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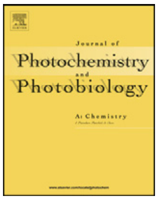

New fluorene derivatives based on 3,9-dihydrofluoreno[3,2-*d*]imidazole (FI): Characterization and influence of substituents on photoluminescence

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ABSTRACT

2,3-Diamino-9,9-dioctylfluorene (DADOF), as a new multifunctional intermediate for π conjugated molecules, was efficiently synthesized via a seven-step procedure with an overall yield of 30%. Novel 9,9-dihydro-9,9-dioctyl-2-phenylfluoreno[3,2-*d*]imidazole (DOFIPh)-type fluorophores with polar substituents were designed and conveniently synthesized from DADOF, and their absorption and fluorescence properties were investigated in solution and in the solid state. The fluorophore DOFIPh exhibits strong blue emission in solid state and fine-tuning of the emission is possible depending on the electronic nature of the substituents.

1. Introduction

Organic molecules or polymers with well-defined π aromatic backbones have attracted tremendous attention in recent years for their applications in organic light-emitting diodes (OLEDs) [1,2], photovoltaic cells [3], plastic lasers [4], and field-effect transistors (FETs) [5]. Changes in the substitutional groups and substitution pattern, conjugation, and molecular electronic structure can bring about very different optical and physical properties for such materials. To design an organic molecule with a specific application in mind, knowledge of the material's structure–property relationship is necessary. With this understanding, the ability to "tune" a class of materials to enhance an explicit property can be achieved. Compared to extended π conjugated polymers, small molecular units with well-defined conjugation lengths generally possess more predictable and reproducible properties, are easier to purify, and are prone to be well characterization. This makes these molecules more attractive than extended π-conjugated polymers for investigations of the structure–property relationship and optimization [6,7].

Due to their rigid planarized oligophenyl unit within the backbone as well as the possibility of facile functionalization at the methylene bridge, fluorene-based derivatives have exhibited unique chemical and physical properties, and emerged as the most promising blue light-emitting materials for OLEDs [8–12], as well as carrier transport materials for FETs [13–15]. Although many fluorene-based polymers, oligomers have been reported, small-molecule fluorene derivatives with good thermal stability and high photoluminescence (PL) efficiency are still rare [16–19]. And there is a need for exploration and optimization of new organic luminophores with better properties.

In the search of new luminophores for use in light-emitting materials, we have given consideration to the benzimidazole core because of its attractive optical properties. The fact that the luminescence of this system is greatly influenced by substituents has also found applications, and phenylbenzo[*d*]imidazole unit has been widely used as building blocks due to its high electron transporting mobility. Among which, 1,3,5-tris(1-phenylbenzo[*d*]imidazol-2-yl)benzene (TPBI) is a widely used electron-transporting and hole-blocking material for fluorescent and phosphorescent dopants [20–23].

And we are interested in whether replacing the phenyl ring in benzimidazole luminophore with an even larger yet flat aromatic system, such as fluorenyl rings, might further advance its properties. In this paper, we present the initial expedient synthesis, full characterization of a series of fluoreno[3,2-*d*]imidazole derivatives with various substituents on the terminal phenyl ring (Fig. 1). The optical absorption and emission characteristics of this system were examined for structure–function relationships. Further, single-crystal X-ray structural determinations was obtained for 2-(4-fluorophenyl)-

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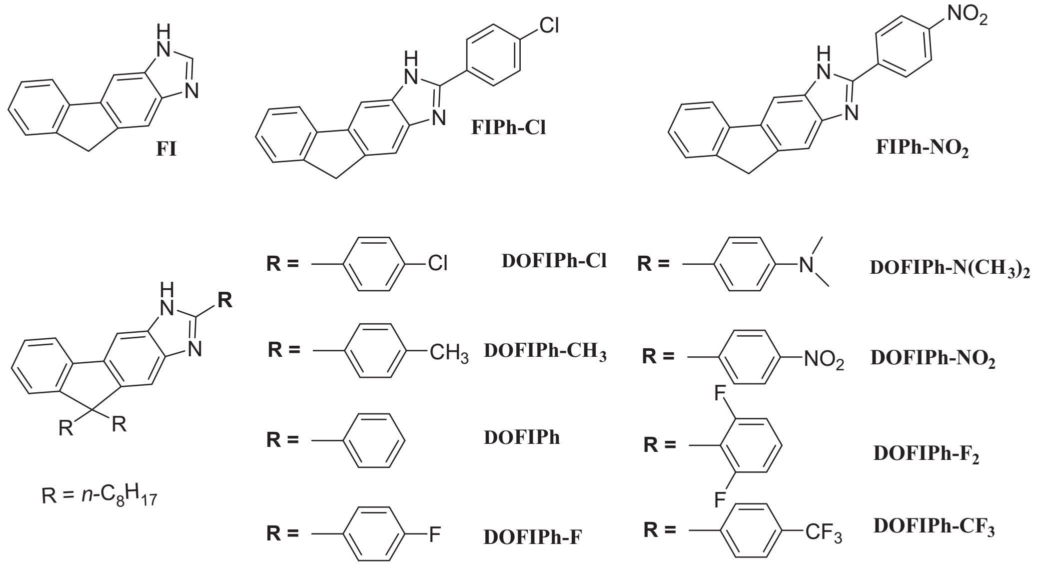


Fig. 1. Chemical structure of the fluoreno[3,2-*d*]imidazole derivatives.

3,9-dihydro-9,9-dioctylfluoreno[3,2-*d*]imidazole (DOFIPh-F); this showed the solid state conformation of the imidazole ring. Firstly, FIPh-Cl and FIPh-NO_2 were synthesized, but both showed poor solubility in common organic solvents. Hence, two octyl groups were introduced to the C-9 position of the fluorene moiety to increase solubility as well as to release intermolecular π–π stacking. We focused our attention on DOFIPhs with different substituents on the terminal phenyl ring to investigate their effects on the absorption and emission properties of these systems. Detailed study on the structure–property relationships for these materials can provide valuable information for molecular design with high performance.

2. Results and discussion

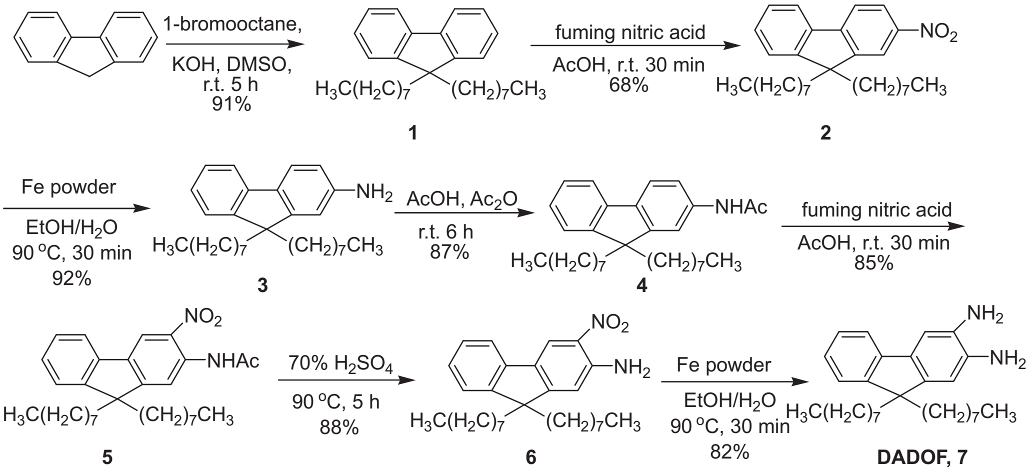
The synthetic strategy employed involved the efficient preparation of the key intermediate 2,3-diamino-9,9-dioctylfluorene (DADOF) from fluorene. A systematic synthetic route for 2,3,6,7-tetraamino-9,9-bisalkylfluorene was reported by Qian and co-workers [24]. And we found that by controlling the reaction time and the amount of fuming nitric acid, nitration of compound 1 in glacial acetic acid gave mono-nitro compound 2 as the main product. As shown in Scheme 1, DADOF was successfully synthesized via a 7-step procedure. Dialkylation of fluorene was accomplished by generation of the fluorenyl anion with KOH in DMSO and subsequent dioctylation with 1-bromooctane at room temperature [25]. 9,9-Dioctyl-2-nitrofluorene 2 was prepared in 68% yield by regioselective nitration at 2-position of 1 with fuming nitric acid in glacial AcOH at room temperature for 30 min. Hydrogenation of 2 with ferrous powder in EtOH/H_2O at 90 °C afforded 2-amino-9,9-dioctylfluorene 3 as a yellow solid in 92% yield. Protection of the amine group of 3 with Ac_2O/AcOH, followed by regiospecific nitration with fuming nitric acid in AcOH, gave 2-acetamido-3-nitro-9,9-dioctylfluorene 5 as a brown solid after column chromatographic purification in total 74% yield by two steps. Removal of acetyl group of 5, followed by hydrogenation with ferrous powder in EtOH/H_2O at 90 °C, provided 2,3-diamino-9,9-dioctylfluorene (DADOF, 7) in 72% yield (for two steps) as yellow oil. MS, ^{1}H, and ^{13}C NMR spectroscopic analysis confirmed formation of this key intermediate.

From the key intermediate 7, all target compounds can be obtained by one-step, concise synthetic procedure. Condensation of 7 with the corresponding aldehydes in dioxane at 95 °C for 8 h gave the desired fluoreno[3,2-*d*]imidazole derivatives in 72–81% yields (Scheme 2). And all target compounds were isolated and purified by column chromatography on silica gel with high purity. These compounds are readily soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, 1,4-dioxane, tetrahydrofuran (THF), and toluene, due to the *n*-octyl substituents, and their molecular structures and purities were verified by ^{1}H NMR spectroscopy, high resolution mass spectroscopy, and element analysis.

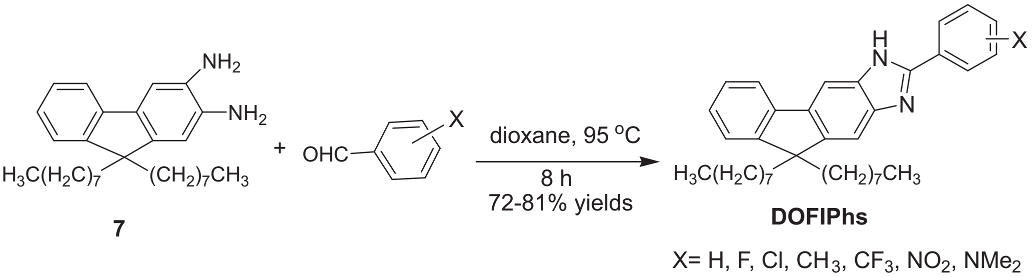
The ORTEP plot of the solid state conformation and the packing view of DOFIPh-F are revealed in Fig. 2 [26]. The ORTEP view of the structure of DOFIPh-F (Fig. 2a) shows the almost planar arrangement of the fluoreno[3,2-*d*]imidazole ring together with the terminal phenyl ring. The fluorene moiety ii forms dihedral angle of 2.02° with the adjacent imidazole ring iii. In contrast, the adjacent phenyl ring iv takes a torsion angle of 23.31° with respect to the fluoreno[3,2-*d*]imidazole moiety. In the crystal lattice, the molecules are stacked in a head-to-tail manner, forming a non-coplanar netlike mode of association, as shown in Fig. 2b. Each two adjacent molecules stack closely through the intermolecular hydrogen bonding of N···H–N with the distance of 2.092(39) Å between the H–N proton of imidazole ring and the adjacent imino nitrogen atom. Also, weak intermolecular forces of F···H–C with the distance of 2.715(3) Å between the fluorine atom and the adjacent H–C proton of the terminal *n*-octyl side chain was observed, as shown in Fig. 2c and d.

The photophysical properties of the compounds were examined by UV–vis and photoluminescent (PL) spectra in dilute CH_2Cl_2, DMSO solutions and in the solid films, as shown in Figs. 3 and 4. Both the photophysical data in these two solvents of different polarity and the PL spectra data of the compounds in thin films are listed in Table 1. In order to study the substituent effect on the optical properties, a series of compounds with various polar groups (i.e., X = H, F, Cl, CH_3, CF_3, NO_2, and NMe_2) substituted on the phenyl ring were studied. Among these polar groups, some are known as strong π-acceptors (i.e., X = NO_2), others are known as intermediate (i.e., X = F, and Cl), besides being classified as electron-withdrawing (i.e., X = F, Cl, CF_3, and NO_2) or electron-donating groups (i.e., X = CH_3, and NMe_2). The results indicated that the photophysical behavior of this electron-deficient heterocyclic system was sensitive to the electronic factors of the substituents.

As it can be observed in Fig. 3a, the UV–vis absorption spectra of all compounds in CH_2Cl_2 were very similar in shape, compound



Scheme 1. Synthesis of 2,3-diamino-9,9-dioctylfluorene 7 (DADOF).



Scheme 2. Synthesis of DOFIPh and its derivatives.

DOFIPh (X = H) exhibited the absorption maximum at 340 nm, which could be ascribed to the π–π^* transition of the molecular backbone. The UV–vis absorption maxima of compounds DOFIPh, DOFIPh-CH_3, DOFIPh-F and DOFIPh-F_2 were almost the same. The UV–vis absorption maxima of DOFIPh-Cl, DOFIPh-CF_3 and DOFIPh-NMe_2 were red-shifted by 5, 8 and 18 nm, respectively, relative to that of DOFIPh, and the enormous red shift of 51 nm as observed in DOFIPh-NO_2 with a broad and featureless absorption band. The effect of the substituent on the absorption properties is not clearly seen. This suggests that the electronic properties of the substituents might not play an important role in the UV–vis absorption spectra. For evaluating the solvatochromism of

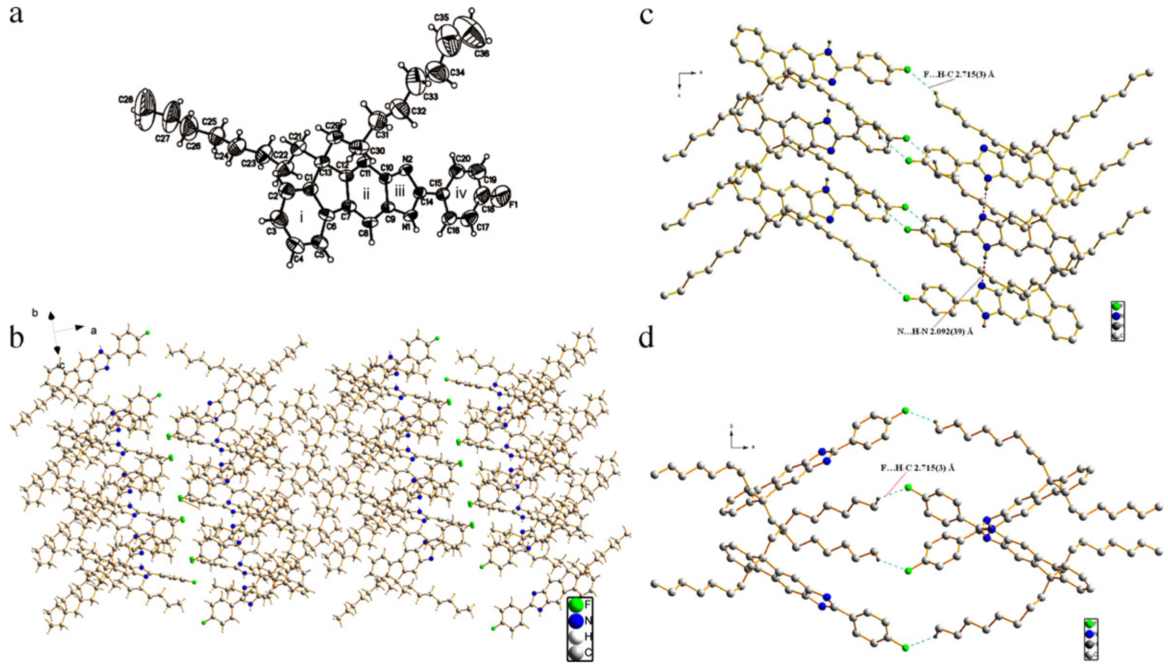


Fig. 2. Crystal structure of DOFIPh-F: (a) ORTEP drawing, (b) a view of the molecular packing structure, (c) a side view, and (d) a top view of the pair of moleculars.

Table 1
Thermal and optical properties of the compounds.

Compound	λ_{abs} (nm)[a]		λ_{em} (nm)[b]			
	CH_2Cl_2	DMSO	CH_2Cl_2	DMSO	film	ϕ_{FL}[c]
DOFIPh	340	342, 356	372, 385	373, 386	389, 442	0.50
DOFIPh-CH_3	341	342, 357	367, 385	368, 384	388, 443	0.41
DOFIPh-NMe_2	358	361	392, 412	414	483	0.45
DOFIPh-F	338	340, 354	366, 383	368, 384	388, 433	0.29
DOFIPh-Cl	345	346, 360	393	395	426	0.45
DOFIPh-F_2	341	329	388	393	391, 417	0.48
DOFIPh-CF_3	348	359	416	427	398, 427	0.54
DOFIPh-NO_2	391	400	421	467	526	0.15

[a] UV–vis absorption wavelengths in dichloromethane or in DMSO at room temperature.
[b] Fluorescence wavelengths in dichloromethane, DMSO or in thin neat films at room temperature.
[c] Fluorescence quantum yields, measured in CH_2Cl_2 solution using a 0.2 M H_2SO_4 solution of quinine sulfate (ϕ_{FL} = 0.55) as a reference.

the fluoreno[3,2-*d*]imidazoles, their UV–vis spectra were measured in DMSO solutions. As shown in Fig. 3b, all derivatives showed almost the same UV–vis spectra regardless of solvent polarity. The absorption spectra underwent small red shifts on going from the CH_2Cl_2 solutions to the DMSO solutions, and their relative order of the values of absorption maxima (λ_{max}) retained the same as observed in solutions, except compound DOFIPh-F_2 (Table 1). These shifts of the UV–vis absorption wavelengths might be affected due to the charge transfer molecule whose energy in ground state changes by solvents. And new absorption bands at 356, 357, 354 and 360 nm for compounds DOFIPh, DOFIPh-CH_3, DOFIPh-F and DOFIPh-Cl were observed in DMSO, respectively, presumably due to the accelerated CT complex formation in the ground state in polar solvent.

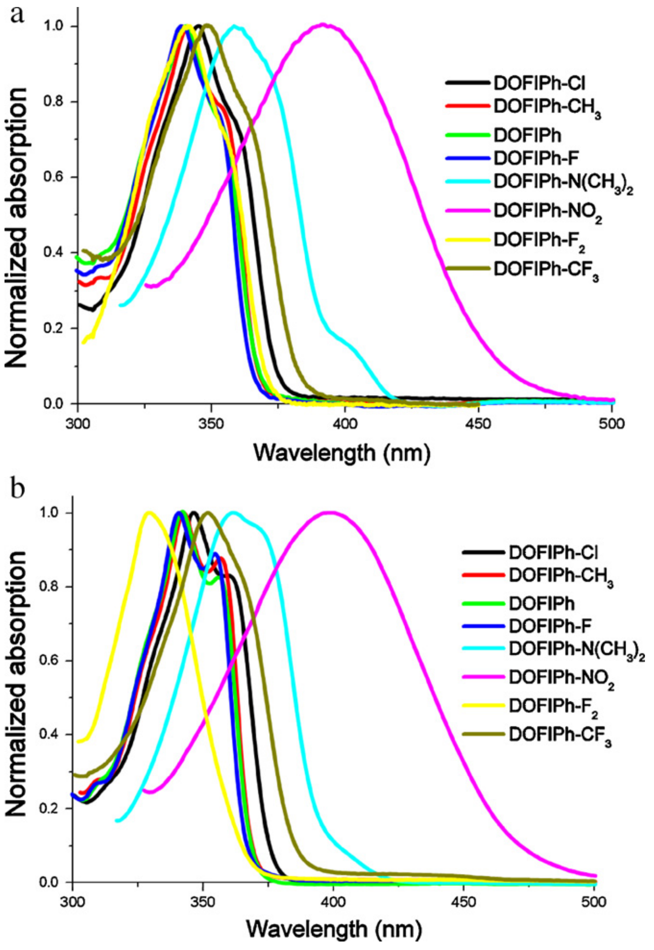


Fig. 3. Normalized absorption spectra of DOFIPhs (1×10^{-5} M) recorded in CH_2Cl_2 solutions (a) and in DMSO solutions (b) at room temperature.

Fig. 4 shows the photoluminescence (PL) spectra recorded upon excitation at absorption maximum at room temperature. In CH_2Cl_2 solution, the fluorescence spectra of DOFIPh showed two peaks at 372 and 385 nm (Fig. 4a) and the fluorescence quantum yield is 0.50, which is comparable to that of quinine sulfate (ϕ_{FL} = 0.55). The fluorescence spectra of compounds DOFIPh-CH_3 and DOFIPh-F were very similar to those of DOFIPh, showing two peaks at ca. 367 and 384 nm. The fluorescence maxima of DOFIPh-Cl and DOFIPh-F_2 were slightly red-shifted relative to those of DOFIPh. It is interesting to note that the fluorescence maxima of DOFIPh-NMe_2, DOFIPh-CF_3 and DOFIPh-NO_2, relative to those of DOFIPh, were red-shifted by 27, 30 and 36 nm, respectively, and compound DOFIPh-NO_2 fluoresced in dichloromethane with emission peaks at ca. 421 nm, probably due to the elongation of the conjugation length and the increased charge-transfer character induced by the fluoroalkyl or nitro groups. All the synthesized compounds were moderate fluorescent in CH_2Cl_2 solution with fluorescence quantum yields in the range of 0.15–0.54. It should be noted that the fluorescence quantum yield of DOFIPh-NO_2 (0.15) is lower than the yields of the other synthesized π-extended fluorenes. In general, the fluorescence quantum yield of a fluorophore containing nitro groups is extremely low because of the decrease in the radiative rate and the increase in the internal conversion rate of an excited state fluorophore [27]. However, this fluorescence quantum yield of DOFIPh-NO_2 is exceptionally higher than the yields of other general nitro-group-containing fluorophores (ϕ_{FL} < 0.01) [28,29]. Next, fluorescence spectra for DOFIPhs were measured in DMSO for certifying the influence of solvent polarity on their emission. As shown in Fig. 4b, most compounds were slightly red-shifted relative to those in CH_2Cl_2. DOFIPh-NMe_2 showed the disappearance of its vibronic band. In the case of DOFIPh-NO_2, the difference in the shift spans ca. 46 nm from CH_2Cl_2 to DMSO. Such large shift observed for DOFIPh-NO_2 in polar solvent may result from the difference in the dipole moments between the delocalized ground state and the highly localized excited one.

PL spectra in the solid state were carried out on films spin-coated onto quartz from chloroform solution. By comparison with the dilute CH_2Cl_2 solutions, the emission spectra of all compounds in solid states showed red-shifts to longer wavelengths by 11–105 nm (Fig. 4c). The red-shifts of the emission observed in the solid state were probably due to the rigid fluoreno[3,2-*d*]imidazole group and its strong intermolecular forces, which drove the molecules to pack at high density, restricted the molecular rotation and increased the π-conjugation significantly, in turn resulting in the red-shifts. In the solid state, the fluorescence maxima of unsubstituted DOFIPh were red-shifted by ca. 57 nm relative to those in CH_2Cl_2 solution, showing two peaks at 389 and 442 nm. Substitution with methyl group (DOFIPh-CH_3) produces a small red-shift in the emission and

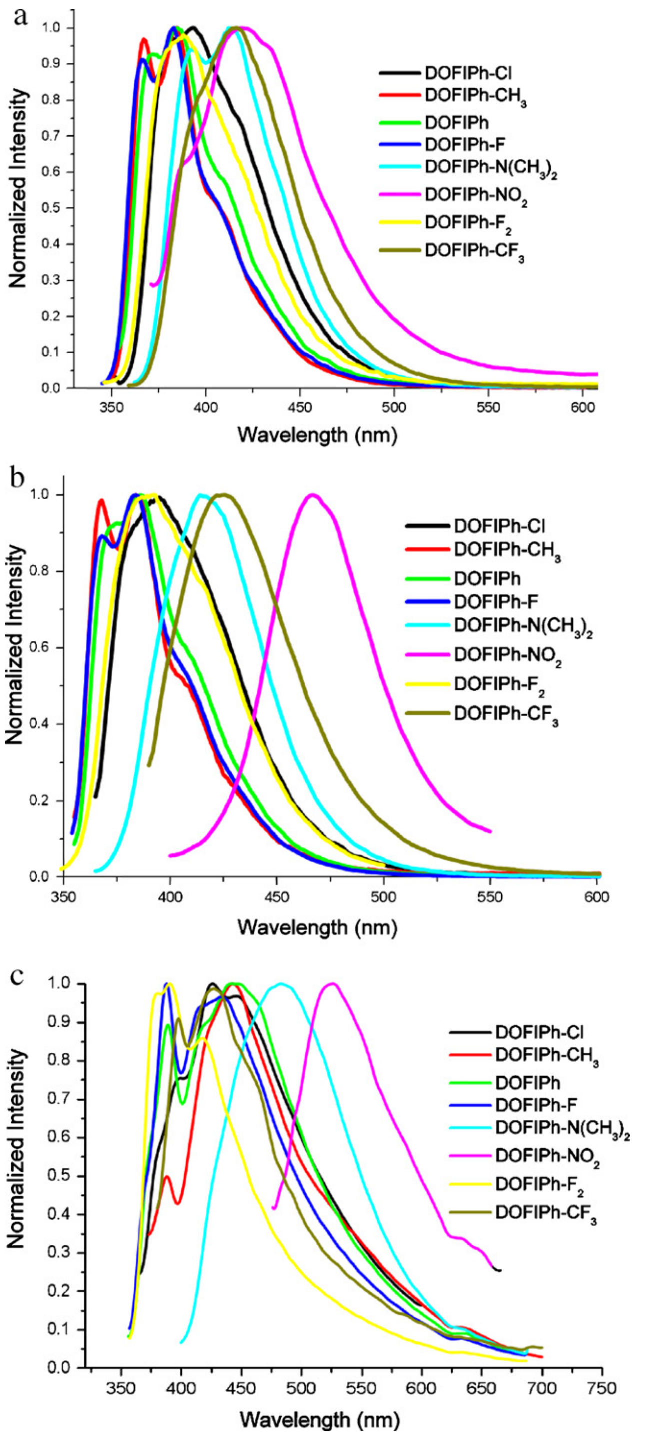


Fig. 4. Normalized fluorescence spectra of DOFIPhs recorded in CH_2Cl_2 solutions (5×10^{-7} M, (a)), in DMSO solutions (5×10^{-7} M, (b)) and in thin neat films (c) excited at the each absorption maximum at room temperature.

shows blue PL (λ_{max} = 443 nm). Halogenation (DOFIPh-F, DOFIPh-Cl, DOFIPh-F_2) produces a noticeable blue-shift in their solid-state PL emission (λ_{max} = 433, 426 and 417 nm, respectively). Also, a similar blue-shift is seen in the solid PL emission of p-CF_3 substituted derivative DOFIPh-CF_3, and blue PL (λ_{max} = 427 nm) was obtained. Derivative DOFIPh-NMe_2 with donor substituent (NMe_2) showed blue-green emission, with a PL emission maximum at 483 nm. Interestingly, compound DOFIPh-NO_2 with strong π-acceptor substituent exhibited a larger red shift (105 nm) than the other DOFIPh derivatives, and showed green PL (λ_{max} = 526 nm). The polar nitro group is also known as good π-acceptor, and has a more planar structure (i.e., sp^2 hybrid orbital). The bathochromic shift in PL emission maximum might be attributed to two factors. Electronically, a conjugative interaction over the entire molecule was better achieved between the polar substituent and the other side of fluoreno[3,2-*d*]imidazole, and also a better packing arrangement due to a more overall molecular planar structure may be achieved in the solid state. Through control of the substituents of DOFIPhs, a broad range of emissions in the visible region can be achieved.

3. Conclusion

In summary, 2,3-diamino-9,9-dioctylfluorene (DADOF), as a new multifunctional intermediate for π conjugated molecules, was efficiently synthesized via a seven-step procedure with an overall yield of 30%. And novel 3,9-dihydro-9,9-dioctyl-2-phenyl fluoreno[3,2-*d*]imidazole (DOFIPh)-type fluorophores with polar substituents were designed and conveniently synthesized, and their absorption and fluorescence properties were investigated in solution and in the solid state. The DOFIPhs were synthesized by condensation of the key intermediate 2,3-biamino-9,9-bioctylfluorene with aldehydes under very mild conditions, which make it possible to incorporate a diverse range of substituents in the DOFIPh core. The fluorophore DOFIPh exhibits strong blue emission in solid state and fine-tuning of the emission is possible depending on the electronic nature of the substituents. Further research regarding the incorporation of these systems usable both as organic light-emitting diodes and as fluorescent probes is under way in our laboratory.

4. Experimental

4.1. General

Commercially available reagents were purchased and were used without further purification unless otherwise mentioned. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (500 MHz) spectrometer in $CDCl_3$ or DMSO-d_6, unless otherwise noted. Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). Coupling patterns are described by abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm) for ^{1}H NMR, and to $CDCl_3$ (77.16 ppm) for ^{13}C NMR, as internal references. The center line of the multiplets of DMSO-d_6 was defined as 2.50 for ^{1}H NMR. Mass spectra were recorded using an EI source (Agilent 5975N instrument). Silica gel plate GF254 was used for thin layer chromatography (TLC) and silica gel H or 300–400 mesh was used for flash column chromatography. Melting points were measured on a Digital Melting Point Apparatus without correction. Yields are shown in terms of those of isolated pure materials. The absorption and fluorescence spectra were recorded using a UV-2501Pc spectrophotometer and a RF-5301 fluorescence spectrophotometer. High-resolution mass spectra (HR-MS) were recorded on an IonSpec 4.7 Tesla FTMS instrument. Elemental analysis was performed on an Elementar Vario EL (Germany) instrument.

4.2. Synthesis

4.2.1. 9,9-Bioctylfluorene (1)

To a solution of fluorene (4.15 g, 0.025 mol), potassium hydroxide (5.6 g, 0.1 mol) in DMSO (50 mL), was added 1-bromooctane (9.65 g, 0.05 mol) at room temperature and the reaction mixture was allowed to stir for 5 h. The reaction mixture was poured into water, and then the mixture was extracted with AcOEt.

The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and then the solvent was evaporated in vacuum. The residue was purified by flash column chromatography using petroleum ether as eluent to afford 1 (8.95 g, yield 91%) as light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.72 (d, J = 7.5 Hz, 2H), 7.36–7.29 (m, 6H), 1.99–1.96 (m, 4H), 1.24–1.06 (m, 20H), 0.84 (t, J = 7.0 Hz, 6H), 0.65–0.63 (m, 4H).

4.2.2. 2-Nitro-9,9-bioctylfluorene (2)

To a solution of 9,9-bioctylfluorene 1 (7.8 g, 20 mmol) in glacial acetic acid (30 mL) was added fuming nitric acid (8 mL) dropwise at 0 °C. After the addition of nitric acid, the resulting solution was allowed to warm to room temperature and was stirred for 30 min. Then the reaction mixture was poured into water (20 mL). The yellow oil was extracted with AcOEt. The combined organic layer was purified by flash column chromatography using petroleum ether:AcOEt (20:1) as eluent to afford 2 (5.9 g, yield 68%) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.27 (dd, J = 8.0, 2.0 Hz, 1H), 8.22 (d, J = 2.0 Hz, 1H), 7.81–7.78 (m, 2H), 7.45–7.38 (m, 3H), 2.03 (m, 4H), 1.26–1.03 (m, 20H), 0.81 (t, J = 7.0 Hz, 6H), 0.62–0.53 (m, 4H).

4.2.3. 2-Amino-9,9-bioctylfluorene (3)

A mixture of ferrous powder (3.3 g, 58 mmol) in H_2O (30 mL) was heated to 90 °C. Concentrated hydrochloric acid (15 mL) was added slowly. Then 2-nitro-9,9-bioctylfluorene 2 (4.35 g, 10 mmol) dissolved in ethanol (30 mL) was added to the mixture, and was stirred vigorously for 30 min. The reaction mixture was filtered and washed with H_2O. The crude solid was purified by flash column chromatography using petroleum ether:AcOEt (10:1) as eluent to afford 3 (3.7 g, yield 92%, Mp = 58–60 °C) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm 7.49 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 7.0 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.0 Hz, 1H), 6.56 (d, J = 2.0 Hz, 1H), 6.51 (dd, J = 8.0, 2.0 Hz, 1H), 5.19 (br, 2H), 1.91–1.741 (m, 4H), 1.18–0.98 (m, 20H), 0.78 (t, J = 7.0 Hz, 6H), 0.57–0.45 (m, 4H).

4.2.4. 2-Acetamido-9,9-bioctylfluorene (4)

To a solution of 2-amino-9,9-bioctylfluorene 3 (3.64 g, 9 mmol) in glacial acetic acid (30 mL) was added acetic anhydride (20 mL) dropwise at room temperature for 6 h. Then H_2O (40 mL) was slowly added. And the mixture was filtered and washed with water. The crude solid was purified by flash column chromatography using petroleum ether:AcOEt (5:1) as eluent to afford 4 (3.5 g, yield 87%, Mp = 147–148 °C) as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.63–7.61 (m, 2H), 7.55 (d, J = 1.5 Hz, 1H), 7.44 (dd, J = 8.0, 1.5 Hz, 1H), 7.31–7.24 (m, 4H), 2.21 (s, 3H), 1.94–1.90 (m, 4H), 1.18–1.02 (m, 20H), 0.81 (t, J = 7.0 Hz, 6H), 0.61–0.57 (m, 4H).

4.2.5. 2-Acetamido-3-nitro-9,9-bioctylfluorene (5)

To a solution of 2-acetamido-9,9-bioctylfluorene 4 (3.1 g, 7 mmol) in glacial acetic acid (30 mL) was added fuming nitric acid (3 mL) dropwise at room temperature. And the resulting solution was stirred for 30 min. Then the reaction mixture was poured into 20 mL water. The solid was filtered under reduced pressure, and the separated solid was washed several times with water. The crude solid was purified by flash column chromatography using petroleum ether:AcOEt (10:1) as eluent to afford 5 (2.9 g, yield 85%, Mp = 67–68 °C) as a brown solid. ^{1}H NMR (500 MHz,$CDCl_3$): δ ppm 10.5 (s,1H), 8.81 (s, 1H), 8.49 (s, 1H), 7.72–7.69 (m, 1H), 7.39–7.33 (m, 3H), 2.33 (s, 3H), 2.04–1.94 (m, 4H), 1.21–1.02 (m, 20H), 0.80 (t, J = 7.0 Hz, 6H), 0.61–0.54 (m, 4H).

4.2.6. 2-Amino-3-nitro-9,9-bioctylfluorene (6)

A mixture of 2-acetamido-3-dinitro-9,9-bioctyl-fluorene 5 (3 g, 6 mmol) in 70% sulfuric acid (20 mL) was heated to 90 °C and stirred for 5 h. The resulting solution was poured into water (20 mL). After cooling, the red precipitate was filtered under reduced pressure. The crude solid was purified by flash column chromatography using petroleum ether:AcOEt (5:1) as eluent to afford 6 (2.4 g, yield 88%, Mp = 156–157 °C) as a dark red solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.41 (s, 1H), 7.64 (d, J = 7.0 Hz, 1H), 7.34–7.26 (m, 3H), 6.76 (s, 1H), 6.29 (br, 2H), 1.98–1.84 (m, 4H), 1.22–1.04 (m, 20H), 0.82 (t, J = 7.0 Hz, 6H), 0.67–0.58 (m, 4H).

4.2.7. 2,3-Biamino-9,9-bioctylfluorene (7)

A mixture of ferrous powder (560 mg, 10 mmol) in H_2O (20 mL) was heated to 90 °C. Then concentrated hydrochloric acid (8 mL) was added dropwise, after that, 2-amino-3-nitro-9,9-bioctylfluorene 6 (450 mg, 1 mmol) dissolved in ethanol (20 mL) was added to the mixture. The mixture was stirred vigorously for 30 min. The reaction mixture was poured into water, and then the mixture was extracted with AcOEt. The combined organic layer was evaporated in vacuum. The residue was purified by flash column chromatography using petroleum ether:AcOEt (3:1) as eluent to afford 7 (344 mg, yield 82%) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.40 (d, J = 8.0 Hz, 1H), 7.16 (m, 2H), 7.08 (t, J = 7.0 Hz, 1H), 6.96 (s, 1H), 6.58 (s, 1H), 3.42 (br, 4H), 1.81–1.74 (m, 4H), 1.13–0.95 (m, 20H), 0.74 (t, J = 7.0 Hz, 6H), 0.60–0.52 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 150.6, 143.9, 141.8, 134.9, 133.7, 133.2, 126.6, 125.4, 122.6, 118.4, 111.3, 108.6, 54.5, 40.7, 31.9, 30.3, 29.8, 29.4, 23.9, 22.7, 14.2. MS (EI) m/z = 420.4 (M^+), calcd for $C_{29}H_{44}N_2$, M = 420.4.

4.2.8. General procedure for synthesis of FIPh-Cl, FIPh-NO_2 and DOFIPhs

A mixture of the corresponding aldehyde (1 mmol) and 2,3-biamino-9,9-bioctylfluorene 7 (420 mg, 1 mmol) or 2,3-biaminofluorene (196 mg, 1 mmol) in dioxane was refluxed for 8 h. The solvent was removed under vacuum and the residue was purified by flash column chromatography using petroleum ether/ethyl acetate as eluent to afford the desired compounds.

4.2.9. 2-(4-Chlorophenyl)-3,9-dihydrofluoreno[3,2-d]imidazole (FIPh-Cl)

White solid, yield 72%. Mp 222–224 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm 13.07 (br, 1H), 8.21 (d, J = 8.5 Hz, 2H), 8.05 (s, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.75 (s, 1H), 7.62 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.27 (m, 1H), 3.98 (s, 2H). MS (EI) m/z = 316.1 (M^+), calcd for $C_{20}H_{13}{}^{35}ClN_2$, M = 316.1.

4.2.10. 2-(4-Nitrophenyl)-3,9-dihydrofluoreno[3,2-d]imidazole (FIPh-NO_2)

Yellow solid, yield 80%. Mp 232–234 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm 13.30 (br, 1H), 8.44–8.39 (m, 4H), 8.09 (s, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.80 (s, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 4.01 (s, 2H). MS (EI) m/z = 327.2 (M^+), calcd for $C_{20}H_{13}N_3O_2$, M = 327.1.

4.2.11. 2-(4-Fluorophenyl)-9,9-dioctyl-3,9-dihydrofluoreno[3,2-d]imidazole (DOFIPh-F)

Light yellow solid, yield 72%. Mp 177–179 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.06 (dd, J = 8.5, 5.0 Hz, 2H), 7.74 (s, 1H), 7.53 (dd, J = 5.5, 3.0 Hz, 1H), 7.47 (s, 1H), 7.23 (dd, J = 6.5, 2.0 Hz, 1H), 7.19–7.17 (m, 2H), 6.99 (t, J = 8.5 Hz, 2H), 1.90–1.83 (m, 4H), 1.08–0.91 (m, 20H), 0.70 (t, J = 7.0 Hz, 6H), 0.55–0.53 (m, 4H). HR-MS: calcd for $C_{36}H_{45}FN_2$ ($[M+H]^+$), 525.3645; found, 525.3644. Anal. calcd for $C_{36}H_{45}FN_2$: C, 82.40; H, 8.64; N, 5.34. Found: C, 82.48; H, 8.53; N, 5.16.

4.2.12. 2-(4-Chlorophenyl)-9,9-dioctyl-3,9-dihydrofluoreno[3,2-d]imidazole
(DOFIPh-Cl)

White solid, yield 77%. Mp 195–196 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.05 (d, J = 8.5 Hz, 2H), 7.83 (s, 1H), 7.63 (dd, J = 5.5, 2.5 Hz, 1H), 7.59 (s, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.33–7.30 (m, 1H), 7.29–7.27 (m, 2H), 2.02–1.91 (m, 4H), 1.18–0.99 (m, 20H), 0.79 (t, J = 7.0 Hz, 6H), 0.66–0.59 (m, 4H). HR-MS: calcd for $C_{36}H_{45}{}^{35}ClN_2$ ([M+H]$^+$), 541.3349; found, 541.3344. Anal. calcd for $C_{36}H_{45}ClN_2$: C, 79.89; H, 8.38; N, 5.18. Found: C, 79.61; H, 8.18; N, 4.96.

4.2.13.
9,9-Dioctyl-2-p-tolyl-3,9-dihydrofluoreno[3,2-d]imidazole
(DOFIPh-CH_3)

Light yellow solid, yield 76%. Mp 160–162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.97 (d, J = 8.0 Hz, 2H), 7.68 (s, 1H), 7.52 (d, J = 6.5 Hz, 1H), 7.47 (s, 1H), 7.23–7.20 (m, 1H), 7.19–7.14 (m, 4H), 2.27 (s, 3H), 1.89–1.84 (m, 4H), 1.10–0.91 (m, 20H), 0.70 (t, J = 7.0 Hz, 6H), 0.59–0.50 (m,4H). HR-MS: calcd for $C_{37}H_{48}N_2$ ([M+H]$^+$), 521.3895; found, 521.3887. Anal. calcd for $C_{37}H_{48}N_2$: C, 85.33; H, 9.29; N, 5.38. Found: C, 85.05; H, 9.12; N, 5.29.

4.2.14.
9,9-Dioctyl-2-phenyl-3,9-dihydrofluoreno[3,2-d]imidazole
(DOFIPh)

Light yellow solid, yield 81%. Mp 138–140 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.17 (dd, J = 7.5, 2.0 Hz, 2H), 7.65 (s, 1H), 7.45 (dd, J = 5.5, 2.5 Hz, 1H), 7.39 (s, 1H), 7.31–7.29 (m, 3H), 7.21 (dd, J = 5.5, 3.0 Hz, 1H), 7.15 (t, J = 3.5 Hz, 2H), 1.85–1.78 (m, 4H), 1.08–0.90 (m, 20H), 0.69 (t, J = 7.0 Hz, 6H), 0.54–0.50 (m, 4H). HR-MS: calcd for $C_{36}H_{46}N_2$ ([M+H]$^+$), 507.3739; found, 507.3738. Anal. calcd for $C_{36}H_{46}N_2$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.50; H, 9.07; N, 5.21.

4.2.15. 2-(4-Nitrophenyl)-9,9-dioctyl-3,9-dihydrofluoreno[3,2-d]imidazole
(DOFIPh-NO_2)

Yellow solid, yield 80%. Mp 173–175 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.33 (d, J = 8.5 Hz, 2H), 8.25 (d, J = 8.5 Hz, 2H), 7.89 (br, 1H), 7.71 (d, J = 6.0 Hz, 1H), 7.66 (br, 1H), 7.33 (d, J = 7.0 Hz, 3H), 2.00–1.98 (m, 4H), 1.17–1.00 (m, 20H), 0.79 (t, J = 7.0 Hz, 6H), 0.63 (m, 4H). HR-MS: calcd for $C_{36}H_{45}N_3O_2$ ([M+H]$^+$), 552.3590; found, 552.3575. Anal. calcd for $C_{36}H_{45}N_3O_2$: C, 78.36; H, 8.22; N, 7.62. Found: C, 78.45; H, 8.36; N, 7.23.

4.2.16. 4-(9,9-Dioctyl-3,9-dihydrofluoreno[3,2-d]imidazol-2-yl)-N,N-dimethylbenzenamine
(DOFIPh-$N(CH_3)_2$)

Yellow solid, yield 75%. Mp 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.91 (d, J = 9.0 Hz, 2H), 7.68 (s, 1H), 7.56 (d, J = 7.0 Hz, 1H), 7.46 (s, 1H), 7.23–7.14 (m, 3H), 6.67 (d, J = 9.0 Hz, 2H), 2.92 (s, 6H), 1.89 (t, J = 8.0 Hz, 4H), 1.10–0.92 (m, 20H), 0.72 (t, J = 7.0 Hz, 6H), 0.58–0.51 (m, 4H). HR-MS: calcd for $C_{38}H_{51}N_3$ ([M+H]$^+$), 550.4161; found, 550.4157. Anal. calcd for $C_{38}H_{51}N_3$: C, 83.01; H, 9.35; N, 7.64. Found: C, 82.75; H, 9.27; N, 7.63.

4.2.17. 2-(2,6-Difluorophenyl)-9,9-dioctyl-3,9-dihydrofluoreno[3,2-d]imidazole
(DOFIPh-F_2)

Yellow solid, yield 74%. Mp 139–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 12.49 (br, 1H), 7.86 (s, 1H), 7.67 (d, J = 6.5 Hz, 1H), 7.59 (s, 1H), 7.37 (d, J = 7.0 Hz, 1H), 7.34–7.29 (m, 2H), 7.26 (t, J = 6.5 Hz, 1H), 6.94 (t, J = 8.5 Hz, 2H), 2.02–2.00 (m, 4H), 1.25–1.08 (m, 20H), 0.84 (t, J = 7.0 Hz, 6H), 0.70 (m, 4H). HR-MS: calcd for $C_{36}H_{44}F_2N_2$ ([M+H]$^+$), 543.3551; found, 543.3541. Anal. calcd for $C_{36}H_{44}F_2N_2$: C, 79.67; H, 8.17; N, 5.16. Found: C, 79.69; H, 8.36; N, 4.96.

4.2.18. 9,9-Dioctyl-2-(4-(trifluoromethyl)phenyl)-3,9-dihydrofluoreno[3,2-d]imidazole
(DOFIPh-CF_3)

Yellow solid, yield 80%. Mp 183–186 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.20 (d, J = 8.0 Hz, 2H), 7.89 (s, 1H), 7.69 (s, 1H), 7.64 (dd, J = 5.0, 3.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.36–7.32 (m, 1H), 7.31–7.28 (m, 2H), 2.02–1.97 (m, 4H), 1.19–1.01 (m, 20H), 0.79 (t, J = 7.0 Hz, 6H), 0.66–0.62 (m, 4H). HR-MS: calcd for $C_{37}H_{45}F_3N_2$ ([M+H]$^+$), 575.3613; found, 575.3615. Anal. calcd for $C_{37}H_{45}F_3N_2$: C, 77.32; H, 7.89; N, 4.87. Found: C, 77.44; H, 7.72; N, 4.75.

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