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Amplifying the Negative Solvatochromism of Pyridinium Phenolates via Fluorene Conjugation

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ABSTRACT:

New chromophores carrying a donor phenolate group and an acceptor pyridyl moiety separated by a fluorene spacer are reported. A progressive elongation of the systems was achieved by the introduction of additional phenyl ring and one or two vinyl linkers using Suzuki–Miyaura or Horner–Wadsworth–Emmons couplings. Zwitterionic forms **FL1** – **FL5** of these donor-bridge-acceptor molecules were generated through consequent *N*-methylation and deprotonation reactions leading to large redshifts in absorbance maxima. UV-vis absorbance studies also revealed negative solvatochromic behavior, with a smooth bathochromic shift observed upon decreasing the solvent polarity. Notably, examples **FL1a** and **FL3** exhibited wide solvatochromic shifts of 235 and 297 nm, respectively, as the solvent polarity gradually lowered from polar water to less polar pyridine. Remarkably, the magnitude of the shift for **FL3** was even greater than that of Reichardt's dye (253 nm) in the same solvent range, which is known to be one of the best performing solvatochromic dyes reported. Apart from extending the conjugation,

the fluorene moiety also allows facile sidechain engineering making these solvatochromic dyes attractive candidates for medium polarity indicators and sensors.

INTRODUCTION

Solvatochromic dyes undergo changes in their photophysical properties with variation in the solvent environment.[1] Apart from being sensitive to the polarity of the environment, these materials can also be involved in solvent specific supramolecular interactions such as hydrogen bonding. This leads to their application not just as solvent polarity sensors, but also as probes to study solvent effects in organic chemistry[2] and supramolecular chemistry[3], for chemical sensing[4-9] as well as for examining biological processes[10-12].

The core design principle of solvatochromic dyes involves electron donating and electron accepting moieties arranged on the molecular structure establishing a dipole.[1, 13] Through electron delocalization in conjugated organic dyes, the molecular dipole changes through interactions with the environment leading to shifts in photophysical properties. Two well-known examples showing negative solvatochromism are Brooker's merocyanine (**BM**)[14] and Reichardt's **Betaine 30** (**Figure 1**).[15] Negative solvatochromic dyes show a bathochromic shift upon decrease of solvent polarity. **Betaine 30** has been used as one of the standards in determining solvent polarity with the $E_T(30)$ scale (kcal mol^{-1}) established based on the molar electronic transition energy of **Betaine 30** in a wide range of solvents.[13] Despite lots of structural variation, **Betaine 30** is still one of the most solvatochromic dyes with a large negative solvatochromic shift of 443 nm between 1,1,1,3,3,3-hexafluoro-2-propanol and tetrachloromethane.[16] **Thiobetaine**, where a sulphur atom replaces the oxygen in the phenolate,[17]

is one example that shows greater negative solvatochromic behaviour than **Betaine 30**. Solvatochromic shifts of 356 and 300 nm were observed for **Thiobetaine** and **Betaine 30**, respectively, from 1,2-ethandiol to thiophene.[17]

Our group has been studying another pyridinium phenolate dye (**POMP**)[18] and we reported a series of its oligophenylene derivatives[19] showing promising solvatochromic behaviour (**Figure 1**). By extending the π system by one phenyl ring, we observed that the magnitude of solvatochromic shift for **OPP(2)-O**$^-$ was 167 nm between water and DMF.[19] This was almost twice the wavelength shift compared to **POMP** and comparable to **Betaine 30** in the same solvent range. Our study showed that extra phenyl ring extension in **OPP(3)-O**$^-$ led to reduced solvatochromic behaviour which we attributed to weak π conjugation of the biphenyl bridge. In addition, these reported molecules are soluble in a limited range of solvents.

To obtain a more solvatochromic system with greater solubility in a wider range of solvents, we decided to examine the use of the fluorene building block while keeping the pyridinium electron acceptor and phenolate electron donor moieties (**Figure 1**). The insertion of a fluorene bridging unit should improve π conjugation.[20] The fluorene unit can also be easily substituted at the sp^3 carbon for improved solubility and functional versatility. Another desirable feature is that this modification would only have a minor electronic effect on the overall system. Thus, a very close analogue of **OPP(2)-O**$^-$ can be obtained.

We report here a series of novel donor-acceptor fluorene-based zwitterions **FL1** – **FL5** (**Figure 1**): where **FL1** and **FL2** are very close analogues of **OPP(2)-O**$^-$ and **OPP(3)-O**$^-$, whereas **FL3** – **FL5** resemble the structure of **BM**. With regards to sidechain engineering for improved solubility, there are either linear octyl groups or branched 2-ethylhexyl variations on

the fluorene subunit. Spectroscopic studies demonstrated that among the obtained zwitterions, **FL1** and **FL3** are more solvatochromic when compared to **OPPs** and **Betaine 30** in the analysed solvent range.

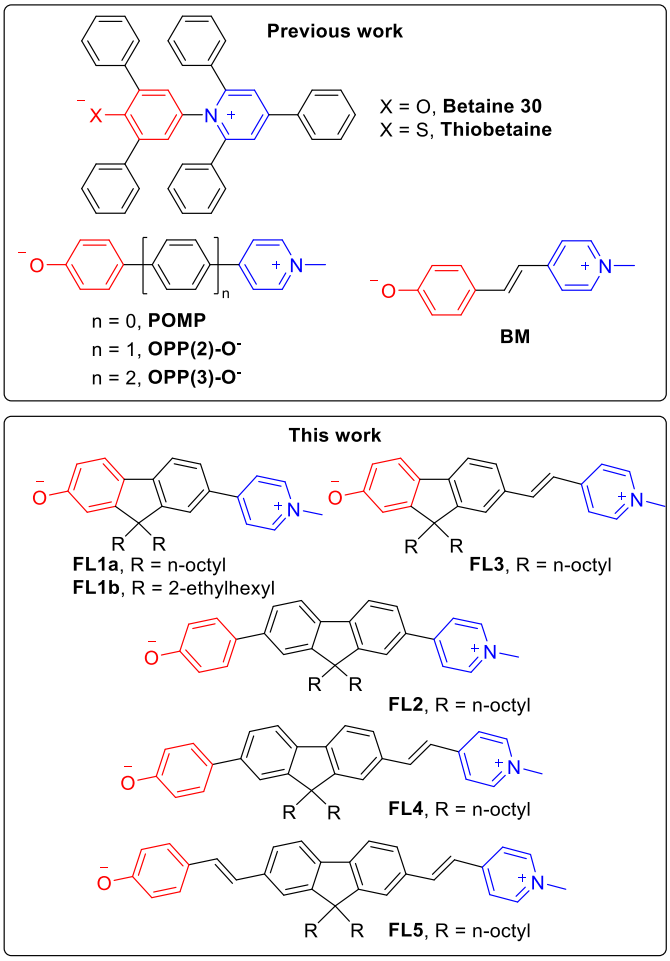


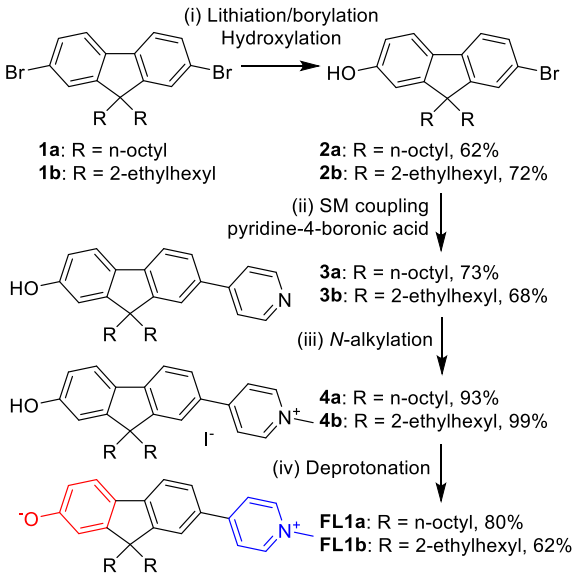
Figure 1. Examples of previously reported negatively solvatochromic pyridinium phenolate dyes (top) and the series of fluorene containing pyridinium phenolates reported in this work.

RESULTS AND DISCUSSION

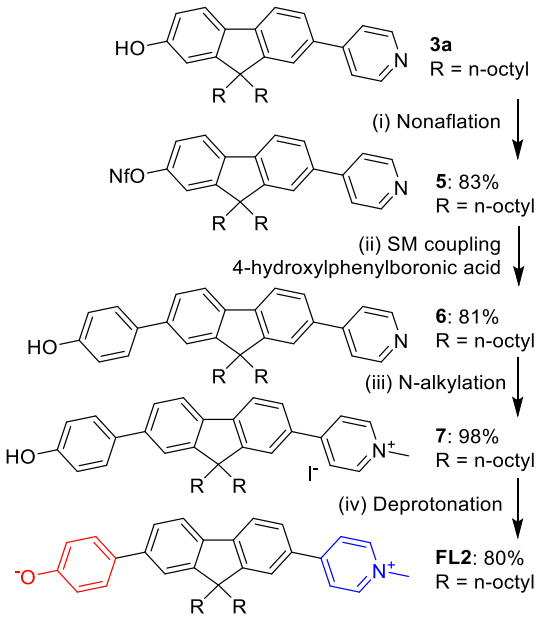
Synthesis of fluorene-spaced donor-acceptor zwitterions

All zwitterions were synthesised starting from 2,7-dibromofluorene. The synthesis of **FL1** and **FL2** began with a lithiation-borylation-hydroxylation sequence resulting in the desired 2-fluorenol **2** (Scheme 1). For **FL1**, an early decision was made to synthesize two fluorene building blocks with n-octyl and 2-ethylhexyl side chains with the intention of achieving greater solvent compatibility with the branched side chain. Suzuki–Miyaura (SM) coupling between compound **2** and pyridine-4-boronic acid gave compound **3** (Scheme 1). *N*-Alkylation followed by deprotonation resulted in **FL1**. Good overall yield across 4 steps of 34% for **FL1a** and 30% for **FL1b** was obtained. The extension of the **FL2** structure was achieved by nonaflation of fluorenol **3a** following by SM coupling with 4-hydroxyphenylboronic acid (Scheme 2). *N*-Methylation and deprotonation gave **FL2** in 24% overall yield from 2,7-dibromofluorene.

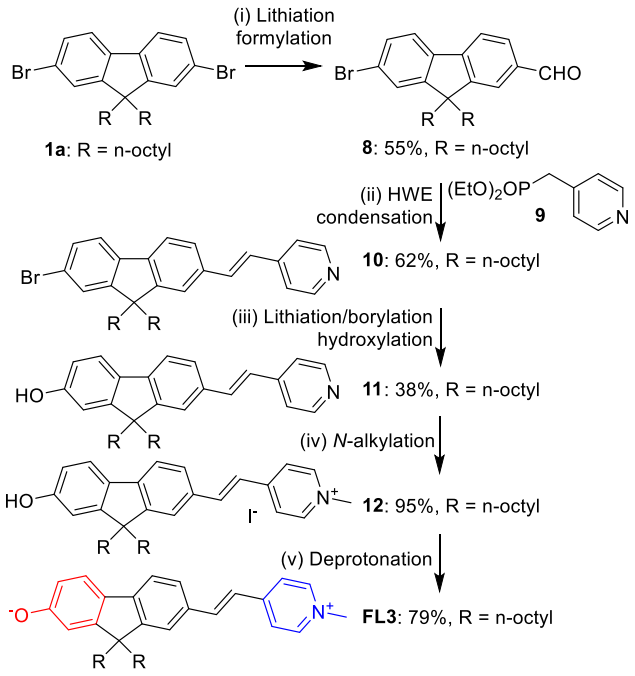
The extended Brooker's merocyanine structures **FL3**, **FL4**, and **FL5** were synthesized starting with the lithiation-formylation of 2,7-dibromofluorene (Scheme 3). Vinylpyridine **10** was obtained by Horner-Wadsworth-Emmons (HWE) condensation. Hydroxylation, *N*-methylation, and deprotonation gave **FL3** in overall yield of 10%. The structural extension for **FL4** was achieved by SM coupling with overall yield of 11% while the extension for **FL5** was achieved by HWE condensation with overall yield of 6% (Schemes 4 and 5). It is noteworthy that the synthetic approach to these molecules is extremely amenable to functional group changes allowing facile tuning of molecular properties, which is not the case for **Betaine 30**.



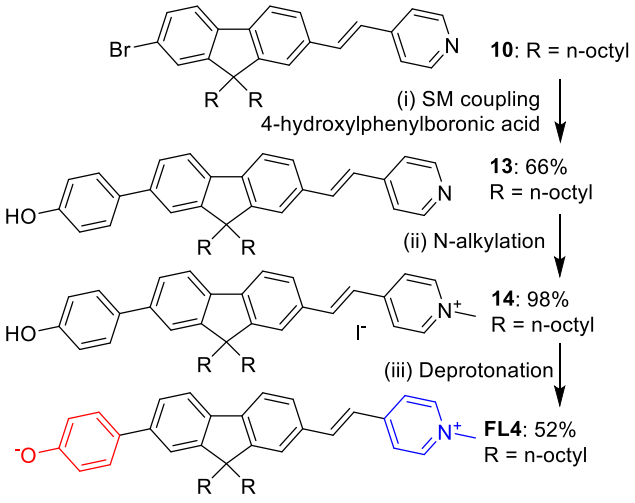
Scheme 1. Synthesis of **FL1a** and **FL1b**. (i) *n*-BuLi (1.05 equiv.), $B(OMe)_3$ (1.1 equiv.), THF, -78 °C to r.t, followed by UHP (2.0 equiv.), MeCN/Et_2O, r.t.; (ii) Pd_2dba_3 (2.5 mol%), $Cy_3P{\cdot}HBF_4$ (6.0 mol%), K_3PO_4 (1.7 equiv.), 1,4-Dioxane/H_2O (2/1, v/v), 100 °C, 16 h; (iii) MeI (4.0 equiv.), Acetone, 55 °C, 16 h; (iv) Et_3N/H_2O.



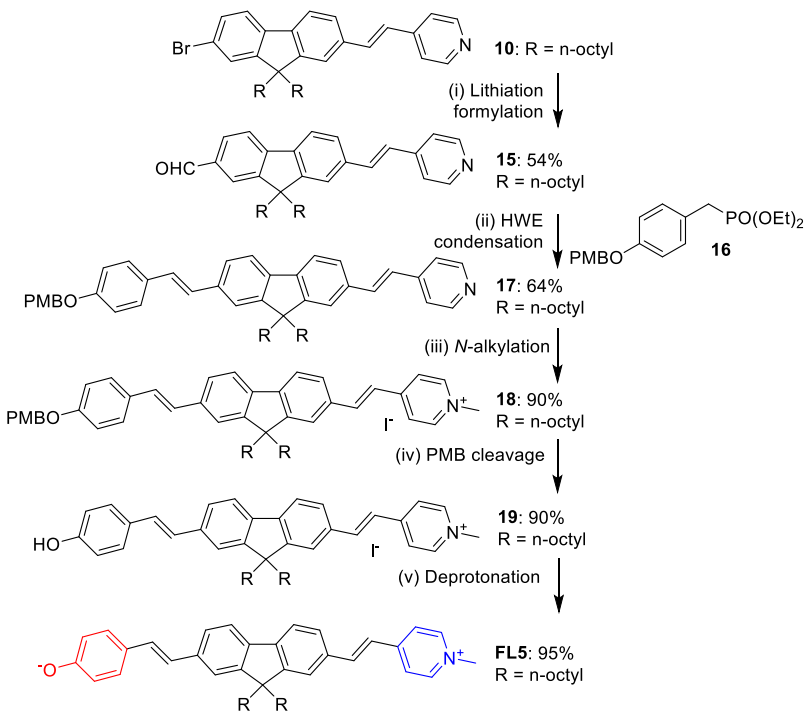
Scheme 2. Synthesis of **FL2**. (i) Nonafluorobutanesulfonyl fluoride (NfF, 1.5 equiv.), Et3N (2.0 equiv.), DMF, 80 °C, 16 h; (ii) Pd_2dba_3 (2.5 mol%), $Cy_3P{\cdot}HBF_4$ (6.0 mol%), K_3PO_4 (1.7 equiv.), 1,4-Dioxane/H_2O (2/1, v/v), 100 °C, 16 h; (iii) MeI (4.0 equiv.), Acetone, 55 °C, 16 h; (iv) Et_3N/H_2O.



Scheme 3. Synthesis of **FL3**. (i) *n*-BuLi (1.05 equiv.), DMF, THF, -78 °C to r.t.; (ii) NaH (3.5 equiv.), DME, 85 °C, 16 h; (iii) *n*-BuLi (1.05 equiv.), $B(OMe)_3$ (1.1 equiv.), THF, -78 °C to r.t, followed by UHP (2.0 equiv.), MeCN/Et_2O, r.t.; (iv) MeI (4.0 equiv.), Acetone, 55 °C, 16 h; (v) Et_3N/H_2O.



Scheme 4. Synthesis of **FL4**. (i) Pd_2dba_3 (2.5 mol%), $Cy_3P{\cdot}HBF_4$ (6.0 mol%), K_3PO_4 (1.7 equiv.), 1,4-Dioxane/H_2O (2/1, v/v), 100 °C, 16 h; (ii) MeI (4.0 equiv.), Acetone, 55 °C, 16 h; (iii) Et_3N/H_2O.



Scheme 5. Synthesis of **FL5**. (i) *n*-BuLi (1.05 equiv.), DMF, THF, -78 °C to r.t.; (ii) NaH (3.5 equiv.), DME, 85 °C, 16 h; (iii) MeI (4.0 equiv.), Acetone, 55 °C, 16 h; (iv) HCl/Dioxane, MeOH, r.t., 16h, followed by Et_3N/H_2O, MeOH.

The obtained intermediates were characterised by ^1H and ^{13}C NMR spectroscopy, ESI-MS and IR spectroscopy. For the deprotonated species **FL1** – **FL5**, only ^1H NMR spectra in DMSO-d_6 were obtained due to stability and/or solubility. The ^1H NMR spectra displayed significant upfield shifts of the most shielded aromatic signals compared to their protonated precursors, which was consistent with what was observed for previously reported OPPs[19].

Photophysical properties

UV-vis spectroscopic analysis of fluorene series was performed and compared against **Betaine 30**.[13, 19] With the alkyl chains on the fluorene unit, solubility of the obtained species was significantly improved over previously reported OPPs.[19] Up to ten solvents of different polarity were chosen including protic polar and aprotic lower polarity solvents: H_2O, MeOH, EtOH, *i*-PrOH, MeCN, DMSO, DMF, DCM and pyridine. The solubility of the compounds in non-polar solvents, such as hexane, toluene, or petroleum spirits, was too low to perform any measurements. In our previous work,[19] we observed that deprotonated forms exist in protic solvents only for a short time, and quickly undergo protonation. Consequently, fresh solutions were prepared just before conducting measurements and an excess of base (more than 20 equivalents) was added to maintain fully deprotonated state in the solution. For the range H_2O – DMF, deprotonation was performed in situ by using OH-forms as precursors and excess 1,1,3,3-tetramethylguanidine (TMG) as base.[19] In case of lower polarity solvents such as DCM and pyridine, the direct use of deprotonated forms of the dyes **FL1** – **FL5** was preferred with no base added due to reduced solubility and to avoid the presence of counterions in the solution.

The absorbance spectra of protonated forms in the range of solvent were first collected before moving on to the deprotonated samples. Spectra for the protonated forms were also studied, and typically, two absorbance maxima were observed in the 300 – 700 nm region (**Figure S1**). The positively charged protonated molecules were only weakly solvatochromic, and the minor shifts of the most red-shifted absorption maxima did not correlate uniformly with the solvent polarity change. These observations were consistent with those for protonated OPP species reported previously.[19] The absorbance maxima for all species were recorded and represented in **Error! Reference source not found.**. **Figure 2** shows **FL1** – **FL5** absorbance

spectra in solvents of different polarity and positions of the most red-shifted absorbance maxima for the most polar and the least polar solvents. It is important to note that when studying the UV-vis absorption spectra of pyridinium phenolate dyes, it is possible to observe absorption bands belonging to protonated and deprotonated forms at the same time. Depending on the dye structure and the solvent environment, the protonated and deprotonated forms will be at a certain equilibrium point. This is the observation in our previous work on OPPs.[19] In solvents of lower polarity, the lower energy absorption bands assigned to the deprotonated form generally exhibited reduced intensity.

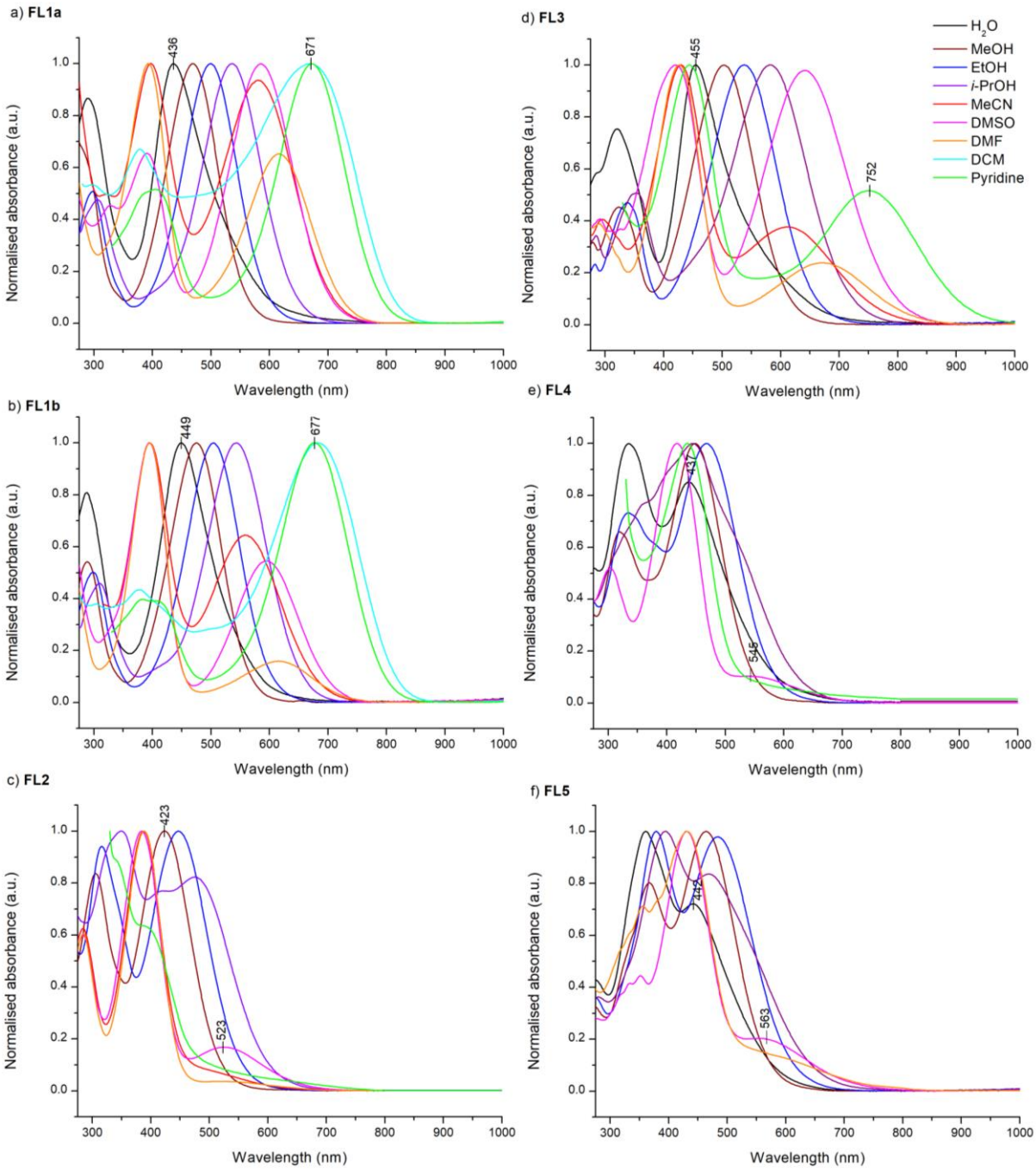


Figure 2. UV-vis absorbance spectra of **FL1 – FL5** in different polarity solvents.

For **FL1a** (**Figure 2a**), the deprotonation induced a shift towards longer wavelengths, where the maxima were 436 nm for the most polar solvent, water, to 671 nm for the least polar solvent, pyridine. That was a change of 235 nm between these two solvent extremes covering the whole visible range. The absorbance profiles for DCM and pyridine even approach the NIR region up to 850 nm, indicating strong negative solvatochromism. We then compared the solvatochromic behaviour of **FL1a** with **FL1b** bearing a branched 2-ethylhexyl chain on a fluorene core with the aim to improve solubility in non-polar solvents. **FL1b** behaved similarly to **FL1a** with the straight alkyl chain in terms of solubility as well as spectroscopic characteristics (**Figure 2b**). The range between H_2O and pyridine for **FL1b** spanned 228 nm. Both dyes gave a remarkable colour change when they were dissolved in different polarity solvents (**Figure 3a and b**). Interestingly, the observed solution colours variations were rather different for the two species and this was attributed to the different relative absorbance of the two main absorption bands. Using a combination of these dyes, it is envisaged that one can take advantage of these variations to increase specificity in chemical sensing applications. We also compared the solvatochromic properties of the **FL1** dyes with that of their reported analogue, **OPP(2)-O$^-$**.[19] In the solvent range in which **OPP(2)-O$^-$** was soluble (i.e. H_2O – DMF), a 139 nm absorption shift was registered for **OPP(2)-O$^-$**, whereas **FL1a** displayed a 179 nm shift (**Error! Reference source not found.**). Therefore, there was a clear effect of the fluorene moiety in **FL1** species in improving the solvatochromic behaviour.

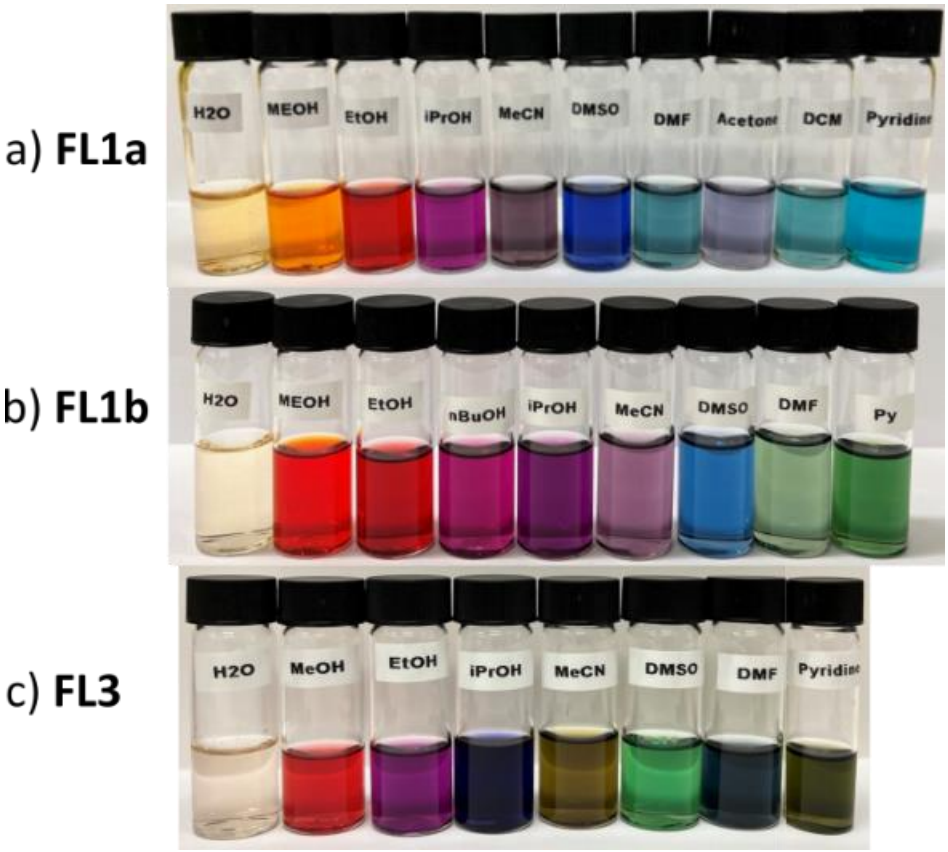


Figure 3. The observed colour change for a) **FL1a**, b) **FL1b** and c) **FL3**.

FL2 is an extension on **FL1** with an additional phenyl ring (**Figure 1**). This increase in the length of the molecule reduced its solubility in water as well as DMF and DMSO. Negative solvatochromic red shifts were observed, but much less significant than for the **FL1** dyes (**Figure 2c**). This was true upon deprotonation in protic solvents (e.g. MeOH – *i*-PrOH). However, for the less polar aprotic range of MeCN to pyridine, the absorbance band associated with the protonated form dominated the spectra with weak redshifted absorbance shoulders for deprotonated form. In these cases, absorbance maxima values for the protonated precursor **7** and **FL2** were almost identical and we could not precisely derive the absorbance maxima values of the deprotonated form based on such small features. Attempts to obtain the fully deprotonated

state in the solutions were not successful. The use of freshly prepared zwitterionic forms, addition of the base, and the use of anhydrous solvent all gave the same spectroscopic results. Additionally, solubility issues arose for these species limiting the studied solvent range. As molecules **FL4** and **FL5** were the most elongated in the series, solvatochromic behaviour similar to **FL2** can be explained in the same way. In these cases, an effective conjugation length was reached where the electron-rich and electron-poor ends of the molecules could not delocalise efficiently and interact with each other.[19] This meant that the extension of the donor-acceptor systems did not help with the improvement in negative solvatochromism.

To directly compare the solvatochromic behaviour of our FL series to **Betaine 30**, electronic transition energies (E_T, kcal/mol) based on the positions of the most red-shifted absorbance maxima of the dyes in each particular solvent were calculated ($E_T = 28591/\lambda_{max}$). Then these parameters were plotted against the solvent polarity scale $E_T(30)$ (**Table S1** and **Figure 4**). The best linear fit was used to interpolate data points, and the fitting parameters were derived (**Table S2**). It is important to note that data points collected in water containing 0.1% MeOH were omitted from the linear fit. Even a small amount of co-solvent greatly affected the behavior of the dyes and solvent mixtures did not interpolate cleanly with pure solvents. The slopes (k) for **FL1a**, **FL1b**, and **FL3** are greater than unity and range from 1.22 to 1.26, meaning that they are more solvatochromic than **Betaine 30** (k =1.00) and comparably solvatochromic to **Thiobetaine** (k = 1.25)[17]. **FL1a** has the highest slope value indicating it has the greatest sensitivity to polarity changes among all of the discussed compounds. Though these compounds have similar slopes, **FL3** shows the largest magnitude of the solvatochromic shift (297 nm vs. 235 nm for **FL1a** and 253 nm for **Betaine 30**, respectively). **FL2** and **FL4** also display comparably steep slopes of 1.23 and 1.13, but in these cases only few data points were used for

interpolation, because for several solvents the broadness or low intensity of the most red-shifted absorption features meant that the absorption maxima position was uncertain. Compound **FL5** showed the lowest slope value of 0.87, but the data point for *i*-PrOH significantly departs from the line of fit. Removal of the *i*-PrOH data point results in a slope of 1.06. Based on the magnitudes of the solvatochromic shifts and the slopes obtained, **FL1a**, **FL1b** and **FL3** are excellent polarity indicators in the explored polarity range.

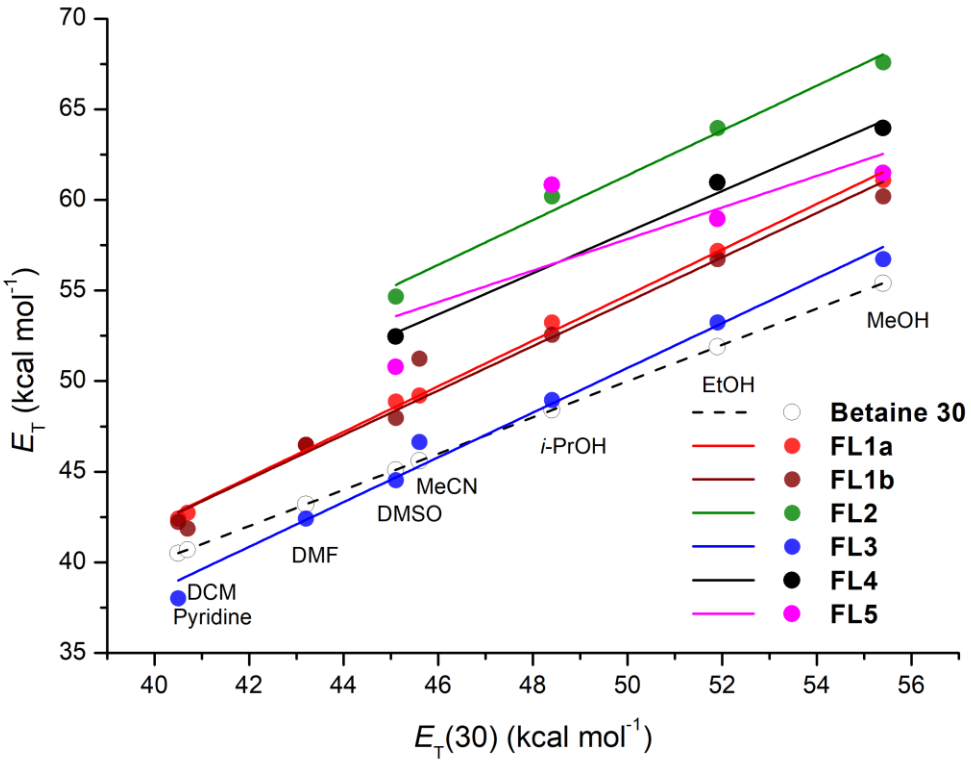


Figure 4. Transition energies of **FL1** – **FL5** and **Betaine 30** (as a reference compound) versus the empirical parameter of polarity $E_T(30)$.

We performed quantum chemical calculations for the fluorene series **FL1** – **FL5** to support the discussions of the observed photophysical behaviour. The alkyl chains were replaced with methyl groups to simplify the calculations without greatly modifying their electronic effects. Geometries were optimised in both vacuum and in methanol using M06-2X functional and 6-31+G(d,p) basis set (**Figure S2**). When molecules are solvated, the consecutive phenyl rings develop a significant twist in case of **FL1** and **FL2**, whereas, their vacuum geometries are planar. This is because regions of concentrated positive and negative charge in a vacuum cannot be screened, and, thus, the molecules have a strong tendency to planarize in order to cancel out the charges as much as possible by conjugation. Meanwhile, in a polar medium, screening is possible, allowing excess opposite charges to remain more spatially separate, and the degree of conjugation can be reduced. However, the vinyl-bridged rings **FL3** – **FL5** have enough space and conjugation strength to stay almost planar even with implicit solvation.

Figure 5 shows comparison of calculated frontier molecular orbital distributions in the fluorene series in vacuum and MeOH at CAM-B3LYP/6-31+G** level of theory. In vacuum for all examples, the HOMOs and LUMOs are delocalised throughout the whole molecular backbone, which was also observed in case of OPPs.[22] As expected, the implicit solvation caused the separation of the orbitals, where the HOMO mostly resides on electron-donor part of the molecule and LUMO on electron-acceptor one. Compared to the vacuum calculations, the HOMO energy levels were lower, but LUMO energies slightly increased, leading to a wider energy gap in polar media consistent with negative solvatochromic behaviour.

In **FL1** and **FL3,** a fair degree of HOMO and LUMO overlap is observed (**Figure 5**), indicating efficient electron delocalization throughout the molecules. For the rest of the examples – **FL2**, **FL4** and **FL5**, the orbitals are in proximity, but they barely overlap with each other. This

reduced electron delocalization is reflected in the higher electronic energy transitions for **FL2**, **FL4**, and **FL5** compared to that of **FL1** and **FL3** (**Figure 4**). However, as discussed in the previous section, the change in energy of the transitions with change in solvent polarity is similar across the series.

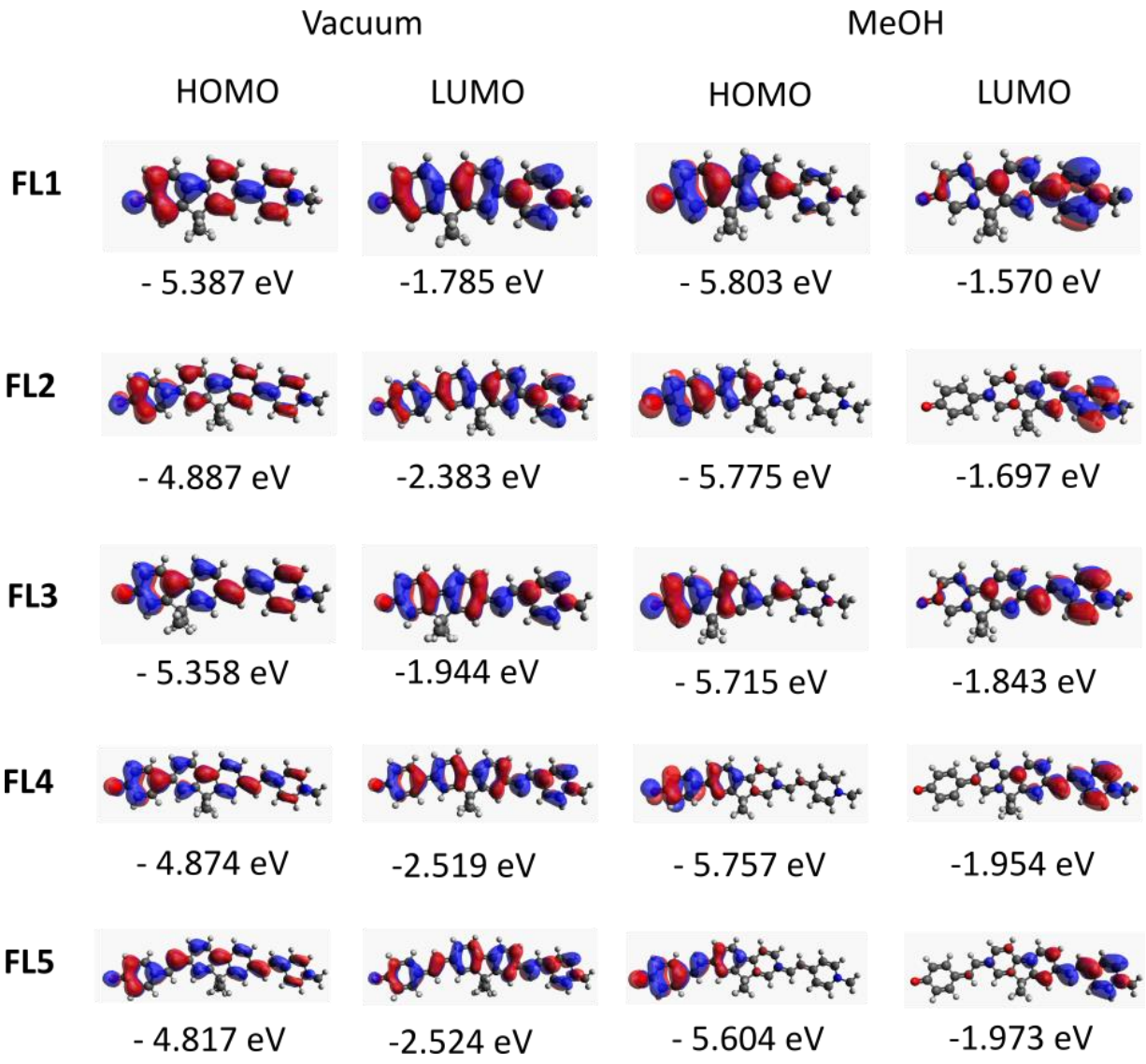


Figure 5. Calculated HOMO and LUMO of **FL1** – **FL5** in vacuum and MeOH using CAM-B3LYP/6-31+G**.

CONCLUSIONS

The extended zwitterionic fluorene molecules with a donor phenolate moiety and an acceptor pyridinium group were synthesised by using SM and HWE coupling chemistry in moderate to excellent yields. The introduction of fluorene spacer with alkyl sidechains afforded increased solubility and improved their spectroscopic characteristics compared to OPPs and **Betaine 30**. The synthetic strategy used is very versatile and allows tuning the structure even further if needed. For example, the donor and acceptor functionalities can be modified or replaced, which is not straight forward for **Betaine 30**. The observed spectroscopic shifts for **FL1** – **FL5** were consistent with the negative solvatochromic behavior. Among the obtained zwitterions, **FL1a**, **FL1b** and **FL3** display solvatochromic behaviour surpassing OPPs and even **Betaine 30** in our studied solvent range. This validated the use of the fluorene building block in our molecular design. The planarization of the molecules with incorporation of a fluorene unit increased π conjugation and electron delocalization. While the original intention of the fluorene 9-position sidechains was to improve solubility, we found that variation of that substitution modulated the UV-vis absorption spectrum profiles resulting in significant observable colour differences by the naked eye.

EXPERIMENTAL SECTION

Theoretical calculations. Following the calculations done for OPPs,[19] we also performed ground-state geometry optimisation with M06-2X functional and 6-31+G(d,p) basis for the fluorene series **FL1** – **FL5** with the GAUSSIAN16 software suite[23]. TD-DFT calculations were also performed at the CAM-B3LYP/6-31+G** level of theory. The calculations were performed under vacuum and with implicit solvation using a polarizable continuum model for MeOH

(ε = 32.61), DMSO (ε = 46.70), and Pyridine (ε = 12.98) implemented in both geometry optimisations and energy calculations.

Materials and methods. Commercial reagents were purchased from Sigma-Aldrich, AK Scientific, Matrix Scientific, Boron Molecular, Ajax Finechem, Univar and Labchem, and were used as delivered. Commercially available nonafluorobutanesulfonyl fluoride (NfF) was stirred with K_2HPO_4/K_3PO_4 (1:1, pH = 12-13) concentrated aqueous buffer for 96 h, filtered and distilled over P_2O_5 to remove perfluorosulfolane[24]. Anhydrous DCM, THF, Et_2O and Toluene were obtained from alumina-packed drying columns[25], anhydrous DMF and Et_3N were obtained by drying over activated molecular sieves. Standard Schlenk techniques were used for air-sensitive reactions. For oxygen-sensitive reactions, solvents were sparged with nitrogen gas for 30 min prior to addition, and the systems were closed with a rubber septum and maintained under positive nitrogen pressure. Purification via flash column chromatography was performed with Merck-Millipore silica gel (Keiselgel 60, 40-63 μm, 230-400 mesh). Thin-layer chromatography was performed on Merck-Millipore Silica gel 60G F254 glass plates, and spots were revealed under 254 nm and 365 nm light from a mercury lamp.

^{1}H NMR (400 MHz, 500 MHz and 600 MHz) and ^{13}C NMR (101 MHz, 126 MHz, 151 MHz) spectra were registered on 400 MHz Jeol, 500 MHz Agilent, 600 MHz Varian spectrometers or Bio600 MHz Bruker Avance III spectrometers. ^{19}F NMR (376 MHz) spectra were obtained on a 400 MHz Jeol spectrometer. ^{1}H NMR and ^{13}C NMR signals were referenced to $CDCl_3$, CD_3OD, $(CD_3)_2CO$ or DMSO-*d*$_6$ solvent peaks. ^{19}F NMR signals were referenced to an external standard of hexafluorobenzene in $CDCl_3$ (-164.9 ppm).

Mass spectra were obtained on an Agilent ESI-TOF-MS spectrometer operating in positive mode from methanol-acetonitrile solutions containing formic acid as a proton source. Infrared

absorption spectra were obtained with a Perkin-Elmer SpectrumOne ATR FT-IR spectrometer in the region of 650 to 4000 cm^{-1}.

UV-vis absorbance spectra were obtained with an Agilent Cary UV-vis Compact Peltier UV-visible spectrometer. For UV-vis measurements solid samples were dissolved in the desired solvent and diluted as necessary (~10^{-5} M); zwitterionic species were maintained in the solution by addition of TMG (>20 equiv.).

Synthetic procedures

*2,7-Dibromo-9,9-bis(3-ethylhexyl)-9H-fluorene (**1b**)*[26]

In a 200 mL Schlenk tube with a magnetic stirrer were added 10.0 g (30.9 mmol, 1.0 equiv.) 2,7-dibromo-*9H*-fluorene, 13.1 g (67.9 mmol, 2.2 equiv.) 2-ethylhexyl bromide (racemic mixture) and 47.5 mg (0.3 mmol, 1.0 mol%) NBu_4Br and vacuum/nitrogen cycles were performed. 14.0 g (349.0 mmol, 11.3 equiv.) NaOH was dissolved in 30 mL water, and then solution was sparged for 30 min. under nitrogen and cannulated to the reaction mixture. The reaction mixture was vigorously stirred at 80 °C for 16 h. The reaction mixture was transferred to a separatory funnel with ethyl acetate and water. The mixture was washed with 3×50 mL water, brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation. The crude product was further purified by distillation giving 16.2 g (96%) of yellow oil.

TLC silica, R_f (Petroleum spirits) = 0.6.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 4H), 7.45 (dd, J = 8.0, 1.8 Hz, 2H), 1.94 (td, J = 5.0, 1.6 Hz, 4H), 1.01 – 0.87 (m, 6H), 0.89 – 0.76 (m, 5H), 0.73 (td, J = 7.1, 2.2 Hz, 10H), 0.55 (dt, J = 7.5, 3.7 Hz, 6H), 0.48 (dq, J = 11.5, 5.8 Hz, 2H).

^{13}C[19] NMR (151 MHz, $CDCl_3$) δ 152.6, 152.6, 152.5, 139.3, 130.3, 130.3, 130.2, 127.7, 127.6, 127.5, 121.2, 121.1, 55.5, 44.5, 34.9, 34.9, 33.8, 33.8, 28.3, 28.2, 27.3, 27.2, 27.2, 22.9, 22.9, 14.2, 10.5, 10.5.

IR (film, cm^{-1}): 2956.7, 2922.5, 2871.4, 2856.8, 1597.9, 1571.4, 1449.2, 1416.9, 1398, 1378.6, 1331.6, 1290.8, 1256.6, 1232.4, 1217.5, 1168.6, 1129.5, 1109.3, 1060.7, 1005.9, 940.6, 879, 832.2, 806.6, 750.9, 725.3, 666.5.

*7-Bromo-9,9-dioctyl-9H-fluoren-2-ol (**2a**)*[27]

In a 200 mL Schlenk tube with a magnetic stirrer was added 4.7 g (8.6 mmol, 1.0 equiv.) of 2,7-dibromo-9,9-dioctyl-*9H*-fluorene (**1a**). After vacuum/nitrogen cycles, 100 mL of anhydrous THF was added. The solution was cooled to -78°C, and 4.0 mL (9.0 mmol, 1.05 equiv.) of *n*-BuLi 2.25 M in hexanes was added dropwise over 5 min. The mixture was stirred at -78 °C for 15 min, then 1.1 mL (9.4 mmol, 1.1 equiv.) of trimethyl borate ($B(OMe)_3$) was added dropwise at -78 °C over a minute. After complete addition, the reaction mixture was stirred for 15 min at -78 °C and then allowed to warm to r.t. and stirred for 16 h. The reaction mixture was transferred to a separatory funnel with diethyl ether and water. The mixture was washed with 3×50 mL water and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the crude product obtained as 4.5 g of yellow oil.

The crude material was transferred with 100 mL diethyl ether to a 250 mL round bottom flask (RBF) equipped with a magnetic stirrer followed by addition of 60 mL acetonitrile and 1.6 g (17.1 mmol, 1.1 equiv.) of urea hydrogen peroxide (UHP). The reaction mixture was stirred at r.t. for 16 h. Then it was quenched with 7 mL saturated $Na_2S_2O_3$ solution and stirred. The reaction mixture was transferred to a separatory funnel with diethyl ether and water. The mixture

was washed with 3×50 mL water, brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation giving 3.95 g of brown oil. The obtained oil was redissolved in petroleum spirits and loaded onto a silica gel plug. The desired material was eluted with EtOAc and the solvent was removed under reduced pressure. Then it was recrystallised twice from MeCN yielding 2.6 g yellow oil which crystallized into a white solid.

TLC silica, R_f (Petroleum spirits:EtOAc) = 0.8.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 1H), 7.45 – 7.42 (m, 1H), 7.42 – 7.39 (m, 2H), 6.80 – 6.77 (m, 2H), 4.82 (s, 1H), 1.94 – 1.82 (m, 4H), 1.26 – 1.17 (m, 4H), 1.17 – 0.99 (m, 17H), 0.83 (t, J = 7.2 Hz, 6H), 0.65 – 0.55 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.5, 152.7, 152.4, 140.0, 133.2, 129.8, 125.9, 120.7, 120.1, 119.8, 114.1, 110.1, 55.3, 40.4, 31.8, 29.9, 29.2, 23.6, 22.6, 14.0.

IR (solid, cm^{-1}): 3301.8, 2924.6, 2849.3, 1614.9, 1589.2, 1488.5, 1465.7, 1445.5, 1404.9, 1356.1, 1321.1, 1291, 1265.6, 1241.7, 1223.3, 1208.9, 1168.4, 1132, 1103.9, 1062.8, 1006.2, 961.8, 913, 866.3, 827.4, 806.2, 752.1, 723, 711.6.

*7-Bromo-9,9-bis(3-ethylhexyl)-9H-fluoren-2-ol (**2b**)*

In a 200 mL Schlenk tube with a magnetic stirrer was added 5.4 g (9.9 mmol, 1.0 equiv.) of 2,7-dibromo-9,9-bis(3-ethylhexyl)-*9H*-fluorene (**1b**). After vacuum/nitrogen cycles, 100 mL of anhydrous THF was added. The solution was cooled to -78 °C, and 4.2 mL (10.5 mmol, 1.06 equiv.) of *n*-BuLi 2.5 M in hexanes was added dropwise over 5 min. The mixture was stirred at -78 °C for 15 min, then 1.3 mL (11.7 mmol, 1.2 equiv.) of $B(OMe)_3$ was added dropwise at -78 °C over a minute. After complete addition, the reaction mixture was stirred for

15 min at -78 °C and then allowed to warm to r.t. and stirred for 16 h. 25 mL MeOH were added to the reaction mixture followed by addition of 1.4 g (14.9 mmol, 1.5 equiv.) of UHP predissolved in 25 mL MeOH. The reaction mixture was stirred at r.t. for 16 h. Then it was quenched with 10 mL saturated $Na_2S_2O_3$ solution and stirred. The reaction mixture was transferred to a separatory funnel with ethyl acetate and water. The mixture was washed with 3×50 mL water, brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation. The obtained oil was redissolved in petroleum spirits and loaded onto a silica gel plug. The desired material collected with DCM:petroleum spirits = 1:1 and the solvent was removed under reduced pressure. After high vacuum drying at 80 °C, 3.4 g (72%) of yellow oil was obtained.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.1 Hz, 1H), 7.45 (dd, J = 6.4, 1.2 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.40 (dd, J = 8.1, 1.7 Hz, 1H), 6.83 (t, J = 3.1 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 4.91 (s, 1H), 1.91 (dd, J = 5.6, 2.6 Hz, 4H), 0.99 – 0.87 (m, 6H), 0.82 (tdd, J = 11.6, 7.2, 4.7 Hz, 6H), 0.78 – 0.66 (m, 10H), 0.54 (td, J = 7.4, 3.3 Hz, 8H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.3, 155.3, 152.7, 152.6, 152.4, 140.3, 133.6, 133.6, 129.9, 129.8, 127.3, 127.3, 120.8, 120.2, 119.4, 119.4, 114.4, 114.3, 114.3, 111.3, 111.3, 111.2, 55.2, 55.2, 44.8, 44.8, 44.7, 44.6, 34.7, 33.7, 33.7, 33.6, 33.5, 28.2, 28.1, 28.1, 27.2, 27.2, 26.9, 26.9, 22.9, 22.8, 14.2, 14.2, 10.6, 10.3.

IR (film, cm^{-1}): 3338.7, 1614.7, 1587.7, 1455.9, 1405.4, 1378, 1348.1, 1310, 1291.9, 1245, 1206.8, 1178.3, 1160.6, 1134.8, 1102.5, 1062.7, 942.4, 876.1, 806.8, 751.8, 739.4, 727.2, 713.4.

*9,9-Dioctyl-7-(pyridin-4-yl)-9H-fluoren-2-ol (**3a**)*

In a 200 mL Schlenk tube with a magnetic stirrer were added 2.0 g (4.1 mmol, 1.0 equiv.) of 7-bromo-9,9-dioctyl-*9H*-fluoren-2-ol (**2a**), 608 mg (4.9 mmol, 1.2 equiv.) of 4-pyridinylboronic acid, 94.3 mg (0.1 mmol, 2.5 mol%) of tris(dibenzylideneacetone)-dipalladium(0) (Pd_2dba_3), 91.0 mg of tricyclohexylphosphine tetrafluoroborate ($PCy_3{\cdot}HBF_4$) (0.2 mmol, 6.0 mol%), and 1.49 g (7.0 mmol, 1.7 equiv.) of K_3PO_4. After vacuum/nitrogen cycles, 30 mL of dioxane and 15 mL of distilled water (2/1, v/v) sparged with nitrogen were cannulated. The reaction mixture was stirred at 100 °C for 16 h. The reaction mixture was filtered via a celite plug, followed by EtOAc wash. The solvents were evaporated from the reaction mixture and the rest was transferred to a separatory funnel with EtOAc and water, and 15 mL of neutral phosphate buffer was also added. The mixture was washed 3 times with water and brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation. The obtained material was loaded onto silica gel. Then it was subjected to purification on a silica plug and the product band was collected with EtOAc:toluene=1:20. High vacuum drying at 80 °C for 14 h yielded 1.16 g (58%) of a yellow oil.

TLC silica, R_f (EtOAc) = 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.3 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.57 (d, *J* = 1.7 Hz, 1H), 6.89 (s, 1H), 6.89 (dd, 2H), 2.06 – 1.90 (m, 4H), 1.28 – 1.16 (m, 4H), 1.16 – 1.00 (m, 18H), 0.80 (t, *J* = 7.1 Hz, 6H), 0.75 – 0.58 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.0, 153.6, 151.4, 150.3, 149.0, 143.3, 134.6, 132.3, 126.1, 122.1, 121.2, 121.1, 119.4, 114.7, 110.7, 55.3, 40.7, 31.9, 30.2, 29.4, 23.9, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 484.35739 Found: 484.35766.

IR (solid, cm^{-1}): 2924.3, 2852.6, 1598.6, 1581.7, 1546.3, 1463.1, 1412.1, 1366.3, 1293.7, 1268.7, 1216.1, 1174, 1126.1, 1100.1, 1067.9, 1038.2, 1008.1, 1001.3, 866.9, 807.1, 753.8, 719.3, 683.8.

*9,9-Bis(3-ethylhexyl)-7-(pyridin-4-yl)-9H-fluoren-2-ol (**3b**)*

In a 200 mL Schlenk tube with a magnetic stirrer were added 3.40 g (7.0 mmol, 1.0 equiv.) of 7-bromo-9,9-bis(3-ethylhexyl)-*9H*-fluoren-2-ol (**2b**), 1.03 g (8.4 mmol, 1.2 equiv.) of 4-pyridinylboronic acid, 160.3 mg (0.18 mmol, 2.5 mol%) of Pd_2dba_3, 154.7 mg (0.42 mmol, 6.0 mol%) of $PCy_3{\cdot}HBF_4$ and 2.52 g (11.9 mmol, 1.7 equiv.) of K_3PO_4. After vacuum/nitrogen cycles, 50 mL of dioxane and 6 mL of distilled water sparged with nitrogen were cannulated. The reaction mixture was stirred at 100 °C for 16 h. The reaction mixture was filtered via a celite plug, followed by EtOAc wash. The solvents were evaporated from the reaction mixture and the rest was transferred to a separatory funnel with EtOAc and water, and 15 mL of neutral phosphate buffer was also added. The mixture was washed 3 times with water and brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation. The obtained material was loaded onto silica gel. Then it was subjected to purification on a silica plug and the product band was collected with DCM:EtOAc =4:1. High vacuum drying at 100 °C yielded 2.31 g (68%) of yellow powder.

TLC silica, R_f (Ethyl acetate) = 0.7.

^1H NMR (500 MHz,$CDCl_3$) δ 8.68 (d, J = 5.3 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 5.5 Hz, 2H), 7.62 – 7.57 (m, 3H), 6.98 – 6.95 (m, 1H), 6.93 (dt, J = 8.1, 2.8 Hz, 1H), 2.09 – 1.89 (m, 4H), 1.01 – 0.92 (m, 2H), 0.92 – 0.75 (m, 12H), 0.72 (t, J = 6.9 Hz, 4H), 0.65 – 0.45 (m, 12H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.5, 157.4, 153.3, 153.3, 153.2, 151.2, 150.4, 149.0, 143.4, 134.1, 134.1, 132.6, 132.5, 126.1, 126.0, 122.5, 122.4, 122.0, 121.2, 119.3, 119.3, 114.9,

114.8, 111.7, 111.7, 55.1, 55.0, 44.8, 44.7, 44.7, 34.7, 33.9, 33.7, 33.7, 28.3, 28.2, 28.1, 27.3, 26.9, 22.9, 14.2, 14.1, 10.6, 10.4, 10.3.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 484.35739 Found: 484.35750.

IR (solid, cm^{-1}): 2955.6, 2919.8, 2870.1, 2856, 1598.9, 1580.4, 1545.3, 1461.6, 1412.2, 1375.1, 1292.9, 1263.2, 1216.5, 1176.5, 1116.8, 1101.5, 1068, 1040.2, 1009.2, 1000.1, 946.6, 891.2, 872, 844.6, 807.1, 753.1, 725.6, 684.2.

*4-(7-Hydroxy-9,9-dioctyl-9H-fluoren-2-yl)-1-methylpyridinium iodide (**4a**)*

In a 10 mL microwave vial with a magnetic stirrer was added 200 mg (0.4 mmol, 1.0 equiv.) of 9,9-dioctyl-7-(pyridin-4-yl)-*9H*-fluoren-2-ol (**3a**). The vial was capped and 5 mL acetone was cannulated followed by transferring 0.1 mL of MeI (1.7 mmol, 4.0 equiv.). The reaction mixture was stirred at 60 °C for 16 h. After completion, the reaction mixture was dried in vacuo. The product was collected as 245 mg (93%) of red foam.

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.75 (s, 1H), 8.94 (d, J = 6.5 Hz, 2H), 8.56 (d, J = 6.6 Hz, 2H), 8.19 (s, 1H), 8.06 (dd, J = 8.1, 1.8 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 2.1 Hz, 1H), 6.79 (dd, J = 8.2, 2.2 Hz, 1H), 4.31 (s, 3H), 2.09 (td, J = 12.0, 11.2, 5.0 Hz, 2H), 1.94 (td, J = 12.9, 12.3, 5.0 Hz, 2H), 1.18 – 1.10 (m, 4H), 1.10 – 0.95 (m, 17H), 0.75 (t, J = 7.1 Hz, 6H), 0.59 – 0.41 (m, 4H).

^{13}C NMR (126 MHz, Acetone-d_6) δ 160.1, 156.7, 154.9, 152.6, 147.2, 146.3, 132.3, 131.5, 128.5, 124.7, 123.3, 122.8, 120.5, 115.8, 111.2, 56.3, 48.2, 40.9, 32.5, 30.6, 30.0, 24.6, 23.3, 14.4.

ESI-MS (positive mode) – Calculated m/z for $[M-I^-]^+$: 498.37304. Found: 498.37348.

IR (film, cm^{-1}): 3214.5, 3027, 2924.1, 2852.9, 1639.6, 1600.7, 1578.8, 1523.1, 1466.7, 1420.6, 1356.1, 1285.8, 1221.5, 1193.4, 1130.2, 1102.5, 1049.8, 868.8, 816.6, 754.1, 723.6.

*4-(9,9-Bis(3-ethylhexyl)-7-hydroxy-9H-fluoren-2-yl)-1-methylpyridin-1-ium iodide (**4b**)*

In a 10 mL microwave vial with a magnetic stirrer was added 203 mg (0.4 mmol, 1.0 equiv.) of 9,9-bis(3-ethylhexyl)-7-(pyridin-4-yl)-*9H*-fluoren-2-ol (**3b**). The vial was capped and 5 mL acetone was cannulated followed by transfer 0.1 mL of MeI (1.7 mmol, 4.0 equiv.). The reaction mixture was stirred at 60 °C for 16 h. After completion, the reaction mixture was dried in vacuo. The product was collected as 262 mg (99%) of yellow-reddish foam.

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.65 (d, J = 4.8 Hz, 1H), 8.93 (q, J = 5.6 Hz, 2H), 8.56 – 8.53 (m, 2H), 8.33 (d, J = 10.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 8.2, 3.5 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.80 (d, J = 8.2 Hz, 1H), 4.31 – 4.29 (m, 3H), 2.20 – 2.12 (m, 2H), 1.98 – 1.88 (m, 2H), 0.96 – 0.55 (m, 19H), 0.55 – 0.39 (m, 12H).

ESI-MS (positive mode) – Calculated m/z for $[M\text{-}I^-]^+$: 498.37304. Found: 498.37301.

IR (solid, cm^{-1}): 3202.9, 2954.7, 2920.4, 2855.2, 1639.5, 1600.1, 1578.7, 1558.9, 1521.1, 1465.8, 1420.6, 1376.8, 1355.1, 1285.9, 1220.1, 1194.6, 1176.5, 1116.8, 1102.8, 1049.5, 948.5, 890.5, 856.1, 814.3, 753.1, 734.9, 724.4.

*7-(1-Methylpyridin-1-ium-4-yl)-9,9-dioctyl-9H-fluoren-2-olate (**FL1a**)*

In a 15 mL centrifuge vial, 50 mg (0.06 mmol, 1.0 equiv.) 4-(7-hydroxy-9,9-dioctyl-*9H*-fluoren-2-yl)-1-methylpyridinium iodide (**4a**) was dissolved in 0.5 mL MeOH, then 10 mL Et_3N aqueous solution (5%, v/v) was added. The solid was filtered and washed with Et_3N aqueous solution two times. After drying under high vacuum, 32 mg (80%) of red solid was obtained.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.73 (d, J = 6.5 Hz, 2H), 8.39 (s, 2H), 7.96 – 7.87 (m, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 6.16 (s, 2H), 4.21 (s, 3H), 1.94 (td, J = 12.6, 4.4 Hz, 2H), 1.74 (td, J = 12.5, 4.4 Hz, 2H), 1.18 – 0.97 (m, 20H), 0.75 (t, J = 7.1 Hz, 6H), 0.71 – 0.61 (m, 2H), 0.58 – 0.45 (m, 2H).

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 498.37304. Found: 498.37311.

*9,9-Bis(3-ethylhexyl)-7-(1-methylpyridin-1-ium-4-yl)-9H-fluoren-2-olate (**FL1b**)*

In a 15 mL centrifuge vial, 50 mg (0.08 mmol, 1.0 equiv.) 4-(9,9-bis(3-ethylhexyl)-7-hydroxy-*9H*-fluoren-2-yl)-1-methylpyridin-1-ium iodide (**4b**) was dissolved in 0.5 mL MeOH, then 10 mL Et_3N aqueous solution (5%, v/v) was added. The solid was filtered and washed with Et_3N aqueous solution two times. After drying under high vacuum, 40 mg (62%) of dark-red solid was obtained.

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.78 (d, J = 6.4 Hz, 2H), 8.42 (d, J = 6.5 Hz, 2H), 8.10 (s, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.53 (d, J = 4.8 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 6.43 (d, J = 19.2 Hz, 2H), 4.22 (s, 3H), 2.10 – 2.00 (m, 2H), 1.85 – 1.72 (m, 2H), 1.01 – 0.57 (m, 23H), 0.58 – 0.38 (m, 11H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-*d*$_6$) δ 158.3, 158.3, 158.2, 154.4, 154.4, 153.2, 153.2, 153.2, 153.1, 151.0, 151.0, 145.7, 145.2, 145.2, 130.8, 130.8, 129.2, 129.2, 127.2, 127.1, 123.3, 123.2, 122.8, 122.8, 122.8, 122.0, 119.4, 119.4, 114.7, 114.6, 111.1, 111.0, 111.0, 54.6, 54.6, 46.7, 46.7, 43.5, 43.4, 43. 3, 34.1, 34.0, 33.2, 33.1, 32.9, 32.8, 27.6, 27.6, 27.1, 27.1, 26.7, 26.7, 26.3, 26.2, 22.0, 22.0, 22.0, 13.7, 13.7, 10.4, 10.3, 9.9, 9.9.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 498.37304. Found: 498.37302.

*9,9-Dioctyl-7-(pyridin-4-yl)-9H-fluoren-2-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**5**)*

In a 25 mL microwave vial with a magnetic stirrer was added 500 mg (1.0 mmol, 1.0 equiv.) of 9,9-dioctyl-7-(pyridin-4-yl)-*9H*-fluoren-2-ol (**3a**). After vacuum/nitrogen cycles, 15 mL of anhydrous DMF was cannulated and 0.3 mL (2.1 mmol, 2.0 equiv.) of anhydrous Et_3N was transferred by syringe. The reaction mixture was stirred with the following addition of 0.3 mL (1.6 mmol, 1.5 equiv.) of -NfF dropwise by syringe. The reaction mixture was stirred at 80 °C for 16 h. After completion, the reaction mixture was evaporated, redissolved with toluene and filtered through a small silica gel plug using toluene:DCM 3:1, 1:1 and then neat DCM. The solvents were removed under reduced pressure and the final product was obtained after high vacuum drying at 80 °C as 623 mg (79%) of yellow oil.

TLC silica, R_f (DCM) = 0.26.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.2 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.29 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 2.02 (td, *J* = 7.3, 4.2 Hz, 4H), 1.24 – 0.96 (m, 21H), 0.80 (t, *J* = 7.2 Hz, 6H), 0.71 – 0.55 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, , $CDCl_3$) δ 153.6, 152.2, 150.1, 149.6, 148.8, 140.6, 140.5, 137.7, 126.5, 121.9, 121.5, 121.4, 120.9, 120.3, 116.5, 56.0, 40.3, 31.9, 29.9, 29.2, 23.9, 22.7, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.52, -108.56, -120.72, -125.69.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 766.29710 Found: 766.29805.

IR (film, cm^{-1}): 2927.6, 2856.4, 1595.9, 1546.9, 1462.4, 1425.2, 1352.3, 1291, 1237.9, 1200.8, 1144, 1125.7, 1096.5, 1033.8, 1009.2, 992.2, 920.9, 885.4, 809.8, 795.8, 747.8, 737.1, 712.8, 698.2, 685.5.

*4-(9,9-Dioctyl-7-(pyridin-4-yl)-9H-fluoren-2-yl)phenol (**6**)*. In a 200 mL Schlenk tube with a magnetic stirrer were added 736 mg (0.96 mmol, 1.0 equiv.) of 9,9-dioctyl-7-(pyridin-4-yl)-*9H*-fluoren-2-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**5**), 265 mg (1.92 mmol, 2.0 equiv.) of (4-hydroxyphenyl)boronic acid, 22.0 mg (0.024 mmol, 2.5 mol%) of Pd_2dba_3, 21.2 mg of $PCy_3{\cdot}HBF_4$ (0.058 mmol, 6.0 mol%), and 611 mg (2.88 mmol, 3.0 equiv.) of K_3PO_4. After vacuum/nitrogen cycles, 15 mL of dioxane and 7.5 mL of distilled water (2/1, v/v) sparged with nitrogen were cannulated. The reaction mixture was stirred at 100 °C for 16 h. After completion, the reaction mixture was evaporated, and then transferred to the separatory funnel with EtOAc and water, and neutral phosphate buffer was also added. The mixture was washed 3 times with water and brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation. The obtained material was loaded onto a small silica plug from toluene and the product band collected with $CHCl_3$. High vacuum drying at 80 °C for 16 h yielded 437 mg (81%) of a yellow solid.

TLC silica, R_f (DCM) = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.60 – 7.55 (m, 3H), 7.54 (d, *J* = 1.5 Hz, 1H), 2.05 (td, *J* = 9.5, 7.0 Hz, 4H), 1.23 – 1.15 (m, 4H), 1.15 – 1.02 (m, 16H), 0.79 (t, *J* = 7.1 Hz, 6H), 0.71 (q, *J* = 7.0 Hz, 4H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.5, 152.2, 151.9, 149.0, 149.2, 142.6, 140.8, 138.8, 136.1, 133.6, 128.5, 126.2, 125.8, 121.4, 121.2, 120.5, 120.4, 116.1, 55.5, 40.5, 31.9, 30.1, 29.3, 29.3, 23.9, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 560.38869 Found: 560.38919.

IR (film, cm^{-1}): 2923.8, 2852.1, 1599.1, 1547, 1519.7, 1464.3, 1448.7, 1412.1, 1374.4, 1274.3, 1255, 1215.4, 1171.8, 1103.9, 1069, 1005.8, 889.4, 838.7, 809.8, 755.8, 707.2, 665.9.

4-(7-(4-Hydroxyphenyl)-9,9-dioctyl-9H-fluoren-2-yl)-1-methylpyridinium iodide (7)

In a 10 mL microwave vial with a magnetic stirrer was added 100 mg (0.18 mmol, 1.0 equiv.) of 4-(9,9-dioctyl-7-(pyridin-4-yl)-*9H*-fluoren-2-yl)phenol (**6**). The vial was capped and 3 mL acetone was cannulated followed by transferring 0.04 mL of MeI (0.71 mmol, 4.0 equiv.). The reaction mixture was stirred at 60 °C for 16 h. After completion, the reaction mixture was dried in vacuo. The product was collected as 127 mg (98%) of yellow oil.

^{1}H NMR (500 MHz, Acetone-d_6) δ 9.27 (d, J = 6.6 Hz, 2H), 8.70 (d, J = 7.0 Hz, 2H), 8.65 (s, 1H), 8.40 (d, J = 1.8 Hz, 1H), 8.14 (dd, J = 8.0, 1.8 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.07 (d, J = 8.6 Hz, 2H), 4.66 (s, 3H), 2.36 – 2.24 (m, 2H), 2.24 – 2.12 (m, 2H), 1.15 – 0.93 (m, 20H), 0.72 (t, J = 7.1 Hz, 6H), 0.69 – 0.62 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, Acetone-d_6) δ 158.5, 156.6, 153.5, 153.4, 146.5, 146.4, 142.5, 139.0, 133.0, 129.0, 128.5, 126.5, 125.1, 123.6, 122.1, 121.7, 121.7, 116.8, 56.6, 48.3, 48.2, 40.6, 32.45, 30.6, 24.6, 23.3, 14.3.

ESI-MS (positive mode) – Calculated m/z for $[M\text{-}I^{-}]^{+}$: 574.40434 Found: 574.40479.

IR (film, cm^{-1}): 3215.8, 3029.6, 2924.4, 2853.3, 1708.3, 1638.5, 1603, 1518.9, 1465.9, 1414.4, 1358.8, 1267.7, 1220.1, 1194.8, 1174, 1138.8, 1105.8, 1089.9, 1050.6, 1001.9, 958.3, 891.3, 843.6, 816.7, 755.4, 723.1, 692.

*4-(7-(1-Methylpyridin-1-ium-4-yl)-9,9-dioctyl-9H-fluoren-2-yl)phenolate (**FL2**)*

In a 15 mL centrifuge vial, 50 mg (0.07 mmol, 1.0 equiv.) 4-(7-(4-hydroxyphenyl)-9,9-dioctyl-*9H*-fluoren-2-yl)-1-methylpyridinium iodide (**7**) was dissolved in 0.5 mL MeOH, then 10 mL Et_3N aqueous solution (5%, v/v) was added. The solid was filtered and washed with Et_3N aqueous solution two times. After drying under high vacuum, 25 mg (62%) of red solid was obtained.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.96 (d, J = 6.5 Hz, 2H), 8.58 (d, J = 6.6 Hz, 2H), 8.21 (s, 1H), 8.08 (dd, J = 8.2, 1.7 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.58 (s, 1H), 7.52 (dd, J = 8.1, 1.6 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 6.50 – 6.42 (m, 3H), 4.31 (s, 3H), 2.16 – 2.03 (m, 4H), 1.14 – 1.07 (m, 3H), 1.07 – 0.96 (m, 17H), 0.72 (t, J = 7.1 Hz, 6H), 0.55 (s, 4H).

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 574.40434 Found: 574.40437.

7-Bromo-9,9-dioctyl-9H-fluorene-2-carbaldehyde (**8**)[28]

In a 200 mL Schlenk tube with a magnetic stirrer was added 4.7 g (8.6 mmol, 1.0 equiv.) of 2,7-dibromo-9,9-dioctyl-*9H*-fluorene (**1a**). After vacuum/nitrogen cycles, 80 mL of anhydrous THF was added. The solution was cooled to -78 °C, and 4.0 mL (9.0 mmol, 1.05 equiv.) of *n*-BuLi 2.25 M in hexanes was added dropwise over 5 min. The mixture was stirred at -78 °C for 1 h, and then quenched with 6.0 mL of DMF added dropwise at -78 °C over a minute. After complete addition, the reaction mixture was stirred for 30 min at -78 °C and the allowed to warm to r.t. and stirred for 16 h. The reaction mixture was quenched with 20 mL 5 M HCl (aq) and allowed to stir for another 2 h at r.t. Then the solvent was removed in vacuo and the rest was transferred to a separatory funnel with diethyl ether and water. The mixture was washed with 3×50 mL water with addition of the neutral phosphate buffer and brine, and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by

rotary evaporation and the crude product obtained. The obtained material loaded onto silica gel and purified on a silica plug, where the product band was gradually eluted with 10% DCM in petroleum spirits to DCM. The compound was recrystallized from MeOH and 2.35 g (55%) of yellow solid was obtained after high vacuum drying.

TLC silica, R_f (petroleum spirits:DCM = 5:1) = 0.4.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.88 – 7.84 (m, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.53 – 7.49 (m, 2H), 2.07 – 1.90 (m, 4H), 1.24 – 1.15 (m, 4H), 1.15 – 0.98 (m, 16H), 0.81 (t, J = 7.2 Hz, 6H), 0.63 – 0.48 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.4, 154.4, 151.3, 147.6, 146.5, 138.7, 135.7, 130.7, 130.6, 126.6, 123.3, 122.4, 120.2, 119.4, 55.8, 40.2, 31.9, 30.0, 29.3, 23.8, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 497.24135 Found: 497.24184.

IR (film, cm^{-1}): 2954, 2917.8, 2850.5, 1697, 1605.2, 1567.4, 1466.9, 1454.6, 1433.6, 1404, 1375.8, 1341.6, 1304, 1258.6, 1234.1, 1202, 1162.3, 1132.4, 1103.1, 1063.3, 1004.4, 919.9, 883.2, 873.6, 813.7, 755.1, 738.4, 723.9, 661.3.

*Diethyl (pyridin-4-ylmethyl)phosphonate (**9**)*[29]

In 50 mL centrifuge tube was dissolved 10 g (61 mmol, 1.0 equiv.) of 4-(chloromethyl)pyridine hydrochloride in 20 mL saturated NaCl brine, then 10 mL toluene was added. Solid $KHCO_3$ was added in small amounts, swirling and allowing CO_2 to be released. Addition was stopped when no more CO_2 evolved even when vigorously shaken. After centrifugation, the organic layer containing acid-free 4-(chloromethyl)pyridine was pipetted off. Another 10 mL toluene was added, the tube was shaken, centrifuged, and the organic layer was pipetted off. The last traces of 4-(chloromethyl)pyridine were collected by carefully adding 5 mL toluene to centrifuge tube

without shaking, then pipetting out the organic layer. Acid-free 4-(chloromethyl)pyridine forms insoluble oligomers within hours at 20 °C, and must be freshly prepared for use.

In a 3-neck 500 mL RBF equipped with a stirrer was placed 2.93 g (73.2 mmol, 1.2 equiv.) NaH (60% in mineral oil) followed by vacuum/nitrogen cycles. Then 150 mL anhydrous toluene was cannulated and 17.3 mL (134.2 mmol, 2.2 equiv.) diethyl phosphate was added. After the reaction mixture was stirred for 30 min at 80 °C, the toluene solution of 4-(chloromethyl)pyridine was transferred and the reaction mixture was left for 16 h at 80 °C. Once it cooled down, the reaction mixture was filtered and rinsed with toluene. The filtrate was directly poured to the silica plug and it was gradually eluted with toluene:DCM mixture, followed by 2% MeOH in DCM. The joined fractions yielded 10 g (71%) of grey oil after high vacuum drying at 80 °C for 16 h.

TLC silica, R_f (2% MeOH in DCM) = 0.1

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, J = 5.9 Hz, 2H), 7.26 – 7.23 (m, 2H), 4.04 (dqd, J = 8.6, 7.1, 1.3 Hz, 4H), 3.13 (d, J = 22.3 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.8, 141.6, 141.5, 125.2, 76.9, 62.6, 62.5, 34.2, 33.1, 16.5, 16.5.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 230.09406. Found: 230.09432.

IR (film, cm^{-1}): 3451.9, 2984.4, 2910, 1637.9, 1602.1, 1560.2, 1498, 1444.4, 1417.5, 1392.8, 1369.1, 1246.9, 1229.9, 1198.1, 1163.1, 1097.7, 1048.2, 1019.7, 963.2, 840.2, 787.1, 744.2, 706.

*(E)-4-(3-(7-Bromo-9,9-dioctyl-9H-fluoren-2-yl)vinyl)pyridine (**10**)*

In 100 mL RBF equipped with a stirrer were placed 1.08 g (2.2 mmol, 1.0 equiv.) 7-bromo-9,9-dioctyl-*9H*-fluorene-2-carbaldehyde (**8**), 0.75 g (3.3 mmol, 1.5 equiv.) diethyl (pyridin-4-

ylmethyl)phosphonate (**9**) and 0.3 g (7.6 mmol, 3.5 equiv.) NaH (60% in mineral oil) followed by vacuum/nitrogen cycles. Anhydrous dimethoxyethane (DME) was cannulated and the reaction mixture was stirred for 48 h at 85 °C. Once it cooled down, the reaction mixture was filtered and rinsed with toluene. The filtrate was evaporated, transferred with ethyl acetate to a separatory funnel and then washed 3 times with water and neutral phosphate buffer. The organic phase was evaporated and the product obtained as yellow oil. It was further loaded onto silica gel and subjected to chromatography. The plug was flushed with petroleum spirits and toluene in order to remove mineral oil and the product was collected with 1-4% EtOAc in toluene. 0.77 g (62%) of light-yellow solid was obtained after high vacuum drying at 80 °C for 16 h.

TLC silica, R_f (DCM) = 0.2 (streaks).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 5.3 Hz, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.54 (dd, J = 7.9, 1.5 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.43 – 7.38 (m, 3H), 7.09 (d, J = 16.3 Hz, 1H), 1.98 (h, J = 6.6 Hz, 4H), 1.26 – 1.17 (m, 4H), 1.17 – 1.01 (m, 17H), 0.82 (t, J = 7.2 Hz, 6H), 0.67 – 0.58 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.4, 151.2, 150.1, 150.0, 145.1, 141.1, 139.6, 135.5, 133.9, 130.2, 126.5, 126.3, 125.5, 121.6, 121.4, 121.0, 120.3, 55.6, 40.4, 31.9, 30.1, 29.3, 29.3, 23.8, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 572.28864. Found: 572.28930.

IR (film, cm^{-1}): 2954.1, 2924.6, 2852.9, 1715.5, 1622.2, 1593.9, 1543, 1496.2, 1455.9, 1405.5, 1376.8, 1295.5, 1259.7, 1216.8, 1131, 1062.3, 1005.3, 991.2, 965.4, 906, 876.8, 849.2, 815.7, 753.8, 732.7.

*(E)-9,9-Dioctyl-7-(3-(pyridin-4-yl)vinyl)-9H-fluoren-2-ol (**11**)*

In a 100 mL Schlenk tube with a magnetic stirrer was added 736 mg (1.3 mmol, 1.0 equiv.) of (*E*)-4-(3-(7-bromo-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)pyridine (**10**). After vacuum/nitrogen cycles, 20 mL of anhydrous THF was added. The solution was cooled to -78 °C, and 0.6 mL (1.4 mmol, 1.05 equiv.) of *n*-BuLi 2.25 M in hexanes was added dropwise. The mixture was stirred at -78 °C for 15 min, then 0.16 mL (1.4 mmol, 1.1 equiv.) of $B(OMe)_3$ was added dropwise at -78 °C. After complete addition, the reaction mixture was stirred for 15 min at -78 °C and the allowed to warm to r.t. and stirred for 16 h. The reaction mixture was transferred to a separatory funnel with diethyl ether and water. The mixture was washed with 3×50 mLwater, 2×4 mL 1 M HCl (aq.) and 15 mL neutral phosphate buffer. Then the organic layer was collected, dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the crude boronic acid product obtained as 697 mg of orange foam.

The crude material was transferred with 20 mL diethyl ether to a 100 mL RBF equipped with a magnetic stirrer followed by addition of 15 mL MeOH and 243 mg (2.6 mmol, 2.0 equiv. based on starting bromide) of UHP. The reaction mixture was stirred at r.t. for 16 h. Then it was quenched with 20 mL saturated $Na_2S_2O_3$ solution and stirred. The reaction mixture was transferred to a separatory funnel with ethyl acetate and water. The mixture was washed with 3×50 mL water, brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation giving 657 mg of orange oil. The obtained oil was loaded onto silica gel and purified via plug. The desired material was collected with 1-10% EtOAc in toluene and the solvent was removed under reduced pressure. After high vacuum drying 251 mg (38%) light yellow solid was obtained.

TLC silica, R_f (Toluene:EtOAc = 10:1) = 0.2.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.50 (dd, J = 8.0, 1.5 Hz, 1H), 7.47 (d, J = 6.2 Hz, 3H), 7.43 (d, J = 16.3 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H), 6.85 (d, J = 7.4 Hz, 2H), 2.02 – 1.88 (m, 4H), 1.24 – 1.17 (m, 4H), 1.17 – 1.00 (m, 17H), 0.81 (t, J = 7.2 Hz, 6H), 0.71 – 0.58 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.1, 153.7, 151.0, 149.2, 146.3, 142.8, 135.1, 133.5, 133.0, 126.6, 124.0, 121.2, 121.2, 121.0, 119.1, 114.5, 110.5, 55.1, 40.7, 32.0, 30.2, 29.4, 23.9, 22.8, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 510.37304. Found: 510.37344.

IR (solid, cm^{-1}): 2924.6, 2850, 1595.4, 1582.7, 1499.1, 1464.6, 1421.2, 1371.4, 1291.2, 1241.7, 1217.7, 1202.2, 1161.4, 1125.8, 1099.1, 1067.6, 1002.6, 966.2, 901.6, 856, 832, 815.9, 754.9, 722.3.

*(E)-4-(3-(7-Hydroxy-9,9-dioctyl-9H-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**12**)*

In a 10 mL microwave vial with a magnetic stirrer was added 90 mg (0.18 mmol, 1.0 equiv.) of (*E*)-9,9-dioctyl-7-(3-(pyridin-4-yl)vinyl)-*9H*-fluoren-2-ol (**11**). The vial was capped and 3 mL acetone was cannulated followed by transferring 0.05 mL of MeI (0.8 mmol, 4.4 equiv.). The reaction mixture was stirred at 60 °C for 16 h. After completion, the reaction mixture was dried in vacuo. The product was collected as 112 mg (96%) of red oil.

^{1}H NMR (500 MHz, Acetone-d_6) δ 9.07 (d, J = 6.4 Hz, 2H), 8.74 (s, 1H), 8.35 (d, J = 6.4 Hz, 2H), 8.19 (d, J = 16.2 Hz, 1H), 8.03 (s, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 16.3 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 9.1 Hz, 2H), 4.55 (s, 3H), 2.20 – 2.09 (m, 2H), 2.05 – 1.96 (m, 2H), 1.20 – 1.13 (m, 4H), 1.13 – 0.97 (m, 17H), 0.76 (t, J = 7.1 Hz, 6H), 0.71 – 0.61 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, Acetone-d_6) δ 159.4, 154.5, 154.4, 151.6, 145.7, 145.3, 143.0, 133.6, 132.7, 129.5, 124.2, 123.2, 122.1, 122.0, 119.8, 115. 5, 111.0, 55.7, 48.1, 40.9, 32.3, 24.5, 23.1, 14.3.

ESI-MS (positive mode) – Calculated m/z for $[M\text{-}I^-]^+$: 524.38869. Found: 524.38908.

IR (film, cm^{-1}): 3213.5, 2924, 2852.1, 1708.5, 1643.9, 1616.3, 1590.3, 1515.4, 1466.7, 1341, 1320.7, 1272.9, 1424.2, 1359.7, 1160.9, 1129.2, 1115.2, 1207.7, 1184.2, 968.5, 868.5, 824.8, 1100.2, 1047, 734.3, 720.8, 699.1.

*(E)-7-(3-(1-Methylpyridin-1-ium-4-yl)vinyl)-9,9-dioctyl-9H-fluoren-2-olate (**FL3**)*

In a 15 mL centrifuge vial, 30 mg (0.05 mmol, 1.0 equiv.) of (*E*)-4-(3-(7-hydroxy-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**12**) was dissolved in 0.5 mL MeOH, then 10 mL Et_3N aqueous solution (5%, v/v) was added. The solid was filtered and washed with Et_3N aqueous solution two times. After drying under high vacuum, 19 mg (79%) of black solid was obtained.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.76 (d, J = 6.5 Hz, 2H), 8.13 (d, J = 6.5 Hz, 2H), 8.02 (d, J = 16.1 Hz, 1H), 7.65 (s, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.43 (s, 1H), 7.41 (d, J = 7.4 Hz, 1H), 6.54 (s, 1H), 6.50 (d, J = 8.5 Hz, 1H), 4.21 (s, 3H), 1.94 – 1.86 (m, 2H), 1.86 – 1.77 (m, 2H), 1.15 (q, J = 7.4 Hz, 4H), 1.12 – 0.95 (m, 19H), 0.76 (t, J = 7.1 Hz, 6H), 0.67 – 0.57 (m, 2H), 0.57 – 0.41 (m, 2H).

ESI-MS (positive mode) – Calculated m/z for $[M\text{-}I^-]^+$: 524.38869. Found: 524.38880.

*(E)-4-(9,9-Dioctyl-7-(3-(pyridin-4-yl)vinyl)-9H-fluoren-2-yl)phenol (**13**)*

In a 200 mL Schlenk tube with a magnetic stirrer were added 1.67 g (2.9 mmol, 1.0 equiv.) of (E)-4-(3-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)vinyl)pyridine (**10**), 0.8 g (5.8 mmol, 2.0 equiv.) of (4-hydroxyphenyl)boronic acid, 69.0 mg (0.07 mmol, 2.5 mol%) of Pd_2dba_3, 64.5 mg of $PCy_3{\cdot}HBF_4$ (0.18 mmol, 6.0 mol%), and 1.86 g (8.8 mmol, 3.0 equiv.) of K_3PO_4. After vacuum/nitrogen cycles, 30 mL of dioxane and 15 mL of distilled water (2/1, v/v) sparged with nitrogen were cannulated. The reaction mixture was stirred at 100 °C for 16 h. After completion, the reaction mixture was evaporated, and then transferred to the separatory funnel with EtOAc and water, and neutral phosphate buffer was also added. The mixture was washed 3 times with water and brine and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation. The obtained material was loaded onto silica gel and eluted though a silica plug with 2-10% EtOAc in toluene. High vacuum drying at 80 °C for 16 h yielded 1.12 g (66%) of an orange solid.

TLC silica, Rf (10% EtOAc in toluene) = 0.2.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 2H), 7.72 (t, J = 8.4 Hz, 2H), 7.59 – 7.53 (m, 4H), 7.53 – 7.50 (m, 2H), 7.48 (d, J = 5.5 Hz, 2H), 7.45 (d, J = 16.4 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 2.03 (dd, J = 11.3, 5.7 Hz, 4H), 1.22 – 1.15 (m, 4H), 1.15 – 1.03 (m, 16H), 0.79 (t, J = 7.1 Hz, 6H), 0.74 – 0.63 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.3, 151.9, 151.8, 149.3, 146.1, 142.4, 140.5, 139.1, 134.9, 134.7, 133.7, 128.5, 126.6, 125.8, 124.6, 121.5, 121.3, 121.2, 120.3, 120.1, 116.0, 55.3, 40.6, 31.9, 30.2, 29.4, 29.3, 23.9, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 586.40434. Found: 586.40486.

IR (film, cm^{-1}): 2923.8, 2852.2, 1632.4, 1593.9, 1551.1, 1518.5, 1464.3, 1417.3, 1376.8, 1337.2, 1269.1, 1240.1, 1216.6, 1171.9, 1135.7, 1104.5, 1066.1, 1004.1, 966, 890.5, 866.8, 842.7, 817.6, 753.7, 672.5.

(E)-4-(3-(7-(4-Hydroxyphenyl)-9,9-dioctyl-9H-fluoren-2-yl)vinyl)-1-methylpyridinium iodide ***(14)***

In a 25 mL microwave vial with a magnetic stirrer was added 500 mg (0.85 mmol, 1.0 equiv.) of (*E*)-4-(9,9-dioctyl-7-(3-(pyridin-4-yl)vinyl)-*9H*-fluoren-2-yl)phenol (**13**). The vial was capped and 10 mL acetone was cannulated followed by transferring 0.21 mL of MeI (3.4 mmol, 4.0 equiv.). The reaction mixture was stirred at 60 °C for 16 h. After completion, the reaction mixture was dried in vacuo. The product was collected as 611 mg (98%) of red foam.

^{1}H NMR (500 MHz, Acetone-d_6) δ 9.04 (d, J = 6.5 Hz, 2H), 8.55 (s, 1H), 8.38 (d, J = 6.8 Hz, 2H), 8.22 (d, J = 16.3 Hz, 1H), 8.01 (s, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.82 (dd, J = 7.9, 1.5 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 6.3 Hz, 1H), 7.63 (dd, J = 7.9, 1.7 Hz, 1H), 7.60 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 4.55 (s, 3H), 2.25 – 2.12 (m, 4H), 1.20 – 1.13 (m, 4H), 1.13 – 1.01 (m, 16H), 0.76 (t, J = 7.1 Hz, 6H), 0.72 – 0.61 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, Acetone-d_6) δ 158.3, 154.5, 153.0, 152.5, 145.9, 144.6, 142.8, 141.8, 139.6, 135.1, 133.0, 129.4, 128.8, 126.3, 124.5, 123.5, 122.9, 121.6, 121.5, 121.0, 116.7, 56.1, 48.1, 40.8, 32.4, 24.6, 23.2, 14.3.

ESI-MS (positive mode) – Calculated m/z for $[M\text{-}I^{-}]^{+}$: 600.41999. Found: 600.42092.

IR (film, cm^{-1}): 3222.7, 3029.6, 2923.2, 2851.9, 1724.6, 1698.5, 1643.9, 1617.5, 1592.6, 1515.7, 1465.5, 1412.4, 1341.4, 1301.1, 1262.8, 1247, 1208.2, 1172.3, 1105.8, 1047.3, 1002.7, 966.1, 873.6, 823.9, 780.7, 754.9, 737.6, 721.8, 667.9.

*(E)-4-(7-(3-(1-Methylpyridin-1-ium-4-yl)vinyl)-9,9-dioctyl-9H-fluoren-2-yl)phenolate (**FL4**)*.

In a 15 mL centrifuge vial, 30 mg (0.04 mmol, 1.0 equiv.) of (*E*)-4-(3-(7-(4-hydroxyphenyl)-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**16**) was dissolved in 0.5 mL MeOH, then 10 mL Et_3N aqueous solution (5%, v/v) was added. The solid was filtered and washed with Et_3N aqueous solution two times. After drying under high vacuum, 13 mg (52%) of red solid was obtained.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (d, J = 6.4 Hz, 2H), 8.21 (d, J = 6.5 Hz, 2H), 8.09 (d, J = 16.2 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.71 (d, J = 7.8 Hz, 1H), 7.63 (s, 1H), 7.60 – 7.52 (m, 2H), 7.46 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.1 Hz, 2H), 4.24 (s, 3H), 2.14 – 2.06 (m, 2H), 2.06 – 1.97 (m, 2H), 1.16 – 1.08 (m, 4H), 1.00 (t, J = 4.6 Hz, 16H), 0.73 (t, J = 7.1 Hz, 3H), 0.62 – 0.47 (m, 4H).

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 600.41999. Found: 600.41981.

*(E)-9,9-Dioctyl-7-(3-(pyridin-4-yl)vinyl)-9H-fluorene-2-carbaldehyde (**15**)*

In a 200 mL Schlenk tube with a magnetic stirrer was added 4.1 g (7.1 mmol, 1.0 equiv.) of (*E*)-4-(3-(7-bromo-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)pyridine (**10**). After vacuum/nitrogen cycles, 60 mL of anhydrous THF was added. The solution was cooled to -78 °C, and 3.0 mL (7.5 mmol, 1.05 equiv.) of *n*-BuLi 2.25 M in hexanes was added dropwise over 5 min. The mixture was stirred at -78 °C for 1 h, and then quenched with 6.0 mL of DMF added dropwise at -78 °C over a minute. After complete addition, the reaction mixture was stirred for 30 min at -78 °C and the allowed to warm to r.t. and stirred for 16 h. The reaction mixture was quenched with 15 mL 5 M HCl and allowed to stir for another 2 h at r.t. The reaction mixture was transferred to a separatory

funnel with ethyl acetate and water. The mixture was washed with 3×50 mL water with addition of the neutral phosphate buffer and brine, and the organic layer was collected. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the crude product obtained. The obtained material was loaded onto silica gel and subjected to purification via silica plug where the product band was gradually eluted with 1-5% EtOAc in toluene. The compound was dried under high vacuum at 80 °C to 2.0 g (54%) of white solid.

TLC silica, R_f (10% EtOAc in Toluene) = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.61 (d, J = 6.1 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.86 – 7.84 (m, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.59 (dd, J = 7.9, 1.5 Hz, 1H), 7.54 (s, 1H), 7.46 – 7.39 (m, 3H), 7.13 (d, J = 16.3 Hz, 1H), 2.13 – 1.96 (m, 4H), 1.23 – 1.15 (m, 4H), 1.15 – 0.99 (m, 16H), 0.80 (t, J = 7.2 Hz, 6H), 0.68 – 0.53 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.4, 153.0, 152.0, 150.2, 147.0, 144.9, 140.5, 136.8, 135.6, 133.7, 130.7, 126.6, 126.3, 123.2, 121.6, 121.5, 121.0, 120.3, 55.5, 40.4, 31.9, 30.0, 29.3, 29.3, 23.9, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 522.37304. Found: 522.37360.

IR (film, cm^{-1}): 2953.6, 2924.1, 2852.9, 1693.3, 1604.3, 1594.3, 1577.6, 1543.6, 1488.1, 1465, 1439.4, 1413.3, 1377.6, 1341.5, 1285.9, 1202, 1153.4, 1128.7, 1100.2, 1067, 1005.6, 991.3, 965.6, 904.1, 850.9, 821.4, 744.3, 721.5.

*Diethyl (4-((4-methoxybenzyl)oxy)benzyl)phosphonate (**16**)*

1) Preparation of (4-((4-methoxybenzyl)oxy)phenyl)methanol[30]. In a 250 mL RBF with a magnetic stirrer were transferred 1.0 g (8.05 mmol, 1.1 equiv.) of 4-(hydroxymethyl)phenol, 3.0 g (21.9 mmol, 3.0 equiv.) of K_2CO_3 and 121.0 mg (0.73 mmol, 10 mol%) of KI. The RBF

was equipped with a condenser and 100 mL of acetone was cannulated. After that 1.0 mL (7.3 mmol, 1.0 equiv.) of 4-methoxybenzyl chloride was transferred by syringe. The reaction mixture was stirred at 60 °C for 16 h and after completion transferred to a separatory funnel with EtOAc. The reaction mixture was washed with water with $Na_2S_2O_5$ addition during the first wash. The organic layer was dried with $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and product was dried in a vacuum oven giving 1.78 g (99%) of yellow solid.

TLC silica, R_f (10% EtOAc in Toluene) = 0.2.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 4.99 (s, 2H), 4.62 (s, 2H), 3.82 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.6, 158.6, 133.4, 129.4, 129.1, 128.8, 115.1, 114.1, 70.0, 65.2, 55.5.

IR (film, cm^{-1}): 3331.2, 2915, 2862.2, 2836.9, 1610.8, 1585.8, 1509.2, 1465.5, 1440.3, 1422.8, 1383.7, 1302.6, 1240.1, 1173.4, 1111.3, 1031.9, 1014.4, 1007.4, 930.8, 871.4, 813.7, 782.8, 734.6, 702.6.

2) Preparation of **16**. In a 100 mL Schlenk tube with a magnetic stirrer 1.5 g (6.1 mmol, 1.0 equiv.) (4-((4-methoxybenzyl)oxy)phenyl)methanol and 90.1 mg (0.2 mmol, 4.0 mol%) tetrabutylammonium iodide ($Bu_4N^+I^-$) were added. After vacuum/nitrogen cycles, 1.6 mL (9.1 mmol, 1.5 equiv.) triethyl phosphate was cannulated. The reaction mixture was stirred for 16 h at 125 °C. Once cooled down, it was evaporated and dried under high vacuum. The obtained oil redissolved in toluene and loaded onto silica gel plug. The desired material collected with EtOAc:toluene = 1:1 and the solvent was removed under reduced pressure. After high vacuum drying at 80 °C overnight 1.09 g (50%) yellow oil was obtained.

TLC silica, R_f (EtOAc) = 0.4.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 2H), 7.21 (dd, J = 8.8, 2.6 Hz, 2H), 6.91 (d, J = 10.2 Hz, 4H), 4.96 (s, 2H), 4.06 – 3.94 (m, 4H), 3.81 (s, 3H), 3.09 (d, J = 21.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 6H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 159.6, 158.0, 130.9, 130.8, 129.4, 129.1, 123.8, 123.7, 115.1, 115.1, 114.1, 69.9, 62.2, 62.2, 55.4, 33.5, 32.4, 16.6, 16.5.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 365.15124. Found: 365.15110.

IR (film, cm^{-1}): 2982, 2908.6, 1611.7, 1585.4, 1509.6, 1465.5, 1442.7, 1422.7, 1385.6, 1300.9, 1239, 1174.3, 1131.2, 1097.7, 1051, 1021.8, 958.3, 871.8, 824, 728.1, 702.9.

*4-((E)-2-(7-((E)-4-((4-Methoxybenzyl)oxy)styryl)-9,9-dioctyl-9H-fluoren-2-yl)vinyl)pyridine (**17**)*

In 100 mL Schlenk tube equipped with a stirrer were placed 855 mg (1.6 mmol, 1.0 equiv.) (*E*)-9,9-dioctyl-7-(3-(pyridin-4-yl)vinyl)-*9H*-fluorene-2-carbaldehyde (**15**), 895 mg (2.5 mmol, 1.5 equiv.) diethyl (4-((4-methoxybenzyl)oxy)benzyl)phosphonate (**16**) and 230 mg (5.7 mmol, 3.5 equiv.) NaH (60% in mineral oil) followed by vacuum/nitrogen cycles. Anhydrous DME was cannulated (20 mL) and the reaction mixture was stirred for 24 h at 85 °C. Once it cooled down, the reaction mixture was filtered and rinsed with toluene. The filtrate was evaporated, transferred with ethyl acetate to a separatory funnel and then washed 3 times with water and brine. The organic phase was evaporated and the product obtained as a yellow oil. Then it was subjected to purification via silica plug and it was flushed with petroleum spirits and toluene in order to remove mineral oil, then the band was gradually eluted with 1-5% EtOAc in toluene. The compound was dried under high vacuum and 834 mg (80%) of yellow solid was obtained.

TLC silica, R_f (Toluene) = 0.2.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, J = 5.1 Hz, 2H), 7.68 (dd, J = 9.2, 7.8 Hz, 2H), 7.53 (dd, J = 7.9, 1.5 Hz, 1H), 7.51 – 7.47 (m, 4H), 7.45 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 9.5 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 5.03 (s, 2H), 3.83 (s, 3H), 2.02 (dd, J = 10.4, 6.3 Hz, 4H), 1.22 – 1.15 (m, 4H), 1.15 – 1.02 (m, 16H), 0.79 (t, J = 7.1 Hz, 6H), 0.70 – 0.61 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.6, 158.7, 151.8, 149.7, 145.6, 142.2, 140.0, 137.2, 134.9, 134.5, 130.5, 129.4, 127.9, 127.8, 127.3, 126.6, 125.6, 124.9, 121.4, 121.0, 120.6, 120.3, 120.1, 115.2, 114.2, 70.0, 55.5, 55.2, 40.6, 31.9, 30.2, 29.4, 29.4, 23.9, 22.7, 14.2.

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 732.47751. Found: 732.47830.

IR (film, cm^{-1}): 2924.4, 2852.6, 1694.4, 1594.8, 1509.3, 1464.9, 1419.6, 1377.1, 1301.7, 1242.5, 1166.7, 1110.1, 1065.4, 1031.1, 1006, 964.4, 823.6, 775.6, 754.9, 731.8, 695.2.

*4-((E)-2-(7-((E)-4-((4-Methoxybenzyl)oxy)styryl)-9,9-dioctyl-9H-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**18**)*

In a 25 mL microwave vial with a magnetic stirrer was added 294 mg (0.4 mmol, 1.0 equiv.) of ((*E*)-2-(7-((*E*)-4-((4-methoxybenzyl)oxy)styryl)-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)pyridine (**17**). The vial was capped and 10 mL acetone was cannulated followed by transfer 0.1 mL of MeI (1.6 mmol, 4.0 equiv.). The reaction mixture was stirred at 60 °C for 16 h. After completion, the reaction mixture was dried in vacuo. The product was collected as 316 mg (96%) of red solid.

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.37 (d, J = 6.9 Hz, 2H), 8.21 (d, J = 16.2 Hz, 1H), 8.00 (s, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.81 (dd, J = 8.0, 1.5 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.60 (dd, J = 8.0, 1.5 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 16.3 Hz, 1H), 7.22 (d, J = 16.3 Hz, 1H), 7.03 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H),

5.07 (s, 2H), 4.55 (s, 3H), 3.81 (s, 3H), 2.19 – 2.12 (m, 4H), 1.21 – 1.14 (m, 4H), 1.13 – 1.01 (m, 16H).

ESI-MS (positive mode) – Calculated m/z for $[M-I]^+$: 746.49316. Found: 746.49416.

IR (film, cm^{-1}): 2924.5, 2853.4, 1643.9, 1618.2, 1593.4, 1511.6, 1466, 1421.8, 1378, 1341.2, 1302.9, 1243.1, 1210.6, 1173.6, 1110.9, 1033, 1004.7, 963.6, 872, 827.8, 754.1, 727.6.

*4-((E)-2-(7-((E)-4-Hydroxystyryl)-9,9-dioctyl-9H-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**19**)*

In a 25 mL microwave vial with a magnetic stirrer was added 175 mg (0.2 mmol, 1.0 equiv.) 4-((*E*)-2-(7-((*E*)-4-((4-methoxybenzyl)oxy)styryl)-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**18**). The vial was capped and 8 mL MeOH was cannulated followed by transfer 3 mL of HCl in dioxane (3.0 M). The reaction mixture was stirred at r.t. for 16 h. After completion, the reaction mixture was dried in vacuo and the solid was recrystallized from MeOH. After drying the product was collected as 90 mg (90%) of red solid.

^{1}H NMR (500 MHz, Methanol-d_4) δ 8.69 (d, J = 6.5 Hz, 2H), 8.16 (d, J = 6.6 Hz, 2H), 8.03 (d, J = 16.2 Hz, 1H), 7.81 (d, J = 7.9 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.57 (s, 1H), 7.54 (dd, J = 8.0, 1.4 Hz, 1H), 7.49 (d, J = 16.2 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 16.3 Hz, 1H), 7.09 (d, J = 16.3 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 4.31 (s, 3H), 2.12 (t, J = 8.2 Hz, 4H), 1.22 – 1.14 (m, 4H), 1.14 – 1.02 (m, 16H), 0.78 (t, J = 7.1 Hz, 6H), 0.60 (dd, J = 15.0, 7.4 Hz, 4H).

^{13}C{1H} NMR (101 MHz, Methanol-d_4) δ 158.6, 155.5, 153.2, 153.0, 145.9, 145.6, 143.7, 140.7, 139.7, 135.2, 130.5, 129.9, 129.4, 129.0, 127.0, 126.8, 124.8, 123.6, 122.7, 121.6, 121.5, 121.2, 116.6, 56.4, 47.6, 41.3, 32.9, 30.8, 30.2, 30.1, 24.8, 23.7, 14.4.

ESI-MS (positive mode) – Calculated m/z for [M-I]+: 626.43564. Found: 626.43609.

IR (film, cm-1): 3019.8, 2924, 2852.6, 1709.7, 1644.5, 1618.1, 1592.7, 1512.6, 1466, 1441.3, 1359.4, 1269.7, 1220, 1184.1, 1169, 1135.9, 1029.8, 963, 866, 829.5, 752.9, 720.5.

*4-((E)-2-(7-((E)-2-(1-Methylpyridin-1-ium-4-yl)vinyl)-9,9-dioctyl-9H-fluoren-2-yl)vinyl)phenolate (**FL5**)*

In a 15 mL centrifuge vial, 50 mg (0.06 mmol, 1.0 equiv.) 4-((*E*)-2-(7-((*E*)-4-hydroxystyryl)-9,9-dioctyl-*9H*-fluoren-2-yl)vinyl)-1-methylpyridinium iodide (**19**) was dissolved in 0.5 mL MeOH, then 10 mL Et_3N aqueous solution (5%, v/v) was added. The solid was filtered and washed with Et_3N aqueous solution two times. After drying under high vacuum, 40 mg (95%) of black solid was obtained.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (d, J = 6.4 Hz, 2H), 8.20 (d, J = 6.4 Hz, 2H), 8.09 (d, J = 16.2 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.82 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.49 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 16.2 Hz, 1H), 6.93 (d, J = 16.2 Hz, 1H), 6.59 (d, J = 8.2 Hz, 2H), 4.24 (s, 3H), 2.15 – 1.92 (m, 4H), 1.17 – 1.09 (m, 4H), 1.09 – 0.93 (m, 16H), 0.73 (t, J = 7.1 Hz, 6H), 0.53 (s, 4H).

ESI-MS (positive mode) – Calculated m/z for $[M+H]^+$: 626.43564. Found: 626.43579.

ASSOCIATED CONTENT

Supporting information

The following files are available free of charge.

^{1}H NMR, ^{13}C NMR spectra for the compounds, (PDF)

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N
C8H17
C8H17
H2O
MEOH
EtOH
iPrOH
MeCN
DMSO
DMF
Acetone
DCM
Pyridine