

## Supporting Information

### Colored Ionic Liquid Based on Stable Polycyclic Anion Salt Showing Halochromism with HCl Vapor

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**Instruments.**  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were recorded on a JEOL JMN-ECA500 spectrometer at room temperature using  $\text{Me}_4\text{Si}$  or residual solvent as an internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy was performed on a SHIMADZU AXIMA-Assurance analyzer using dithranol as a matrix. An elemental analysis was performed on a YANACO MT-5 coder for CHN and a SHIMADZU ICPS-8100 analyzer for Na by Center for Scientific Instrument Renovation and Manufacturing Support, Osaka University. Sonication was performed using a SND US-109 ultrasonic bath sonicator. Centrifugation was performed using KUBOTA Tabletop-4000 separator. Polarized optical microscopy (POM) was performed on a LEICA DM2500 M optical polarizing microscope at room temperature. pH values were measured using HORIBA LAQUA twin pH meter at room temperature. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q20 differential scanning calorimeter under  $\text{N}_2$  flow. X-ray diffraction (XRD) was performed on a D2 Phaser Desktop X-ray Diffractometer with a LYNXEYE XE-T detector (Bruker Co.) using  $\text{Cu K}\alpha$  radiation at 30 kV and 10 mA ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. Thermogravimetric analysis (TGA) was performed on a SII TG/DTA7300 analyzer under  $\text{N}_2$  flow. Electronic spectra were recorded on a SHIMADZU UV-3600 spectrometer at room temperature. Theoretical calculations were performed on a Gaussian 09 program<sup>S1</sup> with a hybrid density functional theory (DFT) method.<sup>S2</sup> Molecular orbital (MO) patterns and electrostatic potential (ESP) mappings as well as molecular models were extracted using a Gauss View software.<sup>S3</sup>

**Materials.** Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used as received. Molecular sieve 4A (MS4A) powder was activated by heating at 300 °C for 3 h under a reduced pressure before use. Compound **2**<sup>S4</sup> and **3**<sup>S5</sup> were prepared according to reported procedures.

**Synthesis of 4.** To a 300-mL flask was added **2** (2.80 g, 5.01 mmol), **3** (10.5 g, 30.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (458 mg, 0.500 mmol), XPhos (953 mg, 2.00 mmol), Cs<sub>2</sub>CO<sub>3</sub> (13.0 g, 39.9 mmol), MS4A powder (2.00 g), and DMF (100 mL). The mixture was degassed and then stirred at 80 °C for 15 h under Ar flow. After the mixture was cooled to room temperature, an insoluble solid in the mixture was removed by a filtration through Celite. To the filtrate was added H<sub>2</sub>O (50 mL) and 6 M aqueous HCl (10 mL) to produce a dark-blue solid. The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. The wet precipitate was dried under air overnight and then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) by a sonication (10 min). After the solution was dried over MgSO<sub>4</sub>, an insoluble solid in the solution was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was collected by a decantation. The collected solution was concentrated under a reduced pressure to give a crude intermediate as a dark-blue solid in a 1-L flask. To the crude intermediate was added 1M NaOH<sub>aq</sub> (250 mL) and EtOH (250 mL). The mixture was stirred at 73 °C for 24 h under air. After the mixture was cooled to room temperature, 6 M aqueous HCl (10 mL) was added dropwise to the mixture to produce a dark-green solid. The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. The precipitate was dispersed in MeOH (100 mL) by a sonication (10 min). The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. This sequence was repeated three times. To the resulting precipitate was added MeOH (100 mL) and 1M NaOH<sub>aq</sub> (7 mL) to dissolve the precipitate by a sonication (60 min). An insoluble solid in the resulting solution was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was collected by a decantation. This sequence was repeated several times until the supernatant solution became almost colorless. The collected

solution was combined and then concentrated under a reduced pressure to give a heptasodium salt of a crude product as a dark-green solid. The salt was dispersed in EtOH (30 mL) by a sonication (10 min). The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. This sequence was repeated three times. The wet precipitate was dried under air overnight and then dissolved in H<sub>2</sub>O (100 mL) by a sonication (10 min). To the resulting solution was added 6 M aqueous HCl (2 mL) dropwise to produce a dark-blue solid. The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. To the wet precipitate was added H<sub>2</sub>O (100 mL) to be sonicated for 10 min and then added 6 M aqueous HCl (2 mL) dropwise. The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. This sequence was repeated several times until the supernatant of the sonicated solution became almost colorless. The precipitate was dispersed in MeOH (100 mL) by a sonication (10 min). The dispersed solid was precipitated by a centrifugation (4000 rpm, 60 min) and then the supernatant solution was removed by a decantation. After this sequence was repeated three times, the resulting precipitate was dried under air overnight and then dried at 60 °C for 2 h under a reduced pressure to give a crude product as a dark-blue blockish solid. The obtained solid was thoroughly crushed by a glass rod to be a powder. The resulting powder was dispersed in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) by a sonication (10 min). The dispersed powder was collected by a filtration and then dried at 60 °C for 3 h under a reduced pressure to give **4** (2.80 g, 3.44 mmol, 69% based on **2**) as an insoluble dark-blue powder. MALDI-TOF mass (positive mode) calcd. for C<sub>46</sub>H<sub>23</sub>O<sub>15</sub> [M+H]<sup>+</sup>: *m/z* = 815. Found: *m/z* = 815. Anal. calcd. for C<sub>46</sub>H<sub>32</sub>O<sub>20</sub> [**4**•5H<sub>2</sub>O]: C, 61.07; H, 3.57; N, 0.00. Found: C, 61.01; H, 3.46; N, 0.00.

**Synthesis of 1-Na.** K<sub>2</sub>CO<sub>3</sub> (2.49 g, 18.0 mmol) and MS4A powder (400 mg) in a 50-mL flask were thoroughly dried by a heat gun under a reduced pressure and then **4** (408 mg, 0.500 mmol), TEG-Br (2.60 mL, 15.0 mmol), and DMF (5 mL) were added to the flask. The mixture was stirred at 60 °C for 63 h under Ar flow. After the mixture was cooled to room temperature, AcOEt (45 mL) was added to the mixture and then an insoluble solid in the mixture was removed by a filtration through Celite. The filtrate in a separating funnel was

washed with a mixture of brine (200 mL) and 6 M aqueous HCl (2 mL). A color of the organic layer turned from green to blue. To the collected organic layer was added NaHCO<sub>3</sub> (2 g) and then the solution was sonicated for 30 min. A color of the solution turned from blue to green. After the solution was dried over Na<sub>2</sub>SO<sub>4</sub>, an insoluble solid in the solution was removed by a filtration. The filtrate was concentrated under a reduced pressure to give a crude product as a dark-green oil. After the obtained oil was diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), Et<sub>2</sub>O (50 mL) was added to the diluted oil and then the mixture was sonicated for 1 min to produce an emulsion. The dispersed liquid in the emulsion was precipitated by a centrifugation (4000 rpm, 5 min) and then the supernatant solution was removed by a decantation. After the precipitated liquid was diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), Et<sub>2</sub>O (50 mL) was added to the diluted oil and then the mixture was sonicated for 1 min to produce an emulsion. The dispersed liquid in the emulsion was precipitated by a centrifugation (4000 rpm, 5 min) and then the supernatant solution was removed by a decantation. This sequence was repeated several times until the supernatant solution became almost colorless. The resulting liquid was dried at room temperature for 1 h under a reduced pressure to give **1-Na** (830 mg, 0.483 mmol, 97% based on **4**) as a sticky dark-green liquid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm) 8.73 (s, 6H), 8.19 (d, 3H, *J* = 1.0 Hz), 8.13 (dd, 3H, *J* = 1.5 and 8.0 Hz), 8.00 (d, 3H, *J* = 8.0 Hz), 4.55–3.41 (m, 36H), 3.22–3.04 (m, 42H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm) 180.61, 167.73, 164.97, 141.17, 134.98, 132.38, 131.80, 131.72, 131.39, 131.04, 130.23, 127.99, 127.19, 71.24, 71.02, 69.94, 69.76, 69.61, 69.49, 69.34, 69.30, 68.24, 67.74, 64.60, 64.44, 57.95, 57.87. MALDI-TOF mass (negative mode) calcd. for C<sub>88</sub>H<sub>106</sub>O<sub>33</sub> [M–Na+H]<sup>–</sup>: *m/z* = 1691. Found: *m/z* = 1691. Anal. calcd. for C<sub>88</sub>H<sub>107</sub>NaO<sub>34</sub> [**1-Na**•1.5H<sub>2</sub>O]: C, 60.72; H, 6.25; N, 0.00; Na, 1.32. Found: C, 60.76; H, 6.28; N, 0.00; Na: 0.93.

**Preparation of a liquid film for 1-Na.** **1-Na** (~0.5 mg) was loaded on a glass plate and then rubbed with muddler to be a green liquid film (Figure S2).

**Theoretical calculations.** Geometry optimization was performed at the B3LYP/6-31G(d,p) level to yield a planar structure with a *D*<sub>3h</sub> symmetry for **TOT** anion and *C*<sub>s</sub> symmetry for **TOT-H** respectively as an energetically global-minimum state, checked by frequency

analysis (Figure S8, Table S1-2). An electronic state was then estimated by the single-point calculations at the B3LYP/6-31++G(d,p) level using atom coordinates for the optimized geometry to yield an energy diagram and an orbital shape of frontier MOs (Figure S9) as well as an ESP mapping on the isodensity surface (Figure S10). Electronic transitions were predicted by the time-dependent (TD) method at the B3LYP/6-31++G(d,p) level using atom coordinates for the optimized geometry and detailed contributions of electronic transitions in some excited states are listed in Table S3-4. Molecular modeling of **1** was performed by a Z-matrix method using a combination of partial structures optimized at the semi-empirical level (Figure S5).

**Evaluation of an experimental  $pK_a$  value.** Aqueous buffer solutions of **1-Na** (0.1 mM) in the range of pH = 1.1–8.4 were prepared using HCl, citric acid, NaOH, and NaHCO<sub>3</sub> (Table S5). Absorbance values of electronic spectra for the solutions were plotted against pH and then the resulting plot was fitted by the Henderson–Hasselbalch equation to give a  $pK_a$  value (see text).

**Evaluation of  $pK_a$  values based on theoretical calculations.**  $pK_a$  values were calculated according to a reported procedure.<sup>S6</sup> Geometry optimization and frequency analysis were performed for an acid and its conjugated base to obtain their Gibbs energies at the B3LYP/6-31++G(d,p) level using the conductor-like polarizable continuum model<sup>S7</sup> for the self-consistent reaction field theory<sup>S8</sup> with solvent parameters optimized for water and the universal force field model<sup>S9</sup> for the cavity of molecules. To correct a  $pK_a$  value based on a calculated  $\Delta G_0$  value, which is a difference of the Gibbs energies between the acid and its conjugated base, a calibration plot (Figure S12) for several tropolone derivatives,<sup>S10</sup> whose experimental  $pK_a$  values are previously reported (Table S6), was prepared and then fitted with a least square line to give values 0.449011307 and -1112.892774 kJ mol<sup>-1</sup> as a scaling factor and the Gibbs energy for a dissociated proton. The resulting  $pK_a$  values of some acids<sup>S6,S10a,S11</sup> including **TOT-H** were listed in Table S7.

**An exposure of a liquid film to HCl vapor.** A glass plate painted with a liquid film of **1-Na** (~0.5 mg) was inserted to a 450-mL glass bottle containing 6 M aqueous HCl (~1 mL) (Figure S13). After standing under HCl vapor for 30 min at room temperature, the plate was ejected from the bottle and then electronic spectra of the exposed liquid film were measured (Figure S14). The exposed liquid film was dissolved in triglyme after standing in air for 20 h at room temperature (Figure S15). The resulting solution was added with an excess amount of NaHCO<sub>3</sub> to neutralize a residual acid and then filtrated to remove inorganic salts. Finally, an electronic spectrum of the filtrated solution was measured (Figure S16). A control experiment using H<sub>2</sub>O instead of 6 M aqueous HCl were also performed (Figure S17 and S18).

## References

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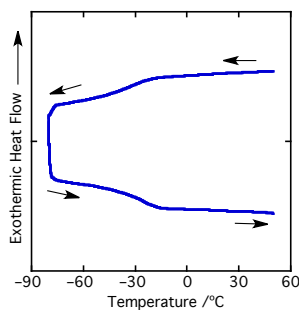
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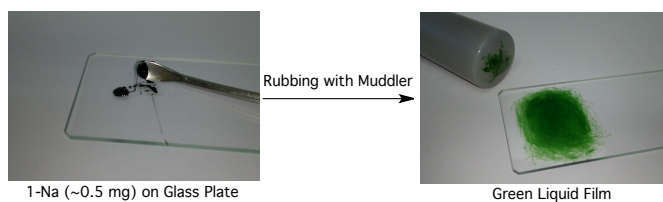
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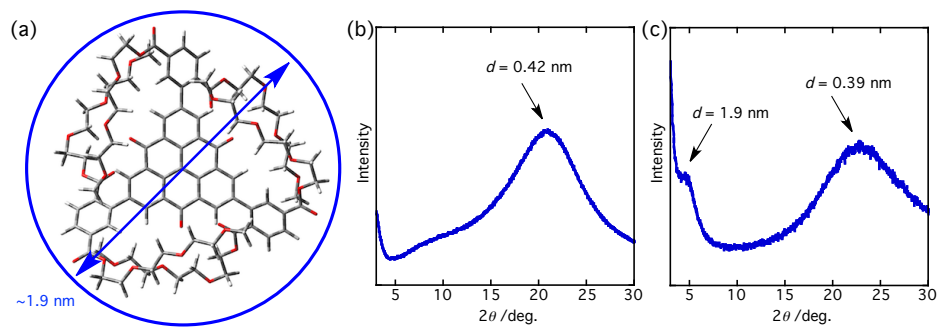
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**Figure S1.** DSC profile (50 °C  $\rightarrow$  -80 °C (5 min hold)  $\rightarrow$  50 °C) of **1-Na**. A 6.430 mg sample of **1-Na** in an aluminum pan was cooled/heated in flowing N<sub>2</sub> at a cooling/heating rate of 5 K/min.

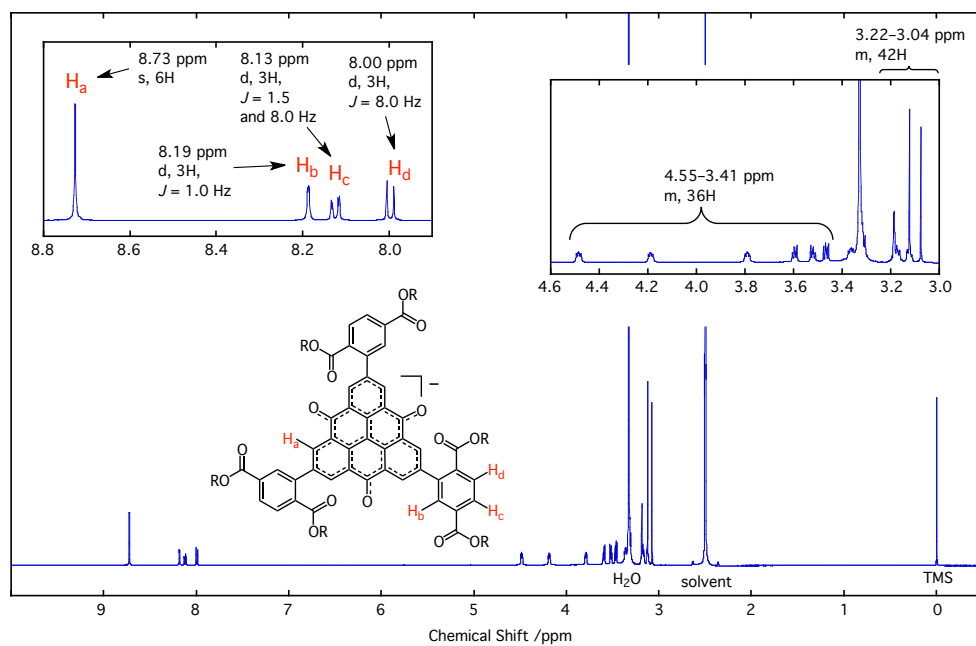


**Figure S2.** Preparation of a liquid film for **1-Na**.

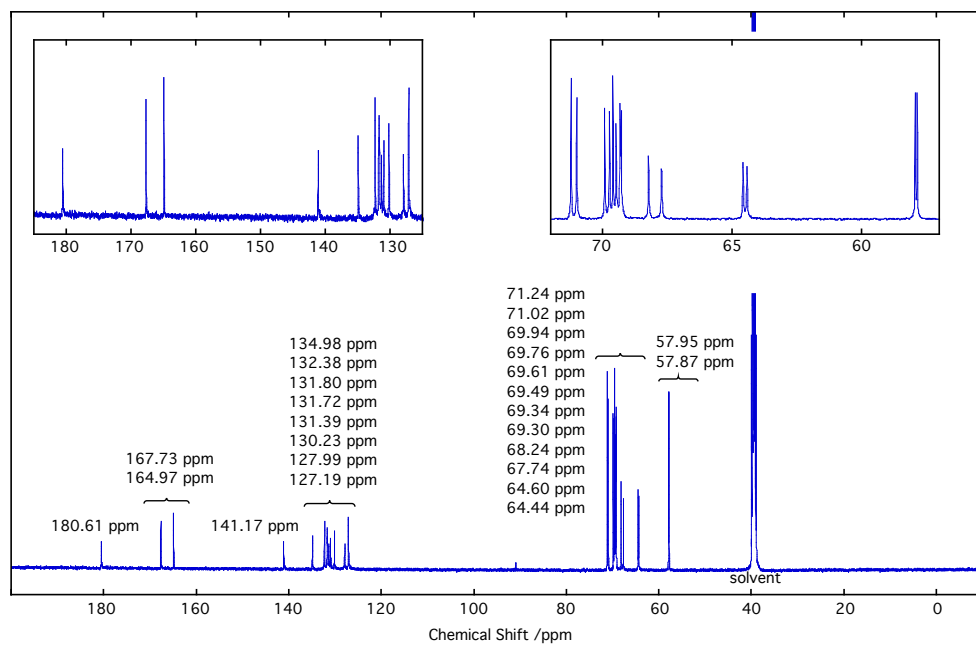


**Figure S3.** (a) A molecular size of **1** estimated by the molecular modeling. XRD profiles of (b) triethylene glycol and (c) a film prepared from **1-Na** liquid exposed to HCl vapor for 30 min on a glass plate at room temperature.





**Figure S6.**  $^1\text{H}$  NMR spectra of **1-Na** in DMSO- $d_6$ .



**Figure S7.**  $^{13}\text{C}$  NMR spectra of **1-Na** in DMSO- $d_6$ .

**Table S1.** Cartesian coordinates for the optimized structure of **TOT** anion.

atom	$X/\text{\AA}$	$Y/\text{\AA}$	$Z/\text{\AA}$
C	0.0000210601	0.0000000002	-0.0000000146
C	2.9223237225	0.0000000002	-0.0000000152
O	4.1650476977	0.0000000004	0.0000000089
C	-1.4611818162	-2.5307455562	-0.0000000148
O	-2.0825050623	-3.6070285028	0.0000000100
C	-1.4611818163	2.5307455565	0.0000000017
O	-2.0825050625	3.6070285028	0.0000000100
C	0.7115458061	-1.2323658428	-0.0000000088
C	2.1409374421	-1.2547188322	-0.0000000030
C	0.0161447496	-2.4813785974	-0.0000000053
C	2.1292559120	-3.6879531542	0.0000000087
H	2.6726896152	-4.6292315819	0.0000000161
C	2.8200094389	-2.4761813197	-0.0000000005
H	3.9054428869	-2.4392593269	0.0000000011
C	0.7344530462	-3.6801856174	0.0000000077
H	0.1596594584	-4.6016874481	0.0000000078
C	-1.4230104030	0.0000000001	-0.0000000115
C	-2.1571277792	-1.2266519237	-0.0000000067
C	-2.1571277792	1.2266519238	-0.0000000030
C	-4.2586217877	-0.0000000002	0.0000000035
H	-5.3455018568	-0.0000000002	0.0000000060
C	-3.5544388249	-1.2040268793	0.0000000000
H	-4.0650140895	-2.1625982444	-0.0000000114
C	-3.5544388249	1.2040268789	0.0000000035
H	-4.0650140900	2.1625982439	0.0000000089
C	0.7115458059	1.2323658433	-0.0000000129
C	0.0161447497	2.4813785976	0.0000000028
C	2.1409374418	1.2547188327	-0.0000000044

C	2.1292559124	3.6879531540	0.0000000001
H	2.6726896154	4.6292315818	0.0000000002
C	0.7344530466	3.6801856175	0.0000000087
H	0.1596594587	4.6016874481	0.0000000072
C	2.8200094393	2.4761813194	0.0000000034
H	3.9054428873	2.4392593262	-0.0000000041

**Table S2.** Cartesian coordinates for the optimized structure of **TOT-H**.

atom	$X/\text{\AA}$	$Y/\text{\AA}$	$Z/\text{\AA}$
C	0.0014523186	-0.0052416874	0.0000000487
C	2.8428875436	-0.0021731675	0.0000000068
O	4.1963730349	0.0781685190	-0.0000000133
C	-1.4734276212	-2.5219518375	0.0000001495
O	-2.0799433632	-3.5931727974	-0.0000000837
C	-1.4646051143	2.5192914139	0.0000000123
O	-2.0732731748	3.5894171694	-0.0000000062
C	0.7109886663	-1.2239953465	0.0000000429
C	2.1520775369	-1.2376123310	0.0000000097
C	0.0162009362	-2.4762968549	0.0000000541
C	2.1275001201	-3.6789147069	-0.0000000308
H	2.6611751821	-4.6237053490	-0.0000000639
C	2.8237709253	-2.4926345028	-0.0000000213
H	3.9110078276	-2.5409900975	-0.0000000551
C	0.7167942615	-3.6665604140	0.0000000091
H	0.1467478354	-4.5899865388	0.0000000215
C	-1.4503191424	-0.0033818770	0.0000000422
C	-2.1766818009	-1.2186986175	0.0000000531
C	-2.1713050641	1.2152123971	0.0000000147
C	-4.2749596053	0.0019168377	-0.0000000397
H	-5.3604212358	0.0043996676	-0.0000000758

C	-3.5759699012	-1.2029324395	-0.0000000031
H	-4.0899471568	-2.1586058450	0.0000000071
C	-3.5703753425	1.2039286305	-0.0000000285
H	-4.0801902813	2.1618608567	-0.0000000583
C	0.7107070177	1.2156683263	0.0000000328
C	0.0219163815	2.4695033092	0.0000000168
C	2.1464922267	1.2268030662	0.0000000232
C	2.1452541392	3.6588187001	0.0000000019
H	2.6819227410	4.6021640943	-0.0000000163
C	0.7343265194	3.6548441002	0.0000000023
H	0.1701990541	4.5821468443	-0.0000000136
C	2.8384973858	2.4698369490	0.0000000061
H	3.9222281888	2.4603443256	-0.0000000066
H	4.5888842927	-0.8035299563	-0.0000000387

**Table S3.** Detailed contributions of electronic transitions in some excited states for **TOT** anion.

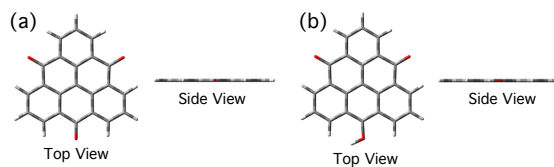
wavelength /nm	oscillator strength	contributions (coefficient)
566.37	0.0821	83 -> 84 (0.70262)
566.36	0.0822	83 -> 85 (0.70263)
		80 -> 85 (0.25848)
384.89	0.0000	81 -> 84 (0.25854)
		82 -> 84 (0.59565)
		80 -> 84 (0.25856)
384.88	0.0000	81 -> 85 (-0.25861)
		82 -> 85 (0.59558)
		80 -> 85 (-0.49159)
363.87	0.0000	81 -> 84 (0.49161)
		82 -> 94 (0.1122)

345.68	0.0916	77 -> 85 (-0.13927)
		78 -> 84 (-0.13396)
		79 -> 85 (0.13396)
		83 -> 87 (0.65832)
345.65	0.0915	77 -> 84 (0.13917)
		78 -> 85 (0.13403)
		79 -> 84 (0.13427)
		83 -> 88 (0.65827)
340.17	0.0076	83 -> 86 (0.70352)
331.81	0.0000	83 -> 89 (0.70513)
331.75	0.0000	83 -> 90 (0.70513)

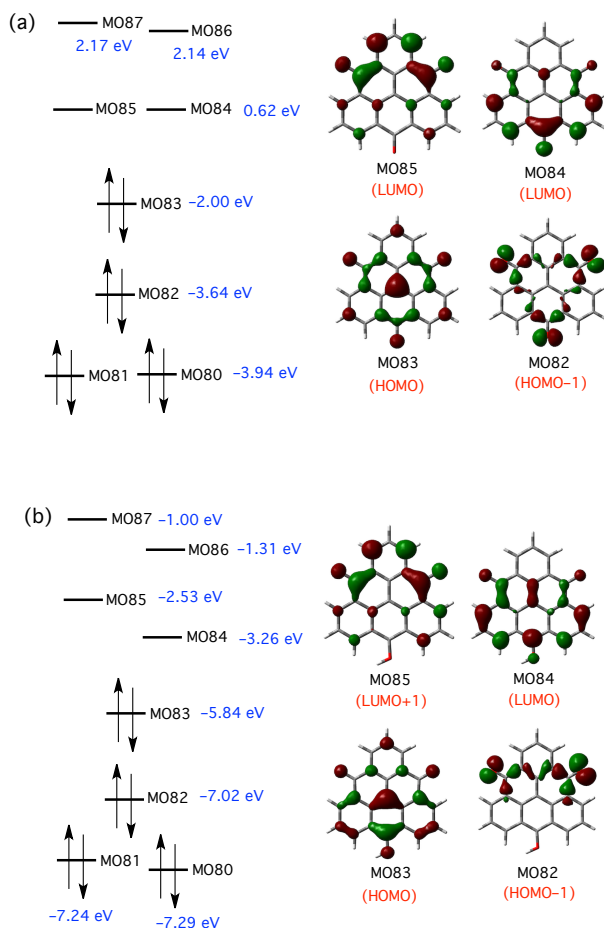
**Table S4.** Detailed contributions of electronic transitions in some excited states for **TOT-H**.

wavelength /nm	oscillator strength	contributions (coefficient)
547.34	0.1401	83 -> 84 (0.70276)
442.88	0.0257	80 -> 84 (-0.10528)
		83 -> 85 (0.69058)
428.21	0.0000	81 -> 84 (0.1246)
		81 -> 85 (0.23222)
		82 -> 84 (0.64783)
410.31	0.0000	81 -> 84 (0.58449)
		82 -> 85 (0.36953)
362.72	0.0001	77 -> 84 (0.14553)
		78 -> 84 (-0.2017)
		80 -> 84 (0.62587)
		83 -> 86 (0.17788)

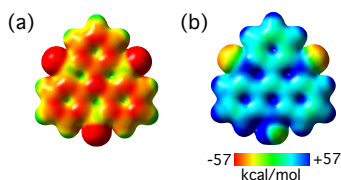
345.66	0.0188	78 -> 84 (0.38481)
		79 -> 84 (0.47737)
		80 -> 84 (0.16364)
		83 -> 86 (-0.29019)
344.56	0.0231	78 -> 84 (-0.32806)
		79 -> 84 (0.50317)
		80 -> 84 (-0.21934)
		83 -> 86 (0.27113)
341.46	0.0000	81 -> 84 (-0.33429)
		81 -> 85 (-0.15223)
		82 -> 84 (0.1655)
		82 -> 85 (0.57274)
325.11	0.0000	81 -> 84 (-0.16394)
		81 -> 85 (0.63412)
		82 -> 84 (-0.19832)
		82 -> 85 (0.13435)
309.62	0.0081	77 -> 84 (0.64448)
		79 -> 85 (-0.16759)
		80 -> 84 (-0.11757)
		83 -> 86 (-0.14395)



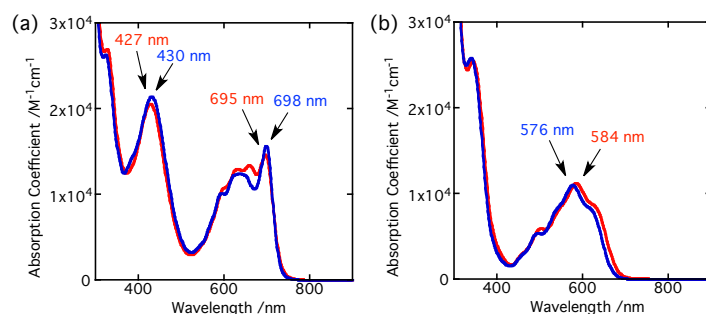
**Figure S8.** Optimized structures of (a) **TOT anion** and (b) **TOT-H**.



**Figure S9.** A diagram of the Kohn–Sham energies and an orbital shape of frontier MOs for (a) **TOT** anion and (b) **TOT-H**.



**Figure S10.** ESP mappings of (a) **TOT** anion and (b) **TOT-H**.



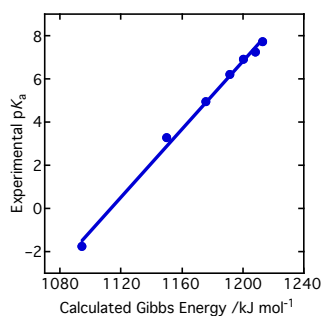
**Figure S11.** Electronic spectra of (a) **1-Na** (0.1 mM) in CH<sub>2</sub>Cl<sub>2</sub> (red line) and THF (blue line) and (b) **1-Na** (0.1 mM, ~4 mL) in CH<sub>2</sub>Cl<sub>2</sub> (red line) and THF (blue line) with a drop (~0.01 mL) of 6 M aqueous HCl. All spectra were concentration independent in the range of 0.025–0.1 mM.

**Table S5.** pH values, compositions, and concentrations of buffer solutions and absorbance values at 640 nm in the electronic spectra (see text).

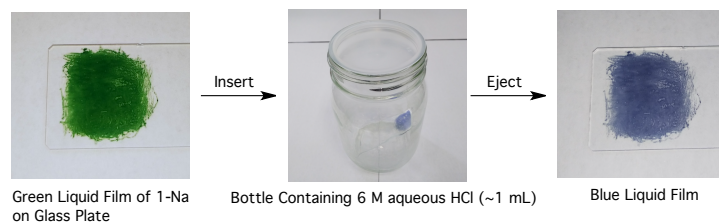
pH	HCl	citric acid	NaOH	NaHCO <sub>3</sub>	abs. at 640 nm
1.1	200 mM	–	–	–	0.503
1.4	100 mM	–	–	–	0.522
1.7	40 mM	60 mM	–	–	0.563
2.0	10 mM	90 mM	–	–	0.629
2.2	–	100 mM	–	–	0.677
2.4	–	90 mM	10 mM	–	0.749
2.7	–	80 mM	20 mM	–	0.830
3.0	–	70 mM	30 mM	–	0.922
3.3	–	60 mM	40 mM	–	1.002
3.8	–	50 mM	50 mM	–	1.063
4.5	–	40 mM	60 mM	–	1.092
5.6	–	30 mM	70 mM	–	1.108
8.4	–	–	–	100 mM	1.113

**Table S6.** Experimental  $pK_a$  and calculated  $\Delta G_0$  values for several tropolone derivatives.

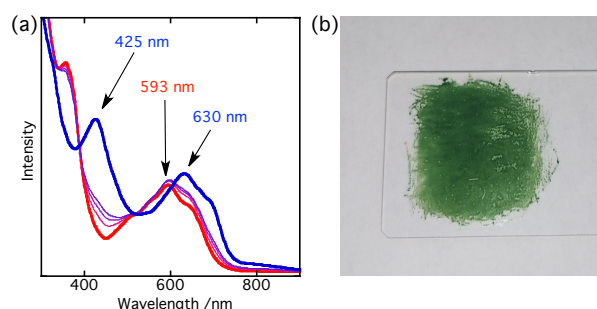
tropolone	exp. $pK_a$ (ref.)	calcd. $\Delta G_0$
unsubstituted	6.92 (S10b)	1200.14
5-OMe	7.75 (S10b)	1212.88
4-Me	7.26 (S10b)	1208.09
4-COMe	6.23 (S10c)	1190.95
5-COMe	4.97 (S10c)	1175.28
5-NO <sub>2</sub>	3.30 (S10d)	1149.84
5-N <sub>2</sub>	-1.72 (S10a)	1094.07

**Figure S12.** Plot prepared from the experimental  $pK_a$  values against the calculated  $\Delta G_0$  values for several tropolone derivatives, fitted with a least square line ( $R = 0.9977$ ).**Table S7.** Calculated  $pK_a$  values for some acids in this work together with their experimental values.

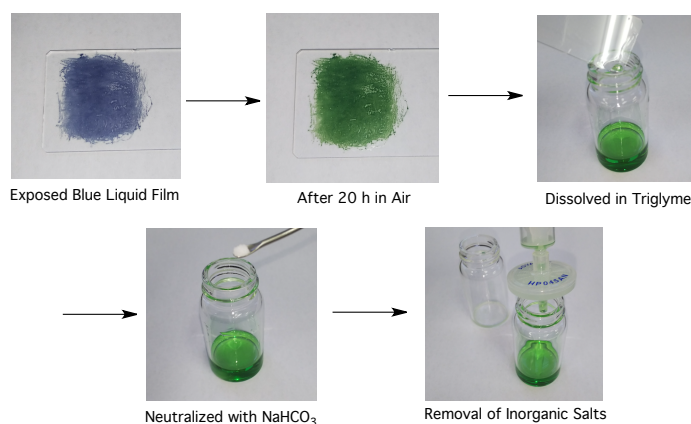
acid	calcd. $pK_a$	exp. $pK_a$ (ref.)
<b>TOT-H</b>	1.47	2.58 (for <b>1-H</b> , see text)
phenol	8.90	9.95 (S11)
tropolone	6.87	6.92 (S10b)
benzoic acid	5.28	4.20 (S6)



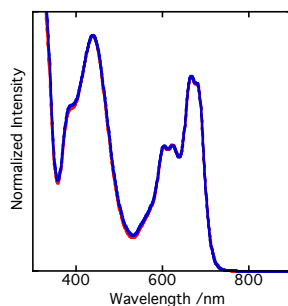
**Figure S13.** A liquid film of **1-Na** exposed to HCl vapor.



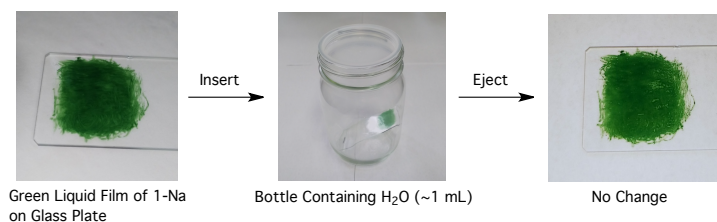
**Figure S14.** (a) Electronic spectra of a film prepared by painting the liquid of **1-Na** over a glass plate soon after standing in a bottle containing 6 M aqueous HCl (~1 mL) for 30 min (red line), 10 min later in air after the exposure (reddish purple line), 20 min (purple line), 30 min (blueish purple line), and 20 h (blue line). (b) The exposed liquid film after 20 h.



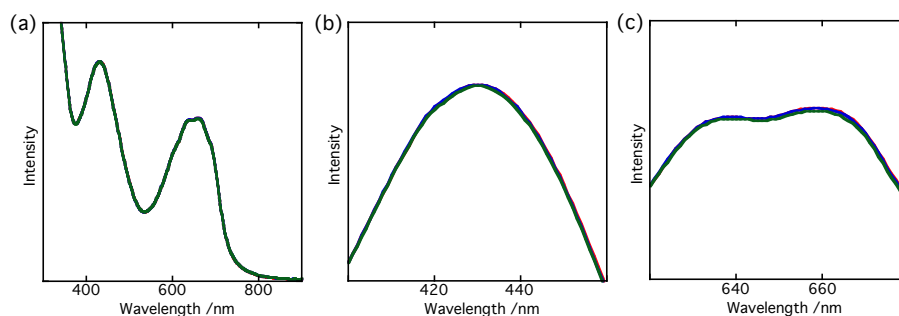
**Figure S15.** A solution of the exposed liquid film neutralized with an excess amount of  $\text{NaHCO}_3$  in triglyme.



**Figure S16.** Normalized electronic spectra for **1-Na** (0.1 mM, red line) and the solution of the exposed liquid film neutralized with an excess amount of  $\text{NaHCO}_3$  (blue line) in triglyme.



**Figure S17.** A control experiment using  $\text{H}_2\text{O}$  instead of 6 M aqueous  $\text{HCl}$ .



**Figure S18.** (a) Electronic spectra of a film prepared by painting the liquid of **1-Na** over a glass plate before the exposure (red line), soon after standing in a bottle containing  $\text{H}_2\text{O}$  (~1 mL) for 30 min (blue line), and 30 min later in air after the exposure (green line). Magnified peaks at (b) 430 nm and (c) 658 nm.