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Electronic Supplementary Information for

# Liquefaction-induced emission enhancement of tetraphenylethene derivatives

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### **Experimental section**

**Materials.** Unless stated otherwise, all other reagents were obtained from commercial sources and used without further purification. Tetra(4-hydroxyphenyl)ethane (**TPE-4OH**),<sup>1</sup> 1-bromo-2-hexyldecane,<sup>2</sup> 1-bromo-2-octyldodecane,<sup>2</sup> 2-octyl-1-dodecanoic acid,<sup>3</sup> **1me**,<sup>1</sup> and **2me**<sup>4</sup> was synthesized and characterized according to the reported method. The reaction was carried out under nitrogen atmosphere. DMAP: *N*,*N*-dimethyl-4-aminopyridine, EDC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide.

**Measurements.** <sup>1</sup>H (500 MHz) and <sup>13</sup>C (126 MHz) NMR measurements were recorded on a Bruker Biospin AVANCE DRX500 instrument, using 0.05% tetramethylsilane (TMS) as an internal standard. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra were obtained with SHIMADZU RF5300PC spectrofluorometer. The absolute luminescence quantum yield ( $\Phi_F$ ) was measured by a Hamamatsu C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and a 150W continuous-wave xenon light source. Fourier transform infrared (FTIR) spectra were observed with a JASCO FTIR-4100 SK spectrometer with a diamond prism kit PKS-ZNSE for (attenuated total reflection) ATR technique. Differential Scanning Calorimetry (DSC) was conducted by METLLER TOLEDO DSC1 Star System with heating rate of 10 °C /min under nitrogen atmosphere. X-ray diffraction (XRD) patterns were obtained by using a Bruker D8Advance / D with Cu K $\alpha$  radiation source (40 kV, 40mA). Optical / Polarization micrographs were obtained by using a TA Instruments SNZ1000 stereoscopic zoom microscope. Viscosity measurement was conducted by using a TA Instruments ARES-G2 Viscometer and Brookfield Engineering DV2T Viscometer. Electron spray ionization mass spectroscopy (ESI-MS) was carried out at Global facility center, Hokkaido University.

# X-ray Crystallography Analyses

Single-crystals of **1me** and **2me** were mounted in the loop using paraffin oil. The data were collected on a Rigaku AFC-7R Mercury diffactometer with graphite monochromated Mo K $\alpha$  radiation (0.71069 Å) and a rotating-anode generator operating at 50 kV and 200 mA. Diffraction data were collected and processed using the CrystalClear program.<sup>5</sup> Structures were solved by direct methods using SHELXS-97.<sup>6</sup> Structural refinements were conducted by the full-matrix least-squares method using SHELXH-97.<sup>6</sup> Non-H atoms were refined anisotropically, and H atoms were refined using the riding model. All calculations were performed using the Yadokari-XG software package.<sup>7</sup>

### Synthesis of 1a and 1b



Scheme S1. Synthetic route for ether compounds 1a and 1b.

In a 50 mL three necked flask, tetra(4-hydroxyphenyl)ethene (**TPE-4OH**, 132 mg, 0.333 mmol), K<sub>2</sub>CO<sub>3</sub> (553 mg, 4.00 mmol) and KI (3.38 mg, 0.0204 mmol) were added into anhydrous DMF (10 mL). An alkyl bromide (2.13 mmol) in anhydrous DMF (2 mL) was then added dropwise, and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, water and CHCl<sub>3</sub> were added. The organic layer was separated and the water layer was extracted with CHCl<sub>3</sub>. The organic layer was combined, washed with brine three times and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the resulting crude product was purified by silica gel column chromatography (n-hexane / CHCl<sub>3</sub> = 5 / 1) to afford **1a** and **1b** as a yellow viscous liquid.

**1a** (61%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 6.91 (8H, d, J = 8.7 Hz), 6.62 (8H, d, J = 8.8 Hz), 3.74 (8H, d, J = 5.8 Hz), 1.78-1.70 (4H, m), 1.42-1.20 (80H, m), 0.87 (24H, t, J = 6.9 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 157.55, 138.26, 136.80, 132.51, 113.58, 70.83, 38.04, 31.93, 31.37, 30.04, 29.71, 29.61, 29.36, 26.89, 22.70, 14.14. HRMS(ESI) Calcd. for C<sub>90</sub>H<sub>148</sub>O<sub>4</sub> [M+H]<sup>+</sup>: *m/z* 1294.1456, Found: *m/z* 1294.1450.

**1b** (35%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 6.90 (8H, d, J = 8.8 Hz), 6.62 (8H, d, J = 8.8 Hz), 3.74 (8H, d, J = 5.7 Hz), 1.76-1.65 (4H, m), 1.42-1.20 (136H, m), 0.88 (24H, t, J = 6.9 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 157.56, 138.27, 136.81, 132.51, 113.59, 70.84, 38.04, 31.94, 31.37, 30.05, 29.67, 29.37, 26.90, 22.72, 14.15; HRMS(ESI) Calcd. for C<sub>106</sub>H<sub>180</sub>O<sub>4</sub> [M+H]<sup>+</sup>: *m/z* 1518.3960. Found: *m/z* 1518.3954..



Scheme S2. Synthetic route for ester compounds 2a-c.

In a 100 mL three necked flask, tetra(4-hydroxyphenyl)ethene (300 mg, 0.757 mmol), DMAP (407 mg, 3.33 mmol) were dissolved in anhydrous CHCl<sub>3</sub> (40 mL). After the solution was cooled, a carbonic acid (3.33 mmol) and EDC·HCl in anhydrous CHCl<sub>3</sub> (15 mL) was added dropwise to the solution. The mixture was stirred at room temperature for 18h. Then the mixture was washed with diluted HCl and H<sub>2</sub>O, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the resulting crude product was purified by silica gel column chromatography using n-hexane / ethyl acetate mixture as an eluent. The volume ratio of n-hexane to ethyl acetate was adjusted according to each molecule. The products were given as a yellow viscous liquid. **2a** (87%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.01 (8H, d, J = 8.6 Hz), 6.82 (8H, d, J = 8.7 Hz), 2.55-2.48 (4H, m), 1.75-1.67 (15H, m), 1.58-1.50 (8H, m), 1.39-1.25 (80H, m), 0.89-0.85 (24H, m). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 174.81, 149.47, 140.69, 139.54, 132.34, 121.06, 45.86, 32.50, 31.84, 31.68, 29.58, 29.44, 29.24, 27.46, 22.63, 14.06. HRMS(ESI) Calcd. for C<sub>90</sub>H<sub>140</sub>O<sub>8</sub> [M+Na]<sup>+</sup>: *m/z* 1372.0446. Found: *m/z* 1372.0440. **2b** (34%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.02 (8H, d, J = 8.8 Hz), 6.82 (8H, d, J = 8.5 Hz), 2.55-2.48 (4H, sep, J = 5.3 Hz), 1.61-1.45 (8H, m), 1.40-1.20 (112H, m), 0.88 (24H, t, J = 6.3 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 174.88, 149.43, 140.69, 139.51, 132.36, 121.08, 45.86, 32.50, 31.92, 29.62, 29.50, 29.45, 29.30, 27.51, 22.71, 14.14. HRMS(ESI) Calcd. for C106H172O8 [M+Na]+: m/z 1596.2950. Found: m/z 1596.2944.

**2c** (87%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.00 (8H, d, J = 8.7 Hz), 6.84 (8H, d, J = 8.7 Hz), 2.50 (8H, t, J = 7.5 Hz), 1.72 (8H, quin, J = 7.5 Hz), 1.21-1.40 (64H, m), 0.88 (12H, t, J = 6.9 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 172.10, 149.39, 140.58, 139.63, 132.33, 120.95, 34.43, 31.93, 29.62, 29.47, 29.35, 29.29, 29.12, 24.91, 22.71, 14.15. HRMS(ESI) Calcd. for C<sub>74</sub>H<sub>108</sub>O<sub>8</sub> [M+Na]<sup>+</sup>: *m/z* 1147.7942. Found: *m/z* 1147.7936.



Fig. S1 XRD patterns of 2c and TPE.



Fig. S2 Photoluminescence spectra of the TPE derivatives 1a, 1b and 2a-c in the dissolved state in THF (dotted line) and the aggregated state (solid line) in the mixed solvent of THF/H<sub>2</sub>O (v/v = 1/99) ( $\lambda_{ex} = 350$  nm).



Fig. S3 Photoluminescence quantum yield of 2a in THF and 2-hexyldenanoic acid with various molar ratio.



Fig. S4 Photoluminescence spectra of 1me (black) and 2me (red) in crystalline state (solid line) and ground state (dashed line).



**Fig. S5** XRD patterns of (a) **1me** and (b) **2me** before ground, after ground, and simulated pattern from single crystal diffraction.



Fig. S6 XRD pattern of 2a at warming after cooling to -196 °C.



**Fig. S7** Polarized light microscopy image of **2a** at room temperature as prepared (left) and after cooling to -196 °C.



Fig. S8 Phase diagram of 2a and 2b, and the mixture of 2a and 2b with various molar ratio.

Identification code	1me	2me	
Empirical formula	$C_{30}H_{28}O_4$	$C_{34}H_{28}O_8$	
Formula weight	452.52	564.56	
Temperature	153(2) K	93(2) K	
Crystal system, space group	monoclinic, P21/n	monoclinic, P21/c	
Unit cell dimensions	$a = 9.6317(3) \text{ Å}$ $\alpha = 90 \circ$	$a = 10.4605(8) \text{ Å}$ $\alpha = 90^{\circ}$	
	$b = 15.5277(6) \text{ Å} \qquad \beta = 92.4928(12)^{\circ}$	$b = 20.3913(13) \text{ Å} \qquad \beta = 102.144(2)^{\circ}$	
	$c = 16.0905(5) \text{ Å} \gamma = 90^{\circ}$	$c = 14.1238(8) \text{ Å} \qquad \gamma = 90^{\circ}$	
Volume	2404.19(14) Å <sup>3</sup>	2945.2(3) Å <sup>^3</sup>	
Z, Calculated density	4, $1.250 \text{ g/cm}^3$	4, $1.273 \text{ g/cm}^3$	
Absorption coefficient	0.082 mm <sup>-1</sup>	0.091 mm <sup>-1</sup>	
F(000)	960	1184	
Crystal size	$0.50\times0.50\times0.20\ mm$	$0.40\times0.40\times0.40~mm$	
Theta range for data collection	3.37 to 27.46 $^\circ$	3.12 to 27.48 °	
Limiting indices	-12<=h<=12, -20<=k<=20, -20<=l<=20	-7<=h<=13, -26<=k<=26, -17<=l<=17	
Reflections collected / unique	$38180 / 5479 [R_{int} = 0.0369]$	$13829 / 6223 [R_{int} = 0.0512]$	
Completeness to theta $=$ 27.46	99.60%	92.10%	
Max. and min. transmission	0.9838 and 0.9602	0.9646 and 0.9646	
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	5479/0/311	6223/0/383	
Goodness-of-fit on $F^2$	1.055	1.078	
Final R indices [I>2sigma(I)]	$R_1 = 0.0510, wR_2 = 0.1073$	$R_1 = 0.0626, wR_2 = 0.1630$	
R indices (all data)	$R_1 = 0.0630, wR_2 = 0.1130$	$R_1 = 0.1279, wR_2 = 0.2300$	
Largest diff. peak and hole	0.259 and -0.200 e. Å <sup>-3</sup>	0.337 and -0.339 e. Å <sup>-3</sup>	

Table S1. Summary of crystallographic data of 1me and 2me.

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