetrachloride (80 mL) was added benzoyl peroxide (300 mg). The reaction mixture was heated at reflux for 1 h. After cooling at rt, formed succinimide was filtered off. The filtrate was concentrated under reduced pressure to give

N-(2-ethylhexyl)-1-bromoacenaphthene-5,6-dicarboxyimide (3.0 g, 7.2 mmol) as pale yellow solid in 60% yield.

Mp: 112–114 °C; ^1H NMR (500MHz, CDCl_3) δ 0.87 (t, J = 6.8 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 1.29–1.40 (m, 8H), 1.93–1.91 (m, 1H), 3.92 (d, J = 19.2 Hz, 1H), 4.08–4.17 (m, 2H), 4.29 (dd, J = 6.8, 19.2 Hz, 1H), 5.92 (d, J = 6.8 Hz, 2H), 7.59 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 8.53 (d, J = 7.3 Hz, 1H), 8.57 (d, J = 7.4 Hz, 1H); IR (KBr): ν 2959 (m), 2927 (m), 2857 (m), 1700 (s), 1656 (s), 1630 (m), 1456 (m), 1418 (m), 1334 (m), 1234 (m), 1174 (m), 755 (m) cm^{-1} ; HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{22}\text{H}_{25}\text{BrNO}_2]$, 414.1070; found:

414.1065. A solution of *N*-(2-ethylhexyl)-1-bromoacenaphthene-5,6-dicarboxylimide (2.98 g, 7.2 mmol) and lithium bromide (1.88 g, 22 mmol) in DMF (40 mL) was heated at 120 °C for 2 h. After cooling at 0 °C in an ice bath, the reaction mixture was poured into ice water (500 mL). Precipitate was filtered, dried under reduced pressure, and recrystallized from methanol to give **1a** (2.11 g, 6.3 mmol) as an orange solid in 88% yield. Mp:

115–117 °C; ^1H NMR (500MHz, CDCl_3) δ 0.87 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H), 1.30–1.40 (m, 8H), 1.88–1.91 (m, 1H), 4.03–4.12 (m, 2H), 7.08 (s, 2H), 7.72 (d, J = 7.1 Hz, 2H), 8.32 (d, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 10.70, 14.11, 23.09, 24.07, 28.75, 30.77, 38.29, 43.97, 122.89, 123.34, 125.04, 127.51,

131.68, 132.89, 144.35, 164.35; IR (KBr): ν 2954 (m), 2925 (m), 2871 (m), 2856 (m), 1703 (s), 1658 (s), 1619 (m), 1456 (m), 1346 (m), 1327 (m), 1229 (s), 1173 (m), 718 (m) cm^{-1} ; HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{22}\text{H}_{24}\text{NO}_2]$, 334.1808; found: 334.1804.

N-(*n*-Octyl)-acenaphthylene-5,6-dicarboxyimides (**1b**)

A solution of **8b** (938 mg, 2.8 mmol), NBS (534 mg, 3.0 mmol) and benzoyl peroxide (70 mg) in carbon tetrachloride (30 mL) was heated at reflux for 1 h. After cooling at rt, formed succinimide was filtered off. The filtrate was concentrated under reduced pressure to give *N*-(*n*-octyl)-1-bromoacenaphthene-5,6-dicarboxyimide (735 mg, 1.9 mmol) as pale yellow solids in 68% yield. Mp: 122–124 °C; ^1H NMR (500MHz, CDCl_3) δ 0.87 (t, J = 7.1 Hz, 3H), 1.28–1.42 (m, 10H), 1.77–1.79 (m, 2H), 3.92 (d, J = 19.5 Hz, 1H), 4.15–4.18 (m, 2H), 4.28 (dd, J = 7.4, 19.5 Hz, 1H), 5.92 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 7.3 Hz, 1H), 7.78 (d, J = 7.3 Hz, 1H), 8.55 (d, J = 7.3 Hz, 1H), 8.58 (d, J = 7.3 Hz, 1H); IR (KBr): ν 2952 (m), 2922 (m), 2853 (m), 1699 (s), 1659 (s), 1631 (m), 1469 (m), 1455 (m), 1417 (m), 1335 (m), 1236 (m), 864 (m), 757 (m) cm^{-1} ; HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{22}\text{H}_{25}\text{BrNO}_2]$, 414.1070; found: 414.1072. Without further purification, a solution of crude *N*-(*n*-octyl)-1-bromoacenaphthene-5,6-dicarboxylimide (785 mg, 1.9 mmol) and lithium bromide (492 mg, 5.7 mmol) in DMF (10 mL) was heated at 120 °C for 2 h. After cooling at 0 °C in an ice bath, the reaction mixture was poured into ice water (200 mL). Precipitate was filtered, dried under reduced pressure, and recrystallized from methanol to give **1b** (441 mg, 1.32 mmol) as orange solids in 70% yield. Mp: 114–116 °C; ^1H NMR (500MHz, CDCl_3) δ 0.90 (t, J = 7.4 Hz, 3H), 1.27–1.41 (m, 10H), 1.69–1.71 (m, 2H), 4.10–4.13 (m, 2H), 7.06 (s, 2H), 7.70 (d, J = 7.1 Hz, 2H), 8.31 (d, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 14.14, 22.68, 27.17, 28.58, 29.27, 29.39, 31.85, 40.36, 122.85, 123.24, 125.01, 127.47, 131.59, 132.90, 144.34, 163.93; IR (KBr): ν 2954 (m),

2925 (m), 2851 (m), 1703 (s), 1659 (s), 1619 (m), 1456 (m), 1345 (m), 1330 (m), 1232 (m), 1163 (m), 1110 (m)

cm^{-1} ; HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{22}\text{H}_{24}\text{NO}_2]$, 334.1808; found: 334.1804.

DPFI (2a)

A solution of **1a** (487 mg, 1.46 mmol) and 2,5-diphenylthiophene 1,1-dioxide **9** (390 mg, 1.46 mmol) in *o*-xylene (15 mL) was heated at reflux for five days. After cooling at rt, the reaction mixture was charged on silica gel column chromatography directly to give a crude product from toluene elution. The product was recrystallized from toluene-hexane (1:1) to afford **2a** (82.0 mg, 0.15 mmol) as yellow crystals in 10% yield. ^1H NMR (CDCl_3 , 500 MHz): Mp: (242–243 °C); δ 0.85 (t, J = 6.9 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H), 1.27–1.36 (m, 8H), 1.87–1.89 (m, 1H), 4.01–4.07 (m, 2H), 7.28 (d, J = 7.4 Hz, 2H), 7.31 (s, 2H), 7.54–7.62 (m, 10H), 8.19 (d, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 10.65, 14.06, 23.05, 24.00, 28.66, 30.67, 38.06, 43.92, 121.95, 123.41, 125.03, 128.37, 128.70, 128.91, 131.03, 131.70, 131.90, 137.30, 139.62, 139.64, 141.80, 164.22; IR (KBr): ν 2956 (m), 2924 (m), 2858 (m), 2372 (w), 2319 (w), 1698 (s), 1661 (s), 1636 (s), 1450 (m), 1338 (s), 1235 (s), 761 (s), 701 (s) cm^{-1} ; MS (EI) m/z 535 (M^+ , 79), 423 (100); HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{38}\text{H}_{33}\text{NO}_2]$, 535.2513; found: 535.2518.

TPFI (3a)

A solution of **1a** (100 mg, 0.30 mmol) and tetracyclone **10** (115 mg, 0.30 mmol) in *o*-xylene (10 mL) was heated at reflux for one day. After cooling at rt, the reaction mixture was charged on silica gel column chromatography directly to give a crude product from toluene elution. The product was recrystallized from toluene-hexane (1:1) to afford **3a** (45.0 mg, 0.065 mmol) as orange crystals in 22% yield. Mp: 281–282 °C; ^1H NMR (CDCl_3 , 500 MHz): δ 0.85 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H), 1.26–1.35 (m, 8H), 1.87 (m, 1H), 4.03–4.06 (m, 2H), 6.61 (d, J

= 7.4 Hz, 2H), 6.87–6.91 (m, 10H), 7.27–7.30 (m, 4H), 7.31–7.35 (m, 6H), 8.13 (d, J = 7.4 Hz, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 10.66, 14.08, 23.07, 24.00, 28.66, 30.67, 38.07, 43.92, 121.78, 123.58, 124.87, 125.82, 126.81, 127.47, 128.42, 129.61, 130.91, 132.01, 132.14, 137.11, 138.65, 138.99, 139.05, 142.10, 142.64, 164.28. IR (KBr): ν 3058 (m), 3028 (m), 2958 (m), 2926 (m), 2858 (m), 1702 (s), 1665 (s), 1653 (s), 1453 (m), 1334 (s), 1236 (s), 756 (m), 698 (s) cm^{-1} . MS (EI) m/z 687 (M^+ , 100), 575 (98); HRMS (FAB, NBA) m/z : calculated for $[\text{C}_{50}\text{H}_{42}\text{NO}_2]$, 688.3218; found: 688.3214.

BFI (4b)

A solution of **1b** (167 mg, 0.50 mmol), 7,7,8,8-tetrabromo-*o*-xylene **11** (210 mg, 0.50 mmol) and potassium iodide (536 mg, 3.23 mmol) in DMF (5 mL) was heated at 80 °C for one day. After cooling at rt, the reaction mixture was quenched with water and extracted with toluene. The separated organic layer was washed with brine and dried over anhydrous sodium sulfate. After removing the dry agent, the solvent was evaporated under reduced pressure. The residue was purified by a silica gel column chromatography to give crude product from dichloromethane-hexane (1:2) as an elution. The crude product was recrystallized from a dichloromethane-hexane solution to give **4b** (54.0 mg, 0.125 mmol) as yellow needles in 25% yield. Mp: 174–175 °C; ^1H NMR (CDCl_3 , 500 MHz): δ 0.87 (t, J = 6.9 Hz, 3H), 1.25–1.45 (m, 10H), 1.70–1.73 (m, 2H), 4.17 (t, J = 7.7 Hz, 2H), 7.55 (m, AA'XX', J_{AX} = 6.1 Hz, 2H), 7.55 (m, AA'XX', J_{AX} = 6.1 Hz, 2H), 8.05 (d, J = 7.3 Hz, 2H), 8.28 (s, 2H), 8.53 (d, J = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.11, 22.65, 27.18, 28.41, 29.25, 29.38, 31.83, 40.42, 119.81, 121.71, 123.04, 127.49, 129.27, 132.49, 133.88, 134.02, 137.16, 142.33, 143.72, 163.92; IR (KBr): ν 2926 (m), 2848 (m), 2361 (m), 2343 (m), 1698 (s), 1664 (s), 1639 (s), 1460 (m), 1332 (m), 1234 (m), 1065 (m), 818 (s), 743 (s) cm^{-1} . MS (EI) m/z 433 (M^+ , 100); HRMS (FAB, N BA) m/z : calculated for $[\text{C}_{30}\text{H}_{28}\text{NO}_2]$, 434.2114; found

434.2113.

NFI (5b)

A solution of **1b** (167 mg, 0.50 mmol), 2,3-bis(dibromomethyl)naphthalene **12** (236 mg, 0.50 mmol) and sodium iodide (450 mg, 3.0 mmol) in DMF (5 mL) was heated at 80 °C for one day. After cooling at rt, the reaction mixture was quenched with water and extracted with toluene. The separated organic layer was washed with brine and dried over anhydrous sodium sulfate. After removing the dry agent, the solvent was evaporated under reduced pressure. The residue was purified by a silica gel column chromatography to give crude product from dichloromethane-hexane (1:2) as an elution. The crude product was recrystallized from a dichloromethane-hexane solution to give **5b** (9.0 mg, 0.02 mmol) as orange needles in 5% yield. Mp: 236–237 °C; ¹H NMR (CDCl₃, 500 MHz): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.25–1.43 (m, 10H), 1.69–1.72 (m, 2H), 4.15 (t, *J* = 7.5 Hz, 2H), 7.52–7.54 (m, AA'XX', *J*_{AX} = 6.4 Hz, 2H), 7.99–8.01 (m, AA'XX', *J*_{AX} = 6.4 Hz, 2H), 8.04 (d, *J* = 7.3 Hz, 2H), 8.39 (s, 2H), 8.43 (s, 2H), 8.53 (d, *J* = 7.3 Hz, 2H); IR (KBr): ν 2952 (m), 2924 (m), 2853 (m), 2359 (m), 2337 (m), 1696 (s), 1660 (s), 1637 (s), 1455 (m), 1403 (m), 1358 (m), 1339 (m) cm⁻¹; HRMS (FAB, NBA) *m/z*: calculated for [C₃₄H₃₀NO₂], 484.2278; found 484.2280. (A satisfactory ¹³C-NMR spectrum of **5b** was not obtained even under high concentration (2 × 10⁻² M) probably due to self-aggregation of the compound.)

X-ray Crystallography

Single crystals of **3a** and **4b** for X-ray analysis were obtained by slow evaporation from a toluene/n-hexane (1:1) solutions. X-ray diffraction data were collected on a Rigaku Rapid Auto diffractometer with graphite-monochromated MoKα (*λ* = 0.71070 Å) radiation, and *Φ* and *ω* scans at a maximum 2*θ* value of 55.08. The structures were solved by a direct method using SIR2004.^[22] All non-hydrogen atoms were refined

anisotropically by full-matrix least-squares on F^2 using SHELXL97.^[23] Hydrogen atoms of **3a** and **4b** were positioned geometrically and refined using a riding model. All calculations were performed using the WinGX program package.^[24] CCDC 1509743 (**3a**, C₅₀H₄₁NO₂) and 1509742 (**4b**, C₃₀H₂₇NO₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **3a**: Crystal System = Triclinic, $a = 11.2876(9) \text{ \AA}$, $b = 12.3471(11) \text{ \AA}$, $c = 14.2761(13) \text{ \AA}$, $\alpha = 105.390(3)^\circ$, $\beta = 93.946(3)^\circ$, $\gamma = 102.520(3)^\circ$, $V = 1855.7(3) \text{ \AA}^3$, space group = $P\bar{1}$, $Z = 2$, $d_{\text{calc}} = 1.231 \text{ mg/mm}^3$, Total refs. = 18244, Unique refs. = 8395, Final R indices [$I > 2\sigma(I)$] $R_I = 0.0905$, $wR_2 = 0.1936$, R indices (all data) $R_I = 0.2363$, $wR_2 = 0.2822$. (CCDC 1509743).

Crystal data for **4b**: Crystal System = Triclinic, $a = 8.7943(6) \text{ \AA}$, $b = 9.6102(7) \text{ \AA}$, $c = 14.6459(13) \text{ \AA}$, $\alpha = 85.498(3)^\circ$, $\beta = 85.333(3)^\circ$, $\gamma = 64.507(2)^\circ$, $V = 1112.28(15) \text{ \AA}^3$, space group = $P\bar{1}$, $Z = 2$, $d_{\text{calc}} = 1.294 \text{ mg/mm}^3$, Total refs. = 10640, Unique refs. = 4892, Final R indices [$I > 2\sigma(I)$] $R_I = 0.0490$, $wR_2 = 0.1218$, R indices (all data) $R_I = 0.0758$, $wR_2 = 0.1501$. (CCDC 1509742).

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Supporting Information Available. Selected absorption and fluorescence spectra, concentration-dependent ^1H NMR of **4b** and **5b**. ^1H and ^{13}C NMR spectra of new compounds **2a**, **3a**, **4b** and **5b**. CIF files of **3a** and **4b**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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Schemes, Figures and Tables

Scheme 1

Scheme 2.

Scheme 3. Synthesis of **2a**, **3a**, **4b**, and **5b** from **1**.

Equation 1

$$\Delta_{\text{SS}} = \nu_{\text{abs}} - \nu_{\text{em}} = \frac{2\Delta\mu^2}{hc a^3} \Delta f + \text{const} \quad (1)$$

Table 1. Absorption and fluorescence spectral data of the π -extended FI derivatives in CH_2Cl_2 .

compounds	λ_{ABS} (log ϵ) ^[a]	λ_{EX} ^[b]	Φ_{SL} ^[c]
1a	305 (3.75), 321 (3.85), 339 (3.94), 355 (4.15), 374 (4.18)	389, 409, 435s	0.04
2a	291 (4.38), 365 (3.82), 422 (4.16)	511	0.02
3a	291 (4.50), 348 (3.71), 366 (3.92), 422 (4.30)	537	0.01
4b	307 (4.48), 328 (4.36), 432 (4.27), 459 (4.32)	493, 525s	0.29
5b	277 (4.76), 354 (4.55), 479 (4.21), 511 (4.27)	571	0.37

[a] Absorption maxima in CH_2Cl_2 . [b] Fluorescence maxima in CH_2Cl_2 . $\lambda_{\text{EX}} = 365 \text{ nm}$ (ca. 10^{-5} M). [c] Fluorescence quantum yields ($\pm 10\%$) in CH_2Cl_2 determined relative to 9,10-diphenylanthracene as an actinometer.

Table 2. Experimental reduction potentials and energy gaps of **2b**, **3b**, **4a** and **5a**, and DFT calculated electronic properties of **2c–5c**.

compounds	E_{red}^1 (V) ^[a]	E_{red}^2 (V) ^[a]	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{cal} (eV) ^[b]	ΔE_{obs} (eV) ^[c]	Dipole moment (Debye)
2	−1.01	−1.41	−6.04	−2.75	3.29	2.46	5.23
3	−1.10	−1.51	−6.17	−2.62	3.55	2.42	5.76
4	−0.97	−1.38	−5.90	−2.76	3.14	2.41	5.45
5	−0.97	−1.37	−5.49	−2.70	2.79	2.09	6.18

[a] vs. Ag/Ag^+ , in 0.1 M $\text{n-Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$, scan rate: 100 mVs^{-1} , $\text{Fc}/\text{Fc}^+ = 0 \text{ V}$. [b] $\Delta E_{\text{cal}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ [B3LYP/6-31G(d)]. [c] From the low energy absorption edge of the absorption spectra in CH_2Cl_2 .

Chaptions of Scheme, Figure and Tables

Scheme 1. Acenaphthene imides **1a** and **1b**, and π -extended FI derivatives **2a**, **3a**, **4b**, **5b**, and **6b**.

Scheme 2. Synthesis of **1a** and **1b** from anhydride **7**.

Scheme 3. Synthesis of **2a**, **3a**, **4b**, and **5b** from **1**.

Figure 1. ORTEP drawings of (a) Top view and (b) side view of **3a**. (c) A packing structure and the closest distance of the FI moieties of **3a**.

Figure 2. ORTEP drawings of (a) top view and (b) side view of **4b**. (c) A columnar π - π stacking structure and closest distance of **4b** moieties. Octyl carbons were omitted for the sake of clarity.

Figure 3. (a) Absorption and (b) normalized fluorescence spectra ($\lambda_{\text{EX}} = 365$ nm, ca. 10^{-5} M) of **1a** and the π -extended FI derivatives, **2a**, **3a**, **4b** and **5b** in CH_2Cl_2 .

Table 1. Absorption and fluorescence spectral data of the π -extended FI derivatives in CH_2Cl_2 .

[a] Absorption maxima in CH_2Cl_2 . [b] Fluorescence maxima in CH_2Cl_2 . $\lambda_{\text{EX}} = 365$ nm (ca. 10^{-5} M). [c]

Fluorescence quantum yields ($\pm 10\%$) in CH_2Cl_2 determined relative to 9,10-diphenylanthracene as an actinometer.

Figure 4. Concentration-dependent ^1H -NMR spectra of aromatic range of **5b** from 1×10^{-4} to 2.0×10^{-2} M at 20°C in CDCl_3 .

Figure 5. Fluorescence colors (photographs) and normalized fluorescence spectra of **5b** in cyclohexane, toluene, CH_2Cl_2 , CH_3CN and CH_3OH (ca. 10^{-5} M, $\lambda_{\text{EX}} = 365$ nm).

Figure 6. a) The Lippert–Mataga plot for **4b** and **5b**; Stokes shift versus the Lippert solvent parameter Δf (correlation for **4b** (---), $y = 9106.5x - 551.36$, $R^2 = 0.8833$, and for **5b** (—), $y = 6653.5x - 347.22$, $R^2 = 0.9254$).

b) Correlation of peak emission wavenumber of with solvent polarity parameter $E_T(30)$ (correlation for **4b** (---), $R^2 = 0.9527$, and for **5b** (—), $R^2 = 0.9362$).

Figure 7. Optimized conformations and calculated spatial electron distributions of the HOMO and LUMO for **2c**–**5c** obtained by DFT calculations at B3LYP/6-31G(d) level.

Table 2. Experimental reduction potentials and energy gaps of **2b**, **3b**, **4a** and **5a**, and DFT calculated electronic properties of **2c**–**5c**.

[a] vs. Ag/Ag^+ , in 0.1 M $n\text{-Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$, scan rate: 100 mVs^{-1} , $\text{Fc}/\text{Fc}^+ = 0 \text{ V}$. [b] $\Delta E_{\text{cal}} = E_{\text{LUMO}} - E_{\text{HOMO}}$

[B3LYP/6-31G(d)]. [c] From the low energy absorption edge of the absorption spectra in CH_2Cl_2 .

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Figure of abstract

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

a)

b)

Figure 7