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Fluorous Biphase Synthesis of a Poly(p-phenyleneethynylene) and its Fluorescent Aqueous Fluorous Phase Emulsion

Jeewoo Lim and Timothy M. Swager*

Heavily fluorinated materials display an array of interesting properties such as thermal and chemical stability, low surface energy, and high resistance to oxidation. These materials can display orthogonal solubility, dissolving in fluorous solvents with limited solubility in organic solvents, allowing for facile purification via liquid-to-liquid extraction and/or fluorous solid phase extraction. Fluorous small molecules, materials, and solvents have been utilized in areas such as fluorous biphase chemistry, liquid crystals, electronics, and arrays for biosample screening. Fluorous phase soluble conjugated polymers have merit both in that they would allow for facile purification and processing and in that they could provide non-toxic platforms for fluorescence-based bioimaging and detection. Furthermore, introduction of rigid perfluoroalkyl chains to the backbone of a conjugated polymer is expected to enhance the material’s quantum yield both in solution and in solid state. We report in this communication the synthesis and properties of two heavily fluorinated poly(p-phenylene ethynylene)s (PPEs), P1 and P2 (Figure 1). Both polymers are highly fluorescent in solution and in thin film. Furthermore, P1, which displays selective solubility in fluorous solvents, can be synthesized via fluorous biphase polymerization, allowing for facile isolation/purification of the polymer after polymerization (Figure 2). The alkoxylated counterpart, P2, shows good solubility in organic solvents but is not soluble in fluorous phase. Selective solubility of P1 in fluorous solvents allows for the creation of a highly fluorescent and stable emulsion in water.

The design principle of P1 was based on qualitative guidelines of fluorous compatibility outlined by Horvath et al. and consists of a) majority fluorine content by weight and b) long perfluoroalkyl chains forming a sheath around the PPE backbone. Furthermore, a rigid, bulky architecture was desired to discourage aggregation of the polymer both in solution and in solid state. The synthesis of the monomer, 1, for a polymer that meets such requirements and the syntheses of P1 and P2 from 1 is outlined in Scheme 1.

When the pentacene derivative 2 was treated with an excess of perfluoro(7-tetradecyne) in xylenes at 145°C, no reaction was observed after 4 days. The lack of reactivity was attributed to the lack of solubility of perfluoro(7-tetradecyne) in xylenes even at elevated temperatures. When the reaction mixture was homogenized with a high-shear mixer at 80°C before raising the temperature to 145°C, the desired two-fold Diels-Alder reactions took place, affording the desired di-adduct, 3, in 86% yield. The reaction gave the syn-isomer as the major product, with a 6:1 syn/anti ratio. This selectivity is in sharp contrast to the Diels-Alder reactions of 2 with hexafluorobutylene and DMAD, in which cases the anti-isomers are observed as major products. The anti isomer displayed sparing solubility in most organic solvents, while the syn isomer was highly soluble, and therefore the synthesis was carried forward using only the syn isomer.

Removal of the TIPS moieties gave the corresponding diacetylene 4. Sonogashira-Hagihara cross coupling polymerization under various conditions between the diacetylene and diiodide 6 gave only oligomeric products. The low degree of polymerization was attributed to the sterically encumbered environment around acetylene moieties of 4. It was therefore envisioned that monomer 1, with reduced steric hindrance around the acetylene functional groups, would yield higher polymers.

When monomer 1 was subjected to Sonogashira-Hagihara cross coupling polymerization in toluene/disopropyl amine solvent system with diiodide 6, higher molecular weight products were obtained, although the products were soluble in organic solvents. It
was expected that more fluorous solvent condition for Sonogashira-Hagihara cross coupling reaction would yield polymers with higher molecular weights, which may subsequently render the material selectively soluble in fluorous solvents. When 5:3:2 toluene/perfluoro(methylcyclohexane)/diisopropyl amine was heated, it was observed that the solvent mixture became monophasic at 82°C, and, upon cooling, the fluorous phase separated out from the organic (toluene/diisopropyl amine) phase cleanly. The Sonogashira-Hagihara cross coupling polymerization between monomer 1 and 6 in this solvent system at 85°C gave, upon cooling, a biphasic mixture in which bright blue fluorescence is localized in the fluorous layer (photograph, Scheme 1). Removal of the organic layer, followed by washing the fluorous layer with methanol, acetone, and ethyl acetate gave P1 in 87% yield. This constitutes a first example of a fluorous biphasic synthesis of a conjugated polymer. The polymer obtained in this manner was optically pure and was used without further purification for photophysical measurements.

When monomer 1 was treated with co-monomer 7 under identical conditions, a complete reversal of solubility was observed, with the fluorescence of the product biphasic mixture localized in the upper organic phase. Removal of the fluorous layer, followed by precipitation of the organic layer into ethanol and washing the solids with acetone, gave P2 in 78% yield.

The normalized absorption and emission spectra of P1, and P2 are shown in Figure 3. Fluorous soluble P1 displays band edge and emission maximum that are both blue-shifted in relation to P2. Small Stokes shift and sharp absorption and emission spectra of P1 (5-6 nm) suggest that the structure of the polymer in solution is highly rigid. Both P1 and P2 are highly fluorescent. Fluorous P1 has a quantum yield of 0.95 in perfluorodecalin and the organic-soluble P2 has a quantum yield of 0.84 in toluene. Furthermore, both polymers exhibit high quantum yields in thin film (0.32 for P1 and 0.42 for P2). The relatively lower thin-film quantum yield of P1 in comparison to P2 could be associated to the flat geometry of the co-monomer 6 relative to 7, resulting in higher degree of aggregation for P1 in solid state than P2.

To compare these properties to a non-fluorinated polymer, a new polymer, P3, featuring a rigid, three-dimensional architecture and dialkyl aryl moiety in the backbone, was synthesized (Scheme 2; for solution absorption and emission spectra, see supporting information Figure S1). This polymer, displayed a reduced solution quantum yield (0.48 in toluene), compared to P1 and P2. The thin-film emission spectrum of P3 showed a broad and red-shifted peak, suggesting large degrees of aggregation, whereas the thin-film emission spectra of P1 and P2 did not display significant shifts from their respective solution spectra (see supporting information, Figure S2). Also, P3 was insoluble in fluorous solvents.

While monomer 1 is soluble in organic solvents including acetonitrile, hexanes, chloroform, ethyl acetate, and THF, and insoluble in non-polar fluorous solvents (such as FC-72, perfluoromethylcyclohexane, and perfluorodecalin), P1 is soluble in those fluorous solvents but is insoluble in organic solvents. The exclusive fluorous solubility of P1 made it difficult to determine degree of polymerization by GPC analysis. Dynamic light scattering (DLS) analysis showed that the average length of P1 is 16 nm, a value which is the typical persistence length of long PPEs.6 DLS measurement in perfluorodecalin also showed similar length distribution. When P1 was end-capped with 1-bromo-4-tert-butylbenzene, no tert-butyl signals were observed in proton NMR spectrum, indicating high degree of polymerization (>20). The organic soluble P2 could be analyzed by GPC, and was shown to have $M_\text{w} = 520$ kDa, $M_\text{n} = 2,850$ kDa, and PDI = 5.48.

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In order to make possible imaging and sensory applications of our fluorous-phase soluble fluorescent polymer, we set out to process fluorous solutions of P1 into a stable emulsion in water with easily modifiable functional groups adorning the surface.

<table>
<thead>
<tr>
<th>Scheme 1</th>
<th>Synthetic routes to P1 and P2. Polymerization conditions: 3:5:1 perfluoro(methylcyclohexane)/toluene/diisopropylamine, 5 mol% Pd(PPh3)4, 7 mol% CuI, 85°C, 4 days. The photographs show reaction mixtures at the end of the reaction irradiated with hand-held long-wave UV lamps.</th>
</tr>
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<tbody>
<tr>
<td>Scheme 2</td>
<td>Structure and synthesis of P3.</td>
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</table>
Perfluorodecalin, which has been approved by the FDA for use as a component in human blood surrogate, was chosen as the fluorous component of the emulsion. When a solution of P1 in perfluorodecalin was added slowly to a hot solution of 2H,2H,3H,3H-perfluorononanoic acid under probe sonication, a turbid and strongly fluorescent emulsion formed. Upon cooling, a relatively monodisperse emulsion was obtained with an average diameter of 245.8 nm and PdI of 0.099 as determined by DLS. The emulsion displayed absorption and emission maxima (Figure 4) identical to P1. The emulsion in PBS buffer was highly fluorescent, with a quantum yield of 0.58. Zeta potential is a useful method of measuring stability of colloids in water, because higher surface charge will discourage aggregation of particles. Colloids with surface potential of ±40 mV and higher are considered to have good stability. Emulsion of perfluorodecalin solution of P1 in water showed Z-potential of -57 mV with 13.2 mV deviation, indicating that the surfaces of the emulsion are sufficiently charged to confer good stability to the overall emulsion.

We have synthesized two PPE’s from a novel, heavily fluorinated building block, 1, and demonstrated that, depending on the choice of the co-monomer, the solubility properties of the materials could be changed drastically. Both polymers were highly fluorescent both in solution and in thin film. The fluorous phase soluble PPE, P1, could be processed into a stable emulsion in PBS buffer (pH 7.4). The emulsion involves a nontoxic fluorous solvent, is highly fluorescent, and has functional groups on the surface, which could be further modified. Report on conjugation of biologically active molecules to the surface of the emulsion is forthcoming.

**Experimental Section**

Detailed experimental procedures and chemical synthesis are described in the Supporting Information.

Received: (will be filled in by the editorial staff)
Published online on (will be filled in by the editorial staff)

**Keywords:** fluorous biphasic synthesis · PPE · Sonogashira-Hagihara polymerization · perfluorodecalin · emulsion

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Figure 4. a) Absorption (dotted) and emission (solid) spectra of the emulsion of perfluorodecalin solution of P1 in pH 7.4 PBS buffer (Q.Y. 0.58), and a pictorial representation of the emulsion particle, and b) photograph of the emulsion before (left) and after (right) irradiation with hand-held laboratory UV lamp.

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A heavily fluorinated molecule with a rigid three-dimensional architecture has been synthesized as a monomer for poly(phenyleneethynylene)s. Fluorous biphasic chemistry has been applied to synthesize a PPE which exhibit selective solubility in fluororous solvents. Fluorous solution of the polymer could be processed into aqueous emulsions that display high fluorescence quantum yields.
Supporting Information for

Fluorous Biphase Synthesis of a Poly(p-phenyleneethynylene) and its Fluorescent Aqueous Fluorous Phase Emulsion

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General. All air- and moisture-sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. Column chromatography was performed using ultra pure silica gel (SILICYCYLE, 40–63 μm). NMR spectra were obtained on a Varian Mercury-300 spectrometer, and all proton chemical shifts are referenced to residual CHCl₃ or C₆D₆, and all fluorine chemical shifts are referenced to an external CFCl₃ standard. High-resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Bruker Daltronics APEX II 3 Tesla FT-ICR-MS. Polymer molecular weights and polydispersity indexes were estimated by gel permeation chromatography (GPC) using a HP series 1100 GPC system. Polystyrene standards were used for calibration, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorimeter (model FL-321, 450 W Xenon lamp) using right-angle detection for solutions and front-face detection for thin films. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent-filled cuvette for solutions and glass slide for thin films. Fluorescence quantum yields of polymer solutions were determined by the optically dilute method using quinine sulfate in 0.1M H₂SO₄, coumarin 6 in ethanol, or 9,10-diphenylanthracene in hexanes as a standards and were corrected for solvent refractive index and absorption differences at the excitation wavelength. Fluorescence quantum yields of polymer thin films were determined using 9,10-diphenylanthracene in poly(methyl methacrylate) (PMMA) (Φ = 0.83). Dynamic light scattering (DLS) data for polymer length distribution was obtained from Wyatt Technologies DynaPro Titan using perfluoromethylcyclohexane and perfluorodecalin as solvents. The emulsion size and Z-potential was obtained from Malvern Zeta Sizer Nano ZS90.

Materials. All solvents were spectral grade unless otherwise noted. Anhydrous toluene and tetrahydrofuran were obtained using a solvent purification system (Innovative Technologies). Perfluorohexyl iodide (C₆F₁₃I) was freshly distilled before use. Diisopropylamine was distilled over calcium hydride. Perfluoromethylcyclohexane and FC-77 (perfluorooctane) was purified according to literature procedures prior to use. All other chemicals were used as received. Solvents for polymerization (perfluoromethylcyclohexane, toluene, and diisopropylamine) were degassed via freeze-pump-thaw prior to use.

Synthesis

Scheme S1. Synthesis of perfluoro(7-tetradecyne) (S4).

3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroct-1-yne (S2). A flame-dried 50 mL round-bottom flask equipped with distillation apparatus was charged with 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-2-methyldec-3-yn-2-ol (S1) (35.3 g, 88 mmol) and NaOH pellets (2.5 g, 61 mmol) under argon. The pressure was reduced to 400 mmHg and the flask was heated to 100°C. The crude product was collected over an hour in a brine/ice bath. The product was washed 3 times with distilled water and was subsequently dried over MgSO₄. Removal of drying agent via filtration gave S2 (13.4 g, 46%) as a clear liquid. B.p. 92-94°C. 1H NMR (300 MHz, CDCl₃): δ 3.07 (t, J_H-F = 5.7 Hz, 1H). 19F NMR (282 MHz, CDCl₃): δ -126.69 (2F), -123.39 (2F), -123.25 (2F), -121.83 (2F), -99.76 (2F), -81.33 (3F).

(Z)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8,9,9,10,10,11,12,13,14,14-hexacosafluoro-7-iodotetradec-7-ene (S3). Compound S2 (27.7 g, 35 mmol) and C₆F₁₃I (33.4 g, 75 mmol) were added to a Parr bomb under N₂, and the reaction was sealed and heated to 220°C. The pressure of the reaction vessel increased initially to 95-100 psi, and was gradually reduced to 28 psi over 4 hours. The reaction was removed from heat and allowed to cool to room temperature before venting. The excess C₆F₁₃I was distilled off at 10 mmHg, and the product (S3, 31.8 g, 80%) was obtained as a clear liquid by distillation at 6 mmHg. B.p. 99-101°C (6 mmHg). 1H NMR (300 MHz, CDCl₃): δ 3.07 (t, J_H-F = 5.7 Hz, 1H). 19F NMR (282 MHz, CDCl₃): δ -126.69 (2F), -123.39 (2F), -123.25 (2F), -121.83 (2F), -99.76 (2F), -81.33 (3F).

Perfluoro(7-tetradecyne) (S4). A flame-dried 100 mL round-bottom flask was charged with anhydrous KOH (10 g, 170 mmol) under argon. Compound S3 (27.7 g, 35 mmol) was added, and the flask was equipped with a 15 cm vigreux column and a short-path distillation
apparatus. The pressure was decreased to 6 mmHg, and the reaction mixture was placed in an oil bath pre-heated to 60°C. The reaction was heated slowly to 105°C. The product collected in the receiving flask was further purified by distillation at 6 mmHg (65–67°C) and S4 (8.8 g, 38%) was obtained as a clear liquid. B.p. 65–67°C (6 mmHg). 1H NMR (300 MHz, CDCl3): blank. 19F NMR (282 MHz, CDCl3): δ -126.43 (4F), -123.14 (4F), -122.83 (4F), -121.61 (4F), -102.44 (4F), -81.04 (6F).

Scheme S2. Synthesis of monomer 1.

**Compound 3.** A flame-dried 25 mL pressure tube was charged with 2' (640 mg, 1.0 mmol), S4 (2.0 g, 3.0 mmol), and xylenes (6 mL). The reaction mixture was degassed by bubbling argon through for 20 minutes while stirring. The reaction vessel was then placed in an oil bath at 80°C. After stirring for 20 minutes, the reaction mixture was homogenized with a high-shear mixer for 20 seconds. The reaction vessel was then sealed and heated to 135°C. The color of the reaction changed gradually from deep blue to yellow over 4 days, at which point the reaction was allowed to cool to room temperature. Solvent and excess S4 was removed via distillation. The crude product was recrystallized in dichloromethane to give the anti isomer (217 mg, 11%). The mother liquor was concentrated and was purified by column chromatography (silica gel, 100% hexanes to 5% dichloromethane) to give the syn isomer, which was further purified by recrystallization in acetone to give compound 3 (800 mg, 0.41 mmol) as rod-like crystals. M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 1.28 (s, 4H), 5.97 (s, 4H), 7.11 (dd, J = 5.4 and 3.3 Hz, 4H), 7.36 (dd, J = 5.4 and 3.3 Hz, 4H). 19F NMR (282 MHz, CDCl3): δ -126.73 (4F), -123.41 (4F), -122.33 (4F), -119.58 (4F), -109.62 (4F), -81.33 (6F). HR-MS (EI): calcd for C76H38F52Si2 1994.1676; found 1994.1624. Syn (3): M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 1.28 (s, 4H), 5.97 (s, 4H), 7.03 (dd, J = 5.4 and 3.3 Hz, 4H), 7.27 (dd, J = 5.4 and 3.3 Hz, 4H). 19F NMR (282 MHz, CDCl3): δ -126.77 (4F), -123.47 (4F), -122.50 (4F), -119.83 (4F), -109.50 (2F), -108.30 (2F), -81.47 (6F). HR-MS (EI): calcd for C76H38F52Si2 1994.1676; found 1994.1624.

**Compound 4.** In a flame-dried 100 mL round bottom flask under argon, 3 (800 mg, 0.41 mmol) was dissolved in anhydrous THF (20 mL). The flask was cooled to -78°C in dry ice/acetone bath. Tetraethyl ammonium fluoride (0.85 mL, 0.85 mmol) solution was added dropwise. The reaction was stirred at -78°C for 30 minutes. After warming up to room temperature, the reaction mixture was diluted with 10 mL ethyl acetate and 40 mL hexanes and subsequently passed through a plug of silica gel. The solvents were evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, hexanes as the eluent) to give 4 as white, foamy solids (690 mg, quantitative). M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 1.28 (s, 4H), 5.97 (s, 4H), 7.11 (dd, J = 5.4 and 3.3 Hz, 4H), 7.36 (dd, J = 5.4 and 3.3 Hz, 4H). 19F NMR (282 MHz, CDCl3): δ -126.77 (4F), -123.47 (4F), -122.50 (4F), -119.83 (4F), -109.50 (2F), -108.30 (2F), -81.47 (6F). HR-MS (EI): calcd for C54H14F52 1673.0157 [M+Na]+; found 1673.0192. 19F NMR (282 MHz, CDCl3): δ -126.73 (4F), -123.41 (4F), -122.33 (4F), -119.58 (4F), -109.62 (4F), -81.33 (6F). HR-MS (EI): calcd for C76H38F52Si2 1994.1676; found 1994.1624.

**Compound 5.** Flame-dried 10 mL Schenk flask was charged with 4 (415 mg, 0.251 mmol), 4-iodophenylethyl trimethylsilane (180 mg, 0.600 mmol), Pd(PPh3)4Cl2 (9.0 mg, 0.013 mmol), and copper(I) iodide (5.0 mg, 0.026 mmol). The flame was evacuated and back-filled with argon three times. Toluene (2 mL) and diisopropyl amine (1 mL), degassed by freeze-pump-thaw, was added via syringe. The reaction mixture was stirred at -78°C for 12 hours. The reaction mixture was poured into 100 mL hexanes / 100 mL aqueous hydrochloric acid (0.1 M). The organic layer was washed with saturated aqueous sodium bicarbonate solution followed by water, dried over MgSO4, and solvent removed under reduced pressure. Crude product was purified by column chromatography (silica gel, 100% hexanes to 5% dichloromethane) to give 5 as off-white solids (478 mg, 95%). M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 3.73 (s, 2H), 5.90 (s, 4H), 7.04 (dd, J = 5.4, 3.1 Hz, 4H), 7.37 (dd, J = 5.4, 3.1 Hz, 4H). 19F NMR (282 MHz, CDCl3): δ -126.70 (4F), -123.38 (4F), -122.47 (4F), -119.86 (4F), -108.89 (2F), -108.57 (2F), -81.34 (6F). HR-MS (EI): calcd for C49H38F52Si2 1673.0157 [M+Na]+; found 1673.0192.

**Monomer 1.** In a 50 mL round bottom flask under argon, 5 (320 mg, 0.160 mmol) was dissolved in 10 mL anhydrous tetrahydrofuran. The solution was cooled to -78°C, and tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 0.340 mL, 0.340 mmol) was added dropwise. The reaction mixture was stirred at -78°C for 30 minutes and warmed up to room temperature, and subsequently passed over a plug of silica gel.
gel, eluting with 25 % ethyl acetate in hexanes. The solvents were removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, 2% dichloromethane in hexanes) to give 2 as an off-white powder (276 mg, 93%). M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 3.26 (s, 2H), 5.95 (s, 4H), 7.06 (dd, J = 5.3, 3.0 Hz, 4H), 7.40 (dd, J = 5.3, 3.0 Hz, 4H). 7.59 (s, 8H). 19F NMR (282 MHz, CDCl3): δ -126.71 (4F), -123.42 (4F), -122.49 (4F), -119.84 (4F), -108.72 (2F), -108.33 (2F), -81.35 (6F). HR-MS (ESI): calcd for C30H22F52 1873.0783 [M+Na]+; found 1873.0822.


1,4-bis(perfluorohexyl)benzene (S5). A 100 ml Schlenk flask equipped with a stir bar was flame-dried and then charged with 1,4-diiodobenzene (3.30g, 10 mmol), Cu powder (5.08 g, 80 mmol), and 2,2’-bipy (156 mg, 1 mmol). The flask was evacuated and back-filled under vacuum (2 days). Polymer length = 16.3 nm. 1H NMR (500 MHz, FC-77, C6D6 external lock): δ 8.15-7.26 (br, 14H), 6.89 (br, 4H), 7.59 (s, 8H). 19F NMR (282 MHz, CDCl3): δ -126.71 (4F), -123.42 (4F), -122.49 (4F), -119.84 (4F), -108.72 (2F), -108.33 (2F), -81.35 (6F).

1,4-dibromo-2,5-bis(perfluorohexyl)benzene (S6). A 50 mL round-bottom flask was charged with S2 (2.00 g, 2.80 mmol), trifluoroacetic acid (20.0 mL), and concentrated H2SO4 (6.0 mL). The reaction mixture was heated to 60°C, and N-bromosuccinimide (1.50 g, 8.43 mmol) was added in portions (250 mg/hr) over 6 hours. The stirring was continued for 48 hours at 60°C, and the reaction mixture was poured into iced water. Yellow precipitate was collected by filtration and was recrystallized twice in ethanol to give S6 as off-white solids (5.61 g, 78%). 1H NMR (300 MHz, CDCl3): δ 7.84 (s, 4H). 19F NMR (282 MHz, CDCl3): δ -126.60 (4F), -123.16 (4F), -122.31 (4F), -119.70 (4F), -118.01 (4F), -111.71 (4F), -81.16 (6F).

1,4-diiodo-2,5-bis(perfluorohexyl)benzene (S7). A 100 mL round-bottom flask was charged with S3 (872 mg, 1.0 mmol), and evaporated and back-filled with argon three times. Anhydrous diethyl ether (8.0 mL) and anhydrous tetrahydrofuran (8.0 mL) were added via syringe. The flask was cooled to -78°C and tert-butyl lithium (1.5 M in pentanes, 3.0 mL, 4.5 mmol) was added dropwise over 15 minutes. The stirring was continued for 1.5 hours at -78°C and diiodoethane (900 mg, 3.2 mmol) was added in one portion. The reaction was stirred in the dark at -78°C for an additional hour and was removed from bath. The stirring continued for an additional 16 hours. Water (50 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (2 X 50 mL). Organic layer was washed twice with dilute NH4OH solution, twice with water, dried over MgSO4. The solvent was removed by evaporation under reduced pressure, and the resulting off-white solids were subjected to sublimation to give S7 as white solids (5.61 g, 93%). M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 8.14 (s, 2H). 19F NMR (282 MHz, CDCl3): δ -126.31 (4F), -122.88 (4F), -121.83 (4F), -118.83 (4F), -107.43 (4F), -90.83 (6F). HR-MS (EI): calcd for C18H2F26I2 965.7825; found 965.7859.

2. A flame-dried 100 mL Schlenk vessel with teflon screw-on cap under argon was charged with monomer 2 (74.35 mg, 0.0402 mmol), monomer 6 (37.67 mg, 0.0390 mmol), Pd(PPh3)4 (2.00 mg, 0.00069 mmol), and CuI (0.20 mg, 0.0011 mmol). In a glove box, perfluoromethylcyclohexane (6 mL), toluene (10 mL), and diisopropyl amine (2 mL) were added. The Shlenk vessel was removed from the glove box and was stirred vigorously at 85°C for 3 days. The reaction mixture, which was initially biphasic, became monophase at c.a. 65°C. After allowing to cool down to room temperature, 10 mL of FC-77 was added. The fluorous (lower) phase, which was fluorescent, was subsequently removed and was washed 3 times with methanol (5 mL each), 3 times with ethyl acetate (5 mL each), and 3 times with acetone (5 mL each). Removal of the fluorous solvents under reduced pressure yielded P1 as a yellow film, which was detached from the flask via sonication in ethanol (20 mL). Ethanol was then removed under reduced pressure to give P1 (89.7 mg, 87%) as a bright yellow film.
**Scheme S3.** Synthesis of P3.

Monomer S8. Flame-dried 10 mL Schenck flask was charged with S7 (180 mg, 0.376 mmol), 4-iodophenylethynyl trimethylsilane (237 mg, 0.790 mmol), Pd(PPh3)2Cl2 (13.2 mg, 0.019 mmol), and copper(I) iodide (7.2 mg, 0.038 mmol). The flask was evacuated and back-filled with argon three times. Toluene (2 mL) and diisopropyl amine (0.5 mL), degassed by freeze-pump-thaw, was added via syringe. The reaction mixture was stirred at 60°C for 16 hours. The reaction mixture was then precipitated into methanol (50 mL). The solids were further cleaned by re-precipitation in methanol three times, followed by re-precipitation in acetone three times. The resulting off-white solids were washed with 10 mL anhydrous tetrahydrofuran under argon. Tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 0.770 mL, 0.770 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 15 minutes, and subsequently passed over a plug of silica gel, eluting with 50% dichloromethane in hexanes. The solvents were removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, 30% dichloromethane in hexanes) to give P3 as an off-white powder (203 mg, 81% over two steps). M.p. > 300°C. 1H NMR (300 MHz, CDCl3): δ 3.27 (s, 2H), 5.86 (s, 4H), 6.96 (dd, J = 5.1, 3.3 Hz, 8H), 7.38 (dd, J = 5.1, 3.3 Hz, 8H), 7.65 (d, J = 5.1 Hz, 4H), 7.75 (d, J = 5.1 Hz, 4H).

P3. A flame-dried 100 mL Schlenk vessel with teflon screw-on cap under argon was charged with monomer S8 (69.92 mg, 0.103 mmol), 1,4-diiodo-2,5-dioctylbenzene (55.43 mg, 0.100 mmol), Pd(PPh3)4 (5.8 mg, 0.050 mmol), and CuI (1.3 mg, 0.070 mmol). In a glove box, toluene (16 mL), and diisopropyl amine (4 mL) were added. The Schlenk vessel was removed from the glove box and was stirred at 75°C for 3 days. The reaction was then precipitated into 100 mL methanol. Yellow precipitates were collected via centrifugation, and the process was repeated three times with methanol, followed by three times with acetone to give P3 (66.7 mg, 68%) as bright yellow solids under vacuum. Mn = 73.7 kDa; PDI = 10.5; DP = 75 (THF-GPC). 1H NMR (500 MHz, THF-d8): δ 7.92 (br, 4H), 7.78 (br, 4H), 7.52 (br, 2H), 7.41 (br, 8H), 6.95 (br, 8H), 6.00 (br, 4H), 1.30-1.60 (br, 24H), 1.44 (br, 4H), 0.98 (br, 10H).

**Photophysical Properties of P1, P2, and P3**

Figure S1. Absorption (black) and emission (red) spectra of P3 in toluene.
**Figure S2.** Thin film absorption (dotted) and emission (solid) spectra of P1 (orange), P2 (black), and P3 (blue).

![Figure S2](image)

**Emulsion Synthesis**

**Table S1.** Emulsion synthesis conditions and the resulting emulsion properties.

<table>
<thead>
<tr>
<th>[P1] in PFD (mg/ml)</th>
<th>Volume of PFD solution (mL)</th>
<th>Volume of 1X PBS buffer</th>
<th>Surfactant</th>
<th>Surfactant Concentration</th>
<th>Emulsion size</th>
<th>Emulsion Z-potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.01</td>
<td>5.0 mL</td>
<td>S1</td>
<td>0.01 M</td>
<td>245.8 ± 43.9 nm</td>
<td>-57 ± 13 mV</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>5.0 mL</td>
<td>S1</td>
<td>0.02 M</td>
<td>242.1 ± 23.6 nm</td>
<td>-79 ± 11 mV</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>5.0 mL</td>
<td>S2</td>
<td>0.0025 M</td>
<td>3~4 μm</td>
<td>-42 ± 6 mV</td>
</tr>
</tbody>
</table>

S1: 2H,2H,3H,3H-perfluorononanoic acid, S2: 8:2 monoPAPS.

In a 50 mL round-bottom flask, surfactant (Table S1, columns 4 and 5) in 5.0 mL PBS buffer was heated to 75°C while stirring. After complete dissolution of the surfactant, P1 (10 μL, 2 mg/ml in perfluorodecalin) was added. The flask was then removed from heat and was sonicated with a probe sonicator at 3 Watts (rms) for 5 minutes. The solution was subsequently allowed to cool to room temperature. Excess surfactant was removed via filtration. The size distribution and Z-potentials of the emulsions are shown in Table S1 (columns 6 and 7).

**NMR Spectra**
Compound S3 1H NMR (cis + trans isomers)
Compound S3 19F NMR (cis + trans isomers)
Compound S4 1H NMR
Compound S4 19F NMR
Compound 4 1H NMR
Compound 4 ^19F NMR
Compound 5 1H NMR
Compound 5 19F NMR
Monomer 1 1H NMR
Monomer 1 19F NMR
Compound S8 1H NMR
FC-77 (solvent only) with C₆D₆ External Lock
P1 in FC-77 (C<sub>2</sub>D<sub>6</sub> External Lock) 1H NMR
P2 1H NMR (CDCl₃)
References for the Supporting Information


