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Fluorous phthalocyanines and subphthalocyanines

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ABSTRACT: Incorporating fluorine atoms into a molecule can endow it with various unique properties that enable materials applications. Selective solubility in fluorous solvents is achieved by a high fluorine content and selective partitioning into perfluorinated liquids over organic and aqueous phases provides orthogonal opportunities for chemistry and materials assembly. Although there are a growing number of partially fluorinated molecules, there are insufficient structural design principles to produce diverse fluorous soluble dyes. Herein, we report the synthesis of six fluorous phthalocyanine and subphthalocyanine dyes, and study their properties in the fluorous phase. Phthalocyanines generally display limited solubility and we also observe apparent aggregation in the fluorous phase. However, the nonplanar subphthalocyanines showed greater solubility. Subphthalocyanines also displayed fluorescence in selected solvents, and their emissive properties were investigated. The materials described expand the library of fluorous dyes, and provide insights for the design of new molecules with fluorous solubility.

KEYWORDS: phthalocyanine, zinc phthalocyanine, subphthalocyanine, fluorescence, fluorine, aggregation, Faraday rotation.

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INTRODUCTION

Fluorine incorporation provides properties of importance to materials chemistry, and has found applications in coating materials [1], pharmaceuticals [2], in vivo drug delivery with perfluorocarbon nanoemulsions [3], and organic electronics [4]. Owing to fluorine’s electronegativity and hydrophobicity, introducing even a single fluorine atom into a molecule can vastly influence its solubility and dipole moment [5]. As a result, there is a growing interest in incorporating fluorine into organic semiconducting materials to enhance device performance. Incorporation of fluorine has also been found to improve chemical, thermal, and photochemical stability [6]. In some cases when the incorporation of fluorine atoms is high, compounds can phase separate from organic and aqueous phases [7]. In 1994, Horváth and Rábai labeled liquids displaying this phase separation as "fluorous" phases, and demonstrated their utility in fluorous biphasic catalysis [8]. Strategies to promote fluorous phase formation and solubility therein mainly rely on the fluorine content of the molecule, and the typical requirement is that there is >50 weight percent fluorine (wt% F) [7]. However, to date examples of dyes that partition to fluorous phases over organic phases are scarce [9]. We are interested to expand this area and have produced fluorous soluble conjugated polymers [10,11], an array of fluorofluorophores [12], and
fluorofluorescent perylene bisimides [13]. Additionally, Sletten and coworkers have recently demonstrated the opportunities of flourous character and reported the first J-aggregate in fluorous media [14], and the synthesis of a branched fluorous tag to create a fluorous soluble porphyrin [15]. All these examples gave rise to noteworthy materials properties, which highlights the uniqueness of the fluorous phase. As a result, we believe many applications await the discovery with the introduction of new fluororous materials.

Fluorous phthalocyanines and subphthalocyanines have attracted our interest as a result of their applications in organic field-effect transistors [16], organic light-emitting diodes [17], photovoltaics [18], nonlinear optical materials [19], and photodynamic therapy [20]. To date there are limited reports describing the properties of phthalocyanines and subphthalocyanines in the fluorous phase [21, 22]. Herein, we report the synthesis of six fluorous soluble phthalocyanines (F-PCs) and subphthalocyanines (F-SubPCs), and elaborate on their structure-property relationship in the fluorous phase.

RESULTS AND DISCUSSION

Synthesis of F-PCs

The synthesis of F-PCs, as shown in Scheme 1, was accomplished by adaptation of a previous literature report [21]. In brief, phthalonitriles 1-3 were reacted with zinc acetate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in n-pentanol to provide the desired F-PCs in 32-43% yields.

F-PCs were characterized by MALDI-TOF MS, UV/vis absorbance spectroscopy, FT-IR, and elemental analysis. The low solubility of F-PCs in deuterated solvents and fluorous solvents prevented the acquisition of nuclear magnetic resonance (NMR) characterization.

Properties of F-PCs

The F-PCs displayed almost no solubility in any organic solvents, regardless of wt% F. THF was the only solvent that showed any, albeit low solubility (< 0.1 mg mL⁻¹) of F-PCs. Fig. 1a–c shows the F-PCs partitioning into the fluorous solvent 2-(trifluoromethyl)-3-ethoxydodecafluorohexane (HFE-7500) rather than dissolving in the organic solvent diethylbenzene (DEB). The HFE-7500 and DEB solvent combination has a low interfacial tension and low upper critical mixing temperature. Although the F-PCs partitioned into HFE-7500, we observed precipitation F-PC-1 and F-PC-2 solutions from this solvent at room temperature (Fig. S1). This was confirmed by the observation that when solutions of F-PC-1 and F-PC-2 were passed through a 0.2 μm syringe filter, the solution was colorless, implying that they likely form aggregates larger than 0.2 μm. The solubility of F-PCs can be increased to ~0.1 mg mL⁻¹ by heating the THF and HFE-7500 solutions to their boiling temperatures (66 °C and 128 °C, respectively). F-PC-3 is slightly more soluble in THF and HFE-7500 than F-PC-1 and F-PC-2, displaying a solubility of ~1 mg mL⁻¹.
Table 1. Summary of photophysical properties of F-PCs

| Compound  | \( \lambda_\text{nm} \) | Molar Extinction Coefficient at \( \lambda_\text{nm} \) |
|-----------|----------------|----------------------------------|
| F-PC-1    | 698 (THF)       | 1.67 (THF)                        |
|           | 650 (HFE-7500)  |                                  |
| F-PC-2    | 698 (THF)       | 2.37 (THF)                        |
|           | 650 (HFE-7500)  |                                  |
| F-PC-3    | 683 (THF)       | 2.84 (THF)                        |
|           | 624 (HFE-7500)  |                                  |

The photophysical properties of F-PCs are summarized in Table 1 and Fig. 1d–f. F-PC-1 is scarcely soluble in heated THF and HFE-7500, and as a result its absorbance spectra was taken in THF and HFE-7500 heated to near their boiling temperatures. When solutions are cooled, the spectra broadens and decreases in intensity (Fig. S1). The heated solution was able to pass through a 0.2 \( \mu \text{m} \) syringe filter, however after cooling no perceptible color is observed in filtered solutions, thereby indicating that F-PC-1 precipitates. The absorbance spectra of F-PC-2 and F-PC-3 were also taken in THF and HFE-7500. The absorbance spectra of F-PC-2 in THF resembles that reported previously [21]. The absorbance of F-PCs in THF showed the typical Soret and Q absorbance bands for phthalocyanines, however a consistent large change in the spectra was observed in for all of the F-PCs in HFE-7500. Specifically, the relative peak intensity of the Q band at \( \sim690 \) nm decreased, while the relative peak intensities of the Soret band at \( \sim360 \) nm, as well as the shoulder at \( \sim650 \) nm increased. A decreased intensity at the \( S \rightarrow S \) band (\( \lambda_\text{abs} \approx 690 \) nm) and an increased intensity of the absorbance at \( \sim650 \) nm is suggestive of H-aggregation in fluorous solvents [24,25].

Synthesis of F-SubPCs

The synthesis of F-SubPCs, as shown in Scheme 2, was accomplished by adapting previous literature procedures [23]. In brief, the phthalonitrile precursors 1-3 were prepared by an S,Ar reaction of the fluoroalkyl thiols and halogenated phthalonitriles. Phthalonitriles 1-3 were then...
reacted with BCl₃ to provide the desired F-SubPCs in 13-29% yields. We note that an alternative synthetic scheme wherein the S-Ar reaction installing the fluoroalkyl thiols is performed on the halogenated subphthalocyanines did not produce the desired F-SubPCs (Scheme S1). The F-SubPCs were characterized by NMR, MALDI-TOF MS, UV/vis absorbance and fluorescence spectroscopy, FT-IR, and elemental analysis. The low solubility of F-SubPC-1 in deuterated solvents prevented the acquisition of NMR characterization.

Scheme 2. Synthesis of Fluorous Subphthalocyanines (F-SubPCs)

Properties of F-SubPCs

The F-SubPCs are consistently more soluble than their F-PCs counterparts despite possessing near identical wt% F. F-SubPC-1 was insoluble in common organic solvents, but was facilely soluble in fluorous solvents such as perfluoromethylcyclohexane (PFMCH), HFE-7500, and FC-770 (> 1 mg.mL⁻¹). F-SubPC-2 and F-SubPC-3 displayed moderate solubility (~1 mg.mL⁻¹) in organic solvents such as chloroform and toluene (PhMe), as well as the mentioned fluorous solvents. We determined the fluorous partition coefficient (P) of F-SubPCs by subjecting each compound to a 1:1 mixture of PFMCH and PhMe, and quantifying the amount in each layer by UV/vis absorbance spectroscopy (Fig. 2a–c). F-SubPC-1, F-SubPC-2, and F-SubPC-3 had a $P = 36$ (97:3 in PFMCH/PhMe), 1.1 (53:47 in PFMCH/PhMe), and 0.044 (4:96 in PFMCH/PhMe), respectively. From these results, we confirm a trend that higher wt% F leads to superior partitioning into fluorous solvents. The low $P$ of F-SubPC-3 may also be reflective of the fact that it is a regioisomeric mixture, and therefore possesses an asymmetric molecular structure.

Fig. 2. Chemical structure and fluorous partition of (a) F-SubPC-1, (b) F-SubPC-2, and (c) F-SubPC-3. Absorbance and emission spectra of (d) F-SubPC-1, (e) F-SubPC-2, and (f) F-SubPC-3.
The photophysical properties of F-SubPCs are summarized in Table 2 and Fig. 2d-f. In PhMe, F-SubPC-2 and F-SubPC-3 were fluorescent possessing quantum yields of 25.1% and 35.2%, respectively. The limited solubility of F-SubPC-1 in PhMe hindered the determination of the quantum yield in PhMe. The F-SubPCs dissolved in PFMCH also displayed a broad absorbance in the visible region, with a small hypsochromic shift. The F-SubPCs were only weakly fluorescent in PFMCH (Fig. 2a-c), and the quantum yields in PFMCH could not be determined.

F-SubPC-2 displayed solubility in both organic and fluorous phases to allow for comparisons, and in fluorous solvent the intensity of longest wavelength band (λₘₐₓ = 590 nm) decrease with a small increase in the absorbance at ~540 nm. This is indicative of H-aggregation in fluorous solvents, which is also likely the cause of fluorescence quenching [26]. However, the F-SubPCs can display fluorescence in fluorous solvents. For instance, F-SubPC-1 is fluorescent in HFE-7500, and shows excellent partition in HFE-7500 over DEB (Fig. S2).

**Faraday Rotation Properties of F-PCs and F-SubPCs**

The Faraday effect, discovered by Michael Faraday two centuries ago, is a ubiquitous magneto-optical effect, describing the rotation of the plane-polarized light traveling through a material along the axis of an applied magnetic field [27]. This effect is quantified by a Verdet constant (V), which is wavelength dependent, and linearly correlated to the applied magnetic field and the thickness of the material (Fig. 3). Recent emergence of organic materials possessing high Verdet constants such as semiconducting polymers [28,29], mesogenic organic molecules [30,31] including phthalocyanines [32,33], and radical-containing polymers [34,35] holds promises in utilizing these materials in processable devices. We have recently discovered that the role of polymer conformation and supramolecular organization affects the electronic delocalization and electromagnetic interactions and thereby modulate the Faraday effect [28,34]. Because we observed H-aggregation of F-PCs and F-SubPCs in fluorous solvents, we

**Table 2. Summary of photophysical properties of F-SubPCs**

| Compound   | Fluorous Partition Coefficient (PFMCH/PhMe) (P) | Molar Extinction Coefficient at λₘₐₓ, 10⁻⁴ L.mol⁻¹.cm⁻¹ | Quantum Yield, % | Fluorescence Lifetime, ns |
|------------|------------------------------------------------|----------------------------------------------------------|-----------------|--------------------------|
| F-SubPC-1  | 36                                             | 595 (PhMe)                                               | – (PhMe)        | – (PhMe)                 |
|            |                                                 | 580 (PFMCH)                                              | 1.46 (PFMCH)    | – (PFMCH)                |
| F-SubPC-2  | 1.1                                            | 595 (PhMe)                                               | 5.23 (PhMe)     | 25.1 (PhMe)              |
|            |                                                 | 586 (PFMCH)                                              | 2.00 (PFMCH)    | 2.72 (PhMe)              |
| F-SubPC-3  | 0.044                                          | 581 (PhMe)                                               | 6.27 (PhMe)     | 35.2 (PhMe)              |
|            |                                                 | 567 (PFMCH)                                              | – (PFMCH)       | 2.87 (PhMe)              |

*Excited at 500 nm. Measured with an integrating sphere excited at 500 nm. Referenced to 1,4-bis(5-phenyloxazol-2-yl)benzene (τ = 1.32 ns, MeOH). Not measured due to low solubility. Not measured due to weak fluorescence.*

![Fig. 3. Schematic image of magneto-optical material displaying a Faraday rotation. The degree of rotation (β) is governed by the materials’ Verdet Constant (V), strength of magnetic field (B), and the thickness of the material (d).](image-url)
hypothesized that the organization in fluorous solvents may give insight into the origins of the Faraday effect, and affect the degree of magnetic rotation. Thus, we sought to investigate the Faraday rotation properties of F-PCs and F-SubPCs in fluorous solvents.

Fig. 4 summarizes the Faraday rotation properties of F-PCs and F-SubPCs in various solvents (also see Fig. S4 for experimental setup). An analog property of the Verdet constant, the molar specific magnetic rotation (deg L mol⁻¹ T⁻¹ m⁻¹), was used to quantify magneto-optical effects in order to accommodate for the solution-phase nature of the samples. Because F-PCs displayed limited solubility in fluorous solvents, the rotation spectra could not be obtained. Instead, rotation spectra for F-PC-2 and F-PC-3 were obtained in THF, displaying largest molar specific magnetic rotations of -3.6 × 10⁻⁴ deg L mol⁻¹ T⁻¹ m⁻¹ and -8.8 × 10⁻⁵ deg L mol⁻¹ T⁻¹ m⁻¹, respectively. The measurement of F-PC-2 was conducted at elevated temperatures due to its low solubility. For F-SubPCs, rotation spectra was obtained in fluorous solvent PFMCH for F-SubPC-1 and F-SubPC-2, and in organic solvent PhMe for F-SubPC-2 and F-SubPC-3. The comparison of the spectra for F-SubPC-2 enables the study of the effect of organic and fluorous solvents on Faraday rotation properties. While we see rotation in fluorous solvent PFMCH (largest molar specific magnetic rotation of -9.3 × 10⁻⁴ deg L mol⁻¹ T⁻¹ m⁻¹), it is lower in intensity than that in organic solvent PhMe (largest molar specific magnetic rotation of -2.4 × 10⁻⁵ deg L mol⁻¹ T⁻¹ m⁻¹). Contrary to our expectations, these results confirm that H-aggregation in fluorous solvents was detrimental to the Faraday effect, however Faraday rotation properties measured in fluorous solvents is unprecedented.

**Fig. 4.** Faraday rotation properties of F-PCs and F-SubPCs. Molar specific magnetic rotation of (a) F-PC-2 and (b) F-PC-3 in THF. Molar specific magnetic rotation of (c) F-SubPC-1 and (d) F-SubPC-2 in PFMCH. Molar specific magnetic rotation of (e) F-SubPC-2 and (f) F-SubPC-3 in PhMe. Spectra for F-PC-1 obtained by heating the solution to its boiling temperature (66 °C).

**EXPERIMENTAL**

**General**

All chemical reagents were purchased from Sigma-Aldrich, Synquest Laboratories, Oakwood Chemicals, Fluoryx Labs, or TCI, and used without purification unless noted otherwise. Thin layer chromatography was performed with Baker-flex Silica Gel 1B-F plates (JT Baker). Flash chromatography was performed using technical grade silica gel with 60 Å pores and 230–400 mesh particle size (Sigma-Aldrich, 717185).

H, C, and F nuclear magnetic resonance (NMR) spectra were recorded on a JEOL model JNM-ECZ500R/S1 spectrometer operating at 500, 126, and 471 MHz,
the precipitate was filtered and collected, and was recrystallized from chloroform to provide colorless crystals 1 (462 mg, 0.426 mmol, 85% yield). \( ^1H \) NMR (500 MHz; acetone-\( d_6 \)): \( \delta \) (ppm) 8.06 (s, 2H), 7.59 (t, \( J = 7.6 \) Hz, 4H), 2.68–2.84 (m, 4H). \( ^13C \) NMR (126 MHz; acetone-\( d_6 \)): \( \delta \) (ppm) 146.08, 134.79, 131.94, 131.85, 117.15, 116.55, 116.20, 112.42, 31.22 (t, \( J = 22 \) Hz), 23.42. \( ^19F \) NMR

respective. For \( ^1H \), \( ^13C \) NMR spectra, deuterated solvent references were used as internal standards (H: 7.26 ppm for CDCl\(_3\), 2.05 ppm for acetone-\( d_6 \); C: 77.16 ppm for CDCl\(_3\), 206.26 ppm for acetone-\( d_6 \)). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m). Direct Analysis in Real Time (DART) mass spectra and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility. Elemental analysis data were obtained at Robertson Microlit Laboratories. Fourier-transform infrared spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. UV/Vis absorbance spectra were obtained on a Cary 4000 UV/Vis spectrophotometer (Agilent Technologies) with a scan rate of 600 nm/min. The instrument was blanked on the solvent prior to obtaining a spectrum. Fluorescence spectra were obtained on a Horiba Jobin Yvon SPEX Fluorolog-3 fluorimeter (model FL-321, 450 W Xenon lamp). Quantum yields were determined by using Horiba Quanta-\( \phi \) integrating sphere. Absorbance and fluorescence data were collected in a quartz cuvette (1 cm path length). Magneto-optical (MO) measurements were performed using our custom Faraday rotation apparatus (see Fig. S4 for experimental setup). Preparation of thin films was unsuccessful, so various solutions of F-PCs and F-SubPCs in organic and fluorous solvents were measured in a quartz cuvette (0.05 cm path length). An analog property of the Verdet constant, the molar specific magnetic rotation (deg.L.mol.\( ^{-1}.T.m^{-1} \)), was used to quantify MO effects in order to accommodate for the solution-phase nature of the samples.

Synthesis

**Compound 1.** A mixture of 4,5-dichlorophthalonitrile (98.5 mg, 0.500 mmol), \textit{1H,1H,2H,2H-}perfluorodecanethiol (504 mg, 1.05 mmol), and anhydrous K\( \text{CO}_3 \) (400 mg, 2.89 mmol) in acetone (5 mL) was stirred at 60 °C for 48 h. Then, 1M HCl aq (10 mL) was added and the product precipitated. The precipitate was filtered and collected, and was recrystallized from chloroform to provide colorless crystals \textit{1} (462 mg, 0.426 mmol, 85% yield). \( ^1H \) NMR (500 MHz; acetone-\( d_6 \)): \( \delta \) (ppm) 8.06 (s, 2H), 7.59 (t, \( J = 7.6 \) Hz, 4H), 2.68–2.84 (m, 4H). \( ^13C \) NMR (126 MHz; acetone-\( d_6 \)): \( \delta \) (ppm) 146.08, 134.79, 131.94, 131.85, 117.15, 116.55, 116.20, 112.42, 31.22 (t, \( J = 22 \) Hz), 23.42. \( ^19F \) NMR
(471 MHz; acetone-\textit{d}): \(\delta\) (ppm) -11.56 (t, \(J = 9.8\) Hz, 3F), -114.36 (m, 2F), -122.14 (m, 2F), -122.35 (m, 2F), -123.18 (m, 2F), -123.67 (m, 2F), -126.65 (m, 2F). DART MS: \(m/z\) calcd. for C.H.F.NS [M]: 606.0058. Found: 606.0071, 607.0155 [M + H], 624.0422 [M + NH], 665.0584 [M + acetone + H].

**F-PC-1.** A mixture of compound 1 (271 mg, 0.250 mmol), Zn(OAc). (12.8 mg, 0.0698 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 50 \(\mu\)L) in \(n\)-pentanol (5 mL) was stirred at 140 °C for 18 h. The reaction mixture was cooled to room temperature and filtered. Further purification was carried out by Soxhlet extraction with MeOH, CHCl, and AcOEt for 24 h each to obtain **F-PC-1** as a dark green solid (114 mg, 0.0625 mmol, 41% yield). NMR and MALDI-TOF MS spectra could not be obtained due to low solubility and aggregation. Elemental Anal. calcd. for C.H.F.N.S.Zn (%): C, 30.55; H, 0.92; N, 2.54. Found: C, 30.53; H, 1.03; N, 3.23. UV-vis (THF): \(\lambda_{\text{max}}\) (log \(e \)) = 369 (4.9), 629 (4.7), 698 (5.2).

**F-PC-2.** **F-PC-2** was synthesized following a previous literature report [21]. A mixture of compound 2 (221 mg, 0.250 mmol), Zn(OAc). (12.8 mg, 0.0698 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 50 \(\mu\)L) in \(n\)-pentanol (5 mL) was stirred at 140 °C for 18 h. The reaction mixture was cooled to room temperature and filtered. Further purification was carried out by Soxhlet extraction with MeOH, CHCl, and AcOEt for 24 h each to obtain **F-PC-2** as a green solid (97.0 mg, 0.0269 mmol, 43% yield). NMR spectra could not be obtained due to low solubility and aggregation. MALDI-TOF MS: \(m/z\) calcd. for C.H.F.N.S.Zn [M]: 3599.8692. Found: 3599.8692. UV-vis (THF): \(\lambda_{\text{max}}\) (log \(e \)) = 366 (5.0), 627 (4.7), 697 (5.4). The characterization is consistent with the previous literature report [21].

**F-PC-3.** A mixture of compound 3 (152 mg, 0.251 mmol), Zn(OAc). (12.8 mg, 0.697 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 50 \(\mu\)L) in \(n\)-pentanol (5 mL) was stirred at 140 °C for 18 h. The reaction mixture was cooled to room temperature and filtered. Further purification was carried out by Soxhlet extraction with MeOH, CHCl, and AcOEt for 24 h each to obtain **F-PC-3** as a teal green solid (50.1 mg, 0.0201 mmol, 32% yield). NMR spectra could not be obtained due to low solubility and aggregation. MALDI-TOF MS: \(m/z\) calcd. for C.H.F.N.S.Zn [M + H]: 2488.9604. Found: 2488.9574. Elemental Anal. calcd. for C.H.F.N.S.Zn (%): C, 34.72; H, 1.13; N, 4.50. Found: C, 35.00; H, 0.56; N, 4.87. UV-vis (THF): \(\lambda_{\text{max}}\) (log \(e \)) = 357 (5.0), 616 (4.7), 683 (5.5).

**F-SubPC-1.** **F-SubPC-1** was synthesized following a previous literature report [23]. Compound 1 (462 mg, 0.426 mmol) was added to a dried flask, and BCl (1.0 M in \(p\)-xylene, 0.450 mL) was added dropwisely. Then, the reaction mixture was stirred at 160 °C in a pre-heated oil bath for 30 min. Upon cooling the reaction mixture to room temperature, it was diluted with FC-770 (5 mL) and transferred to a separation funnel. The fluorous layer was washed with chloroform (10 mL), acetone (10 mL), water, (10 mL), brine (10 mL), dried with MgSO, and evaporated to dryness under reduced pressure. Further purification was carried out by Soxhlet extraction with acetone for 72 h to obtain **F-SubPC-1** as a dark purple solid (63.2 mg, 0.0191 mmol, 13% yield). NMR spectra could not be obtained due to low solubility and aggregation. MALDI-TOF MS: \(m/z\) calcd. for C.H.B.C.I.F.N.S. [M]: 3297.9009. Found: 3297.9106. UV-vis (HFE-7500): \(\lambda_{\text{max}}\) (log \(e \)) = 359 (4.3), 592 (4.2).

**F-SubPC-2.** Compound 2 (265 mg, 0.300 mmol) was added to a dried flask, and BCl (1.0 M in \(p\)-xylene, 0.300 mL) was added dropwisely. Then, the reaction mixture was stirred at 160 °C in a pre-heated oil bath for 30 min. Upon cooling the reaction mixture to room temperature, it was diluted with FC-770 (5 mL) and transferred to a separation funnel. The fluorous layer was washed with chloroform (10 mL), acetone (10 mL), water, (10 mL), brine (10 mL), dried with MgSO, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel using CHCl as an eluent, and the fraction containing **F-SubPC-2** (R = 0.60) was collected and evaporated to
dryness to provide a dark purple solid (50.2 mg, 0.0185 mmol, 19% yield). H NMR (500 MHz; CDCl3): δ (ppm) 8.76 (s, 6H), 3.38–3.49 (m, 12H), 2.49–2.64 (m, 12H). -F NMR (471 MHz; CDCl3): δ (ppm) -80.79 (t, J = 9.8 Hz, 18F), -113.94 (m, 12F), -121.87 (m, 12F), -122.87 (m, 12F), -123.19 (m, 12F), -126.17 (m, 12F). MALDI-TOF MS: m/z calcd. for C21H25F24N20S: [M + H]+: 720.9762. Found: 720.9765.

CONCLUSIONS

In summary, we have described the synthesis and characterization of fluorous phthalocyanines and subphthalocyanines. F-PC-1 and F-PC-2 displayed limited solubility in both organic and fluorous solvents, whereas F-PC-3 was more soluble in fluorous solvents. The absorbance spectra of F-PCs in organic and fluorous solvents showed different trends, suggestive of H-aggregation in fluorous solvents. On the other hand, the nonplanar F-SubPCs were showed improved solubility in fluorous solvents, and followed the trend of higher wt% F displaying higher fluorous solubility. The F-SubPCs were fluorescent in organic solvents and HFE-7500, but were only weakly fluorescent in PFMC, which is also suggestive of H-aggregation. We have also studied the Faraday rotation properties of F-PCs and F-SubPCs in fluorous and organic solvents. The compounds described in this report pave the way for the discovery of functional fluorous soluble phthalocyanines and subphthalocyanines. Further characterization of the properties of F-PCs and F-SubPCs is underway, and we anticipate these compounds will find applications as new fluorous soluble/dispersible materials.

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Supporting Information

Supplementary figures, spectral data (NMR, MALDI TOF-MS) are given in the Supporting Information. This material is available free of charge via the internet at http://worldscinet.com/jpp/jpp.shtml.

REFERENCES

1. Anton BD. 1998; 10: 1197-1205.
2. Müller K, Faeh C and Diederich F. Science 2007; 317: 1881-1886.
3. Rapoport N. In Escoffre J-M, Bouakaz A, eds. Therapeutic Ultrasound. Cham: Springer International Publishing, 2016; 221-241.

4. Ragni R, Punzi A, Babudri F and Farinola GM. European J. Org. Chem. 2018; 2018: 3500-3519.

5. Fuchibe K, Morikawa T, Shigeno K, Fujita T and Ichikawa J. Org. Lett. 2015; 17: 1126-1129.

6. Sun H, Putta A, Kloster JP and Tottempudi UK. Chem. Commun. 2012; 48: 12085-12087.

7. Horváth IT, Curran DP and Gladysz JA. In Handbook of Fluorous Chemistry. John Wiley & Sons, Ltd, 2005; 1-4.

8. Horváth IT and Rábai J. Science 1994; 266: 72-75.

9. Kobayashi N and Fukuda T. In Kim S-H, ed. Functional Dyes. Amsterdam: Elsevier Science, 2006; 1-45.

10. Lim J and Swager TM. Angew. Chemie - Int. Ed. 2010; 49: 7486-7488.

11. Takeda Y, Andrew TL, Lobez JM, Mork AJ and Swager TM. Angew. Chemie Int. Ed. 2012; 51: 9042-9046.

12. Sletten EM and Swager TM. J. Am. Chem. Soc. 2014; 136: 13574-13577.

13. Yoshinaga K and Swager TM. Synlett 2018; 29: 2509-2514.

14. Cao W and Sletten EM. J. Am. Chem. Soc. 2018; 140: 2727-2730.

15. Miller MA and Sletten EM. Org. Lett. 2018; 20: 6850-6854.

16. Melville OA, Lessard BH and Bender TP. ACS Appl. Mater. Interfaces 2015; 7: 13105-13118.

17. Baeg K-J, Binda M, Natali D, Caironi M and Noh Y-Y. Adv. Mater. 2013; 25: 4267-4295.

18. de la Torre G, Bottari G and Torres T. Adv. Energy Mater. 2017; 7: 1601700.

19. Oluwole DO, Yagodin A V., Mkhize NC, Sekhosana KE, Martynov AG, Gorbunova YG, Tsivadze AY and Nyokong T. Chem. Eur. J. 2017; 23: 2820-2830.

20. Lo P-C, Rodríguez-Morgade MS, Pandey RK, Ng DKP, Torres T and Dumoulin F. Chem. Soc. Rev. 2020.

21. GüröI, Gümüş G, Musluoğlu E, Arslan Y and Ahsen V. J. Porphyr. Phthalocyanines 2013; 17: 555-563.

22. Mori S and Shibata N. Beilstein J. Org. Chem. 2017; 13: 2273-2296.

23. Eder GM, Walker BR and McGrier PL. RSC Adv. 2017; 7: 29271-29274.

24. Bilgiçli AT, Günsel A, Kandaz M and Özkaya AR. Dalt. Trans. 2012; 41: 7047-7056.

25. Bayda M, Dumoulin F, Hug GL, Koput J, Gorniak R and Wojcik A. Dalt. Trans. 2017; 46: 1914-1926.

26. Adachi K, Chayama K and Watarai H. Soft Matter 2005; 1: 292-302.

27. Faraday M. Philos. Trans. R. Soc. London 1846; 136: 1-20.

28. Wang P, Jeon I, Lin Z, Peeks MD, Savagatrup S, Kooi SE, Van Voorhis T and Swager TM. J. Am. Chem. Soc. 2018; 140: 6501-6508.

29. Gangopadhyay P, Koeckelberghs G and Persoons A. Chem. Mater. 2011; 23: 516-521.

30. Vandendriessche S, Van Cleuvenbergen S, Willot P, Hennrich G, Srebro M, Valev VK, Koeckelberghs G, Clays K, Autschbach J and Verbiest T. Chem. Mater. 2013; 25: 1139-1143.

31. Vleugels R, Steverlynck J, Bruullot W, Koeckelberghs G and Verbiest T. J. Phys. Chem. C 2019; 123: 9382-9387.

32. Stephens PJ, Suëtaak W and Schatz PN. J. Chem. Phys. 1966; 44: 4592-4602.

33. Shashoua VE. J. Am. Chem. Soc. 1965; 87: 4044-4048.

34. Wang P, Lin S, Lin Z, D. Peeks M, Van Voorhis T and M. Swager T. J. Am. Chem. Soc. 2018; 140: 10881-10889.

35. Lim C-K, Ju Cho M, Singh A, Li Q, Jin Kim W, Sub Jee H, L. Fillman K, H. Carpenter S, L. Neidig M, Baev A, T. Swihart M and N. Prasad P. Nano Lett. 2016; 16: 5451-5455.
List of Captions

Fig. 1. Chemical structure and fluorous partition of (a) F-PC-1, (b) F-PC-2, and (c) F-PC-3. Overlaid normalized absorbance spectra of (d) F-PC-1, (e) F-PC-2, and (f) F-PC-3 in organic solvent THF and in fluorous solvent HFE-7500. Spectra for F-PC-1 obtained by heating the solutions to their boiling temperatures (66 °C for THF, 128 °C for HFE-7500).

Fig. 2. Chemical structure and fluorous partition of (a) F-SubPC-1, (b) F-SubPC-2, and (c) F-SubPC-3. Absorbance and emission spectra of (d) F-SubPC-1, (e) F-SubPC-2, and (f) F-SubPC-3.

Fig. 3. Schematic image of magneto-optical material displaying a Faraday rotation. The degree of rotation ($\beta$) is governed by the materials’ Verdet Constant ($V$), strength of magnetic field ($B$), and the thickness of the material ($d$).

Fig. 4. Faraday rotation properties of F-PCs and F-SubPCs. Molar specific magnetic rotation of (a) F-PC-2 and (b) F-PC-3 in THF. Molar specific magnetic rotation of (c) F-SubPC-1 and (d) F-SubPC-2 in PFMCH. Molar specific magnetic rotation of (e) F-SubPC-2 and (f) F-SubPC-3 in PhMe. Spectra for F-PC-1 obtained by heating the solution to its boiling temperature (66 °C).

Scheme 1. Synthesis of fluorous phthalocyanines (F-PCs)

Scheme 2. Synthesis of Fluorous Subphthalocyanines (F-SubPCs)

Table 1. Summary of photophysical properties of F-PCs

Table 2. Summary of photophysical properties of F-SubPCs

Graphical Abstract
Fig. 1. Chemical structure and fluorous partition of (a) F-PC-1, (b) F-PC-2, and (c) F-PC-3. Overlaid normalized absorbance spectra of (d) F-PC-1, (e) F-PC-2, and (f) F-PC-3 in organic solvent THF and in fluorous solvent HFE-7500. Spectra for F-PC-1 obtained by heating the solutions to their boiling temperatures (66 °C for THF, 128 °C for HFE-7500).
Fig. 2. Chemical structure and fluorous partition of (a) F-SubPC-1, (b) F-SubPC-2, and (c) F-SubPC-3. Absorbance and emission spectra of (d) F-SubPC-1, (e) F-SubPC-2, and (f) F-SubPC-3.
Fig. 3. Schematic image of magneto-optical material displaying a Faraday rotation. The degree of rotation ($\beta$) is governed by the materials’ Verdet Constant ($V$), strength of magnetic field ($B$), and the thickness of the material ($d$).
Fig. 4. Faraday rotation properties of F-PCs and F-SubPCs. Molar specific magnetic rotation of (a) F-PC-2 and (b) F-PC-3 in THF. Molar specific magnetic rotation of (c) F-SubPC-1 and (d) F-SubPC-2 in PFMCH. Molar specific magnetic rotation of (e) F-SubPC-2 and (f) F-SubPC-3 in PhMe. Spectra for F-PC-1 obtained by heating the solution to its boiling temperature (66 °C).
Scheme 1. Synthesis of fluorous phthalocyanines (F-PCs)
Scheme 2. Synthesis of Fluorous Subphthalocyanines (F-SubPCs)
| Compound | $\lambda_{\text{abs}}$, nm | Molar Extinction Coefficient at $\lambda_{\text{abs}}$, $10^5$ L.mol$^{-1}$.cm$^{-1}$ |
|----------|-----------------|--------------------------------------------------|
| F-PC-1   | 698 (THF)       | 1.67 (THF)                                      |
|          | 650 (HFE-7500)  |                                                  |
| F-PC-2   | 698 (THF)       | 2.37 (THF)                                      |
|          | 650 (HFE-7500)  |                                                  |
| F-PC-3   | 683 (THF)       | 2.84 (THF)                                      |
|          | 624 (HFE-7500)  |                                                  |
Table 2. Summary of photophysical properties of F-SubPCs

| Compound | Fluorous Partition Coefficient (PFMCH/PhMe) (P) | λ\(_{\text{abs}}\), nm | Molar Extinction Coefficient at λ\(_{\text{abs}}\), 10\(^{-4}\) L.mol\(^{-1}\).cm\(^{-1}\) | λ\(_{\text{em}}\), nm | Quantum Yield (\(\phi\), %) | Fluorescence Lifetime (\(\tau\), ns) |
|----------|--------------------------------------------------|---------------------|-------------------------------------------------|---------------------|-------------------------------|-----------------------------------|
| F-SubPC-1 36 | 595 (PhMe) 580 (PFMCH) | 585 (PhMe) 1.46 (PFMCH) | 606 (PhMe) – (PhMe) | 606 (PhMe) – (PhMe) | 587 (PFMCH) – (PFMCH) | 587 (PFMCH) – (PFMCH) |
| F-SubPC-2 1.1 | 595 (PhMe) 586 (PFMCH) | 600 (PhMe) 5.23 (PhMe) | 605 (PhMe) 2.00 (PFMCH) | 605 (PhMe) 2.00 (PFMCH) | 588 (PFMCH) – (PFMCH) | 588 (PFMCH) – (PFMCH) |
| F-SubPC-3 0.044 | 581 (PhMe) 567 (PFMCH) | 594 (PhMe) 6.27 (PhMe) | 594 (PhMe) – (PFMCH) | 594 (PhMe) – (PFMCH) | 573 (PFMCH) – (PFMCH) | 573 (PFMCH) – (PFMCH) |

\(\text{Excited at } 500 \text{ nm. Measured with an integrating sphere excited at } 500 \text{ nm. Referenced to 1,4-bis(5-phenyloxazol-2-yl)benzene }\ (\tau = 1.32 \text{ ns, MeOH). Not measured due to low solubility. Not measured due to weak fluorescence.}\)
Graphical Abstract

- F-PCs
- Organic Fluorous
- F-SubPCs
- Organic Fluorous

✓ >50 wt% F
✓ Photophysical Studies in Fluorous Solvents
✓ Faraday Rotation Properties