Supporting Information

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

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Table of Contents

I. General remarks ............................................................................................................. S3

II. Synthesis of phosphonium salts .................................................................................. S3

III. Physical and photophysical properties of phosphonium salts .............................. S8

IV. X-Ray structure determination .................................................................................. S10

V. Fluorescence decay profiles of 1·PF$_6$ in different states ........................................ S13

VI. Excitation of 1·PF$_6$ in different states .................................................................... S13

VII. References ................................................................................................................. S14

VIII. Copies of $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra ................................................ S15
I. General remarks

NMR spectra were obtained on a Bruker AV II-400 (Germany). The $^1$H NMR chemical shifts were measured relative to DMSO-$d_6$ or CDCl$_3$ as the internal reference (DMSO-$d_6$: $\delta = 2.50$ ppm; CDCl$_3$: $\delta = 7.26$ ppm). The $^{13}$C NMR chemical shifts were given using DMSO-$d_6$ or CDCl$_3$ as the internal standard (DMSO-$d_6$: $\delta = 39.52$ ppm; 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. DMSO-$d_6$ and CDCl$_3$ were purchased from Alfa. Other reagents and solvents were obtained from Chengdu Kelong Chemical Reagent Factory. Silica gel (size: 45-75 µm, relative surface area: 600-800 m$^2$/g) was purchased from Qingdao Haiyang Chemical Factory. The 1-(bromomethyl)pyrene were prepared according to the literature procedures.[1]

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 N$_2$. The reaction system was then evacuated and backfilled with 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), CH$_2$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$_2$Cl$_2$ for 3 times. The combined organic phases were dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel (MeOH/CH$_2$Cl$_2$) to afford the desired product.

![Tributyl(pyren-1-ylmethyl)phosphonium bromide (1·Br)](image)

**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$_2$Cl$_2$ = 1/15, v/v) afforded 1·Br as a white solid (953.4 mg, 96% yield). $^1$H NMR (DMSO-$d_6$, 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. $^{13}$C NMR (DMSO-$d_6$, 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. $^{31}$P NMR (DMSO-$d_6$, 162 MHz): $\delta$ = 34.36 ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{38}$P [M]$^+$ 417.2706, found 417.2697. Elemental analysis calcd (%) for M+H$_2$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$_2$)](image)
Following the general procedure, **1·Br** (497.5 mg, 1.0 mmol) and LiNTf$_2$ (574.2 mg, 2.0 mmol) were used. Purification via column chromatography on silica gel (MeOH/CH$_2$Cl$_2$ = 1/20, v/v) afforded **1·NTf$_2$** as a white solid (674.2 mg, 97% yield).

$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 0.78$ (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. $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta = 18.0, 18.4, 23.0$ (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, 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. $^{19}$F NMR (DMSO-$d_6$, 376 MHz): $\delta = -78.72$ ppm. $^{31}$P NMR (DMSO-$d_6$, 162 MHz): $\delta = 34.40$ ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{38}$P [M]$^+$ 417.2706, found 417.2707. Elemental analysis calcd (%) for M+H$_2$O: C 52.02, H 5.63, N 1.96, found: C 52.20, H 5.60, N 1.79.

[Diag 1]

**Tributyl(pyren-1-ylmethyl)phosphonium hexafluorophosphate (1·PF$_6$)**

Following the general procedure, **1·Br** (497.5 mg, 1.0 mmol) and KPF$_6$ (368.1 mg, 2.0 mmol) were used. Purification via column chromatography on silica gel (MeOH/CH$_2$Cl$_2$ = 1/20, v/v) afforded **1·PF$_6$** as a white solid (524.8 mg, 93% yield).

$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 0.77$ (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. $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta = 18.0, 18.5, 23.0$ (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. $^{19}$F NMR (DMSO-$d_6$, 376 MHz): $\delta = -69.15, -71.04$ ppm. $^{31}$P
NMR (DMSO-$d_6$, 162 MHz): $\delta = 34.38, -130.98, -135.37, -139.76, -144.15, -148.54, -152.94, -157.33$ ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{38}$P [M]$^+$ 417.2706, found 417.2698. Elemental analysis calcd (%) for M+H$_2$O: C 60.00, H 6.94, found: C 60.77, H 6.60.

Tributyl(pyren-1-ylmethyl)phosphonium tetrafluoroborate (1·BF$_4$)

Following the general procedure, 1·Br (497.5 mg, 1.0 mmol) and NaBF$_4$ (219.6 mg, 2.0 mmol) were used. Purification via column chromatography on silica gel (MeOH/CH$_2$Cl$_2$ = 1/20, v/v) afforded 1·BF$_4$ as a white solid (454.8 mg, 90% yield).

$^1$H NMR (DMSO-$d_6$, 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. $^{13}$C NMR (DMSO-$d_6$, 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. $^{19}$F NMR (DMSO-$d_6$, 376 MHz): $\delta = -148.21$, $-148.24$ ppm. $^{31}$P NMR (DMSO-$d_6$, 162 MHz): $\delta = 34.40$ ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{38}$P [M]$^+$ 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/CH₂Cl₂ = 1/15, v/v) afforded 2·Br as a white solid (1.1310 g, 98% yield). ¹H NMR (DMSO- d₆, 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. ¹³C NMR (DMSO-d₆, 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. ³¹P NMR (DMSO-d₆, 162 MHz): δ = 32.44 ppm. HRMS (ESI⁺): calcd for C₃₅H₄₄P [M⁺] 495.3175, found 495.3123. Elemental analysis calcd (%) for M+H₂O: C 70.82, H 7.81, found: C 71.02, H 7.67.

![Triocetyl(pyren-1-ylmethyl)phosphonium bromide (3·Br)](image)

Triocetyl(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/CH₂Cl₂ = 1/20, v/v) afforded 3·Br as a white solid (1.2353 g, 93% yield). ¹H NMR (DMSO- d₆, 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. ¹³C NMR (DMSO-d₆, 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. \(^{31}\)P NMR (DMSO-\(d_6\), 162 MHz): \(\delta = 34.01\) ppm. HRMS (ESI\(^+\)) : calcd for C\(_{41}\)H\(_{62}\)P [M]\(^+\) 585.4584, found 585.4575. Elemental analysis calcd (%) for M+H\(_2\)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/CH\(_2\)Cl\(_2\) = 1/20, v/v) afforded 4·Br as a white solid (1.0854 g, 85% yield). \(^1\)H NMR (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. \(^{13}\)C NMR (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. \(^{31}\)P NMR (CDCl\(_3\), 162 MHz): \(\delta = 28.86\) ppm. HRMS (ESI\(^+\)) : calcd for C\(_{40}\)H\(_{48}\)P [M]\(^+\) 573.3645, found 573.3643. Elemental analysis calcd (%) for M+H\(_2\)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/CH₂Cl₂ = 1/15, v/v) afforded 5·Br as a white solid (1.0350 g, 93% yield). ¹H NMR (DMSO-d₆, 400 MHz): δ = 5.95 (d, J = 15.6, 2H), 7.58-7.69 (m, 12H), 7.79-7.84 (m, 5H), 7.94 (d, J = 9.2Hz, 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. ¹³C NMR (DMSO-d₆, 100 MHz): δ = 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. ³¹P NMR (DMSO-d₆, 162 MHz): δ = 22.55 ppm. HRMS (ESI⁺): calcd for C₃₅H₂₆P [M]+ 477.1767, found 477.1764. Elemental analysis calcd (%) for M+H₂O: 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 \(1\cdot\text{PF}_6\) were obtained by slow evaporation of an ethyl acetate solution and light yellow block crystals tributyl(pyren-1-ylmethyl)phosphonium bis((trifluoromethyl)sulfonyl)amide \(1\cdot\text{NTf}_2\) were obtained by slow diffusion of Et\(_2\)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 Ka radiation (\(\lambda = 0.71073 \ \text{Å}\)) 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·PF₆) and tributyl(pyren-1-ylmethyl)phosphonium bis((trifluoromethyl)sulfonyl)amide (1·NTf₂).

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Figure S2. ORTEP drawing of the single crystal of 1·PF₆ (left) and 1·NTf₂ (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·PF₆ in different states

![Fluorescence decay profiles of 1·PF₆](image)

Figure S5. Fluorescence decay profiles of the pristine powder (left) and ground sample (right) of 1·PF₆.

V. Excitation of 1·PF₆ in different states

![Excitation spectra of 1·PF₆](image)

Figure S6. Excitation of the pristine powder and ground sample of 1·PF₆ monitored in different emission wavelength.

After grinding, red-shifted excitation could be observed for the ground sample of 1·PF₆, which was in accordance with the enhanced π–π interactions of the adjacent pyrene planes in the amorphous phase emerged by grinding.
VII. References

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