

Electronic Supplementary Information (ESI) for

## **Unexpected Photostability Improvement of Aromatics in Polyfluorinated Solvents**

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## 1. General experimental procedure:

All chemicals and solvents were purchased from Acros Organics, Aldrich, TCI America, Matrix Scientific, Synquest and used without further purification unless otherwise specified in the text. Solvents such as DMSO,  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT) were dried over flame-dried 4Å molecular sieves. TLCs were run on aluminium-backed silica gel G<sub>254</sub> TLC plates with 200  $\mu$ m thickness from Sorbent Technologies, Inc. All NMR spectral studies were carried out using CDCl<sub>3</sub> unless otherwise specified. <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded on either Varian 200 MHz or JEOL 400 MHz NMR spectrometers. Mass spectra (FAB positive ion) were obtained from University of Nebraska–Lincoln mass spectra center; mass spectra (EI model) were obtained from University of Minnesota mass spectra center, mass spectra ESI UV-visible spectral studies were performed with Cary 5000 UV-Vis-NIR Spectrophotometer (Varian Inc.). Fluorescence spectral studies were conducted with Fluoromax–4 Spectrofluorometer (Horiba Jobin Yvon). All absorption and emission spectra measurements were done using spectrophotometric grade cyclohexane. Fluorescence quantum yields were determined in spectrophotometric grade cyclohexane using 9,10-diphenylanthracene as a reference standard. The concentration of fluorescent samples is below 10<sup>-6</sup> M (maximum absorption is below 0.05 for all compounds measured). There is no excimer formation observed. Photochemical stability studies were performed in chloroform (Aldrich) and HFE-7200 (3M) solvents.

### General synthetic procedure

A mixture of bromoanthracene (1 equivalent) and copper powder (5 equivalents) in a mixture of dry DMSO and dry trifluorotoluene was heated to 135 °C under nitrogen. At 135 °C, perfluorooctyl iodide (2.5 equivalents) was added dropwise and reaction was carried out for 4 to 20 hrs under nitrogen. Then the reaction flask was cooled to room temperature and quenched with cold water. The product was extracted with mixture of trifluorotoluene and dichloromethane; organic phases were combined, washed with DI water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained and further purified by recrystallization from dichloromethane or continue extraction with HFE-7200.

#### 1a. Synthesis of 9,10-bis-perfluorooctyl-anthracene (compound 7)

A mixture of 9,10-dibromoanthracene (0.34 g, 1 mmol), Cu powder (0.64 g, 10 mmol) were added into a 100 ml two-neck round-bottom flask and purged with nitrogen for 10 minutes. Under nitrogen flow, anhydrous  $\alpha,\alpha,\alpha$ -trifluorotoluene (14 ml), DMSO (6 ml) was added to above mixture and heated at 135 °C with stirring for 15 minutes. Perfluorooctyl iodide (1.33 ml, 5 mmol) was added in 0.05 ml portions every 5 minutes. Reaction was carried out in nitrogen atmosphere at 135 °C with stirring for 4 hours. After 4 hours, the reaction flask was cooled to room temperature, and the reaction mixture was quenched with cold DI water (100 ml) and extracted with  $\alpha,\alpha,\alpha$ -trifluorotoluene (20 ml), dichloromethane (140 ml) to give sticky crude product after removal of the solvents. Recrystallization with dichloromethane gave pure **1** as a white-yellow powder in a yield of 0.44 g (43%) with mp 128-132 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  8.43 (d, 4H), 7.62 (dd, J=7.6, 3.3Hz, 4H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -80.56 (t, 21.36 Hz, 6F), -90.89 (m, 4F), -116.78 (m, 4F), -121.14 (m, 4F), -121.32 (m, 4F), -121.64 (m, 4F), -122.48 (m, 4F), -125.91 (m, 4F); MS (LR-FAB,); m/z (M<sup>+</sup>) 1014.0 (calcd for C<sub>30</sub>H<sub>8</sub>F<sub>34</sub>: 1014.3); Elemental analysis; Calcd (%) for (C<sub>30</sub>H<sub>8</sub>F<sub>34</sub>): C 35.52, H 0.78; found C 35.17, H 0.74

#### 1b. Synthesis of 2,6,9,10-tetrakis-perfluorooctyl-anthracene (compound 8)

A mixture of 2,6,9,10-tetrabromoanthracene (4.95 g, 0.01 mol), Cu powder (13 g, 0.2 mol) were added into a 250 ml two-neck round-bottom flask and purged with nitrogen for 15 minutes. Anhydrous DMSO (12 ml) and HFE-7200 (36 ml) were added and heated at 115 °C with stirring for 15 minutes. Perfluorooctyl iodide (26 ml, 0.1 mol) was added in 3 ml portions every 10 minutes. Reaction was carried out in nitrogen atmosphere at 115 °C with stirring for 20 hours. After 20 hours the reaction flask was cooled to room temperature and the reaction mixture was quenched with cold DI water (500 ml) and extracted with HFE-7200 (80 ml), after removal of HFE-7200 solvent, 12 g (64%) product were obtained. Analytical pure product was obtained by recrystallization from HFE-7200. Characterization: mp 94-96°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 9.0 (s, 2H), 8.75 (d, 2H), 7.85 (d, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -80.57 (t, 23.34 Hz, 12F), -90.91 (m, 8F), -111.62 (m, 8F), -116.81 (m, 8F), -121.46 (m, 8F), -121.84 (m, 8F), -122.86 (m, 8F), -126.08 (m, 8F); MS (LR-FAB); m/z (M<sup>+</sup>) 1850.0 (calcd for C<sub>46</sub>H<sub>6</sub>F<sub>68</sub>: 1850.4); Elemental analysis; Calcd (%) for C<sub>46</sub>H<sub>6</sub>F<sub>68</sub> C 29.85, H 0.32; found C 29.67, H 0.19.

### 1c. Synthesis of 1,3,6,8-tetrakis-perfluorooctyl-pyrene (compound 10)

1,3,6,8-tetrabromopyrene (0.15 g, 0.28 mmol), copper powder (0.53g, 8.26 mmol) were added into a 100 ml two-neck round-bottom flask and purged with nitrogen for 15 minutes. Anhydrous α,α,α-trifluorotoluene (7 ml) and anhydrous DMSO (3 ml) was added to above mixture and heated at 135 °C with stirring for 15 minutes. Perfluorooctyl iodide (1.1 ml, 4.13 mmol) was added in 0.1 ml portions every 5 minutes. Reaction was carried out in nitrogen atmosphere at 135 °C with stirring for 20 hours. After 20 hours, the reaction flask was cooled to room temperature and the reaction mixture was quenched with cold DI water (75 ml). Mixture was then suction filtered and then the solid materials were repeated treated with 15% HCl aqueous solution to remove copper containing compounds. Ashy colored crude product was obtained after filtration. Continuous extraction using HFE-7200 for one day to give white crystalline material (0.069 g, 15%) with a mp 166-168°C; <sup>1</sup>H NMR (CDCl<sub>3</sub> and HFE-7100): δ 8.95 (s, 4H), 8.80 (s, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub> and α,α,α-trifluorotoluene): δ -81.21 (t), -121.98.61 (m), -122.71 (m), -123.35 (m), -126.25(m), 129.58 (m), 137.28 (m); MS (LR-EI positive mode): m/z (M<sup>+</sup>) 1875.4 (instrument calibration drifted up by 1.5 mass units), calcd for C<sub>48</sub>H<sub>6</sub>F<sub>68</sub>: 1874.4.

### 1d. Synthesis of 3,5,8-tris-perfluorooctyl-1,10-phenanthroline (compound 12)

A mixture of 0.504 g (1.02 mmol) of 3,5,6,8-tetrakis-bromo-1,10-phenanthroline, 1.291 g (20.3 mmol) of Cu powder was added into a 50 ml three-neck round bottom flask equipped with a magnetic stir bar and a reflux condenser. The system was purged with N<sub>2</sub> for 15 min. 17 ml dry TFT and 6 ml dry DMSO were added and the reaction mixture was heated to reflux. Under nitrogen protection, 2.7 ml (5.58 g, 10.22 mmol) of perfluorooctyl iodide (C<sub>8</sub>F<sub>17</sub>I) was added drop wise over a period of 20 min. The reaction was stopped after 48 h and cooled down to room temperature. The reaction mixture was then mixed with 400 ml TFT, sonicated, and washed with 5x120 ml concentrate NH<sub>4</sub>OH solution, until no blue color aqueous solution layer is seen, followed by 4x150 ml D.I. H<sub>2</sub>O wash. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed by distillation. The crude product was recrystallised from hot CHCl<sub>3</sub> to give 0.638 g of light brown material. Yield: 44%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 9.56 (br, 2H), 8.93(s, 1H), 8.70(s, 1H), 8.46(s, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) -80.74 (m, 9F), -104.70(t, J=14 Hz, 2F), -110.64(m, 4F), -119.41(br, 2F), -120.74(m, 8F), -121.50(m, 14F), -122.39(br, 6F), -125.80(m, 6F). Elemental Analysis: Calcd C<sub>36</sub>H<sub>5</sub>F<sub>51</sub>N<sub>2</sub>: C, 30.14%; H, 0.35%; N, 1.95%; Found: C, 30.19 %; H, 0.24 %; N, 1.88 %. LR-MS (ESI, positive ion detection) calcd for C<sub>36</sub>H<sub>6</sub>F<sub>51</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 1434.9, found: 1435.1.

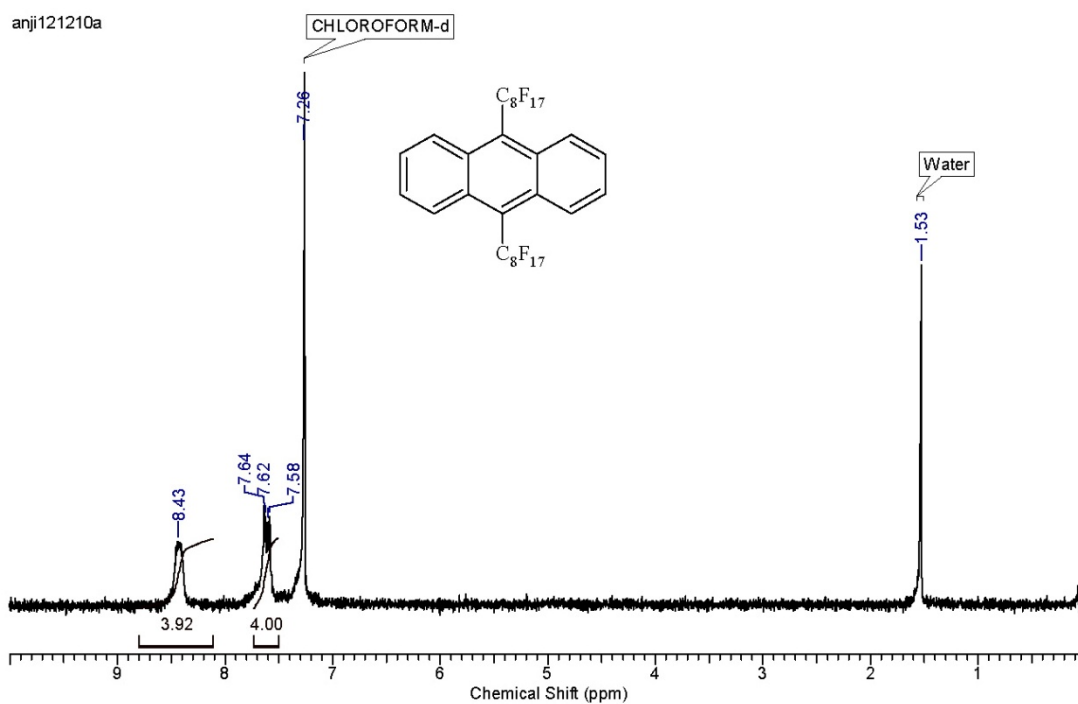


Figure S-1.  $^1\text{H}$  NMR spectrum of 9,10-bis(perfluorooctyl)anthracene.

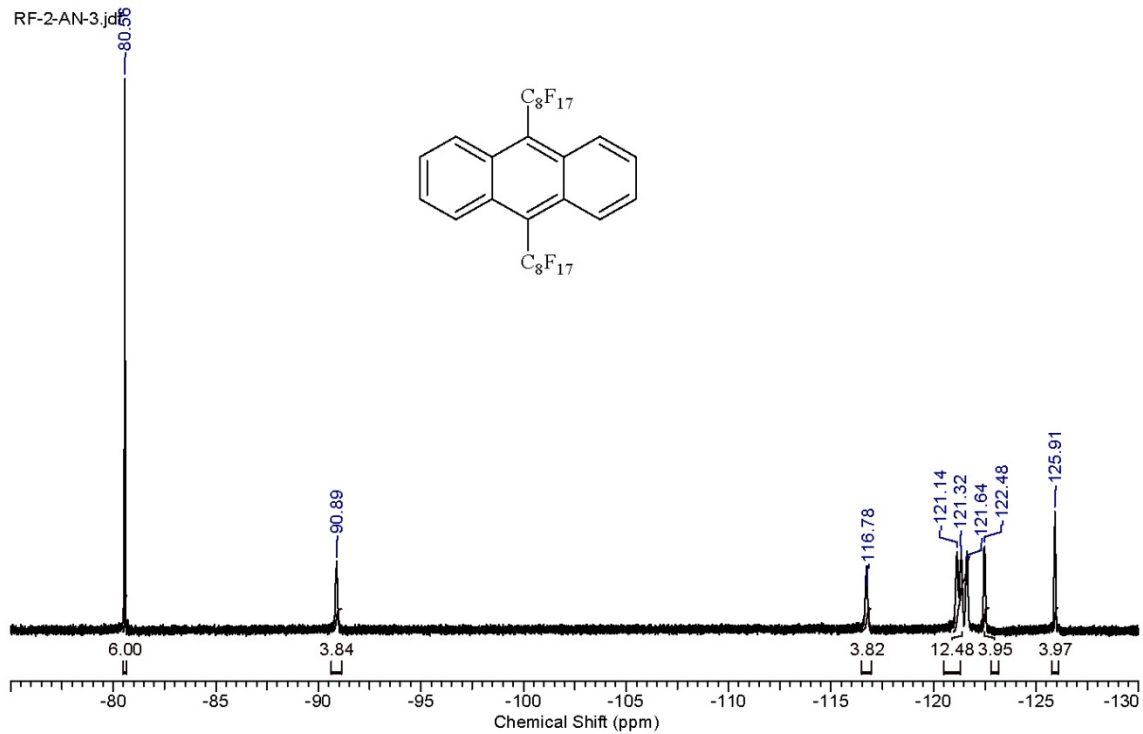


Figure S-2.  $^{19}\text{F}$  NMR spectrum of 9,10-bis(perfluorooctyl)anthracene.

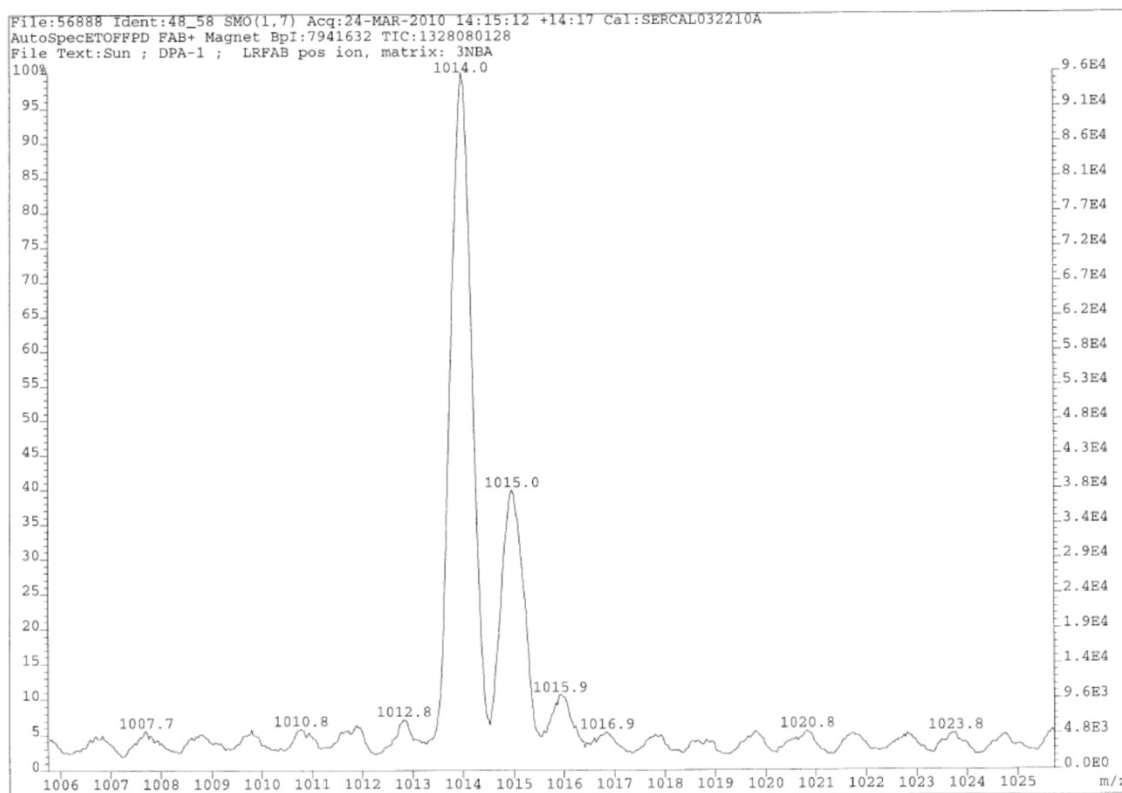


Figure S-3. Mass spectrum of 9,10-bis(perfluorooctyl)anthracene.

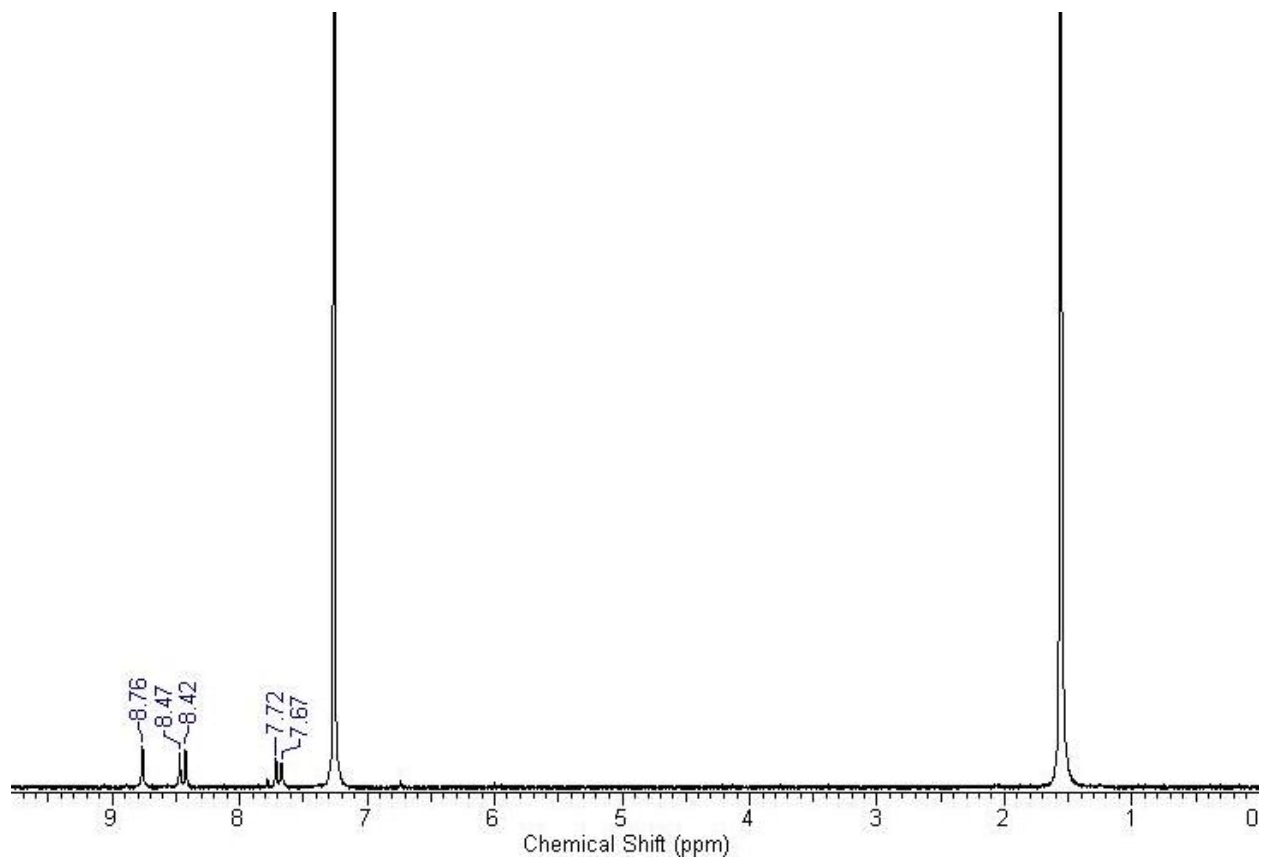
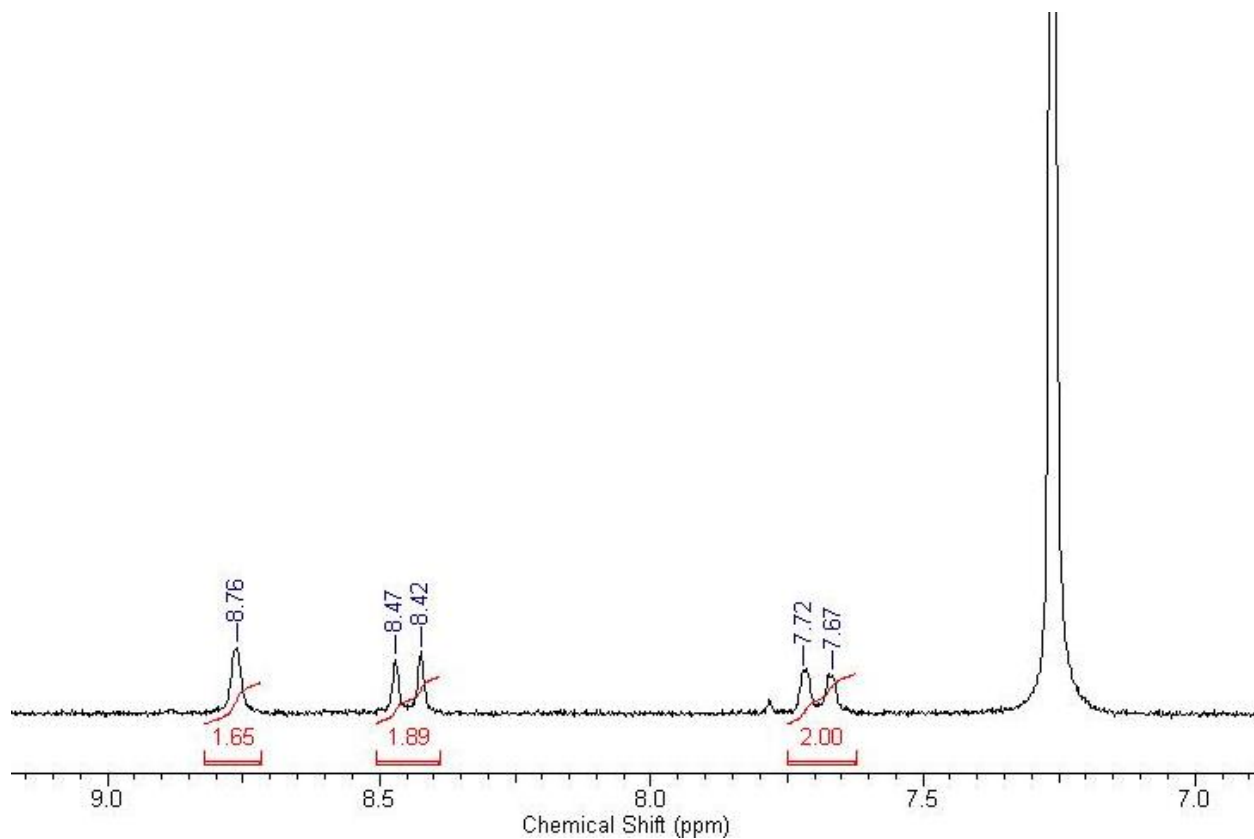


Figure S-4.  $^1\text{H}$  NMR spectrum of 2,6,9,10-tetrafluorooctylanthracene.



Zoom in region of Figure S-4.  $^1\text{H}$  NMR spectrum of 2,6,9,10-tetrafluorooctylanthracene. The small peak at 7.58 ppm is the  $^{13}\text{C}$  satellite peak of  $\text{CHCl}_3$ .

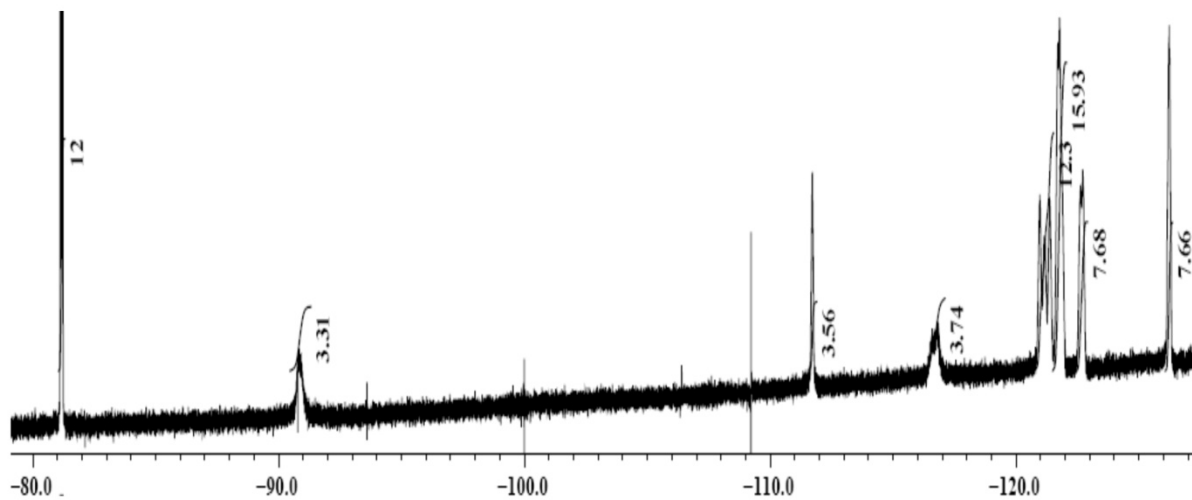


Figure S-5.  $^{19}\text{F}$  NMR spectrum of 2,6,9,10-tetrafluorooctylanthracene in  $\text{CDCl}_3 + \alpha, \alpha, \alpha$ -trifluorotoluene (TFT) (20:80).



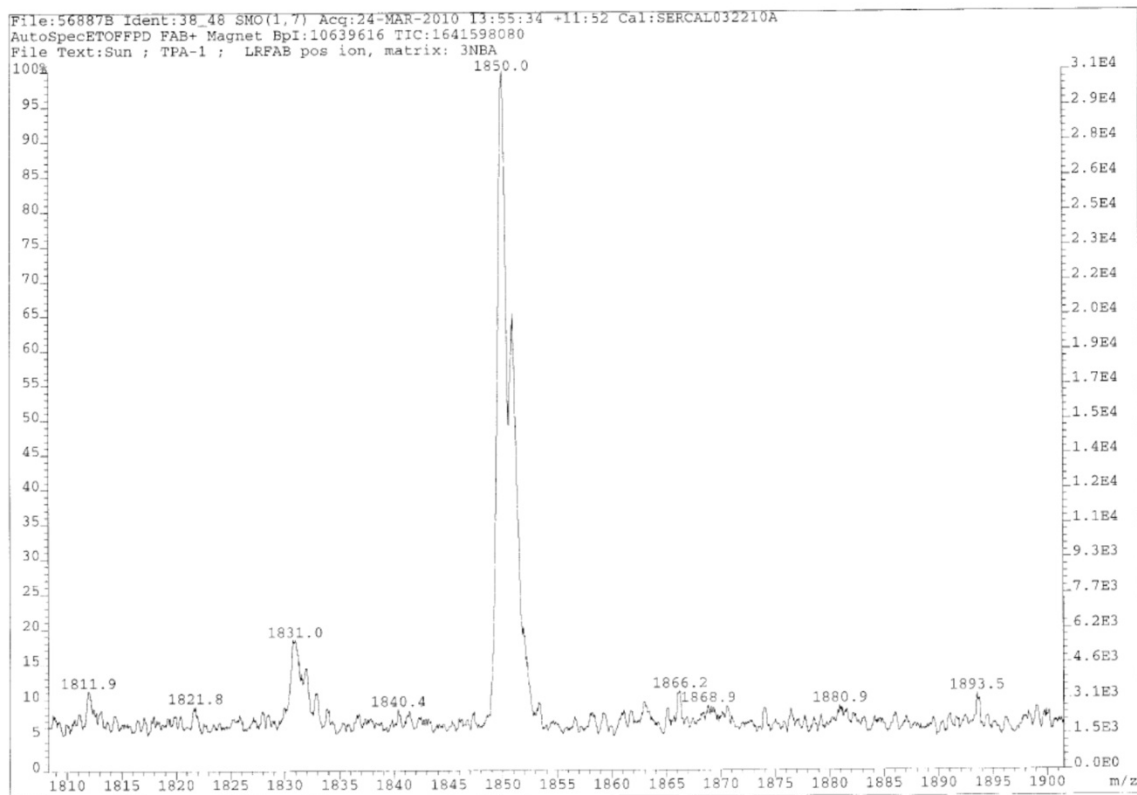


Figure S-6. Mass spectrum of 2,6,9,10-tetrafluorooctylanthracene.

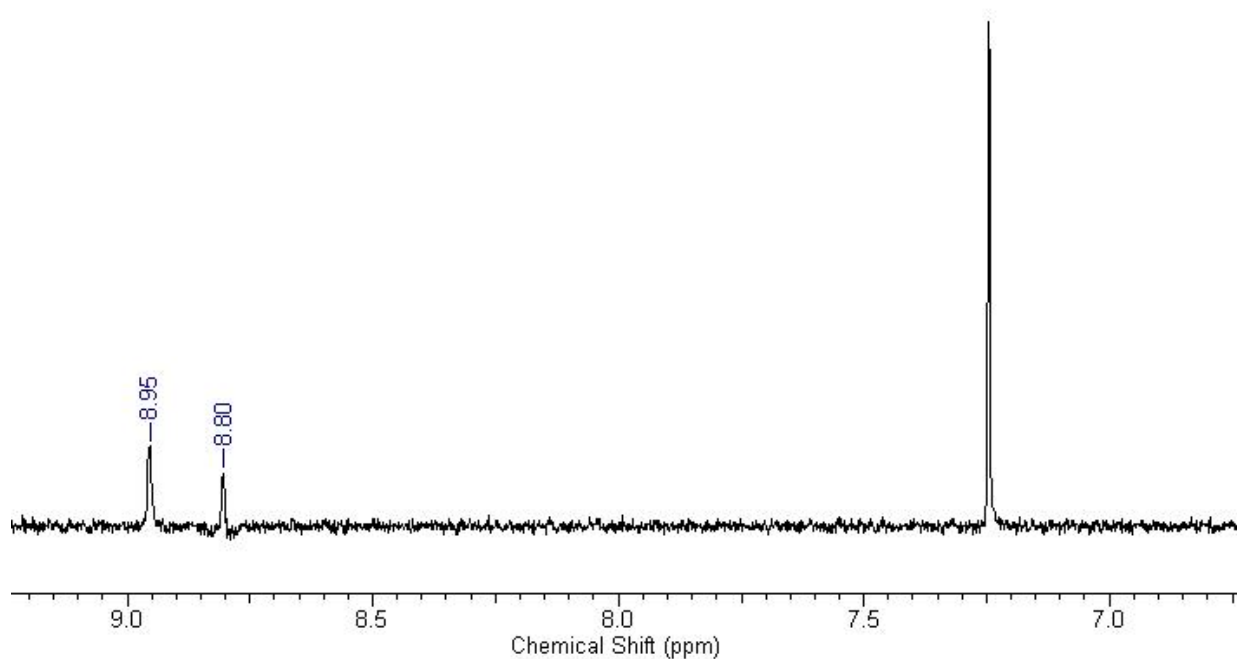


Figure S-7.  $^1\text{H}$  NMR spectrum of 1,3,6,8-tetrafluorooctylpyrene in  $\text{CDCl}_3$ +HFE-7100(20:80).

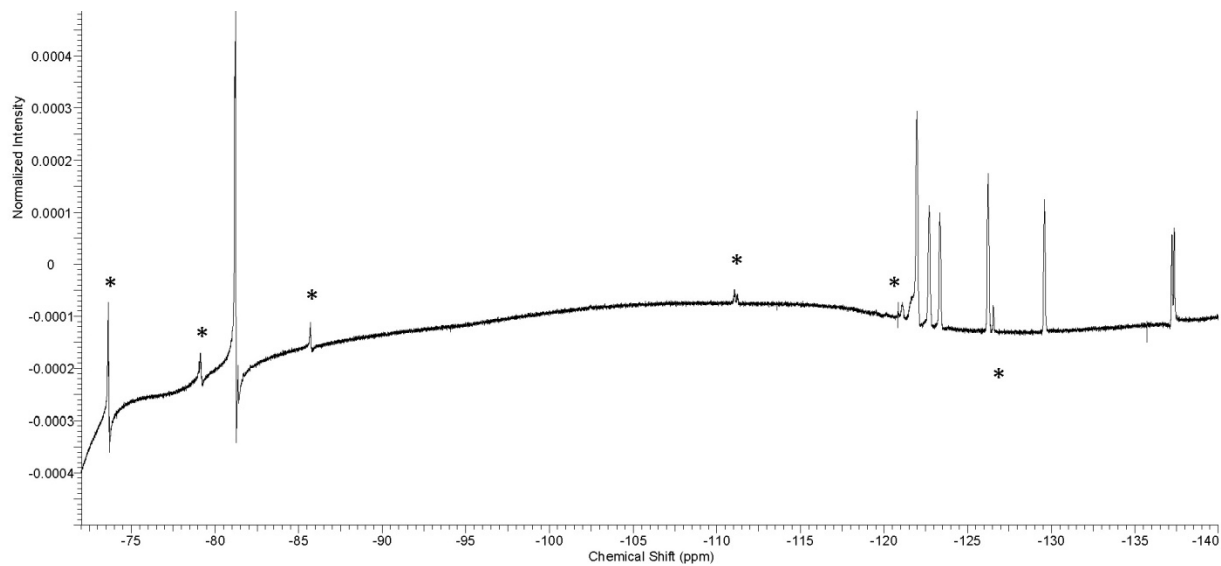
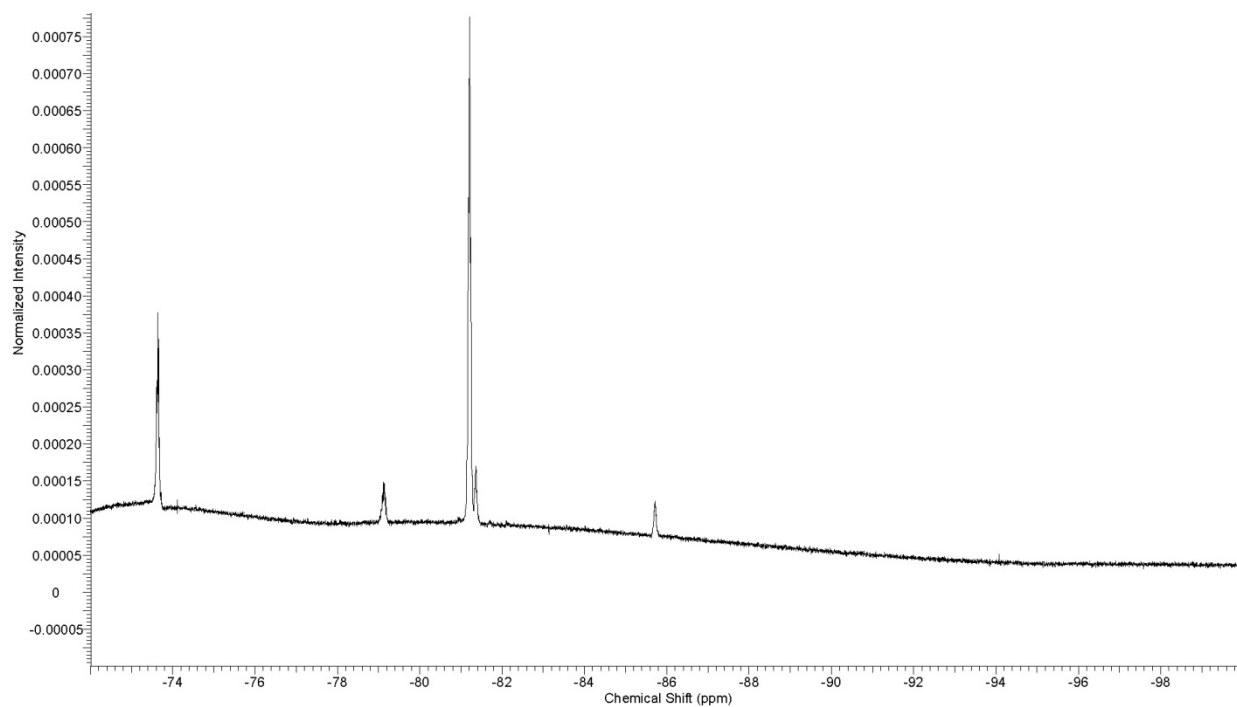
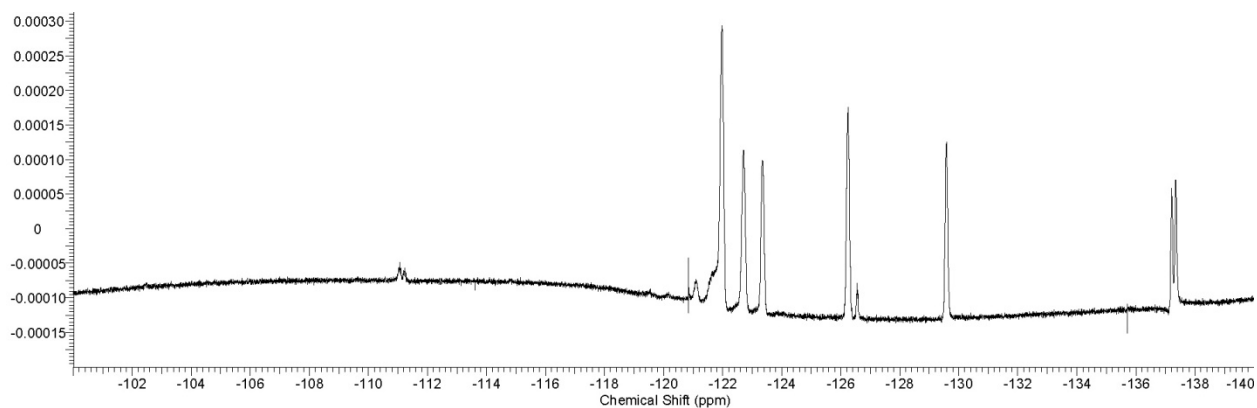


Figure S-8:  $^{19}\text{F}$  NMR spectrum of 1,3,6,8-tetrafluorooctylpyrene in  $\text{CDCl}_3$ +TFT(20:80). Peaks labeled with \* are from HFE solvents.



Locally phased zoom in region of Figure S-8.  $^{19}\text{F}$  NMR spectrum of 1,3,6,8-tetrafluorooctylpyrene in  $\text{CDCl}_3+\text{TFT}(20:80)$ :



Locally phased zoom in region of Figure S-8.  $^{19}\text{F}$  NMR spectrum of 1,3,6,8-tetrafluorooctylpyrene in  $\text{CDCl}_3+\text{TFT}(20:80)$ :

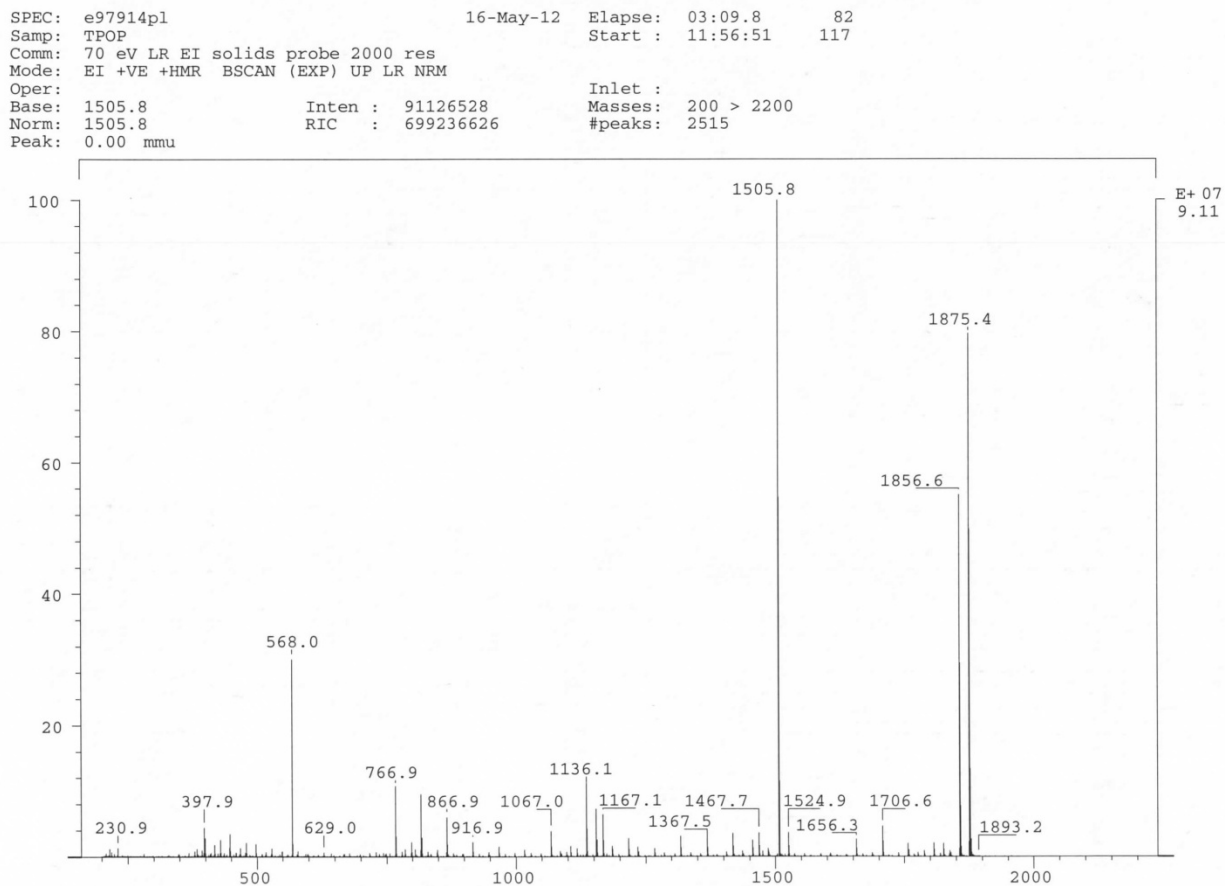


Figure S-9. Mass spectrum of 1,3,6,8-tetra-perfluorooctylpyrene.

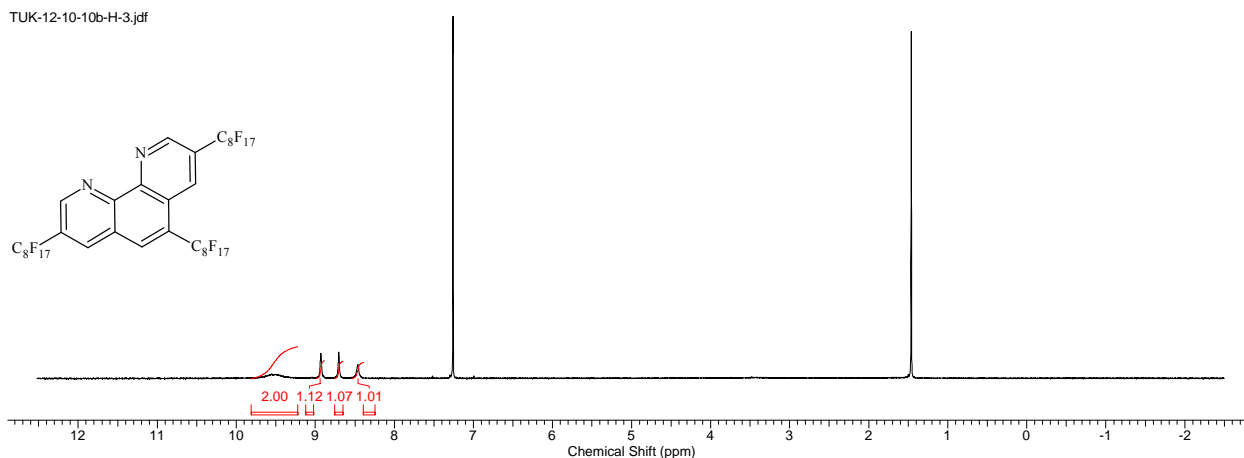


Figure S-10. <sup>1</sup>H NMR (400 MHz) spectrum of 3,5,8-tris-perfluorooctyl-1,10-phenanthroline taken in CDCl<sub>3</sub> at 58 °C.

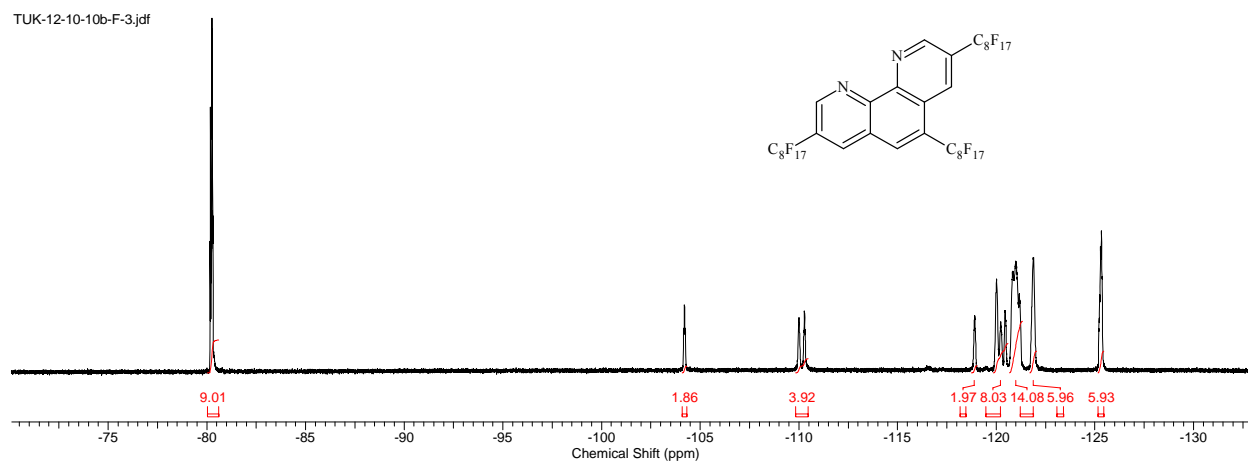


Figure S-11.  $^{19}\text{F}$  NMR (376 MHz) spectrum of 3,5,8-tris-perfluorooctyl-1,10-phenanthroline taken in  $\text{CDCl}_3$  at  $58^\circ\text{C}$ .

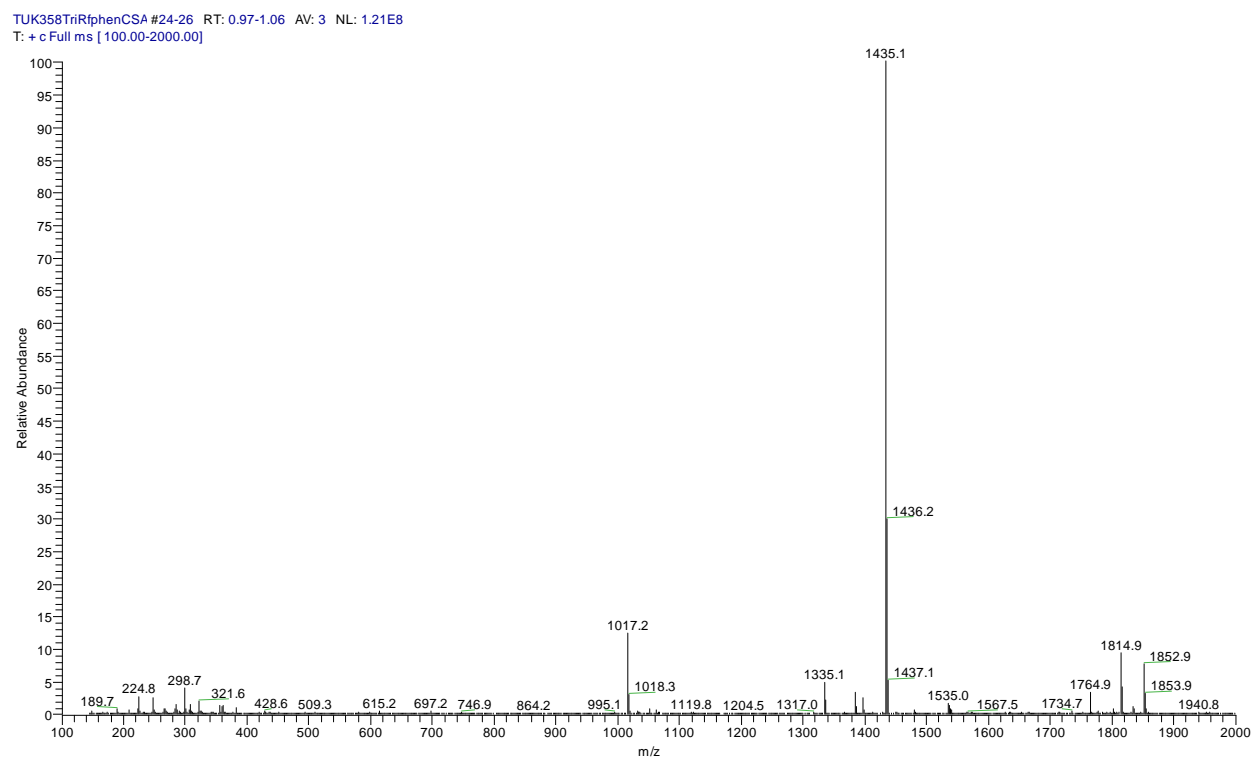


Figure S-12. ESI-MS spectrum of 3,5,8-tris-perfluorooctyl-1,10-phenanthroline in a mixture of acetonitrile and dichloromethane. 2 drops of chlorosulfonic acid was added to protonate the compound.

## 2. Photophysical and photostability testing results

### 2a. Absorption and emission spectra

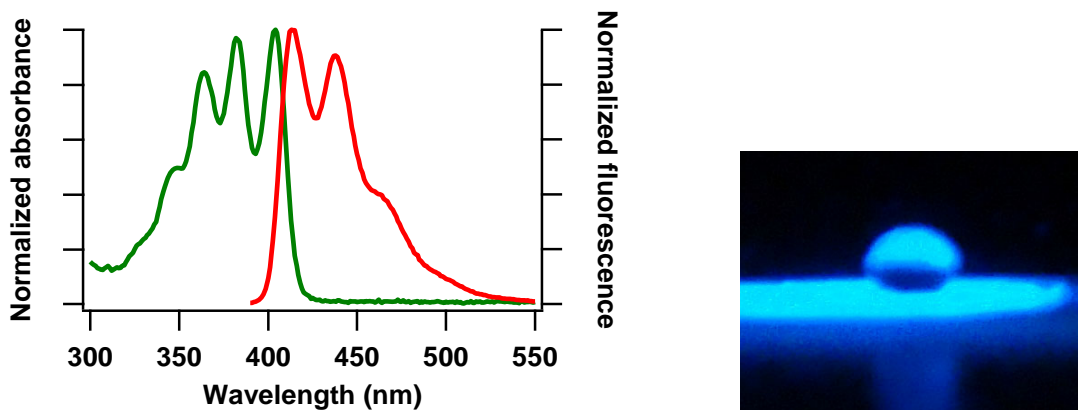


Figure S-13. Normalized absorption and emission spectra of compound (8) in cyclohexane (left) and picture of its solid sample under long UV light (right), a water droplet is sitting on top of the solid sample.

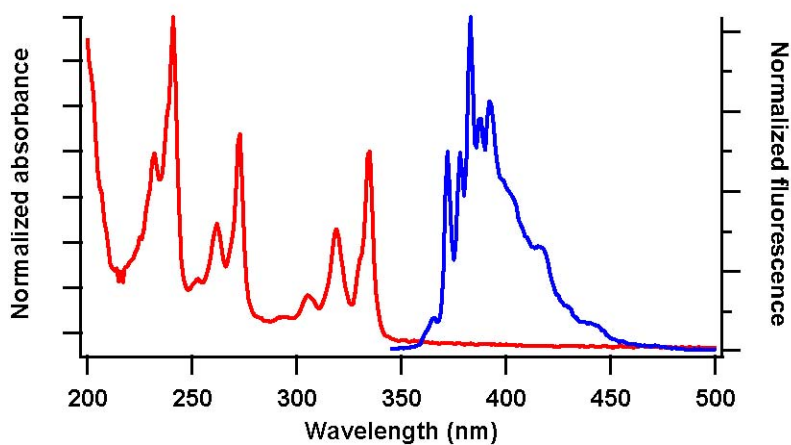


Figure S-14. Absorption (red) and emission (blue) spectra of pyrene in cyclohexane.

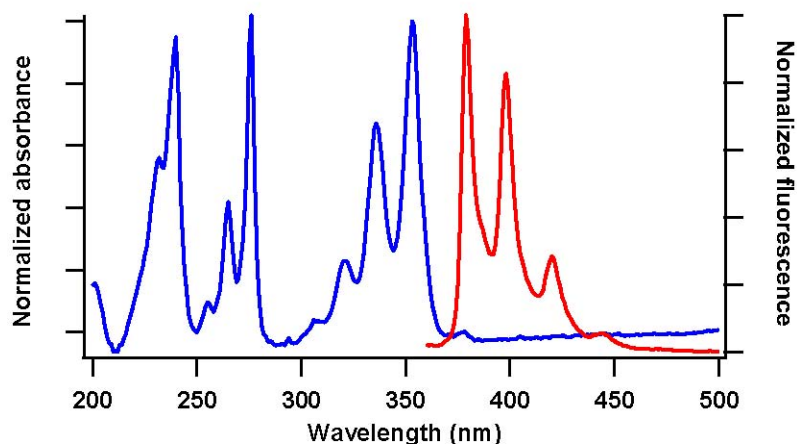


Figure S-15. Absorption (blue) and emission (red) spectra of 1,3,6,8-tetra-perfluorooctylpyrene in cyclohexane+HFE-7200(80:20).

**Table S-1.** Photophysical properties of anthracenes and pyrenes

Compounds	Abs. Q(0,0)	Em Q(0,0)	$\Delta\lambda/\text{nm}$	$\Phi$
1	404	415	11	0.68 <sup>c</sup>
2	398	402	4	0.58 <sup>c</sup>
3	376	377	1	0.27 <sup>a</sup>
4	394	406	12	0.90 <sup>b</sup>
5	403	405	2	0.1 <sup>c</sup>
6	402	403	1	0.48 <sup>c</sup>
7	409	413	4	0.97 <sup>e</sup>
8	403	414	11	0.83 <sup>e</sup>
9	335	372	37	0.32 <sup>d</sup>
10	353	379	26	0.41 <sup>c</sup>

a. Ref<sup>2</sup>; b. Ref<sup>3</sup>; c. Ref<sup>1</sup>; d. Ref<sup>4</sup>; e. This work.

### Procedure for photostability test

Photostability studies were performed using Newport solar simulator consisting a model 69911 power supply, a model 67005 lamp house, a 300 watt xenon lamp, a focus lens, and a 1.5 AM filter as the light source. The light intensity was 3.58 sun determined with a Newport 91150V Reference Solar Cell and Meter. The distance between samples and light focus lens was 30 cm. Studies were conducted in air-saturated solution at room temperature by using solvents chloroform and HFE-7200. The photostability of

the respective samples were determined using UV-Vis spectra by Cary 5000 UV-Vis-NIR spectrophotometer.

All 9,10-disubstituted anthracene derivatives and pyrene were dissolved in chloroform with a concentration of  $10^{-5}$  M and used for photostability test. For compounds **8** and **10**, due to their less solubility in chloroform, photostability studies were carried out at a concentration of  $10^{-6}$  M in chloroform. For better comparing solvents effect, further photostability study of compounds **7**, **8** were carried out in polyfluorinated solvent, HFE-7200, with a concentration of  $10^{-6}$  M. Though compound **10** was carried out in HFE-7200 with a concentration of  $10^{-5}$  M, we still observed increased photostability of compound **10** in HFE-7200 compared to that in chloroform. Compounds **11** and **12** were determined at  $10^{-5}$  M in  $\text{CHCl}_3$  and HFE-7200.

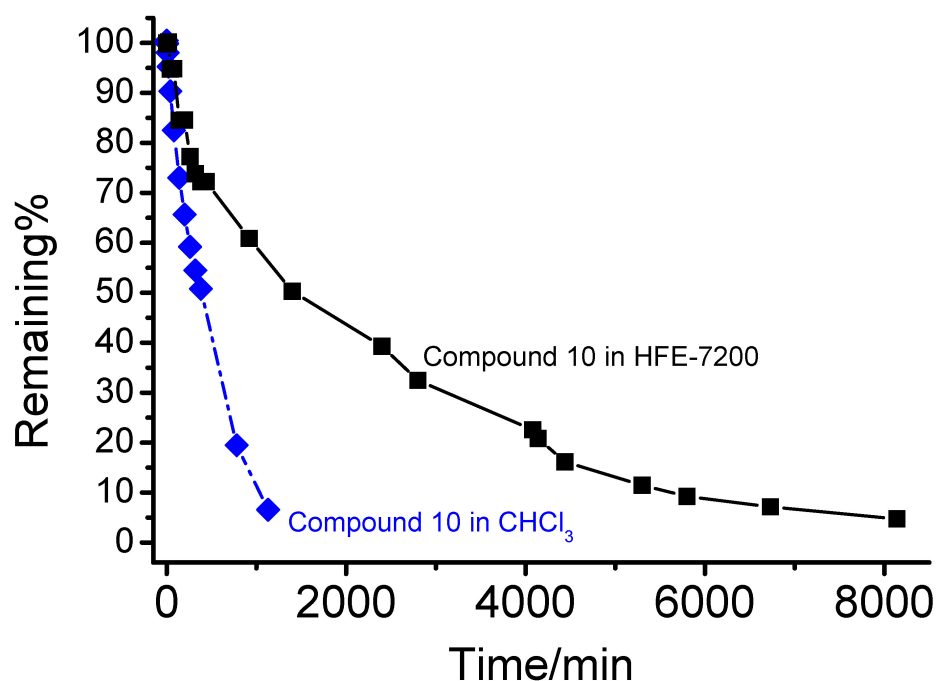


Figure S-16. Plot of % remaining vs time of sample exposure in minutes for compound 10 in  $\text{CHCl}_3$  and in HFE-7200. 1.5 AM solar light with light intensity of 3.58 sun. (Under the same condition, pyrene decomposes in less than 10 min.)



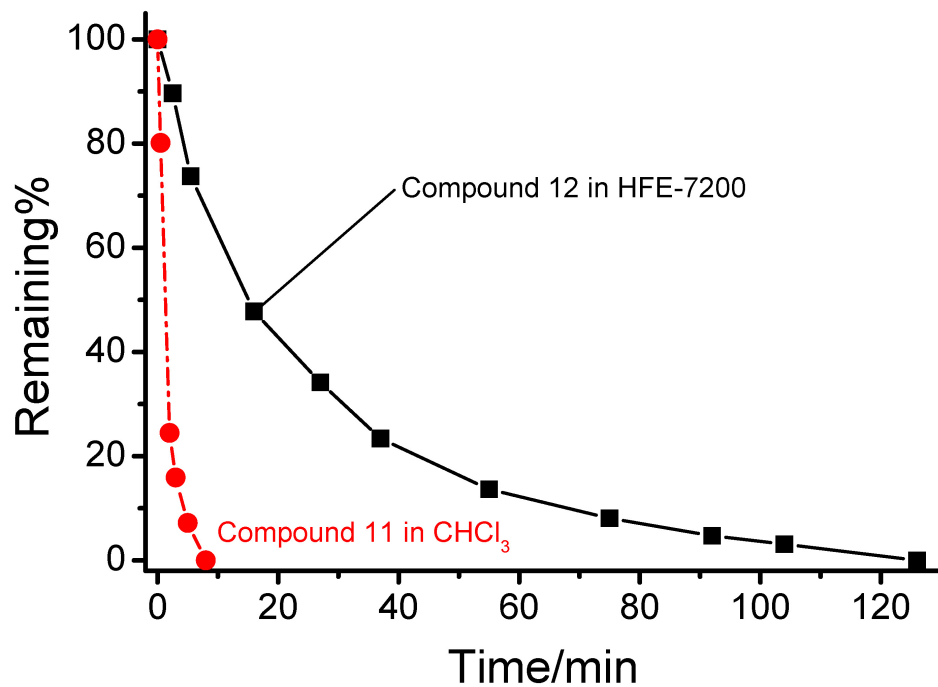


Figure S-17: Plot of remaining% vs. time of sample light exposure for phenanthroline in CHCl<sub>3</sub> (red line) and 3,5,8-tris(perfluorooctyl)-1,10-phenanthroline in HFE-7200 (black line). 1.5 AM solar light with light intensity of 3.58 sun.

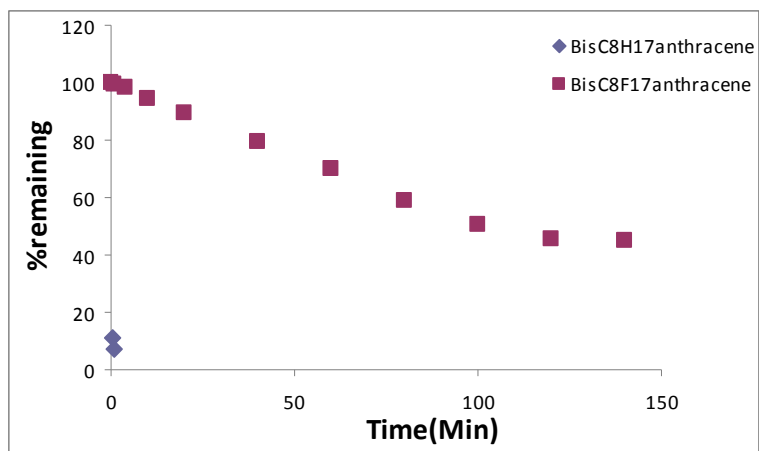


Figure S-18. Plot of % remaining vs time of sample exposure in minutes for compound 13 (BisC8H17anthracene) and compound 7 (BisC8F17anthracene) in  $\text{CHCl}_3$ . 1.5 AM solar light with light intensity of 3.58 sun. (Under the same condition, compound 13 decomposes in less than a minute.)

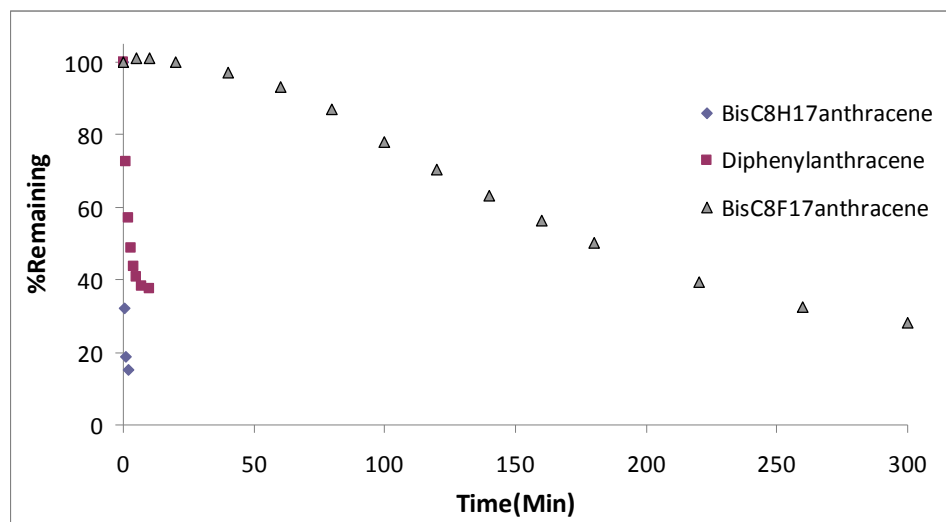


Figure S-19. Plot of % remaining vs time of sample exposure in minutes for compound 4, 7, and 13 in deaerated  $\text{CHCl}_3$  solution. 1.5 AM solar light with light intensity of 3.58 sun.

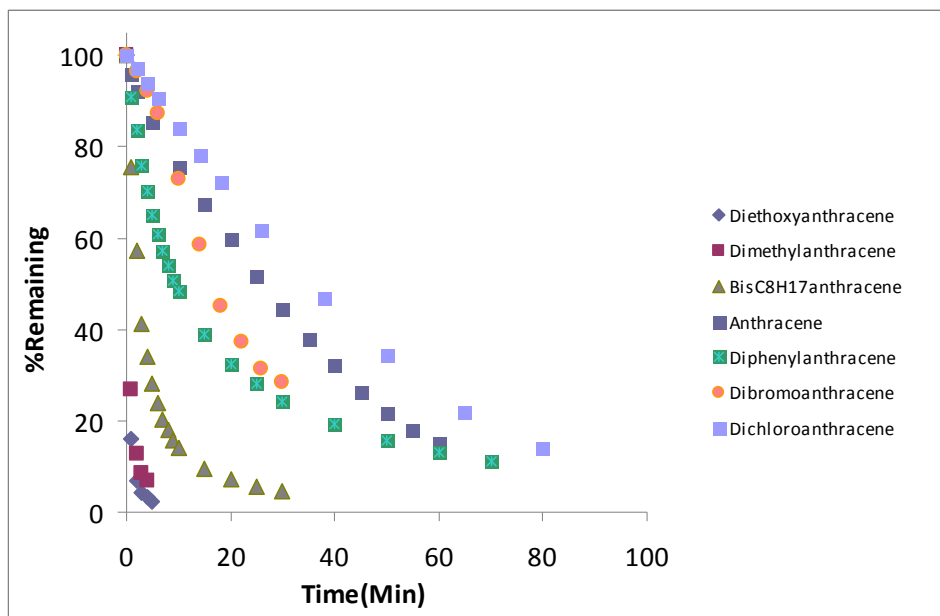


Figure S-20. Plot of % remaining vs time of sample exposure in minutes for compound 1-6 and 13 in HFE-7200 1.5 AM solar light with light intensity of 3.58 sun.

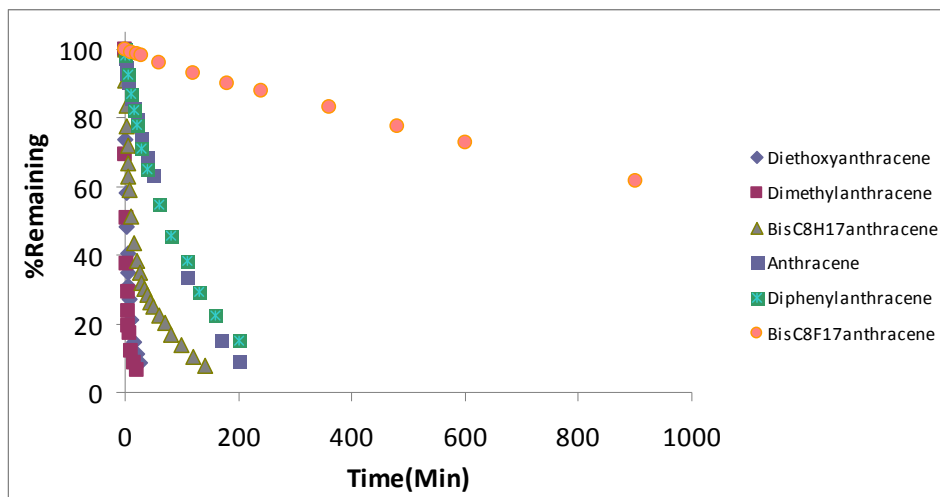


Figure S-21. Plot of % remaining vs time of sample exposure in minutes for compound 1-4, 7, and 13 in cyclohexane. Note: compound 7 has very low solubility; it was tested with its saturated solution. Compounds 8, 10, and 12 are not soluble in cyclohexane. 1.5 AM solar light with light intensity of 3.58 sun.

### 3. References

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