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# Supporting Information for

# A kinetically protected pyrene: molecular design, bright blue emission in the crystalline state and aromaticity relocation in its dicationic species

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#### 1. Instrumentation and Materials

<sup>1</sup>H NMR (400 MHz or 300 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded with JEOL JNM-ECX 400 and 300 spectrometers at ambient temperature by using tetramethylsilane as an internal standard. The high-resolution MS were measured by a JEOL JMS-700 MStation spectrometer and a BRUKER Autoflex II MALDI TOF MS. The high-resolution atmosphere pressure chemical ionization (APCI) MS were performed on a BRUKER DALTONICS micrOTOF using positive and negative ion modes. X–ray crystallographic data were recorded at 100 K on a Rigaku R-AXIS RAPID/S using Mo-K $\alpha$  radiation. The diffraction data were processed with Crystal Structure of the Rigaku program, solved with the SIR-97 program and refined with the SHELX-97 program.<sup>[S1]</sup>

UV/Vis absorption spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570. CV measurements were conducted in a solution of 0.1 M TBAPF<sub>6</sub> in dry dichloromethane with a scan rate of 100 mV/s at room temperature in an argon-filled cell. A glassy carbon electrode and a Pt wire were used as a working and a counter electrode, respectively. An Ag/Ag<sup>+</sup> electrode was used as reference electrodes, which were normalized with the half-wave potential of ferrocene/ferrocenium<sup>+</sup> (Fc/Fc<sup>+</sup>) redox couple.

TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All other solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification. For spectral measurements, spectral-grade chloroform was purchased from Nacalai Tesque.

#### 2. Experimental Section

**1,3,6,8-Tetrakis(3,3,4,4-tetramethyl-1,3,2-dioxabororanyl)pyrene** 5: A solution of 1,3,6,8-tetrabromopyrene (5.0 g, 9.66 mmol), 4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (20 ml, 0.138 mol) and Et<sub>3</sub>N (30 ml, 0.216 mol) in dry toluene (100 ml) was degassed with argon for 30 min. To the mixture, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (1.0 g, 1.84 mmol) was added, and the resultant solution was refluxed under argon atmosphere for 2 days. The progress of the reaction was monitored by APCI mass spectroscopic analysis. After cooled to room temperature, the organic products were extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with cool water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. Precipitation from CH<sub>2</sub>Cl<sub>2</sub>/ toluene gave the pure compound **5** (5.0 g, 7.08 mmol, 74%) as a light gray solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.16 (s, 4H), 8.98 (s, 2H), and 1.49 (s, 48H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.29, 137.96, 129.41, 123.96, 83.82, and 25.09 ppm; HR-MS (Spiral MALDI): *m*/*z*: calcd for C<sub>40</sub>H<sub>54</sub>B<sub>4</sub>O<sub>8</sub>, 706.4185 [*M*]<sup>+</sup>; found: 706.4198; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 280 (23637), 291 (38808), 366 (36219), and 386 (46860) nm.

**1-Bromo-4-mesityloxynaphthalene 6**: To a solution of 1-(mesityloxy)naphthalene (2.0 g, 7.63 mmol) in CH<sub>3</sub>CN (100 ml) was added NBS (1.5 g, 8.43 mmol) under nitrogen in the dark for 3 h. After the reaction was completed, the solvent was evaporated under reduced pressure. The oil residue was purified by chromatography on silica gel (hexane), which gave **6** (2.4 g, 6.74 mmol, 90%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.53 (d, *J* = 8.0 1H), 8.22 (d, *J* = 8.4 1H), 7.69-7.60 (m, 2H), 7.49 (d, *J* = 8.0 1H), 6.95 (s, 2H), 6.22 (d, *J* = 8.0 1H), 2.33 (s, 3H), and 2.08 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 153.34, 148.70, 134.82, 132.75, 130.83, 129.71, 129.46, 127.89, 127.03, 126.21, 126.18, 122.45, 113.76, 106.72, 20.81, and 15.99 ppm; HR-MS (EI): *m/z*: calcd for C<sub>19</sub>H<sub>17</sub>O<sub>1</sub>Br<sub>1</sub>, 340.0463 [*M*]<sup>+</sup>; found: 340.0459; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 304 and 318 (sh) nm.

**2-(4-(Mesityloxy)naphthalene-1-yl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane 9**: To a solution of **6** (2.0 g, 5.87 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bis(1,3,2-dioxaborolane) (2.1 g, 8.27 mmol), and KOAc (3.6 g, 36.7 mmol) in 1,4-dioxane (10 ml) was degassed by three freeze-pump-thaw cycles. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), dichloromethane adduct (150 mg, 0.18 mmol) was added to the solution through counter flow argon, the mixture was heated at 85 °C for 14 h. The reaction mixture was poured to water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The solid residue was purified by chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:3), which gave **9** (1.4 g, 3.61 mmol, 61%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.81 (d, *J* = 8.4 1H), 8.53 (d, *J* = 8.4 1H), 7.85 (d, *J* = 7.6 1H), 7.87-7.52 (m, 2H), 6.95 (s, 2H), 6.33 (d, *J* = 7.6 1H), 2.34 (s, 3H), 2.07 (s, 6H), and 1.39 (s, 12H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.29, 148.78, 138.54, 136.65, 134.60, 130.92, 129.61, 128.31, 127.01, 125.07, 124.82, 122.04, 105.44, 83.43,

24.93, 20.84, and 15.99 ppm; HR-MS (EI): m/z: calcd for C<sub>25</sub>H<sub>29</sub>O<sub>3</sub><sup>10</sup>B, 387.2246 [M]<sup>+</sup>; found: 387.2242; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max} = 303$ , 312 (sh) nm.

**1,3,6,8-Tetrakis(4-(mesityloxy)naphthalene-1-yl)pyrene 1**: A mixture of aqueous 0.5 M K<sub>3</sub>PO<sub>4</sub> solution (20 ml) and THF (30 ml) was degassed by three freeze-pump-thaw cycles. Compound **5** (300 mg, 0.42 mmol), **6** (630 mg, 1.84 mmol), and Buchwald catalyst<sup>[52]</sup> (see scheme 2) (70 mg, 20 mol%) were added to the solution through counter flowed by argon, the mixture was heated at 60°C for 8 h. After cooled to room temperature, the reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The solid residue was purified by chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:2). Recrystallization from CHCl<sub>3</sub>/hexane gave **1** (169 mg, 0.14 mmol, 32%) as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 60°C):  $\delta$  = 8.61 (d, *J* = 8.0 4H), 8.05 (s, 2H), 7.69 (s, 4H), 7.58-7.51 (m, 8H), 7.43-7.36 (m, 8H), 6.96 (s, 8H), 6.47 (d, *J* = 7.6 4H) 2.34 (s, 12H), and 2.16 (s, 24H) ppm; <sup>13</sup>C NMR (100 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  = 153.09, 148.85, 135.36, 134.53, 133.98, 130.96, 129.78, 129.68, 129.61, 128.56, 128.40, 126.53, 125.70, 125.11, 124.77, 124.75, 122.24, 120.20, 105.65, 20.84, and 16.21 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for C<sub>92</sub>H<sub>74</sub>O<sub>4</sub>, 1242.5582 [*M*]<sup>+</sup>; found, 1242.5576; UV-vis (toluene):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 372 (41253) nm.

**1,3,6,8-Tetrakis(4,5-bis(mesityloxy)anthracen-9-yl)pyrene 2**: A mixture of aqueous 0.5 M K<sub>3</sub>PO<sub>4</sub> solution (5 ml) and THF (5 ml) was degassed by three freeze-pump-thaw cycles. Compound **5** (18 mg, 0.03 mmol), **7** (60 mg, 0.11 mmol), and Buchwald catalyst (5 mg, 20 mol%) were added to the solution through counter flowed by argon, the mixture was heated at 50°C for 8 h. After cooled to room temperature, the reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The solid residue was purified by chromatography on silica gel (CHCl<sub>3</sub>), which gave **2** (20 mg, 0.010 mmol, 40%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 60°C):  $\delta$  = 9.88 (s, 4H), 8.16 (s, 2H), 7.52 (s, 4H), 7.26 (d, *J* = 8.8 8H), 7.07 (t, *J* = 8.4 8H), 6.94 (s, 16H), 6.28 (d, *J* = 7.2 8H) 2.32 (s, 24H), and 2.15 (s, 48H) ppm; <sup>13</sup>C NMR of **2** could not be measured due to the low solubility; HR-MS (Spiral MALDI) *m*/*z*: calcd for C<sub>144</sub>H<sub>122</sub>O<sub>8</sub>, 1978.9134 [*M*]<sup>+</sup>; found, 1978.9120; UV-vis (toluene):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 353 (sh, 32176), 372 (44969), 392 (57927), and 414 (53649) nm.

**4,5,9,10-Tetrakis(4-(mesityloxy)naphthalen-1-yl)pyrene 3**: A mixture of aqueous 0.5 M K<sub>3</sub>PO<sub>4</sub> solution (30 ml) and THF (30 ml) was degassed by three freeze-pump-thaw cycles. Compound **8** (100 mg, 0.15 mmol), **9** (700 mg, 1.80 mmol), and Buchwald catalyst (100 mg, 0.13 mmol) was added to the solution through counter flowed by argon, the mixture was heated at 60°C for 10 h. After cooled to room temperature, the reaction mixture was poured into water and extracted with  $CH_2Cl_2$ . The organic layer was dried over  $Na_2SO_4$  and the solvent was removed under reduced pressure. The solid residue was purified by chromatography on silica gel  $(CH_2Cl_2/hexane = 1:3)$ , followed by recycling GPC. Recrystallization from  $CHCl_3/hexane$  gave

**3** (35 mg, 0.03 mmol, 18%) as a white solid. <sup>1</sup>H NMR (400 MHz,  $C_2D_2Cl_4$ , 100°C):  $\delta = 8.47$  (d, J = 8.0 4H), 7.73 (d, J = 8.0 4H), 7.67 (s, 2H), 7.64 (d, J = 8.0 4H), 7.47 (t, J = 8.0 4H), 7.31 (t, J = 8.0 4H), 7.03 (d, J = 8.0 4H), 6.91 (s, 8H), 6.03 (d, J = 8.0 4H) 2.33 (s, 12H), and 1.99 (bs, 24H) ppm; <sup>13</sup>C NMR (100 MHz,  $C_2D_2Cl_4$ ):  $\delta = 153.03$ , 149.33, 137.93, 134.85, 134.61, 132.39, 131.23, 130.41, 129.80, 127.55, 126.96, 126.58, 126.31, 125.47, 125.26, 124.94, 124.57, 122.25, 105.62, 20.84, 16.15 and 16.06 ppm; HR-MS (Spiral MALDI): m/z: calcd for  $C_{92}H_{74}O_4$ , 1242.5582 [*M*]<sup>+</sup>; found, 1242.5587; UV-vis (toluene):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 304 (50530),, 322 (sh, 42194), 353 (27810), 380 (sh, 1975), nm.

3. <sup>1</sup>NMR Spectra



**Figure S1.** <sup>1</sup>H NMR spectrum of **5** in CDCl<sub>3</sub> at room temperature.



**Figure S2.** <sup>13</sup>C NMR spectrum of **5** in CDCl<sub>3</sub> at room temperature.



**Figure S3.** <sup>1</sup>H NMR spectrum of **1** in  $C_2D_2Cl_4$  at 60°C.



**Figure S4.** <sup>13</sup>C NMR spectrum of **1** in  $C_2D_2Cl_4$  at room temperature.



**Figure S5.** <sup>1</sup>H NMR spectrum of **2** in  $C_2D_2Cl_4$  at 60°C.



**Figure S6.** <sup>1</sup>H NMR spectrum of **3** in  $C_2D_2Cl_4$  at 100°C.



**Figure S7.** <sup>13</sup>C NMR spectrum of **3** in  $C_2D_2Cl_4$  at room temperature.



4. HR-MS

Figure S8. HR-Spiral-MALDI-TOF mass spectrum of 5.



Figure S9. HR-Spiral-MALDI-TOF mass spectrum of 1.



Figure S10. HR- Spiral-MALDI -TOF mass spectrum of 2.



Figure S11. HR- Spiral-MALDI -TOF mass spectrum of 3.

## 5. Cyclic Voltammetry



**Figure S12.** Cyclic voltammogram (CV) and differential pulse voltammogram of **1**, **2** and **3** in CH<sub>2</sub>Cl<sub>2</sub>. Conditions; 0.1 M TBAPF<sub>6</sub>, Scan rate = 0.1 V s<sup>-1</sup>, [1] = 1.0 mM, [2] = 0.5 mM, [3] = 0.5 mM, working electrode: glassy carbon; counter electrode: Pt.

6. UV-vis Absorption and Fluorescence Spectra



Figure S13. UV-vis-NIR absorption and fluorescence spectra of 1-3 in toluene.



**Figure S14.** UV-vis-NIR absorption spectral change of **1** upon the oxidation with  $SbCl_5$ . Inset; Photographs of solution of **1** with the addition of 40 eq. of  $SbCl_5$  (left) and of 320 eq. (right).

Electrolysis UV spectrum of 1



**Figure S15.** UV-vis-NIR absorption spectra of  $1^{+}$  generated with SbCl<sub>5</sub> (in blue) and electrolysis (in red) at 0.8 V in CH<sub>2</sub>Cl<sub>2</sub>.

# 7. MO Calculations by DFT Method



**Figure S16.** Molecular orbital diagrams of **1**', **2**' and **3**'. Mesityl groups were replaced by methyl groups

# 8. ESR Spectra



**Figure S17.** ESR spectra of **1** upon the oxidation with 0.5 eq. of  $BCl_5$  (top) at RT,  $-20^{\circ}C$ ,  $-60^{\circ}C$  and  $-90^{\circ}C$  and (bottom) at  $-95^{\circ}C$  with simulation (solvent:  $CH_2Cl_2$ ).

9. NICS values



**Figure S18.** NICS(0) values at the selected positions of a) **1**, b) **1**<sup>+</sup>, c) **1**<sup>+</sup>, d bond lengths.

# 10. X-Ray Crystal Structures

Table S1. Crystal data and structure refinement for 5.

Empirical formula	C40H54B4O8
Formula weight	706.07
Temperature	103(2) K
Wavelength	0.71075 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.2939(4) Å
	$b = 10.7476(4)$ Å $\beta = 109.6730(10)$ °
	c = 15.7067(5) Å
Volume	1954.19(11) Å <sup>3</sup>
Ζ	2
Density (calculated)	1.200 Mg/m <sup>3</sup>
Absorption coefficient	$0.080 \text{ mm}^{-1}$
F(000)	756
Crystal size	0.20 x 0.13 x 0.12 mm <sup>3</sup>
Theta range for data collection	3.20 to 25.35°
Index ranges	$-14 \le h \le 14, -12 \le k \le 12, -18 \le l \le 18$
Reflections collected	26936
Independent reflections	3550 [R(int) = 0.0399]
Completeness to theta = $25.35^{\circ}$	99.5 %
Max. and min. transmission	0.9905 and 0.9842
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3550 / 4 / 268
Goodness-of-fit on F <sup>2</sup>	1.065
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0742, wR_2 = 0.2098$
R indices (all data)	$R1 = 0.0826, wR_2 = 0.2218$
Largest diff. peak and hole	0.721 and −0.293 e.Å <sup>-3</sup>



**Figure S19.** X-ray crystal structure of **5**. (a) Top view and (b) side view. Thermal ellipsoids were scaled to 50% probability.

**Table S2**. Crystal data and structure refinement for 1.

Empirical formula	C120H106O4	
Formula weight	1612.05	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 12.656(2) Å	$\alpha = 72.271(3)^{\circ}$
	b = 12.875(2) Å	$\beta = 84.227(3)$ °
	c = 16.048(3) Å	$\gamma = 63.603(3)^{\circ}$
Volume	2229.3(7) Å <sup>3</sup>	
Ζ	1	
Density (calculated)	1.201 Mg/m <sup>3</sup>	
Absorption coefficient	$0.071 \text{ mm}^{-1}$	
F(000)	858	
Crystal size	0.30 x 0.20 x 0.05 mm	3
Theta range for data collection	1.80 to 25.00°	
Index ranges	$-14 \leq h \leq 15, -13 \leq k \leq$	$15,-12 \leq l \leq 19$
Reflections collected	11554	
Independent reflections	7713 [ <i>R</i> (int) = 0.0337]	
Completeness to theta = $25.00^{\circ}$	98.4%	
Absorption correction	Empirical	
Max. and min. transmission	0.9965 and 0.9791	
Refinement method	Full-matrix least-squa	ares on $F^2$
Data / restraints / parameters	7713 / 0 / 538	
Goodness-of-fit on F <sup>2</sup>	1.027	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0798, wR_2 = 0.2$	054
R indices (all data)	$R_1 = 0.1348, wR_2 = 0.2$	467
Largest diff. peak and hole	0.522 and -0.429 e.Å $^{\!\!-\!\!3}$	



**Figure S20.** X-ray crystal structure of **1**. (a) Top view; (b) Side view. Thermal ellipsoids were scaled to 50% probability.

## **Table S3**. Crystal data and structure refinement for 2

Empirical formula	C144H122O8
Formula weight	1980.42
Temperature	103(2) K
Wavelength	0.71075 Å
Crystal system	Orthorhombic
Space group	Fddd
Unit cell dimensions	a = 22.3697(12) Å
	b = 23.8656(14) Å
	c = 59.021(4) Å
Volume	31509(3) Å <sup>3</sup>
Ζ	8
Density (calculated)	$0.835 \text{ Mg/m}^3$
Absorption coefficient	$0.051 \text{ mm}^{-1}$
F(000)	8400
Crystal size	0.10 x 0.06 x 0.03 mm <sup>3</sup>
Theta range for data collection	3.04 to 23.50°
Index ranges	$-25 \le h \le 25, -26 \le k \le 26, -66 \le l \le 66$
Reflections collected	89710
Independent reflections	5795 [R(int) = 0.1138]
Completeness to theta = $23.50^{\circ}$	99.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9985 and 0.9950
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5795 / 438 / 411
Goodness-of-fit on F <sup>2</sup>	1.129
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1258, wR_2 = 0.3171$
R indices (all data)	$R_1 = 0.2317, wR_2 = 0.3914$
Largest diff. peak and hole	0.283 and -0.194 e.Å <sup>-3</sup>

\*The contributions to the scattering arising from the presence of the disordered solvents in the crystals were removed by use of the utility SQUEEZE in the PLATON software package.<sup>[S3]</sup>



Figure S21. X-ray crystal structure of 2. Thermal ellipsoids were scaled to 20% probability.

## **Table S4**. Crystal data and structure refinement for 3

Empirical formula	C92H74O4
Formula weight	1243.51
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 42.2144(8) Å
	$b = 8.82075(16)$ Å $\beta = 117.2730(10)$ °
	c = 23.4233(4) Å
Volume	7752.4(2) Å <sup>3</sup>
Ζ	4
Density (calculated)	$1.065 \text{ Mg/m}^{3}$
Absorption coefficient	$0.064 \text{ mm}^{-1}$
F(000)	2632
Crystal size	$0.22 \ge 0.05 \ge 0.05 \ \text{mm}^3$
Theta range for data collection	3.23 to 27.48°
Index ranges	$-54 \leq h \leq 54, -11 \leq k \leq 11, -30 \leq l \leq 30$
Reflections collected	65154
Independent reflections	8886 [ <i>R</i> (int) = 0.0661]
Completeness to theta = $27.48^{\circ}$	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.9968 and 0.9861
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	8886 / 0 / 439
Goodness-of-fit on F <sup>2</sup>	1.054
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0613, wR_2 = 0.1714$
R indices (all data)	$R_1 = 0.0797, wR_2 = 0.1852$
Largest diff. peak and hole	0.366 and −0.318 e.Å <sup>-3</sup>

\*The contributions to the scattering arising from the presence of the disordered solvents in the crystals were removed by use of the utility SQUEEZE in the PLATON software package.<sup>[S3]</sup>



Figure S22. X-ray crystal structure of 3. Thermal ellipsoids were scaled to 50% probability.



**Figure S23**. Crystal packing view of **1**. For clarity, pyrene units are shown as a space-filling model, and hydrogen atoms and solvent molecules are omitted.

#### 11. References

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