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# Reversibly/Irreversibly Stimuli-Responsive Inks Based on N-Heteroacene Liquids

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#### **General Method**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. Chemical shift of <sup>1</sup>H and <sup>13</sup>C NMR signals were quoted to tetramethylsilane ( $\delta = 0.00$ ) and ( $\delta = 77.00$ ) as internal standards, respectively. FT-IR spectra were measured with a Perkin-Elmer Spectrum Two FT-IR Spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were collected on a JEOL JMS-S3000 instrument using dithranol as a matrix. Elemental analyses were carried out with Perkin-Elmer instruments Series II CHNS/O Analyzer 2400II. UV/Vis absorption spectra were measured with a Perkin-Elmer Lambda35 UV-vis Spectrometer. Fluorescent spectra were measured with a Perkin-Elmer LS45 Luminescence Spectrophotometer. XRD patterns were obtained using a SHIMADZU XRD-6100 X-RAY DIFFRACTOMETER using Ni-filtered Cuk<sup>[]</sup> radiation. The density functional theory (DFT) calculations were carried out using Wavefunction SPARTAN'16 programs. The ground-state geometries were optimized at the B3LYP/6-31G\* level of theory.<sup>1</sup>

Diffraction data for **PyC**, **PyC-H<sup>+</sup>** and **BzC** were collected at -173 °C on a Bruker Apex II Ultra X-ray diffractometer equipped with a Mo *K* $\alpha$  radiation ( $\lambda = 0.71073$ Å). Intensity data were processed using the APEX3 software. The structure solutions and the corresponding refinements were carried out by using the Yadokari-XG<sup>2-3</sup> graphical interface. The positions of the non-hydrogen atoms were determined by a dual-space method using the SHELXT-2014/5<sup>4</sup> program and refined on *F*<sup>2</sup> by full-matrix least-squares techniques using the SHELXL program (version 2017/1, 2018/1 and 2018/3).<sup>5</sup> All the non-hydrogen atoms were refined with anisotropic thermal parameters, while all the hydrogen atoms were placed using AFIX instructions. For compound **PyC-H**<sup>+</sup>, the nitrogen- and oxygen-bound hydrogens were found in a difference Fourier map and refined with  $U_{iso}(H) = 1.2U_{eq}(N)$  and  $1.5U_{eq}(O)$ ; the O–H distances were restrained using DFIX instruction, and H–O–H angles were restrained using DANG instruction. Attempts to model some solvent molecules (H<sub>2</sub>O) were not successful due to heavily disorder of the molecules. The diffuse electron density associated with the solvent molecules was removed by the PLATON/SQUEEZE program.<sup>6</sup> Details of the crystal data and a summary of the intensity of data collection parameters of X-ray crystallography are listed in Table S1.

All reagents and solvents were purchased from FUJIFILM Wako Pure Chemical Co, Tokyo Chemical Industry Co., ltd, Kanto Chemical co., inc, or Aldrich, and used as received. **PyC** and **BzC** were prepared according to the procedures of the literature.<sup>7</sup>



Scheme S1. Synthesis of PyL and BzL.

## 2,3-(3,7,11-trimethyl-1-dodecyloxy)-6,7-pyridyl-quinoxaline (PyL)

To a suspension of **2** (0.62 g, 1.0 mmol) and Pd/C (0.067 g) in dry EtOH (100 mL) at 0 <sup>°</sup>C was added dropwise hydrazine monohydrate (4.0 mL). After reflux for 4 h, the reaction mixture was filtrated through Celite under Ar, and then evaporated. The crude product was heated with 2,2<sup>°</sup>-pyridil (0.25 g, 1.2 mmol) in dry EtOH (35 mL) under Ar for 24 h. The reaction mixture was cooled to room temperature and extracted with CHCl<sub>3</sub> three times. The combined organic layers

were washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography (silica, CHCl<sub>3</sub>), and dried under vacuum to afford **PyL** as a light yellow liquid (0.24 g, 32.4%). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) = 271(4.02), 371(3.57); IR(ATR):  $\nu$ = 2964, 2921, 2868, 1613, 1585, 1565, 1497, 1496, 1360, 1219, 1171, 1087, 1042, 998, 845, 789, 777, 741, 620, 560 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): $\delta$  7 $\delta$  8.44 (m, 2H), 7.79-7.72 (m, 4H), 7.47 (m, 2H), 7.22 (m, 2H), 4.22-4.20 (m, 4H), 2.01-1.02 (m, 34H), 1.00-0.98 (d, 6H), 0.86-0.84 (m, 18H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): $\delta$  157.81, 153.34, 149.66, 148.84, 138.55, 136.36, 124.28, 122.59, 107.32, 67.76, 39.37, 37.39, 37.31, 35.75, 35.68, 32.81, 30.17, 27.97, 24.82, 24.41, 22.71, 22.62, 19.77, 19.71 ppm; MS(MALDI-TOF): m/z calcd: 737.13 [M]<sup>+</sup>; found: 737.81; elemental analysis: calcd (%) for CHNO: C77.90, H 10.00, N 7.50; found: C 78.21, H 9.85, N 7.60.

#### 2,3-(3,7,11-trimethyl-1-dodecyloxy)-6,7-diphenyl-quinoxaline (BzL)

To a suspension of **2** (0.62 g, 1.0 mmol) and Pd/C (0.15 g) in dry EtOH (100 mL) at 0 <sup>•</sup>C was added dropwise hydrazine monohydrate (4.0 mL). After reflux for 4 h, the reaction mixture was filtrated through Celite under Ar, and then evaporated. The crude product was heated with benzil (0.25 g, 1.2 mmol) in dry EtOH (40 mL) under Ar for 24 h. The reaction mixture was cooled to room temperature and extracted with CHCl<sub>3</sub> three times. The combined organic layers were washed with brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography (silica, hexane/CHCl<sub>3</sub> = 4/1 (v/v)), and dried under vacuum to afford **BzL** as a light yellow liquid (0.28 g, 38.1%). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) = 265(4.29), 374(3.72); IR(ATR): v= 2954, 2925, 2870, 1617, 1495, 1468, 1383,

1356, 1341, 1251, 1213, 1170, 1062, 1025, 979, 916, 846, 810, 764, 698, 611, 563, 547 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):δ □7.49-7.48 (m, 4H), 7.44 (m, 2H), 7.33 (m, 6H), 4.23 (m, 4H), 1.98-0.99 (m, 34H), 0.91-0.85 (m, 24H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 152.85, 150.60, 139.58, 138.35, 129.76, 128.17, 128.11, 107.25, 67.68, 39.33, 37.35, 37.26, 35.76, 35.68, 32.77, 30.13, 27.93, 24.76, 24.37, 22.66, 22.56, 19.73, 19.62 ppm; MS(MALDI-TOF): m/z calcd: 735.13 [M]<sup>+</sup>; found: 735.82; elemental analysis: calcd (%) for CHNO: C 81.69, H 10.15, N 3.81; found: C 81.94, H 10.17, N 3.86.





Figure S2. POM observations of (a) **PyL** and **PyL-H**<sup>+</sup> (b) **BzL** and **BzL-H**<sup>+</sup>. The exposure time for **PyL** and **BzL** to HCl vapor is 1 h. A and P indicate analyzer and polarizer axis, respectively.



Figure S3. XRD patterns of (a) **PyL** (black) and **PyL-H**<sup>+</sup> (red) and (b) **BzL** (black) and **BzL-H**<sup>+</sup> (red).



Figure S4. <sup>1</sup>H NMR spectra of (a) **PyL** and **PyL+H**<sup>+</sup>and (b) **BzL** and **BzL+H**<sup>+</sup>.

Identification code (file name)	PyC (2py_merge)	<b>PyC-H</b> <sup>+</sup> (isd41_sq_merge)	BzC (ISDrev_merge)
CCDC	1954914	1954915	1954916
Empirical formula	$C_{20}H_{16}N_4O_2$	$C_{20}H_{25}Cl_3N_4O_5$	$C_{22}H_{18}N_4O_2$
Formula weight	344.37	507.79	342.38
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_{1}/n$	<i>P</i> -1	<i>I</i> 2/ <i>a</i>
Unit cell dimensions	$a = 7.7189(8) \text{ Å} \qquad \alpha = 90^{\circ}$	a = 7.0736(17) Å $\alpha$ = 78.032(2)°	$a = 6.8207(13) \text{ Å}  \alpha = 90^{\circ}$
	$b = 12.8637(13) \text{ Å } \beta = 90.306(1)^{\circ}$	$b = 9.491(2) \text{ Å} \qquad \beta = 85.170(3)^{\circ}$	$b = 14.526(3)$ Å $\beta = 93.214(2)^{\circ}$
	$c = 16.8268(16) \text{ Å } \gamma = 90^{\circ}$	$c = 18.928(4) \text{ Å}  \gamma = 85.818(3)^{\circ}$	$c = 16.989(3) \text{ Å}  \gamma = 90^{\circ}$
Volume	1670.8(3) Å <sup>3</sup>	1236.7(5) Å <sup>3</sup>	1680.6(6) Å <sup>3</sup>
Ζ	4	2	4
Density (calculated)	1.369 mg/m <sup>3</sup>	1.364 mg/m <sup>3</sup>	1.353 mg/m <sup>3</sup>
Absorption coefficient	0.092 mm <sup>-1</sup>	0.408 mm <sup>-1</sup>	0.088 mm <sup>-1</sup>
<i>F</i> (000)	720	528	720
Crystal size	$0.370 \times 0.300 \times 0.210 \ mm^3$	0.240 x 0.070 x 0.030 mm <sup>3</sup>	0.320 x 0.130 x 0.110 mm <sup>3</sup>
Theta range for data collection	1.993 to 27.495°	2.197 to 27.493°	1.846 to 27.500°
Index ranges	-9<=h<=9, -10<=k<=16, -	-9<=h<=9, -12<=k<=12, -	-8<=h<=5, -17<=k<=18, -
	21<=l<=21	24<=l<=24	21<=l<=19
Reflections collected	9023	13574	4453
Independent reflections	3734 [ <i>R</i> (int) = 0.0170]	5471 [R(int) = 0.0320]	1840 [ <i>R</i> (int) = 0.0186]
Completeness to theta = $25.242^{\circ}$	99.8%	98.3 %	99.3%
Data / restraints / parameters	3734 / 0 / 237	5471 / 17 / 318	1840 / 0 / 120
Goodness-of-fit on $F^2$	1.060	1.151	1.072
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0351, wR_2 = 0.0897$	$R_1 = 0.0759, wR_2 = 0.1736$	$R_1 = 0.0377, wR_2 = 0.0990$
R indices (all data)	$R_1 = 0.0402, wR_2 = 0.0941$	$R_1 = 0.0847, wR_2 = 0.1773$	$R_1 = 0.0400, wR_2 = 0.1012$
Largest diff. peak and hole	0.274 and -0.190 e.Å-3	0.916 and -0.720 e.Å <sup>-3</sup>	0.311 and -0.218 e.Å <sup>-3</sup>

## Table S1. Crystal data and structure refinement for $PyC,\,PyC\text{-}H^{+}$ and BzC



Figure S5. UV–vis and FL spectra of (a) PyL and PyL-H<sup>+</sup>and (b) BzL and BzL-H<sup>+</sup>.



Figure S6. DFT calculations of (a) **PyC**, (b) **PyC-H**<sup>+</sup>, (c) **BzC** and (d) **BzC-H**<sup>+</sup>.



Figure S7. (a) UV-vis absorption and (b) FL spectra for adsorption/desorption behavior of **PyL**, **PyL-H**<sup>+</sup>, **BzL** and **BzL-H**<sup>+</sup> to HCl vapor.



Figure S8. Repeatability tests of **BzL**. (a) UV-vis and (b) FL spectra, and (c) photographs. Exposure time of HCl vapor from HClaq and air are 5 min and 10 min, respectively.



Figure S9. Photographs of for adsorption/desorption behavior of **PyL**, **PyL-H**<sup>+</sup>, **BzL** and **BzL-H**<sup>+</sup> to HCl vapor. Texts were written on glass substrates.

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