

***Supporting Information***

***Preparation of organic mechanochromic fluorophores with  
simple structures and promising mechanochromic  
luminescence properties***

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## Table of Contents

<b>I. General remarks</b> .....	S3
<b>II. Synthesis of phosphonium salts</b> .....	S3
<b>III. Physical and photophysical properties of phosphonium salts</b> .....	S8
<b>IV. X-Ray structure determination</b> .....	S10
<b>V. Fluorescence decay profiles of 1·PF<sub>6</sub> in different states</b> .....	S13
<b>VI. Excitation of 1·PF<sub>6</sub> in different states</b> .....	S13
<b>VII. References</b> .....	S14
<b>VIII. Copies of <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P NMR spectra</b> .....	S15

## I. General remarks

NMR spectra were obtained on a Bruker AV II-400 (Germany). The  $^1\text{H}$  NMR chemical shifts were measured relative to  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  as the internal reference ( $\text{DMSO-}d_6$ :  $\delta = 2.50$  ppm;  $\text{CDCl}_3$ :  $\delta = 7.26$  ppm). The  $^{13}\text{C}$  NMR chemical shifts were given using  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  as the internal standard ( $\text{DMSO-}d_6$ :  $\delta = 39.52$  ppm;  $\text{CDCl}_3$ :  $\delta = 77.16$  ppm). Fluorescence emission spectra were obtained using a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer (Japan). Absorption spectra were obtained on a HITACHI U-2910 spectrometer (Japan). The ESI-TOF mass spectra were recorded with a Shimadzu LCMS-IT-TOF instrument (Japan). Fluorescence lifetime data were determined on a HORIBA TEMPRO-01 instrument (Japan). Differential scanning calorimetry (DSC) data was performed using a TA instrument DSC-Q200 1474 (USA) with rate = 5 °C/min and range = 40 to 230 °C. All the tests were performed in Sichuan University, Chengdu.

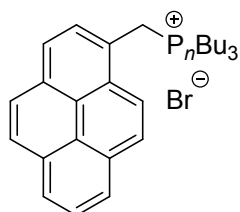
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.  $\text{DMSO-}d_6$  and  $\text{CDCl}_3$  were purchased from Alfa. Other reagents and solvents were obtained from Chengdu Kelong Chemical Reagent Factory. Silica gel (size: 45-75  $\mu\text{m}$ , relative surface area: 600-800  $\text{m}^2/\text{g}$ ) was purchased from Qingdao Haiyang Chemical Factory. The 1-(bromomethyl)pyrene were prepared according to the literature procedures.<sup>[1]</sup>

## II. Synthesis of phosphonium salts

**General procedure for the synthesis of phosphonium salts:** A Schlenk tube with a magnetic stir bar was charged with bromomethylarene (2.0 mmol), trisubstituted phosphine (3.0 mmol) and EtOAc (10.0 mL) under  $\text{N}_2$ . The reaction system was then evacuated and backfilled with  $\text{N}_2$  for twice. After stirring at 75 °C for 8 h, the precipitate was filtered, washed by EtOAc to get the target phosphonium salt with bromide as the anion.

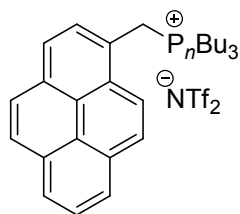
**General procedure for the anion exchange:** A Schlenk tube with a magnetic stir bar was charged with phosphonium bromide (1.0 mmol), metal salt with the target anion (2.0 mmol),  $\text{CH}_2\text{Cl}_2$  (10.0 mL) and deionized water (5.0 mL). The resulting mixture

was stirred at room temperature for 24 h. Then the organic phase was separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> for 3 times. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to afford the desired product.



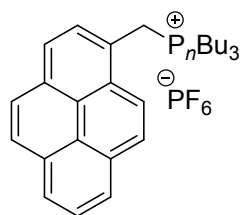
### Tributyl(pyren-1-ylmethyl)phosphonium bromide (**1·Br**)

Following the general procedure, 1-(bromomethyl)pyrene (590.3 mg, 2.0 mmol), tributylphosphine (0.75 mL, 3.0 mmol) and EtOAc (10.0 mL) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/15, v/v) afforded **1·Br** as a white solid (953.4 mg, 96% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  = 0.76 (t, *J* = 7.2 Hz, 9H), 1.23-1.39 (m, 12H), 2.24-2.32 (m, 6H), 4.69 (d, *J* = 15.6 Hz, 2H), 8.10-8.17 (m, 2H), 8.23 (dd, *J* = 8.8 Hz, *J* = 12.0 Hz, 2H), 8.34-8.40 (m, 4H), 8.64 (d, *J* = 9.2 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz):  $\delta$  = 18.0, 18.5, 23.0 (d, *J* = 4.6 Hz), 23.7, 23.8, 123.8, 124.0 (d, *J* = 9.3 Hz), 124.1, 124.7 (d, *J* = 2.6 Hz), 125.6 (d, *J* = 3.1 Hz), 126.0, 126.2, 127.1, 127.7, 128.3, 128.6, 129.4 (d, *J* = 4.7 Hz), 129.9 (d, *J* = 5.1 Hz), 130.6, 131.1 (d, *J* = 3.4 Hz), 131.2 ppm. <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, 162 MHz):  $\delta$  = 34.36 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>38</sub>P [M]<sup>+</sup> 417.2706, found 417.2697. Elemental analysis calcd (%) for M+H<sub>2</sub>O: C 67.57, H 7.82, found: C 67.83, H 8.06.



### Tributyl(pyren-1-ylmethyl)phosphonium bis((trifluoromethyl)sulfonyl)amide (**1·NTf<sub>2</sub>**)

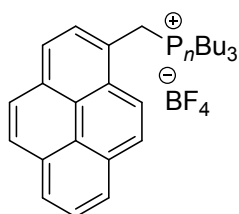
Following the general procedure, **1·Br** (497.5 mg, 1.0 mmol) and LiNTf<sub>2</sub> (574.2 mg, 2.0 mmol) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/20, v/v) afforded **1·NTf<sub>2</sub>** as a white solid (674.2 mg, 97% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ = 0.78 (t, *J* = 7.2 Hz, 9H), 1.25-1.40 (m, 12H), 2.20-2.28 (m, 6H), 4.62 (d, *J* = 16.0 Hz, 2H), 8.10-8.17 (m, 2H), 8.25 (dd, *J* = 8.8 Hz, *J* = 14.0 Hz, 2H), 8.37-8.41 (m, 4H), 8.58 (d, *J* = 9.2 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ = 18.0, 18.4, 23.0 (d, *J* = 4.6 Hz), 23.7, 23.8, 123.6 (d, *J* = 2.0 Hz), 123.8 (d, *J* = 9.2 Hz), 124.1, 124.8 (d, *J* = 2.3 Hz), 125.7 (d, *J* = 3.5 Hz), 126.0, 126.3, 127.1, 127.7, 128.3, 128.6, 129.4 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 5.2 Hz), 130.6, 131.1 (d, *J* = 3.3 Hz), 131.2 ppm. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 376 MHz): δ = -78.72 ppm. <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, 162 MHz): δ = 34.40 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>38</sub>P [M]<sup>+</sup> 417.2706, found 417.2707. Elemental analysis calcd (%) for M+H<sub>2</sub>O: C 52.02, H 5.63, N 1.96, found: C 52.20, H 5.60, N 1.79.



### Tributyl(pyren-1-ylmethyl)phosphonium hexafluorophosphate (**1·PF<sub>6</sub>**)

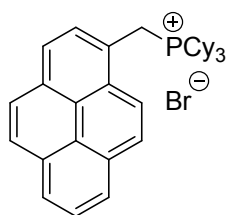
Following the general procedure, **1·Br** (497.5 mg, 1.0 mmol) and KPF<sub>6</sub> (368.1 mg, 2.0 mmol) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/20, v/v) afforded **1·PF<sub>6</sub>** as a white solid (524.8 mg, 93% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ = 0.77 (t, *J* = 7.2 Hz, 9H), 1.24-1.38 (m, 12H), 2.21-2.28 (m, 6H), 4.64 (d, *J* = 15.6 Hz, 2H), 8.11-8.15 (m, 2H), 8.23 (dd, *J* = 8.8 Hz, *J* = 12.4 Hz, 2H), 8.35-8.40 (m, 4H), 8.60 (d, *J* = 9.2 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ = 18.0, 18.5, 23.0 (d, *J* = 4.5 Hz), 23.7, 23.8, 123.7, 123.9 (d, *J* = 9.4 Hz), 124.1, 124.8 (d, *J* = 2.6 Hz), 125.7 (d, *J* = 3.2 Hz), 126.0, 126.3, 127.1, 127.7, 128.3, 128.6, 129.4 (d, *J* = 4.9 Hz), 129.9 (d, *J* = 5.2 Hz), 130.6, 131.1 (d, *J* = 3.6 Hz), 131.2 ppm. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 376 MHz): δ = -69.15, -71.04 ppm. <sup>31</sup>P

NMR (DMSO-*d*<sub>6</sub>, 162 MHz):  $\delta$  = 34.38, -130.98, -135.37, -139.76, -144.15, -148.54, -152.94, -157.33 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>38</sub>P [M]<sup>+</sup> 417.2706, found 417.2698. Elemental analysis calcd (%) for M+H<sub>2</sub>O: C 60.00, H 6.94, found: C 60.77, H 6.60.



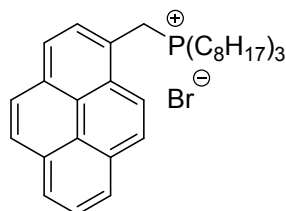
### Tributyl(pyren-1-ylmethyl)phosphonium tetrafluoroborate (1·BF<sub>4</sub>)

Following the general procedure, **1·Br** (497.5 mg, 1.0 mmol) and NaBF<sub>4</sub> (219.6 mg, 2.0 mmol) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/20, v/v) afforded **1·BF<sub>4</sub>** as a white solid (454.8 mg, 90% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  = 0.78 (t, *J* = 7.2 Hz, 9H), 1.24-1.41 (m, 12H), 2.20-2.28 (m, 6H), 4.62 (d, *J* = 16.0 Hz, 2H), 8.10-8.16 (m, 2H), 8.24 (dd, *J* = 8.8 Hz, *J* = 12.4 Hz, 2H), 8.36-8.41 (m, 4H), 8.58 (d, *J* = 9.2 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz):  $\delta$  = 18.0, 18.5, 23.0 (d, *J* = 4.5 Hz), 23.7, 23.8, 123.7 (d, *J* = 1.7 Hz), 123.8 (d, *J* = 9.2 Hz), 124.1, 124.8 (d, *J* = 2.6 Hz), 125.7 (d, *J* = 3.2 Hz), 126.0, 126.3, 127.1, 127.7, 128.3, 128.6, 129.4 (d, *J* = 5.1 Hz), 129.9 (d, *J* = 5.1 Hz), 130.6, 131.1 (d, *J* = 3.4 Hz), 131.2 ppm. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 376 MHz):  $\delta$  = -148.21, -148.24 ppm. <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, 162 MHz):  $\delta$  = 34.40 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>38</sub>P [M]<sup>+</sup> 417.2706, found 417.2696. Elemental analysis calcd (%) for M: C 69.06, H 7.59, found: C 68.59, H 6.90.



### Tricyclohexyl(pyren-1-ylmethyl)phosphonium bromide (2·Br)

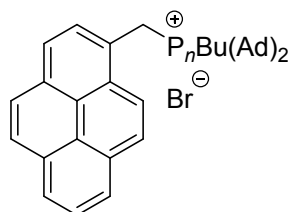
Following the general procedure, 1-(bromomethyl)pyrene (590.3 mg, 2.0 mmol), tricyclohexylphosphine (840.6 mg, 3.0 mmol) and EtOAc (10.0 mL) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/15, v/v) afforded **2·Br** as a white solid (1.1310 g, 98% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ = 1.13 (t, *J* = 12.4 Hz, 3H), 1.26 (q, *J* = 12.4 Hz, 6H), 1.45 (q, *J* = 12.4 Hz, 6H), 1.58-1.70 (m, 9H), 1.88-1.91 (m, 6H), 2.71 (q, *J* = 12.4 Hz, 3H), 4.77 (d, *J* = 12.4 Hz, 2H), 7.99 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 8.14 (t, *J* = 7.6 Hz, 1H), 8.24 (dd, *J* = 8.8 Hz, *J* = 14.0 Hz, 2H), 8.36-8.42 (m, 4H), 8.68 (d, *J* = 9.2 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ = 25.3, 26.4 (d, *J* = 3.6 Hz), 26.5 (d, *J* = 11.9 Hz), 30.7, 31.1, 124.0, 124.1, 124.7 (d, *J* = 8.4 Hz), 124.8 (d, *J* = 2.1 Hz), 125.7 (d, *J* = 2.7 Hz), 126.1, 126.4, 127.2, 127.7, 128.4, 128.5, 129.0 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 5.5 Hz), 130.6, 131.0 (d, *J* = 2.9 Hz), 131.3 ppm. <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, 162 MHz): δ = 32.44 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>35</sub>H<sub>44</sub>P [M]<sup>+</sup> 495.3175, found 495.3123. Elemental analysis calcd (%) for M+H<sub>2</sub>O: C 70.82, H 7.81, found: C 71.02, H 7.67.



### **Trioctyl(pyren-1-ylmethyl)phosphonium bromide (3·Br)**

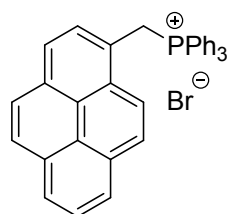
Following the general procedure, 1-(bromomethyl)pyrene (590.3 mg, 2.0 mmol), trioctylphosphine (1.34 mL, 3.0 mmol) and EtOAc (10.0 mL) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/20, v/v) afforded **3·Br** as a white solid (1.2353 g, 93% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ = 0.81 (t, *J* = 7.2 Hz, 9H), 1.06-1.29 (m, 36H), 2.24-2.31 (m, 6H), 4.66 (d, *J* = 16.0 Hz, 2H), 8.11-8.16 (m, 2H), 8.24 (dd, *J* = 9.2 Hz, *J* = 15.2 Hz, 2H), 8.35-8.40 (m, 4H), 8.65 (d, *J* = 9.2 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ = 13.9, 17.8, 18.2, 20.5 (d, *J* = 4.6 Hz), 22.0, 28.1 (d, *J* = 14.3 Hz), 30.0 (d, *J* = 11.2 Hz), 31.1, 123.3, 123.5 (d, *J* = 9.3 Hz), 123.7, 124.4, 125.2, 125.5, 125.8, 126.6, 127.2, 127.9, 128.2, 128.8 (d, *J* =

4.1 Hz), 129.5 (d,  $J = 5.0$  Hz), 130.2, 130.7, 130.9 ppm.  $^{31}\text{P}$  NMR (DMSO- $d_6$ , 162 MHz):  $\delta = 34.01$  ppm. HRMS (ESI $^+$ ): calcd for  $\text{C}_{41}\text{H}_{62}\text{P}$   $[\text{M}]^+$  585.4584, found 585.4575. Elemental analysis calcd (%) for  $\text{M}+\text{H}_2\text{O}$ : C 72.01, H 9.43, found: C 72.02, H 8.67.



#### **Butyl-di-(1-adamantyl)-(pyren-1-ylmethyl)phosphonium bromide (4·Br)**

Following the general procedure, 1-(bromomethyl)pyrene (590.3 mg, 2.0 mmol), cyclohexyldiphenylphosphine (1.0756 g, 3.0 mmol) and EtOAc (20.0 mL) were used. Purification via column chromatography on silica gel (MeOH/ $\text{CH}_2\text{Cl}_2 = 1/20$ , v/v) afforded **4·Br** as a white solid (1.0854 g, 85% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 0.79$  (t,  $J = 7.2$  Hz, 3H), 1.32-1.41 (m, 2H), 1.51-1.52 (m, 2H), 1.60-1.68 (m, 12H), 2.00-2.07 (m, 12H), 2.26-2.39 (m, 8H), 4.66 (d,  $J = 13.2$  Hz, 2H), 7.71 (dd,  $J = 2.0$  Hz,  $J = 8.0$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.92 (d,  $J = 8.8$  Hz, 1H), 8.00-8.06 (m, 2H), 8.15-8.20 (m, 3H), 8.68 (d,  $J = 9.6$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 13.5$ , 14.3, 16.3, 16.6, 19.3, 19.7, 25.0 (d,  $J = 13.1$  Hz), 26.4 (d,  $J = 6.0$  Hz), 27.9 (d,  $J = 8.7$  Hz), 35.7, 37.4 (d,  $J = 3.0$  Hz), 41.5, 41.8, 123.4 (d,  $J = 9.0$  Hz), 124.2, 124.4, 124.8 (d,  $J = 2.8$  Hz), 125.2 (d,  $J = 2.1$  Hz), 125.7, 126.0, 126.5, 127.3, 128.2, 128.4, 128.8 (d,  $J = 3.8$  Hz), 129.6 (d,  $J = 5.4$  Hz), 130.5, 131.0 (d,  $J = 2.7$  Hz), 131.3 ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta = 28.86$  ppm. HRMS (ESI $^+$ ): calcd for  $\text{C}_{40}\text{H}_{48}\text{P}$   $[\text{M}]^+$  573.3645, found 573.3643. Elemental analysis calcd (%) for  $\text{M}+\text{H}_2\text{O}$ : C 73.31, H 7.80, found: C 72.70, H 7.99.

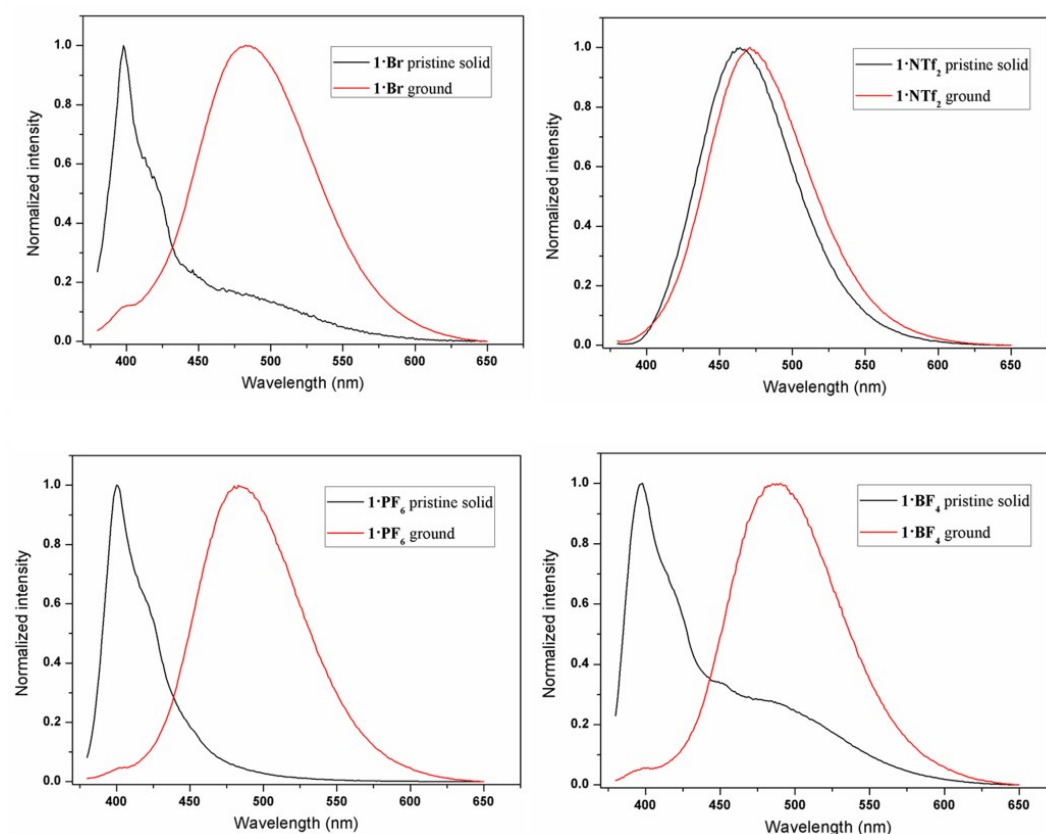


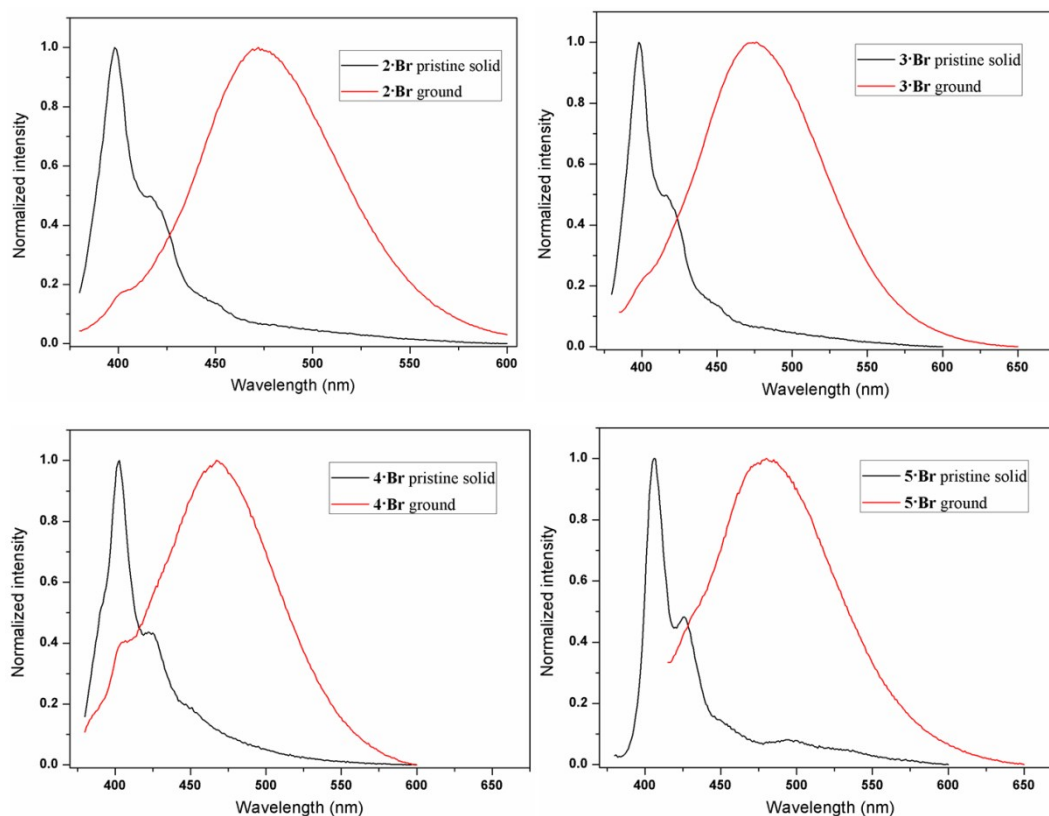


### Triphenyl(pyren-1-ylmethyl)phosphonium bromide (**5·Br**)

Following the general procedure, 1-(bromomethyl)pyrene (590.3 mg, 2.0 mmol), triphenylphosphine (786.9 mg, 3.0 mmol) and EtOAc (10.0 mL) were used. Purification via column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/15, v/v) afforded **5·Br** as a white solid (1.0350 g, 93% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  = 5.95 (d, *J* = 15.6, 2H), 7.58-7.69 (m, 12H), 7.79-7.84 (m, 5H), 7.94 (d, *J* = 9.2 Hz, 1H), 8.06 (t, *J* = 7.6 Hz, 1H), 8.11-8.15 (m, 2H), 8.20-8.25 (m, 2H), 8.31 (d, *J* = 7.6 Hz, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz):  $\delta$  = 26.6 (d, *J* = 45.9 Hz), 117.6, 118.4, 121.7 (d, *J* = 9.3 Hz), 123.4, 123.8, 124.4 (d, *J* = 2.8 Hz), 125.1 (d, *J* = 3.7 Hz), 125.9, 126.2, 127.0, 127.6, 128.5, 129.8 (d, *J* = 5.2 Hz), 130.2 (d, *J* = 1.0 Hz), 130.4 (d, *J* = 12.3 Hz), 130.7 (d, *J* = 5.8 Hz), 131.1 (d, *J* = 1.1 Hz), 131.2 (d, *J* = 3.8 Hz), 134.6 (d, *J* = 9.8 Hz), 135.4 (d, *J* = 2.7 Hz) ppm. <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, 162 MHz):  $\delta$  = 22.55 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>35</sub>H<sub>26</sub>P [M]<sup>+</sup> 477.1767, found 477.1764. Elemental analysis calcd (%) for M+H<sub>2</sub>O: C 73.05, H 4.90, found: C 73.59, H 4.76.

### III. Physical and photophysical properties of phosphonium salts





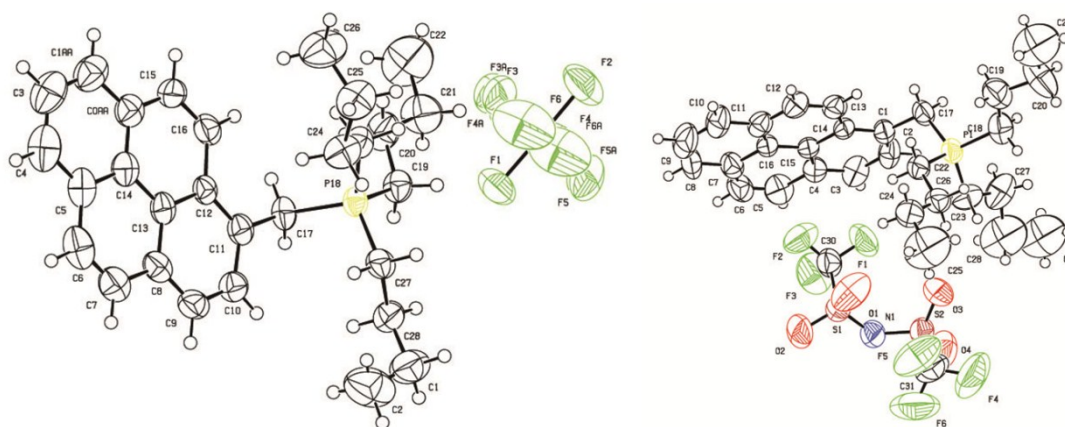
**Figure S1.** Fluorescence emission spectra of phosphonium salts in different states in solid state (excited at the corresponding maximum excitation wavelength).

#### IV. X-Ray structure determination

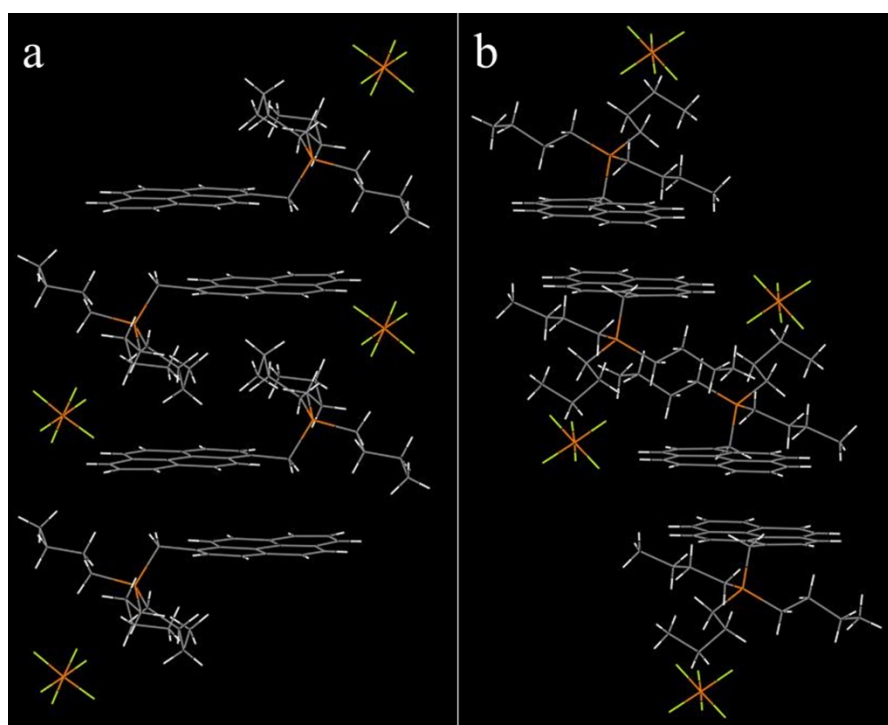
Colorless block crystals of tributyl(pyren-1-ylmethyl)phosphonium hexafluorophosphate  $\mathbf{1} \cdot \text{PF}_6$  were obtained by slow evaporation of an ethyl acetate solution and light yellow block crystals tributyl(pyren-1-ylmethyl)phosphonium bis((trifluoromethyl)sulfonyl)amide  $\mathbf{1} \cdot \text{NTf}_2$  were obtained by slow diffusion of  $\text{Et}_2\text{O}$  to the MeOH solution in refrigerator. X-Ray single-crystal diffraction data were collected on a Oxford Xcalibur E CCD area-detector diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\omega$  scan mode. The crystal parameters, data collection and refinement results for the compound are summarized in Table S1.

**Table S1. Crystallographic Data for tributyl(pyren-1-ylmethyl)phosphonium hexafluorophosphate ( $1 \cdot \text{PF}_6$ ) and tributyl(pyren-1-ylmethyl)phosphonium bis((trifluoromethyl)sulfonyl)amide ( $1 \cdot \text{NTf}_2$ ).**

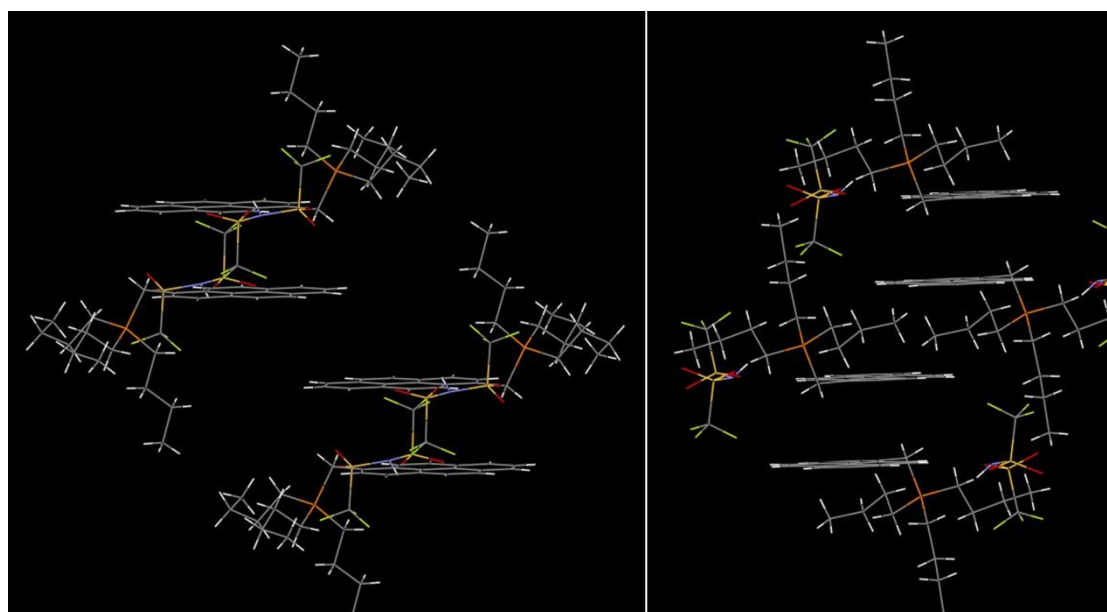
	$1 \cdot \text{PF}_6$	$1 \cdot \text{NTf}_2$
empirical formula	$\text{C}_{29}\text{H}_{38}\text{F}_6\text{P}_2$	$\text{C}_{31}\text{H}_{38}\text{F}_6\text{NO}_4\text{PS}_2$
formula weight (M)	562.53	697.71
temperature (K)	293(2)	100(2)
wavelength ( $\text{\AA}$ )	0.71073	0.71073
crystal system	triclinic	triclinic
space group	$P-1$	$P-1$
$a$ ( $\text{\AA}$ )	10.7112(6)	10.7725(3)
$b$ ( $\text{\AA}$ )	11.0294(6)	16.6577(5)
$c$ ( $\text{\AA}$ )	13.6960(5)	18.3152(7)
$\alpha$ (deg)	107.945(4)	98.142(3)
$\beta$ (deg)	96.334(4)	94.137(3)
$\gamma$ (deg)	107.336(5)	92.423(2)
$V$ ( $\text{\AA}^3$ )	1432.53(12)	3240.38(19)
$Z$	2	2
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.304	1.432
$\mu$ ( $\text{mm}^{-1}$ )	0.207	2.593
$F(000)$	592	1460
crystal size (mm)	0.30 $\times$ 0.20 $\times$ 0.20	0.80 $\times$ 0.80 $\times$ 0.50
reflns collected	11380	27178
unique reflns	5842	12306
$R_{\text{int}}$	0.0205	0.0550
goodness-of-fit on $F^2$	1.068	1.047
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0634, 0.1793	0.0715, 0.1911



**Figure S2.** ORTEP drawing of the single crystal of  $1 \cdot \text{PF}_6$  (left) and  $1 \cdot \text{NTf}_2$  (right) with 50% probability thermal ellipsoids.

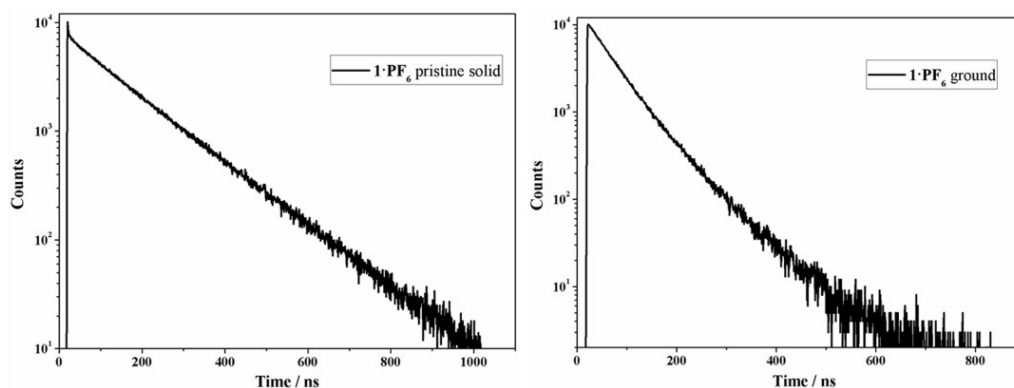


**Figure S3.** Molecular stacking of the single crystals of  $1 \cdot \text{PF}_6$ : side view (left) and front view (right).



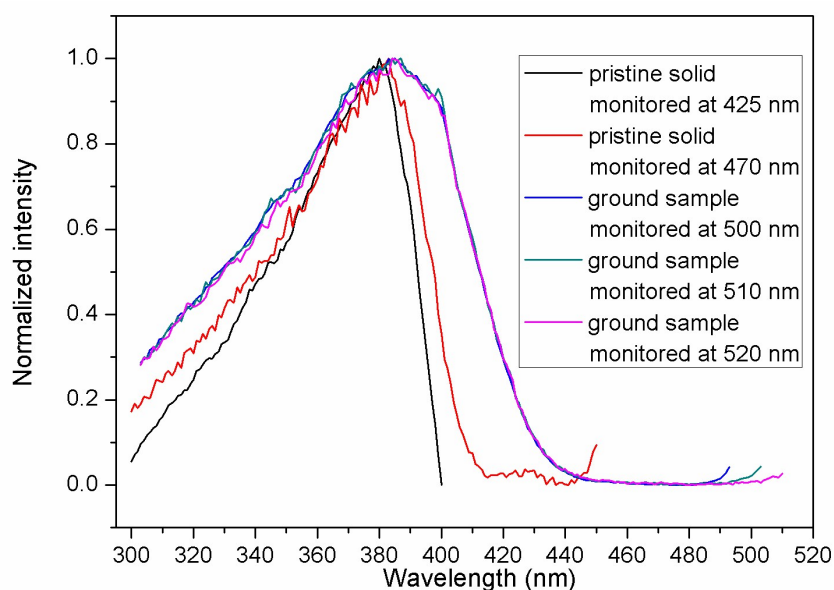
**Figure S4.** Molecular stacking of the single crystals of  $1 \cdot \text{NTf}_2$ : side view (left) and front view (right).

## V. Fluorescence decay profiles of $1\text{-PF}_6$ in different states



**Figure S5.** Fluorescence decay profiles of the pristine powder (left) and ground sample (right) of  $1\text{-PF}_6$ .

## V. Excitation of $1\text{-PF}_6$ in different states



**Figure S6.** Excitation of the pristine powder and ground sample of  $1\text{-PF}_6$  monitored in different emission wavelength.

After grinding, red-shifted excitation could be observed for the ground sample of  $1\text{-PF}_6$ , which was in accordance with the enhanced  $\pi\text{-}\pi$  interactions of the adjacent pyrene planes in the amorphous phase emerged by grinding.

## VII. References

- [1] S. Y. Park, J. H. Yoon, C. S. Hong, R. Souane, J. S. Kim, S. E. Matthews, J. Vicens, *J. Org. Chem.* **2008**, *73*, 8212.

# VIII. Copies of $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ and $^{31}\text{P}$ NMR spectra

