Supporting information

Rationally Designed Molecular D–A–D Triad for Piezochromic and Acidochromic Fluorescence On–Off Switching

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General experimental procedures

Synthetic details. m-BHHDCS, m-HDCS, and HH were synthesized according to the procedure shown in Scheme S1. All chemicals were purchased commercially, and used without further purification. The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into vanillin solution (9.0 g of vanillin and 1.5 mL of concentrated sulfuric acid in 300 mL of MeOH), KMnO₄ solution (3 g of KMnO₄, 20 g of K₂CO₃, and 5 mL of 5% NaOH solution in 300 mL of water), or phosphomolybdic acid solution (250 mg phosphomolybdic acid in 50 mL EtOH). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60). Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. The usual work-up refers to washing the quenched reaction mixture with brine, drying the organic extracts over anhydrous MgSO₄ and evaporating under reduced pressure using a rotary evaporator.

Spectroscopic Characterization. ¹H-NMR spectrum was recorded on a Bruker, Avance-300 (300 MHz) in CDCl₃ solution. ¹³C-NMR spectrum was recorded on a Bruker, Avance-500 (500 MHz) in CDCl₃ solution. Chemical shift values were recorded as parts per million relative to tetramethylsilane

as an internal standard unless otherwise indicated, and coupling constants in Hertz. Mass spectra were recorded on a JEOL, JMS 600W spectrometer using electron impact (EI) or chemical ionization (CI), and JEOL JMS AX505WA spectrometer using fast atom bombardment (FAB) method. Significant fragments are reported in the following fashion: m/z (relative intensity). Elemental analysis was carried out using a CE instruments, EA1110 elemental analyzer. UV-visible absorption spectra were recorded on a Shimazu, UV-1650 PC spectrometer. Photoluminescence emission and excitation spectra were obtained using a Varian, Cary Eclipse Fluorescence spectrophotometer, correcting the spectra for the sensitivity of the detection system and the characteristics of the lamp, respectively. The relative fluorescence quantum yield of solutions were measured using 9,10-diphenylanthracence (DPA) in benzene as a standard reference (1×10⁻⁴ mol L⁻¹, $\Phi_{\rm F}$ = 83%). The absolute $\Phi_{\rm F}$ values of thin films on quartz plates were measured using a 6-inch integrating sphere (Labsphere, 3P-GPS-060-SF) equipped with a 325-nm CW He-Cd laser (Omnichrome, Series 56) and a PMT detector (Hamamatsu, PD471) attached to a monochromator (Acton Research, Spectrapro-300i). Time-resolved fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique with a FluoTime200 spectrometer (PicoQuant) equipped with a PicoHarp300 TCSPC board (PicoQuant) and a PMA182 photomultiplier (PicoQuant). The excitation source was a 377 nm picoseconds pulsed diode laser (PicoQuant, LDH375) driven by a PDL800-D driver (PicoQuant) with fwhm ~70 ps. The multi-exponential least square fitting procedure was carried out with the Fluofit software (PicoQuant), taking into possible double excitations of the IRF within the deconvolution. Mean decay times τ_{av} were obtained from the individual lifetimes τ_i and amplitudes a_i of multiexponential evaluation through

$$\tau_{av} = \frac{\sum_{i} a_{i} \tau_{i}^{2}}{\sum_{i} a_{i} \tau_{i}}$$

X-ray Analysis. WAXS measurements were performed on a GADDS (Bruker, Germany) equipped with a 2D area detector, operating at 3 kW.

Cyclic voltammetry measurements. Cyclic voltammetry experiments were carried out with a model 273A (Princeton Applied Research) using an one-compartment electrolysis cell consisting of a platinum working electrode, a platinum wire counter electrode, and a quasi Ag^+/Ag reference electrode. The measurements were done in 0.2 mM DCM solution with 0.1M tetrabutylammonium hexafluorophosphate(n-Bu₄NPF₆) as supporting electrolyte at a scan rate of 50 mV/s. Each oxidation potential was calibrate with ferrocene as a reference.

Computational Details. Geometry optimizations of the extended (C_2 symmetry) and stacked (C_i) configuration of m-BHCDCS were done by density functional theory (DFT) employing the dispersion-corrected functional wB97XD in vacuo. MO energies (wB97XD) were calculated in dichloromethane (DCM) with the polarizable continuum model (PCM). Time-dependent (TD) DFT calculations were done with the B3LYP functional in DCM. All calculations were performed employing the 6-311G* basis with the Gaussian09 program package:

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Scheme S1. The synthetic scheme of m-BHHDCS 1

9-(6-bromohexyl)-1-methyl-9H-pyrido[3,4-b]indole. 1,6-dibromohexane (1.52 ml, 9.90 mmol) was added to a solution of the harmane (1.00 g, 6.60 mmol) and NaH (60% in mineral oil, 660 mg, 16.5 mmol) in dry THF (27.5 mL) at 0°C. This mixture was stirred at room temperature for 10 h. The resulting reaction mixture was poured into water and extracted with ethylacetate (EA). The organic phase was dried over MgSO₄ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography with EA gave white powder (1.48 g, 65 %). ¹H NMR (500 MHz, CDCl₃): δ 8.32 (d, *J*=5.5 Hz, 1 H), 8.11 (d, *J*=7.5 Hz, 1 H), 7.83 (d, *J*=5.5 Hz, 1 H), 7.58 (t, *J*=8.0 Hz, 1 H), 7.45 (d, *J*=8.5 Hz, 1 H), 7.27 (t, *J*=7.5 Hz, 1 H), 4.53 (t, *J*=7.7 Hz, 2 H), 3.38 (t, *J*=6.5 Hz, 2 H), 3.04 (s, 3 H), 1.89 – 1.82 (m, 4 H), 1.53 – 1.43 (m, 4 H). ¹³C NMR (125 MHz, CDCl₃): δ 141.5, 141.2, 138.0, 135.1, 129.1, 128.1, 121.5, 121.4, 119.6, 112.9, 109.6, 44.7, 33.4, 32.5, 30.7, 27.9, 26.1, 23.5. HRMS (FAB) calcd. for C₁₈H₂₂BrN₂ (M⁺+1) 345.0966, found 345.0961.

2,5-bis(6-(1-methyl-9H-pyrido[3,4-b]indol-9-yl)hexyloxy)terephthalaldehyde. 9-(6-bromohexyl)-1-methyl-9H-pyrido[3,4-b]indole (1.20 g, 3.48 mmol) and K₂CO₃ (721 mg, 5.22 mmol) were added to a solution of the 2,5-dihydroxyterephthalaldehyde (262 mg, 1.58 mmol) in dry DMF (3.5 mL) at room temperature. This mixture was stirred at 50°C for overnight. After cooling to room temperature, the mixture was poured into water and extracted with EA. The organic phase was dried over MgSO₄ and the solvent was evaporated in vacuo. The dark yellow powder were obtained by reprecipitation from dichloromethane (DCM) and methanol (MeOH) and used without further purification for next step.

(2Z)-3,3'-(2,5-bis(6-(1-methyl-9H-pyrido[3,4-b]indol-9-yl)hexyloxy)-1,4-phenylene)bis(2-(3,5-

bis(trifluoromethyl)phenyl)acrylonitrile) (m-BHHDCS) (1). The mixture of crude powder of 2,5bis(6-(1-methyl-9H-pyrido[3,4-b]indol-9-yl)hexyloxy)terephthalaldehyde (500 mg, 0.719 mmol) and (4-Cyanomethyl-phenyl)-acetonitrile (400 mg, 1.58 mmol) in tetrahydrofuran (THF, 7 mL) and *tert*butyl alcohol (7 mL) was stirred at 50°C. Tetrabutylammonium hydroxide (TBAH, 1.0 M solution in methanol, 0.07 mL) was slowly dropped into the mixture and stirred for 1 h. The resulting precipitate was filtered and purified by column chromatography using dichloromethane. m-BHHDCS powder (359 mg, 42 %) was obtained by reprecipitation from DCM and MeOH. ¹H NMR (500 MHz, CDCl₃): δ 8.30 (d, *J*=5.0 Hz, 2 H), 8.09 (d, *J*=10.5 Hz, 2 H), 8.08 (s, 2 H), 8.06 (s, 4H), 7.90 (s, 2 H), 7.88 (s, 2 H), 7.82 (d, *J*=5.0 Hz, 2 H), 7.54 (t, *J*=7.5 Hz, 2 H), 7.43 (d, *J*=8.5 Hz, 2 H), 7.24 (t, *J*=8.3 Hz, 2 H), 4.55 (t, *J*=7.7 Hz, 4 H), 4.13 (t, *J*=6.5 Hz, 4 H), 3.02 (s, 6 H), 1.92 – 1.85 (m, 8 H), 1.65 – 1.45 (m, 8 H). ¹³C NMR (125 MHz, CDCl₃): δ 151.7, 141.5, 141.2, 138.7, 138.1, 136.7, 135.1, 133.3, 133.0, 132.7, 129.1, 128.1, 126.1, 125.7, 122.9, 121.5, 121.4, 119.6, 117.1, 112.9, 111.4, 109.7, 109.6, 69.3, 44.8, 30.7, 29.0, 26.7, 26.0, 23.5. MS *m*/z (FAB, relative intensity): 1165 (M⁺, 1), 460 (2), 391 (4), 359 (2), 307(21), 289 (12), 219 (7), 154 (100), 136 (68). HRMS (FAB) calcd. for C₆₄H₅₃F₁₂N₆O₂ (M⁺) 1165.4038, found 1165.4043.



Scheme S2. The synthetic scheme of protonated m-BHHDCS

9,9'-(6,6'-(2-((Z)-2-(3,5-bis(trifluoromethyl)phenyl)-2-cyanovinyl)-5-(2-(3,5-

bis(trifluoromethyl)phenyl)-2-cyanovinyl)-1,4-phenylene)bis(oxy)bis(hexane-6,1-diyl))bis(1methyl-9H-pyrido[3,4-b]indol-2-ium) chloride (**m-BHHDCSH**⁺**CI**⁻) (**1**') ¹H NMR (500 MHz, CDCl₃): δ 8.36 (t, *J*=5.5 Hz, 2 H), 8.25 (d, *J*=5.0 Hz, 2 H), 8.25 (d, *J*=8.0 Hz, 2 H), 8.10 (s, 2H), 8.06 (s, 4 H), 7.90 (s, 2 H), 7.89 (s, 4 H), 7.80 (t, *J*=7.5 Hz, 2 H), 7.61 (d, *J*=8.5 Hz, 2 H), 7.47 (t, *J*=7.5 Hz, 2 H), 7.24 (t, *J*=8.3 Hz, 2 H), 4.64 (t, *J*=7.0 Hz, 4 H), 4.16 (t, *J*=7.3 Hz, 4 H), 3.44 (s, 6 H), 1.96 – 1.80 (m, 8 H), 1.68 – 1.48 (m, 8 H). ¹³C NMR (125 MHz, CDCl₃): δ 151.7, 144.2, 138.9, 137.4, 136.7, 133.9, 133.8, 133.0, 132.7, 132.0, 129.0, 126.1, 125.8, 124.0, 123.0, 122.3, 121.8, 119.9, 117.1, 114.9, 111.5, 110.6, 109.8, 69.1, 45.3, 30.8, 28.9, 26.6, 25.9, 18.0.



Scheme S3. The synthetic scheme of m-HDCS 2

(2Z,2'Z)-3,3'-(2,5-bis(hexyloxy)-1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)

phenyl)acrylonitrile) (m-HDCS) (2). The mixture of 2,5-bis(hexyloxy)terephthalaldehyde (2.05 g, 6.13 mmol) and (4-Cyanomethyl-phenyl)-acetonitrile (3.41 g, 13.5 mmol) in *tert*-butyl alcohol (60 mL) was stirred at 50°C. Tetrabutylammonium hydroxide (TBAH, 1.0 M solution in methanol, 0.61 mL) was slowly dropped into the mixture and stirred for 1 h. The resulting precipitate was filtered and purified by column chromatography using dichloromethane. m-HDCS powder (3.42 g, 69 %) was obtained by reprecipitation from DCM and MeOH. ¹H NMR (500 MHz, CDCl₃): δ 8.15 (s, 2 H), 8.11 (s, 4 H), 7.92 (br s, 2 H), 7.91 (s, 2 H), 4.16 (t, *J*=6.5 Hz, 4 H), 1.90 – 1.82 (m, 4 H), 1.55 – 1.48 (m, 4 H), 1.40 – 1.34 (m, 8 H), 0.90 – 0.80 (m, 6 H). ¹³C NMR (125 MHz, CDCl₃): δ 151.9, 139.0, 136.9, 133.0, 132.7, 126.1, 125.8, 124.0, 122.8, 121.9, 117.2, 111.4, 109.6, 69.6, 31.5, 29.1, 25.9, 22.5, 13.9. MS *m*/*z* (FAB, relative intensity): 367 (M⁺+1, 88), 349 (27), 309 (2), 257 (19), 235 (8), 217 (28), 201 (55), 181 (2), 157 (3), 143 (4), 127 (100), 109 (9), 91 (45), 75 (4). HRMS (FAB) calcd. for C₄₀H₃₆F₁₂N₂O₂ (M⁺) 804.2585, found 804.2576.



Scheme S4. The synthetic scheme of HH 3

9-hexyl-1-methyl-9H-pyrido[**3,4-b**]**indole (HH) (3)** 1-bromohexane (0.185 ml, 1.32 mmol) was added to a solution of the harmane (200 mg, 1.32 mmol) and NaH (60% in mineral oil, 132 mg, 3.29 mmol) in dry THF (5.5 mL) at 0°C. This mixture was stirred at room temperature for 10 h. The resulting reaction mixture was poured into water and extracted with ethylacetate (EA). The organic phase was dried over MgSO₄ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography with EA gave white powder (212 mg, 72 %). ¹H NMR (500 MHz, CDCl₃): δ 8.32 (d, *J*=5.5 Hz, 1 H), 8.11 (d, *J*=7.5 Hz, 1 H), 7.83 (d, *J*=5.0 Hz, 1 H), 7.57 (t, *J*=8.3 Hz, 1 H), 7.45 (d, *J*=8.5 Hz, 1 H), 7.26 (t, *J*=7.5 Hz, 1 H), 4.51 (t, *J*=7.7 Hz, 2 H), 3.04 (s, 3 H), 1.86 – 1.79 (m, 2 H),

1.46 – 1.41 (m, 2 H), 1.40 – 1.29 (m, 4 H), 0.90 – 0.87 (t, J=7.0 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ 141.5, 141.2, 137.9, 135.2, 129.1, 128.0, 121.5, 121.3, 119.5, 112.9, 109.7, 45.0, 31.5, 30.8, 26.6, 23.5, 22.5, 13.9. MS *m*/*z* (FAB, relative intensity): 367 (M⁺+1, 88), 349 (27), 309 (2), 257 (19), 235 (8), 217 (28), 201 (55), 181 (2), 157 (3), 143 (4), 127 (100), 109 (9), 91 (45), 75 (4). HRMS (FAB) calcd. for C₁₈H₂₃N₂ (M⁺+1) 267.1861, found 267.1861.



Figure S1 Photo images of various powders of m-BHHDCS (1) and m-BHCDCS under room light (upper) and 365 nm UV light (lower). (a) Pristine powders (left), ground powders (middle), and HCl (aq) treated powders of m-BHHDCS (1). (b) H_2O (l) added powders (left) and Na2CO3 (aq) added powders (right) of m-BHHDCS (1) were obtained to identify pH effect on fluorescence change. (c) Pristine powders (left) and HCl (aq) added (right) powders of m-BHCDCS were used as references.



Figure S2 Fluorescence changes by treatment of (a) HCl (aq) to pristine 1A powder (b) Na_2CO_3 to acidified 1C powder.



Figure S3 Excitation photoluminescence (PL) spectra of 1 (red line), 2 (black line), and 1/HCl (blue line) in CHCl₃ solution

	E ⁰ _{ox} [V] ^a	E ⁰ _{red} [V] ^a	E_g^{opt} [eV] solution. ^b	HOMO [eV] ^c	LUMO [eV]
m-BHHDCS 1	1.46	-0.70		-5.66	-3.48 ^c
m-HDCS 2	1.72	-0.71	2.43	-5.92	-3.49 ^c
N-Hexylharmane 3	1.46		·	-5.66	

Table S1. Electrochemical data and molecular orbital energies of 1, 2, and 3

a. Measured in DCM-TBAPF₆ (0.1 M), concentration = 2×10^{-3} M , 25°C, V = 100 mV \cdot s⁻¹ , versus Ag /Ag⁺

b. Estimated using the onset of the UV–Vis spectra in 1,2-dichloroethane (DCE).

c. Estimated by the comparison with ferrocene (-4.8 eV), using Koopmans theorem, which identifies the electron affinity with the HOMO energy.

d. Estimated according to the equation $E_{LUMO} = E_{HOMO} - E_{g}^{opt}$.



Figure S4. (a) UV-Vis absorption spectra of 2 (black line) and 2/HCl (red line) in CH₃Cl solution (b) PL spectra of 2 and 2/HCl in CH₃Cl solution excited at $\lambda_{ex} = 450$ nm



Figure S5. (a) UV-Vis spectral changes in a mixture solution of 3 upon the addition of HCl (b) PL spectral changes in a mixture solution of 3 upon the addition of HCl (c) UV-Vis spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl (d) PL spectral changes in a mixture solution of 2/3 upon the addition of HCl.



Figure S6. ¹H-NMR (300 MHz) spectra of **1** (upper) and **1**/HCl (lower) in CDCl₃ solution at room temperature. Inset: schematic representation of reaction of m-BHHDCS (**1**) with HCl.

¹³ C-NMR chemical shifts of 1	¹³ C-NMR chemical shifts of 1/HCl
151.7	151.7
141.5	144.2
141.2	138.9
138.7	137.4
138.1	136.7
136.7	133.9
135.1	133.8
133.3	133.0
133.0	132.7
132.7	132.0
129.1	129.0
128.1	126.1
126.1	125.8
125.7	124.0
122.9	123.0
121.5	122.3
121.4	121.8
119.6	119.9
117.1	117.1
112.9	114.9
111.4	111.5
109.7	110.6
109.6	109.8
69.3	69.1
44.8	45.3
30.7	30.8
29.0	28.9
26.7	26.6
26.0	25.9
23.5	18.0

Figure S7. ¹³C-NMR (125 MHz) chemical shifts of **1** (left) and **1**/HCl (right) in a CDCl₃ solution at room temperature



Figure S8. Fluorescence decay profiles (upper blue lines) of (a) m-BHHDCS solution (CHCl₃, 1×10^{-5} M), (b) m-BHHDCS/HCl solution (CHCl₃, 1×10^{-5} M/ 1×10^{-4} M) with 377 nm excitation. IRFs are represented in red, fits in black; lower blue lines are the residuals.



Figure S9. Fluorescence decay profile (upper blue lines) of (a) an m-BHHDCS spin-coated film, (b) an m-BHHDCS **1a** film, and (c) an m-BHHDCS **1b** film with 377 nm excitation. IRFs are represented in red, fits in black; lower blue lines are the residuals.



Figure S10. Fluorescence images and fabrication processes (for detail; please see following sentences) of various thin films of m-BHHDCS 1

Detailed fabrication process of thin films

We prepared an as-spin cast film of m-BHHDCS **1** (see **Figure S10**) by simple spin-coating on a glass substrate from a CHCl₃ solution (0.5 wt% m-BHHDCS in CHCl₃) without the use of another matrix. Interestingly, as-spin cast film exhibited strong orange fluorescence, which is distinctly different from precipitate powder (also called pristine powder, see **Scheme 1b** and **Figure S1a**) with quenched luminescence. We attribute this to the centrifugal force occurred during spin-coating process. The centrifugal force may act as shearing force like mechanical grinding and smearing. In contrast, the process of preparing pristine powder was not interrupted by any other perturbation such as mechanical force, so that they remain in the thermodynamically stable phase (crystalline phase). In this sense, piezochromism of the thin films correspond well with that of the powders. When CHCl₃ vapor was treated, the luminescence completely quenched (vapor annealed **1a** film, see **Scheme 1c** and **Figure S10**). The vapor annealed film also exhibited HCl (g) sensitivity. The orange fluorescence turned on promptly in response to HCl (g) with a high contrast ratio (ca. ~50). The reversibility was confirmed by treating triethylamine (TEA) vapor.



Figure S11. Chemical structure of triphenylsulfonium triflate used as a photo acid generator (PAG) in this work.