Improved solid-state photomechanical materials by fluorine substitution of 9-anthracene carboxylic acid

Lingyan Zhu(1), Fei Tong(1), Christopher Salinas(2), Muhanna K. Al-Muhanna(3) ,Fook S. Tham(1), David Kisailus(2,4), Rabih O. Al-Kaysi(5)*, and Christopher J. Bardeen(1)*

(1)Department of Chemistry
University of California, Riverside
501 Big Springs Road
Riverside, CA 92521

(2)Department of Chemical and Environmental Engineering
University of California, Riverside
900 University Avenue
Riverside, CA 92521

(3) King Abdulaziz City for Science and Technology
P.O Box 6086, Riyadh 11442
Kingdom of Saudi Arabia

(4)Materials Science and Engineering Program
University of California, Riverside
900 University Avenue
Riverside, CA 92521

(5) Department of Basic Sciences
College of Science and Health Professions-3124
King Saud bin Abdulaziz University for Health Sciences/
King Abdullah International Medical Research Center
Ministry of National Guard Health Affairs
Riyadh 11426 (Kingdom of Saudi Arabia)

*christopher.bardeen@ucr.edu
*kaysir@ksau-hs.edu.sa and rabihalkaysi@gmail.com

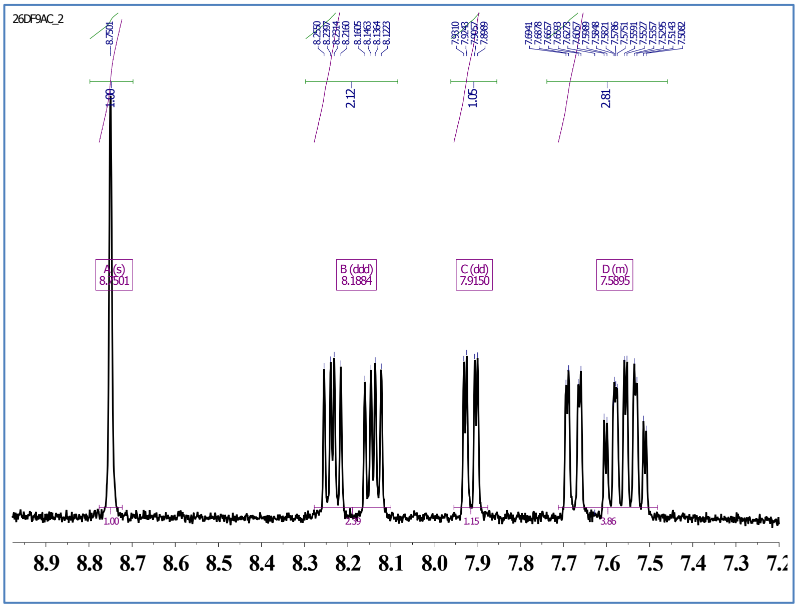
Supporting Information

1. ^{1}H-NMR of 4F-9AC and synthesis of Fluoro-Anthracene carboxylic acids
2. Spectroscopic properties of Fluoro-Anthracene carboxylic acids
3. Photomechanical properties of **9AC** and **4F-9AC**
4. Crystallographic information of **2F-9AC, 4F-9AC, 2,6DF-9AC and 10F-9AC**

1. Synthesis of Fluoro-Anthracene carboxylic acids

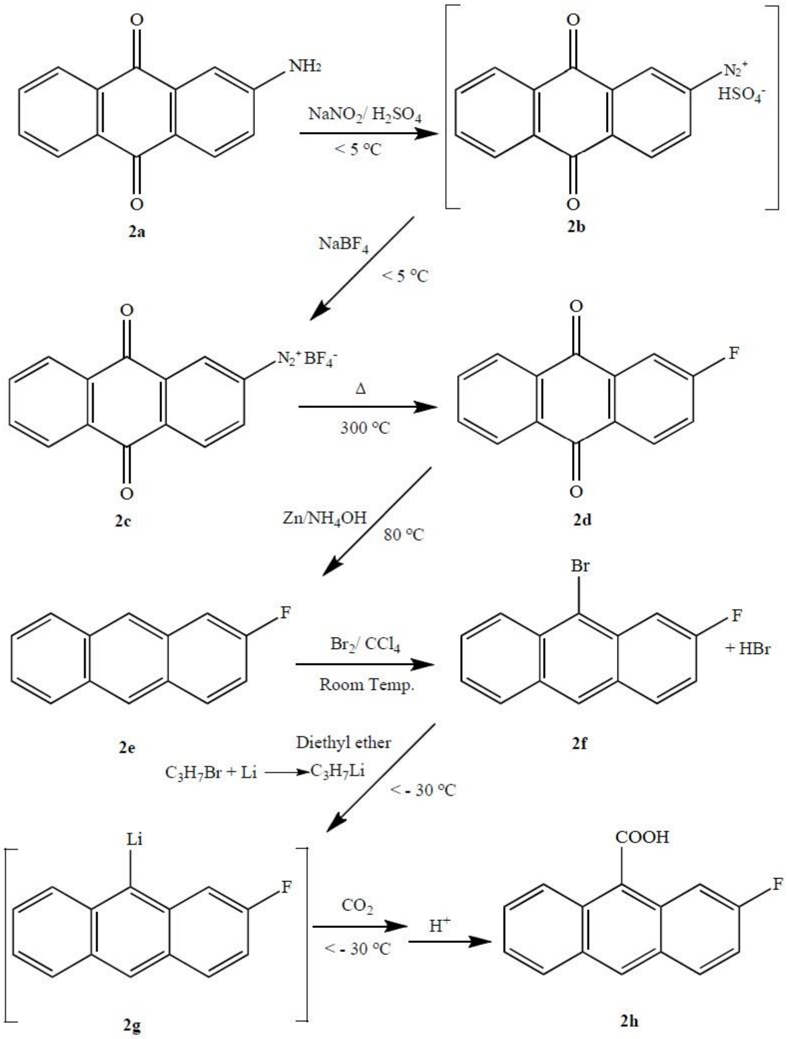
Materials: All starting materials were purchased from Tokyo Chemical Company (TCI) and used without further purification. Dry diethyl ether was distilled over lithium aluminum hydride and stored over activated molecular sieves (4 **Å**). All other organic solvents were distilled over anhydrous $CaCl_2$ prior to use. Equipment: For the low temperature bath we used Lab Armor bath beads stored at -80 °C. Glassware were kept dry in an oven at 60 °C prior to use. IR measurements were performed using IR Affinity-1 FTIR from Shimadzu. GC-MS was collected using Shimadzhu GCMS-QP2010 using a 30 m long general-purpose capillary GC column. Melting point were determined inside sealed capillary tubes. The synthesis of 10F-9AC is described in a previous paper ["Crystal structures and photophysical properties of 9-anthracene carboxylic acid derivatives for photomechanical applications," L. Zhu, R. O. Al-Kaysi, R. J. Dillon, F. S. Tham and C. J. Bardeen, *Cryst. Growth Des.*, **11**, 4975-4983 (2011)].

__4-Fluoro-9-Anthracene Carboxylic Acid (4F-9AC)__: Synthesis of this compound is reported in the article.



^{1}H NMR of 4F-9AC (**1h**) in DMSO-d6

<u>Synthesis of 2-Fluoro-9-Anthracene Carboxylic Acid (2h)</u>: Synthesis of this compound followed a similar method to the one used to synthesize **4F-9AC** as mentioned in the article. Synthesis scheme is depicted in Scheme S1.



Scheme S1: Scheme for the synthesis of Synthesis of **2F-9AC (2h**)

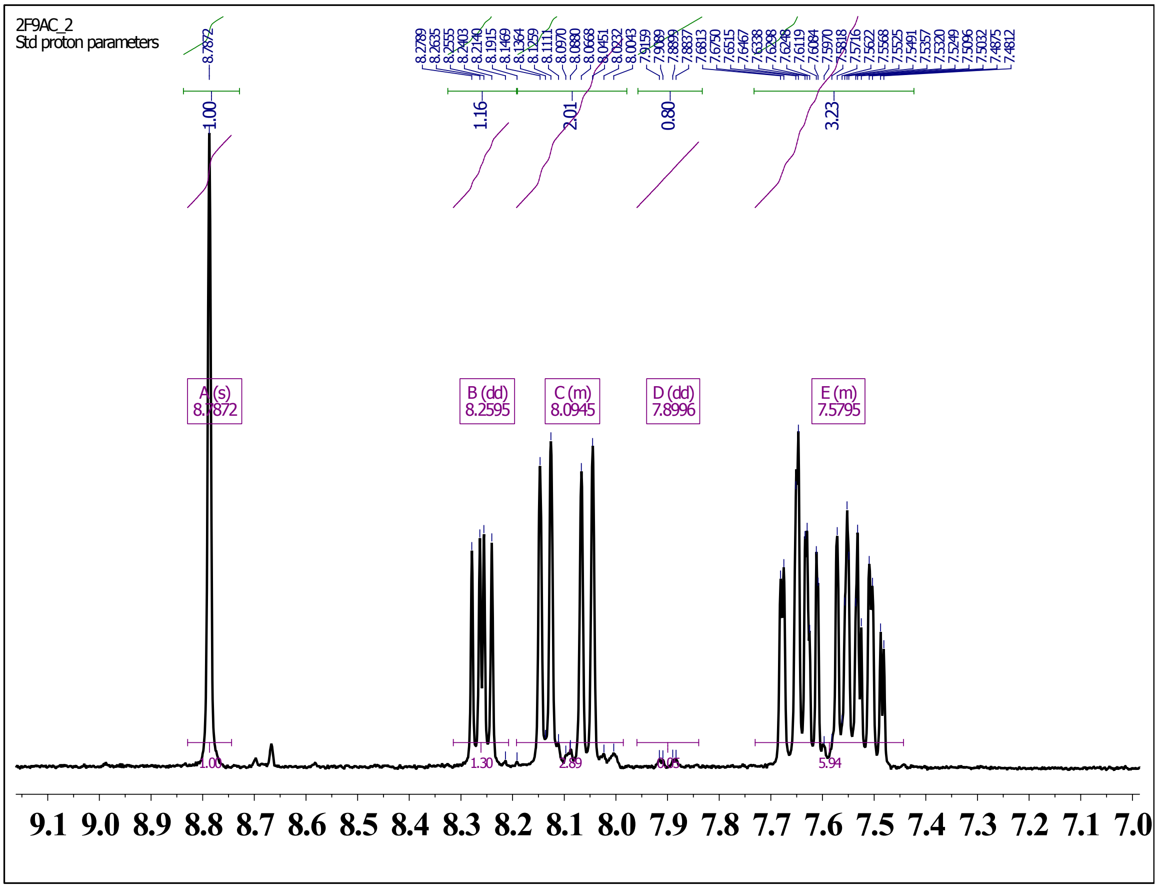
<u>2-Anthraquinone Diazonium Tetrafluoroborate</u> **2c**: The salt was prepared in a similar procedure used for **1c**. Starting with **2a** (3 g, 0.013 moles) followed by precipitation of the tetrafluoroborate salt with $NaBF_4$ to yield **2c** pale brown powder (3.87 g, 90% yield).

2-Fluoro-Anthraquinone **2d**: Following a similar procedure to that described for **1c**, we started with **2c** (3.87 g, 0.012 moles) to yield **2d** as yellow needle-like crystals (2.1 g, with 77% yield) with a mp of 198-200 °C (literature mp: 202 °C[1-2]). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.48 (1H, m), 7.83 (2H, m), 7.96 (1H, dd), 8.31 (2H, m), 8.39 (1H, dd). GC-MS: 100% pure with a major peak at M^+ = 226 and fragments at 198 (loss of one CO), 170 (loss of two CO).

2-Fluoroanthracene **2e**: Following a similar procedure to that described for **1e**, we started with **2d** (1.95 g, 0.0086 moles). After reaction, recrystallization from 1-propanol yielded 2-fluoroanthrancene **2e** as pale green plates (1.47 g, 87% yield) with a mp of 208-211 °C (literature mp: 212 °C[3]). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.27 (1H, m), 7.46 (2H m), 7.57 (1H, dd), 8.00 (3H, m), 8.35 (1H, s), 8.43 (1H, s). GC-MS : 100% pure product with a very strong major peak corresponding to M^+ = 196.

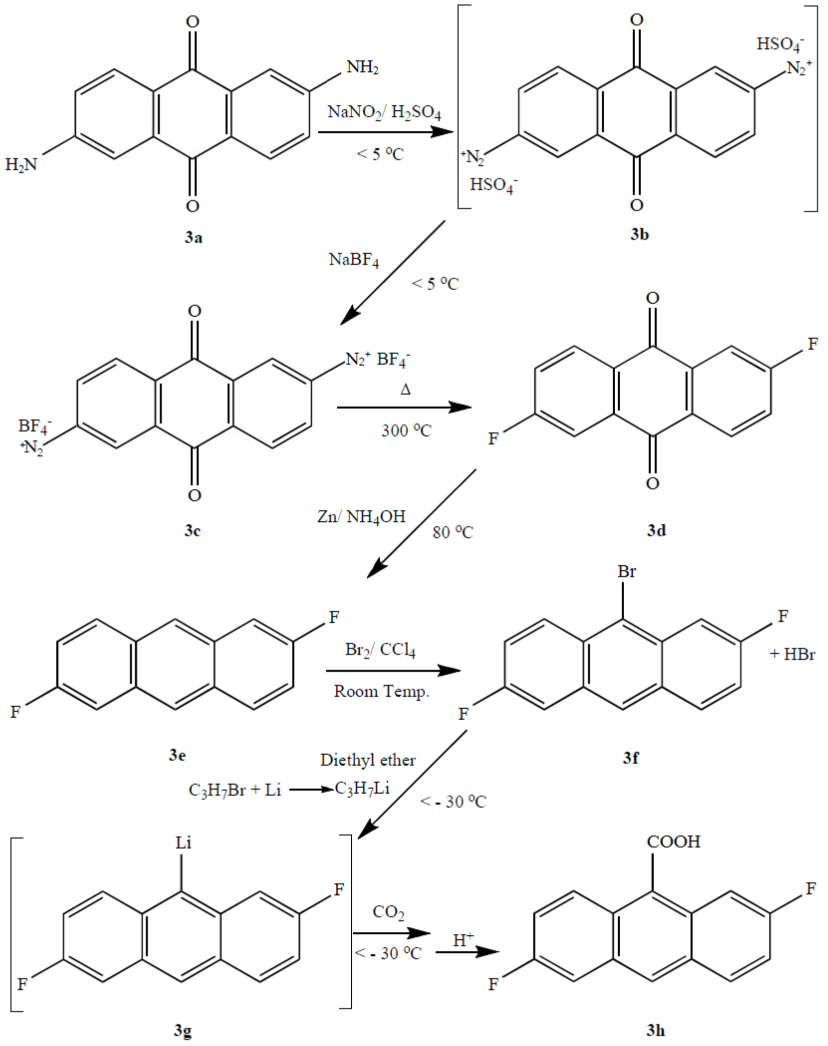
9-Bromo-2-Fluoroanthracene **2f**: Following a similar method to that described for of **1f**, we started with **2e** (1.35 g, 0.007 moles). Reaction with one equivalent Bromine followed by column chromatography gave **2f** as a yellow powder (1.76 g, 93% yield) with a mp of 110-114 °C (literature mp: 118-119 °C[4]). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.30 (1H, m), 7.51 (1H, m), 7.64 (1H, m), 8.01 (1H, d), 8.13 (1H, dd), 8.45 (1H, s), 8.47 (1H, d). GC-MS revealed that the product was only 94% **2f**, with two equal intensity peaks at M^+ = 276 and 274 corresponding to a monobrominated product and fragment peaks at 196 and 194 corresponding to loss of one bromine. There was 6% unreacted **2e**.

2-Fluoro-9-Anthracene carboxylic acid **2F-9AC**: Following a similar method to that described for **4F-9AC**, we started with dry **2f** (1.0 g, 0.0036) and reacted it with n-propyl lithium (prepared by reacting 1.6 mL n-bromopropane with 0.24 g Li wire) and then with CO_2. Compound **2F-9AC** was a yellow crystalline powder (0.58 g, 67% yield) with a mp of 230-231 °C. ^1H NMR ($CDCl_3$) δ (ppm): 7.59 (4H, m), 8.10 (2H, dd), 8.26 (1H, s), 8.78 (1H, s). ν_{max} (KBr disc) cm^{-1}: 3500-2800 (COOH), 1679 (CO), 1635 (C=C), 1459, 1255, 1172, 737.



^1H NMR of 2F-9AC **(2h)** in DMSO-d6.

***<u>2, 6-Difluoro-9-Anthracene Carboxylic Acid (2,6DF-9AC)</u>*:** Synthesis of this compound followed a similar method to the one used to synthesize **4F-9AC** as mentioned in the article. Synthesis scheme is depicted in Scheme S2.



Scheme S2: Scheme for the synthesis of 2**,6DF-9AC** (**3h**)

<u>2, 6-Anthraquinone Diazonium Tetrafluoroborate</u> **3c**: Following a similar method to that described for **1c**, we started with **3a** (4 g, 0.017 moles). After reaction, precipitation of

the tetrafluoroborate salt with $NaBF_4$ (12 g) yielded **3c** (pale brown powder, 5.89 g, 81% yield).

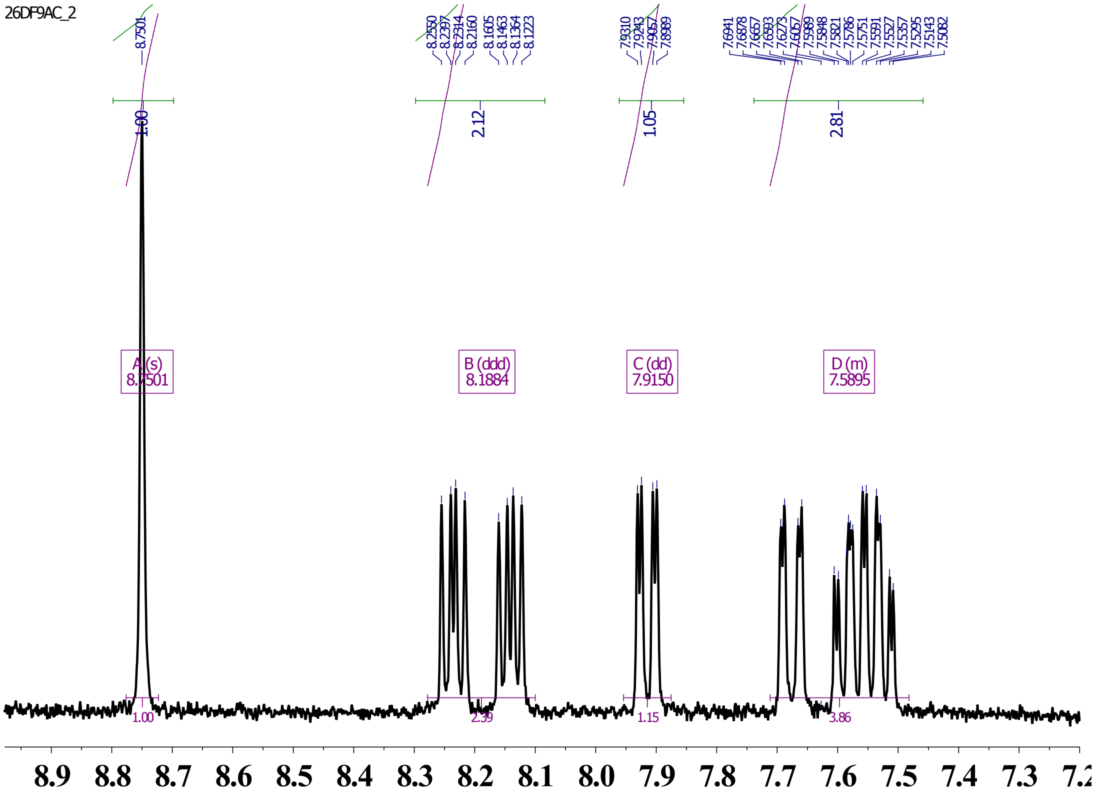
2, 6-Difluoro-Anthraquinone **3d**: Thermal decomposition of **3c** (3.87 g, 0.012 moles) yielded **3d** as yellow crystals (1.6 g, with 48% yield) with a mp of 216 °C (literature mp: 228-229[2]). ^1H NMR ($CDCl_3$) δ (ppm): 7.48 (2H, m), 7.95 (2H, d), 8.36 (2H, dd). GC-MS: 100% pure with a major peak at $M^+ = 244$ and fragments at 216 (loss of one CO) and 188 (loss of two CO).

2, 6-Difluoroantracene **3e**: Reduction of **3d** (1.6 g, 0.0065 moles) for 3 days gave **3e** as a pale green powder (1.2 g, 86% yield). ^1H NMR ($CDCl_3$) δ (ppm): 7.29 (2H, m), 7.55 (2H, d), 7.97 (2H, dd), 8.39 (2H, s). GC-MS: 98% pure product with a very strong major peak corresponding to $M^+ = 214$.

9-Bromo-2,6-Difluoroanthracene **3f**: Bromination of **3e** (0.4 g, 0.0019 moles) with one equivalent Bromine while the reaction mixture is being stirred over ice followed by column chromatography gave **3f** as a yellow powder (0.42 g, 77% yield) with a mp of 118-120 °C. GC-MS: revealed that the product was 99% **3f**, with two equal intensity peaks M^+ 294 and 292 corresponding to a monobrominated product and fragment peaks at 215, 213, 193, 146 and 106. There was only 1% of a dibromo derivative.

2, 6-Difluoro-9-Anthracene Carboxylic Acid **2,6DF-9AC**: Dry **3e** (0.41 g, 0.0014 moles) was reacted with n-propyl lithium (prepared by reacting 0.8 mL n-bromopropane with 0.24 g Li wire) and then with CO_2. Extraction with organic solvents followed by precipitation of the **2, 6DF-9AC** with HCl and recrystallization from ethanol/water gave pure **2, 6DF-9AC** yellow powder crystals (0.25 g, 70% yield) with a mp of 241-242 °C.

^{1}H NMR ($CDCl_3$) δ(ppm): 7.56 (2H, m), 7.68 (1H, dd), 7.92 (1H, dd), 8.19 (2H, ddd), 8.75 (1H, s). ν_{max} (KBr disc) cm^{-1}: 3500-2800 (COOH), 1689 (CO), 1640 (C=C), 1469, 1187, 1251, 797.



^{1}H NMR of 2,6DF-9AC (**3h**) in DMSO-d6.

2. Spectroscopic properties of Fluoro-Anthracene carboxylic acids

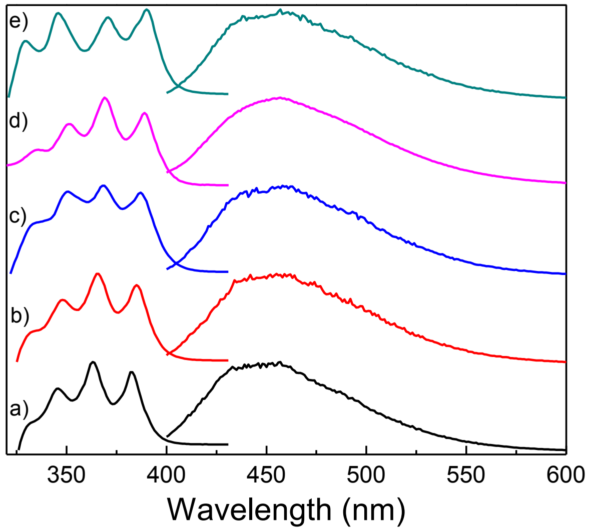
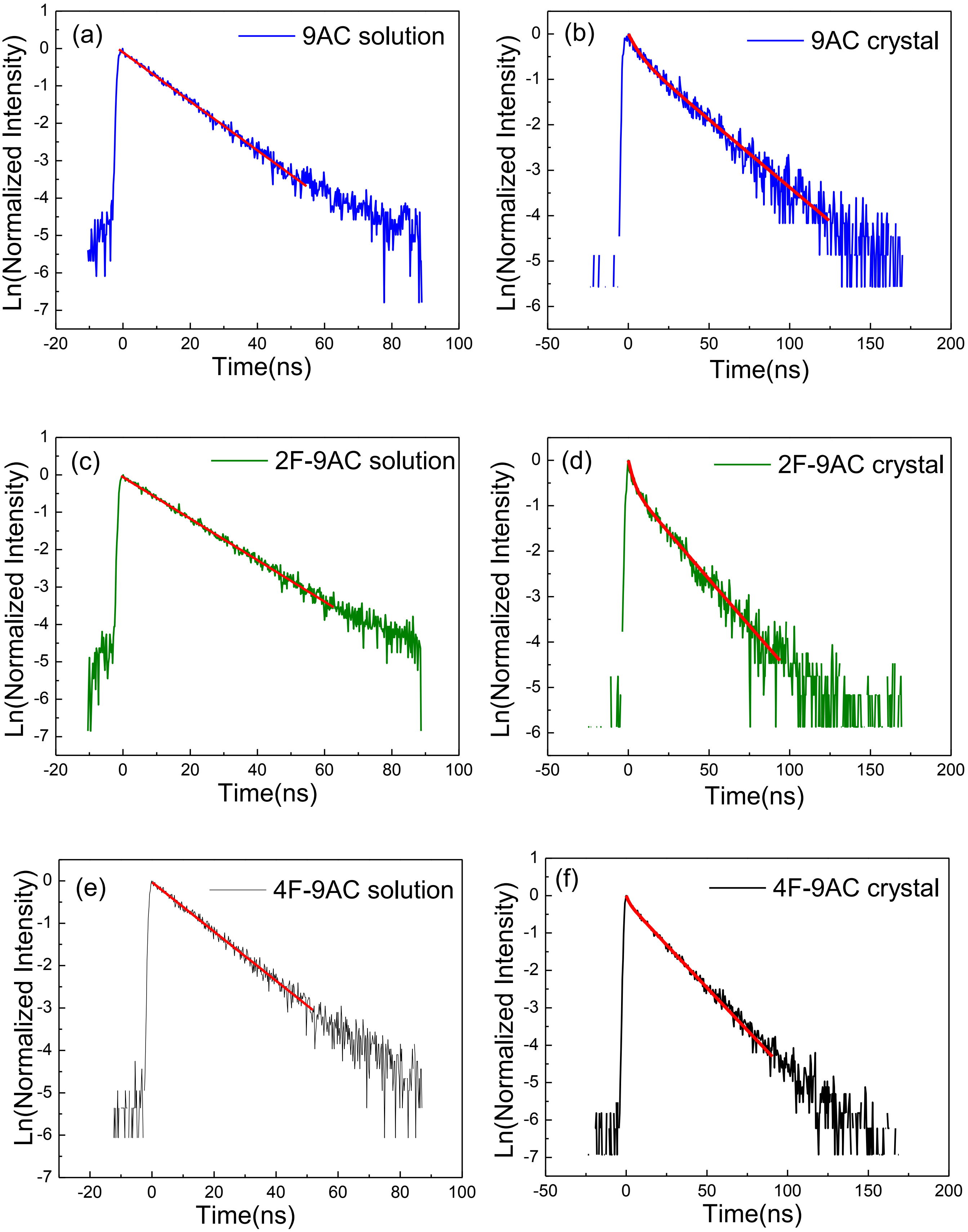


Figure S1. Absorption and emission spectroscopy of anthracene-9-carboxylic acid (9AC) and its fluorinated derivatives in tetrahydrofuran solution: (a) anthracene-9-carboxylic acid (9AC); (b) 4-fluoro-9-anthracene carboxylic acid (4F-9AC); (c) 2-fluoro-anthracene-9-carboxylic acid (2F-9AC); (d) 10-fluoro-anthracene-9-carboxylic acid (10F-9AC) and (e) 2,6-difluoro-anthracene-9-carboxylic acid (2,6DF9AC). The solid line plots are the absorption spectra, and the dotted line plots are the fluorescence spectra.


(a)
9AC solution
Ln(Normalized Intensity)
Time(ns)
1
0
-1
-2
-3
-4
-5
-6
-7
-20
0
20
40
60
80
100
(b)
9AC crystal
Ln(Normalized Intensity)
Time(ns)
0
-1
-2
-3
-4
-5
-6
-50
0
50
100
150
200
(c)
2F-9AC solution
Ln(Normalized Intensity)
Time(ns)
1
0
-1
-2
-3
-4
-5
-6
-7
-20
0
20
40
60
80
100
(d)
2F-9AC crystal
Ln(Normalized Intensity)
Time(ns)
0
-1
-2
-3
-4
-5
-6
-50
0
50
100
150
200
(e)
4F-9AC solution
Ln(Normalized Intensity)
Time(ns)
0
-1
-2
-3
-4
-5
-6
-7
-20
0
20
40
60
80
100
(f)
4F-9AC crystal
Ln(Normalized Intensity)
Time(ns)
1
0
-1
-2
-3
-4
-5
-6
-7
-50
0
50
100
150
200

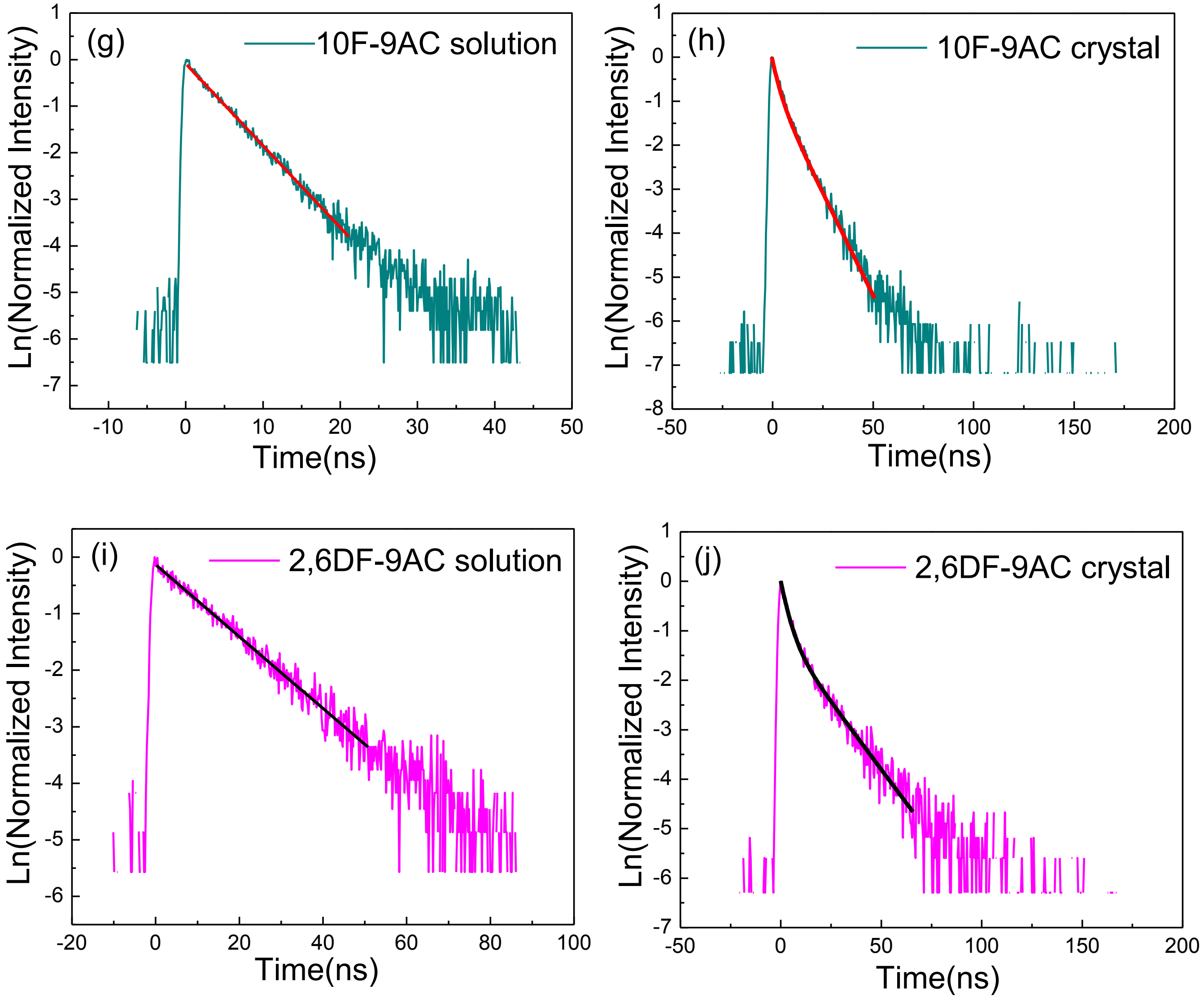


Figure S2. Fluorescence lifetime delay and exponential fitting of **9AC** and its derivatives; Solution samples were fitted single exponentially and crystal samples were fitted biexponentially: (a) **9AC** solution in THF; (b) **9AC** crystal film; (c) **2F-9AC** solution in THF; (d) **2F-9AC** crystal film; (e) **4F-9AC** solution in THF; (f) **4F-9AC** crystal film; (g) **10F-9AC** solution in THF; (h) **10F-9AC** crystal film; (i) **2,6DF-9AC** solution in THF; (j) **2,6DF-9AC** crystal film.

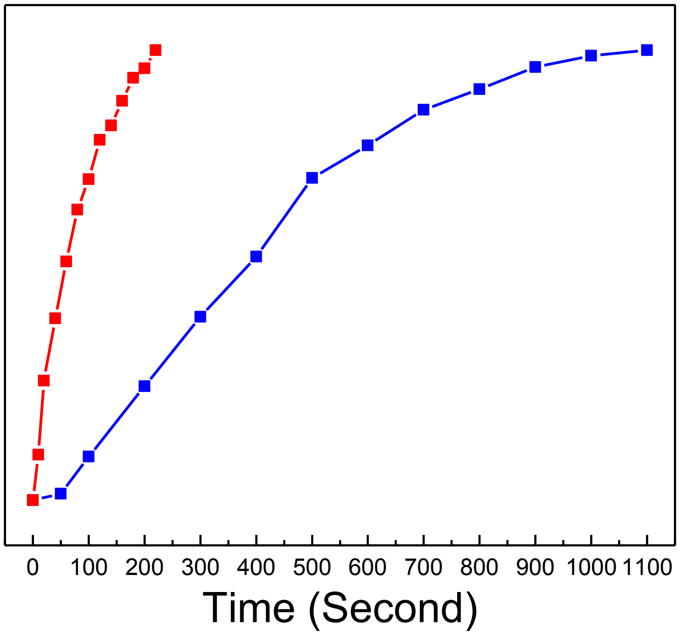


Figure S3. Fluorescence recovery half time of **2,6DF-9AC** (red plot) and **10F-9AC** (blue plot).

3. Photomechanical properties of 9AC and 4F-9AC.

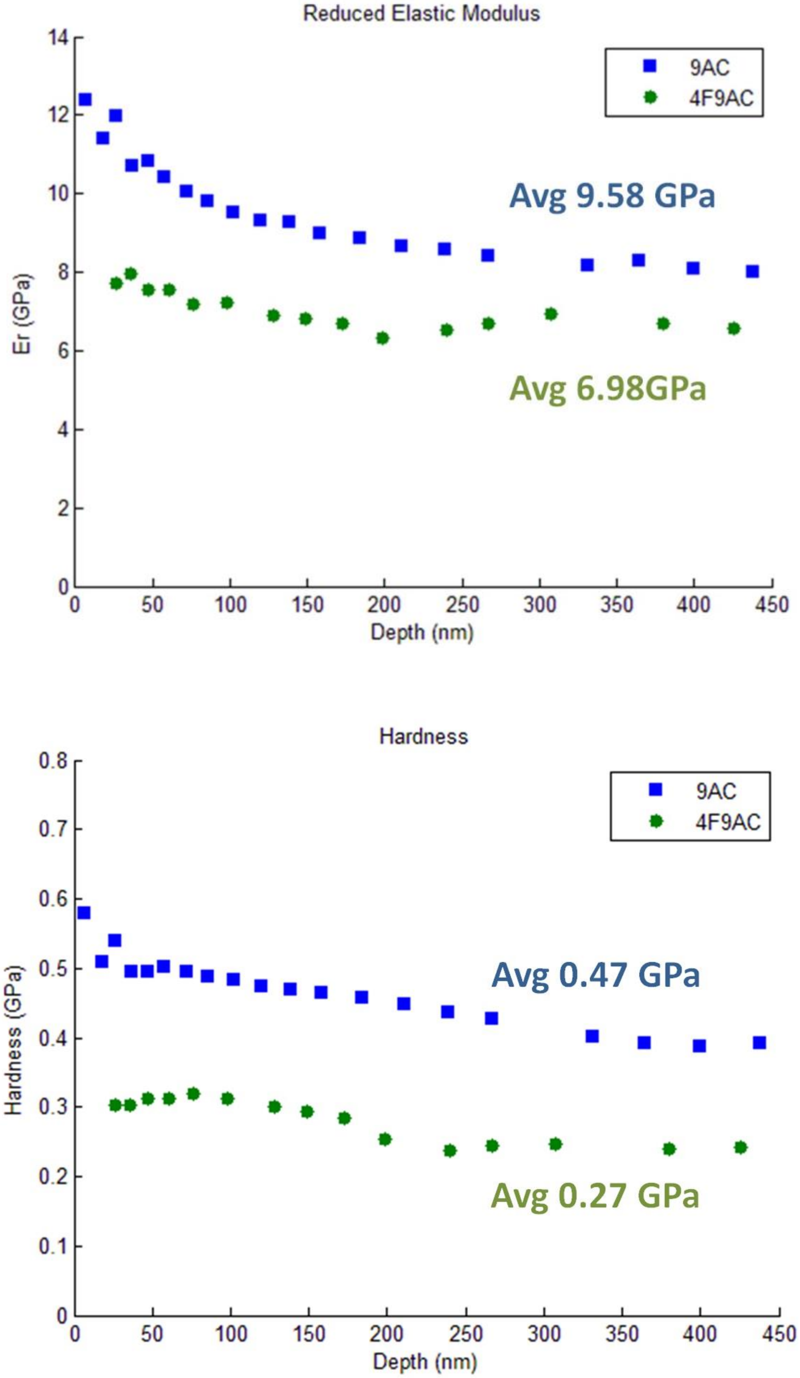


Figure S4. Reduced Elastic Modulus and Hardness of **9AC** and **4F-9AC**.

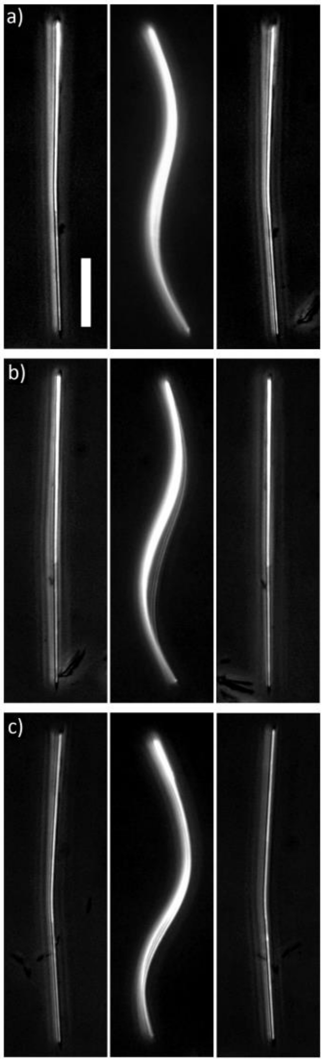


Figure S5. Snapshots of repeated cycles of a 4F-9AC crystalline needle's photo-induced twisting and recovery: a) 1st cycle; b) 30th cycle; c) 60th cycle. The irradiation source was a 100 Watt Hg lamp. The scale bar is 20 μm for all images. After the 60th cycle, the water surrounding the sample evaporated. In the process of adding water to the microscope slide, the needle floated away.

4. Crystallographic information of 2F-9AC, 4F-9AC, 2,6DF-9AC and 10F-9AC

2F-9AC

There was one partially occupied (79% occupied) molecule of $C_{15}H_9O_2F$ and one partially occupied (21% occupied) molecule of $C_{14}H_9F$ present in the asymmetric unit of the unit cell.

4F-9AC

There was one molecule of $C_{15}H_9O_2F$ present in the asymmetric unit of the unit cell. The F-atom was in a disordered position (disordered site occupancy ratio was 55%/45%). The structure was refined as a pseudo-merohedral twin, (twin law, 1 0 0 0 -1 0 0 0 -1, major/minor component twin ratio was 76%/24%).

2,6DF-9AC

There was one disordered molecule of $C_{15}H_8F_2O_2$ present in the asymmetric unit of the unit cell. The F-atoms at the C2 and C6 positions were disordered (disordered site occupancy ratio was 71%/29%). The disordered-symmetry is a 2-fold rotation about the C9-C10 axis. The structure was refined as a monoclinic pseudo-merohehral twin (TWIN 1 0 0 0 -1 0 0 0 -1, major/minor twin component ratio was 95%/5%).

10F-9AC

There was one disordered molecule of $C_{15}H_9FO_2$ present in the asymmetry unit of the unit cell. The disorder was at the partially occupied F and Br atom positions. The disordered site occupancy ratio was 95% and 5%, respectively. DELU, SIMU, and EADP restraints were used to stabilize the Br-atom anisotropic refinement. Attempts to resolve the minor non-merohedral twinning were unsuccessful when the structure model converged to R1 = 7.31% (higher than non-twin convergence, R1 = 7.03% at identical 2θ resolution). This was probably due to the unresolved overlapped twinning intensities (twin law rotation about reciprocal axis 0 0 1 and the minor component was about 20%) during the data integration process since the crystal thickness was only 0.02 mm.

References

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