**Electronic Supplementary Information** 

# Exploring the local solvation structure of redox molecules in a mixed solvent

# for increasing the Seebeck coefficient of thermocells

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## **1. Experimental Section**

#### Chemicals

*p*-chloranil (CA) was purchased from Tokyo Chemical Industry (TCI) and recrystallized with toluene and 1-propanol. Tetrabuthylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was purchased from TCI and recrystallized with ethanol. Dehydrated ethanol and acetonitrile were purchased from Wako Pure Chemical Corporation.

#### Thermoelectric measurement

The Preparation of the electrolyte of  $CA^{-/2-}$  and the thermoelectric measurement were carried out under Ar atmosphere.  $CA^{-}$  and  $CA^{2-}$  were prepared by electrochemical reduction of neutral CA. CA (1 mM) and TBAPF<sub>6</sub> (0.1 M) dissolved in acetonitrile (20 mL) was injected in one side of an H-shape cell separated by a glass filter in the middle, and the same electrolyte without CA was injected in the other side of the cell. Pt coil, Ag wire, and Pt coil were used as working, reference, and counter electrodes, respectively.  $CA^{-}$  and  $CA^{2-}$  were prepared by applying constant -0.5 and -1.1 V vs Ag pseudo electrode, respectively. Fig. S2a shows the time-course charge of the reduction. Both coulombic efficiencies were above 90 %, and we confirmed the preparation of  $CA^{-}$  and  $CA^{2-}$ .

The prepared solutions were mixed, and various concentrations of EtOH (0, 0.04, 0.25, or 1.3 M) were added. Then, we obtained the acetonitrile electrolytes containing  $CA^{-/2-}$  (0.5 mM) redox couple and various concentrations of EtOH (0, 0.04, 0.25, or 1.3 M). The electrolyte was put into an H-shaped cell with magnetic stirrers (Fig. S1a).

The temperature on one side was cooled by a water circulator, and the temperature on the other side was heated by a ribbon heater, forming temperature differences between the two sides of the thermocell (Fig. S1a and S2b). Pt wire and GC plate were used as the electrodes, and the voltage was recorded by a source meter 2401 (Keithley). The temperatures of both sides of the cell were monitored by thermocouples (TM201, AS ONE). Two thermocouples were immersed in the stirred electrolyte and held near the electrode to measure temperature of the electrolyte. The thermocell was covered by septum stoppers to prevent the electrolyte from vaporization. Diameters of the Pt wire and GC plate are 1.0 and 3.0 mm, respectively. The distance between the electrodes is 9.5 cm.

#### **Current-voltage measurement**

Current-voltage measurement was conducted by ALS 620 (BAS) under Ar atmosphere. The same experimental as in the thermoelectric measurement was used to record the output current while applying a temperature difference and monitoring the temperature of the electrolyte. Pt wire was used as the electrodes. When the temperature difference between the hot and cold electrodes was around 5 K, the current-voltage was measured by sweeping the voltage from the open circuit voltage to 0 V with stirring the electrolyte. The scan rate was  $0.5 \text{ mV s}^{-1}$ . Pt wires were used as electrodes, and the current values were recorded by a source meter 2401 (Keithley).

#### **Continuous power generation**

Continuous power generation of the thermocell was carried out using an acetonitrile electrolyte containing  $CA^{-/2-}$  (0.5 mM, each) redox couple, TBAPF<sub>6</sub> (0.1 M), and EtOH (1.3 M) under the Ar atmosphere. The temperature on one side was cooled by a water circulator, and the temperature on the other side was heated by a hot plate (Fig. S2c). GC plate (Fig. S1d) was used as the electrodes at both cold and hot sides, and the current values were recorded by a source meter 2401 (Keithley). The temperature difference between the hot and cold electrodes was kept between 12 and 13 K, and the current was measured while applying a constant voltage of 16.7 mV. The temperatures of both sides of the cell were monitored by a couple of thermocouples (TM201, AS ONE). Two thermocouples were immersed in the stirred electrolyte and held near the electrode to measure temperature of the electrolyte. The thermocell was covered by septum stoppers to prevent the electrolyte from vaporization.

#### **UV-Vis spectroscopy**

UV-Vis spectroscopy was conducted with a UV-vis spectrometer (V770. JASCO) at room temperature at the 200 to 600 nm wavelength. The sample preparation and measurement were executed under an inert gas atmosphere. Acetonitrile solutions of CA (0.5 mM) and TBAPF<sub>6</sub> (0.1 M) with various concentrations of EtOH (0–5 M) were prepared and put into a quartz cell (For neutral CA). In addition, the bulk electrolysis was performed at constant potentials of -0.7 and -1.4 V vs Ag/Ag<sup>+</sup> to prepare the reduced CA species, CA<sup>--</sup> and CA<sup>2-</sup>, respectively. Each reduced electrolyte was mixed with various concentrations of EtOH and acetonitrile electrolytes of CA<sup>--</sup> or CA<sup>2--</sup> (0.5 mM), TBAPF<sub>6</sub> (0.1 M), and EtOH (0–5 M) were prepared and put into a quartz cell (For CA<sup>--</sup> and CA<sup>2-</sup>).

#### Square wave voltammetry at various temperatures (VT-SWV)

VT-SWV was measured with ALS 620 (BAS) using an acetonitrile solution containing 1.0 mM of CA and 0.1 M of TBAPF<sub>6</sub> with various EtOH concentrations under N<sub>2</sub> gas flow. GC plate,  $Ag/Ag^+$ , and Pt wire were used as the working, reference, and counter electrodes, respectively. N<sub>2</sub> gas was bubbled into the electrolyte during the measurement. Temperature of the electrolyte was controlled with a Peltier temperature-controlling equipment (NDC-100, NISSIN Japan). Temperature of the electrolyte was monitored by a thermocouple (TM201, AS ONE, Japan), which was immersed in the electrolyte and its tip was held near the working electrode.

The observed redox potential shifts of the CA<sup>•-/2-</sup> redox pair with changing temperatures are shown in Fig. S21. The slope of the graph shows a  $\Delta E/\Delta T$  value of the redox pair. Considering the  $\Delta E/\Delta T$  of Ag/Ag<sup>+</sup> reference electrode is ca. +0.2 mV K<sup>-1</sup>,<sup>1</sup> the S<sub>e</sub> can be estimated by adding 0.2 mV K<sup>-1</sup> to the value of  $\Delta E/\Delta T$ . The estimated S<sub>e</sub> values were converted into the values of redox entropy ( $\Delta S_{rc}$ ) by using Eq. 1, as shown in Table S2.

Electrochemical impedance spectroscopy measurement

Electrochemical impedance measurement was carried out with ALS 620 (BAS) for the acetonitrile solution containing CA (1.0 mM), TBAPF<sub>6</sub> (0.1 M), and various concentrations of EtOH (0, 0.04, 0.25, or 1.3 M). Glassy carbon electrode, Ag/Ag<sup>+</sup> electrode, and Pt wire were used as the working electrode, reference electrode, and counter electrode, respectively. The impedance of the redox reactions of CA<sup>0/•-</sup> and CA<sup>•-/2-</sup> was measured at the redox potentials of -0.277 (CA<sup>0/•-</sup>) and -1.085 (CA<sup>•-/2-</sup>) V vs Ag/Ag<sup>+</sup> reference electrode, respectively. The frequency was changed in the range of 1 Hz ~ 100 kHz, and the potential amplitude was set at 10 mV.

### **2. DFT Calculations**

#### **Theoretical Models and Calculations**

We theoretically investigated the equilibrium geometries, electronic states, and electronic excitations of CA<sup>-</sup>, CA<sup>2-</sup>, and local solvation structures (clusters) composed of CA<sup> $-/2^-$ </sup> and several EtOH molecules. For all the geometry optimization calculations, we employed the Kohn–Sham density functional theory (DFT) along with the B3LYP functional<sup>2–4</sup> and cc-pVDZ basis set.<sup>5,6</sup> With the acetonitrile solvation effects incorporated using the polarizable continuum model (PCM),<sup>7</sup> we studied the EtOH solvation configurations. The self-consistent-field stability analysis<sup>8,9</sup> was performed for all the electronic states to make sure that they have reliable electronic configurations.

First, we obtained the equilibrium geometries of CA<sup>--</sup> and CA<sup>2-</sup> using Gaussian 16.<sup>10</sup> Both of the geometries belong to the  $D_{2h}$  point group. The ground-state term symbols for CA<sup>--</sup> and CA<sup>2-</sup> are  ${}^{2}B_{2g}$  and  ${}^{1}A_{g}$ , respectively. We then performed the so-called host-ligand coordination search implemented in CONFLEX 9.11 This is a brute-force scatter search to locate many local-energy-minimum geometries of host-ligand systems. In our calculations, we regarded CA<sup>+-</sup> (or CA<sup>2-</sup>) as a host and one EtOH molecule as a ligand to thoroughly examine the local solvation structure. CONFLEX 9 generated 2592 (=  $12 \times 6^3$ ) geometries of CA<sup>-/2-</sup>... EtOH solvation structure, in which one EtOH molecule was arranged in different locations (i.e., 12 vertices of a regular icosahedron) and different orientations (i.e., six-fold rotation around each of the x, y, and z axes) around CA<sup>-/2-</sup>. The 2592 geometries were used to start geometry optimization with Gaussian 16.10 This CONFLEX/Gaussian-hybrid host-ligand search successfully yielded 1333 geometries for CA<sup>+-</sup>···EtOH and 1698 geometries for CA<sup>2-...</sup>EtOH. The lowest-energy group among the resultant geometries consists of geometries in which the OH group of EtOH is bound to an O atom of  $CA^{-/2-}$ . The second- and third-lowest energy groups consist of geometries in which the OH group of EtOH is bound to a Cl atom and two Cl atoms of CA<sup>--/2-</sup>, respectively. In each of the groups, we focused on the geometry that has no imaginary-frequency normal modes and is energetically stable. Such geometries in the lowest, second-lowest, third-lowest energy groups are denoted by  $CA^{-/2-}(O)$ . EtOH, CA<sup>-/2-</sup>(Cl)…EtOH, and CA<sup>-/2-</sup>(2Cl)…EtOH, respectively. Here, O, Cl, and 2Cl in parentheses indicate the constituent atom(s) of  $CA^{-/2-}$  to which the OH group is bound.

We further obtained equilibrium geometries of local solvation structures including several EtOH molecules as follows. Focusing on  $CA^{*-/2-}(O)^{*-}EtOH$  and  $CA^{*-/2-}(Cl)^{*-}EtOH$ , we inverted the EtOH geometry with respect to the center of the six C atoms of  $CA^{*-/2-}$  to yield an additional EtOH geometry. The subsequent geometry optimization using Gaussian 16 yielded equilibrium geometries without any imaginary-frequency normal modes. These geometries are denoted by  $CA^{*-/2-}(2O)^{*-}2EtOH$  and  $CA^{*-/2-}(2Cl)^{*-}2EtOH$ . Because the binding between an OH group and an O atom of  $CA^{*-/2-}$  is relatively strong, we further obtained equilibrium geometries of  $CA^{*-/2-}(3O)^{*-}3EtOH$  and  $CA^{*-/2-}(4O)^{*-}4EtOH$ , including three and four EtOH molecules, respectively, to examine the solvation capability. Let us note that we constructed the initial geometries including four EtOH molecules, required to start the optimization, by performing two-fold rotation of the EtOH geometries in  $CA^{*-/2-}(2O)^{*-}2EtOH$  around the axis passing through the two O atoms of  $CA^{*-/2-}$ . Simple removals of an EtOH molecule from them yielded initial geometries including three EtOH

molecules.

To address the question of how the level of theory can affect the energetics of EtOH solvating around  $CA^{-/2-}$ , we also performed single-point calculations using the aug-cc-pVTZ basis set<sup>5,6,12</sup> with and without the Grimme's D3 dispersion correction and Becke–Johnson damping (D3BJ).<sup>13</sup>

To obtain UV-Vis absorption spectra, we performed time-dependent density functional theory (TD-DFT) calculations<sup>5,6,12,14</sup> with the aug-cc-pVTZ basis set.<sup>5,6,12</sup> Every stick spectrum we obtained was convoluted with a Gaussian function with a half width at half maximum (HWHM) of 0.333 eV. We also performed single-point TD-DFT calculations of CA<sup> $-/2^-$ </sup> in a polarizable continuum that describes the EtOH solvation. These calculations correspond to the extreme case of a high EtOH concentration within the PCM framework. Through the comparison between explicit and implicit (*i.e.*, PCM) considerations of the EtOH solvation around CA<sup> $-/2^-$ </sup>, we examined the effects of the hydrogen bonding, a molecular nature of the EtOH solvation, on the UV-Vis absorption spectra.

## 3. Geometry Optimization and Absorption Peak Assignment of CA species

#### **Optimized Geometries**

Fig. S15a and S16a and Fig. S15b and S16b show the potential energy changes and geometries for the EtOH solvating around the O atoms of CA<sup>+-</sup> and CA<sup>2-</sup>, respectively. All the energies in Fig. S15 (S16) are relative to the reference energy of CA<sup>+-/2-</sup> and two (four) EtOH molecules at infinite separation; in other words, the energy of every structure in Fig. S15 and S16 corresponds to the negative of the binding energy. The binding energy is positive both for CA<sup>+-</sup> and CA<sup>2-</sup> (Fig. S15 and S16, black solid circles). The binding energy for CA<sup>2-</sup> is much greater than that for CA<sup>+-</sup> (*e.g.*, 26.9 kcal mol<sup>-1</sup> for CA<sup>2-</sup>(2O)...2EtOH and 15.4 kcal mol<sup>-1</sup> for CA<sup>+-</sup>(2O)...2EtOH). Thanks to the out-of-plane contact structure, multiple EtOH molecules can be readily bound to the O atoms of CA<sup>+-/2-</sup> without incurring strong steric clashes (Fig. S16). The total binding energy is indeed almost additive with respect to the number of EtOH (at least up to four) and is greater in CA<sup>2-</sup> than in CA<sup>+-</sup> (52.6 and 30.6 kcal mol<sup>-1</sup> for four EtOH adsorption to CA<sup>2-</sup> and CA<sup>+-</sup>, respectively).

When using a highly accurate basis set, aug-cc-pVTZ,<sup>5,6,12</sup> with and without the Grimme's D3 dispersion correction and Becke–Johnson damping (D3BJ),<sup>13</sup> the binding energies become somewhat smaller (Fig. S15 and S16, green diamonds and orange squares), but the aforementioned energetic features remain unchanged.

The EtOH solvation around  $CA^{2-}$  is energetically stronger than that around  $CA^{-}$  because hydrogen bonding with the O atoms of  $CA^{2-}$  is strong. This is evident as the pronounced electronegative charges of the O atoms of  $CA^{2-}$  and the short distance between an OH group and its nearby O atom of  $CA^{2-}$ . In fact, the natural atomic charges<sup>15</sup> of the O atoms of  $CA^{2-}$  (-0.83e) are more electronegative than those of  $CA^{-}$  (-0.64e). Besides, the H atom of an OH group is close to an O atom of  $CA^{2-}$ ; for example, the H···O distance is 1.61 Å for  $CA^{2-}(O)$ ···EtOH and 1.81 Å for  $CA^{-}(O)$ ···EtOH. As compared to the EtOH solvation around the O atoms of  $CA^{--}$  and  $CA^{2-}$  (Fig. S15), that around the Cl atoms is noticeably weak (Fig. S17), which is consistent with the long H···Cl distance (*e.g.*, 2.42 Å for  $CA^{2-}(Cl)$ ···EtOH and 2.58 Å for  $CA^{--}(Cl)$ ···EtOH).

#### **Absorption Peak Assignments**

#### • Observed UV-Vis spectra of CA species

The UV-Vis spectrum of neutral CA was measured in acetonitrile electrolyte (0.5 mM CA and 0.1 M TBAPF<sub>6</sub>), and the absorption peak of only neutral CA species was observed at 288 nm (Fig. S5b). Then, we applied constant potentials of -0.7 and -1.4 V (vs Ag/Ag<sup>+</sup>) to prepare the two reduced species, CA<sup>+-</sup> and CA<sup>2-</sup>, respectively. After the reduction of neutral CA to CA<sup>+-</sup> at -0.7 V, the absorption peak of neutral CA disappeared, and the CA<sup>+-</sup> radical anion appeared at 321, 420, and 448 nm (Fig. S5b).<sup>16,17</sup> After the further reduction by applying -1.4 V, the absorption peak at 359 nm was observed, which is assigned to CA<sup>2-</sup> anion.<sup>17,18</sup> These results confirm that the first reduction at -0.28 V in Fig. S5a corresponds to the reduction of CA to CA<sup>+-</sup> and the second reduction at -1.1 V corresponds to the reduction of CA<sup>+-</sup> to CA<sup>2-</sup>.

#### Calculated UV-Vis spectra of CA species

To conduct the peak assignments of the UV-Vis absorption spectra and examine the effects of the EtOH solvation on the spectra, we performed TD-DFT calculations<sup>14</sup> with the aug-cc-pVTZ basis set.<sup>5,6,12</sup> Note that for the peak assignments, we use the symbols of the frontier orbitals of neutral CA shown in Fig. S7 (*e.g.*,  $\pi^*(b_{2g})$ ), as well as the multi-electron term symbols for CA<sup>•-/2-</sup> (*e.g.*, <sup>2</sup>B<sub>2g</sub>), because the orbitals are fairly similar to those of CA<sup>•-/CA<sup>2-</sup></sup>. The overall profiles of the theoretical spectra for CA<sup>•-</sup> (Fig. S9a, black curve) and CA<sup>2-</sup> (Fig. 2a, bottom and S9b, black curve) without EtOH are similar to those of the experimental ones (Fig. S5b and S6b–c).

In the convoluted spectrum of CA<sup>--</sup> without EtOH (Fig. S9a and S10a, black curves), a strong sharp peak, a weak peak, and a broad peak appear at 219, 273, and ~415 nm, respectively, which correspond to the experimental peaks at 214, 321, and ~450 nm. All these are associated with  $\pi^* \leftarrow \pi$  ( $\pi^*$ ) excitations. Specifically, three  ${}^{2}B_{3u} \leftarrow {}^{2}B_{2g}$  excitations at 219, 274, and 428 nm (three intense sticks labeled  ${}^{2}B_{3u}$ , Fig. S9a) are attributed mainly to the  $\pi^*(a_u) \leftarrow \pi(b_{1g})$  excitation, the  $\pi^*(b_{3u}) \leftarrow \pi^*(b_{2g})$  and  $\pi^*(a_u) \leftarrow \pi(b_{1g})$  excitations, and the  $\pi^*(b_{2g}) \leftarrow \pi(b_{3u})$  excitation, respectively. One  ${}^{2}A_u \leftarrow {}^{2}B_{2g}$ ( $\pi^*(a_u) \leftarrow \pi^*(b_{2g})$ ) excitation at 406 nm, together with the  ${}^{2}B_{3u} \leftarrow {}^{2}B_{2g}$  excitation at 428 nm, gives rise to the broad peak at ~415 nm. Although not evident in the theoretical peak owing to its broadness, the peak splitting associated with these two excitations actually appears in the experimental peak at ~450 nm (420 and 448 nm, Fig. S5b and S6b).

In the convoluted spectrum of CA<sup>2-</sup> without EtOH (Fig. 2a, bottom, S9b, and S10b, black curves), a strong sharp peak, a small shoulder on it, and a broad peak appear at 221, 253, and 379 nm, respectively, which correspond to the experimental peaks at 223, 258, and 359 nm. The sharp peak and the shoulder are attributed primarily to the  $\pi^*(a_u) \leftarrow \pi(b_{1g})$  and Rydberg( $b_{3u}$ )  $\leftarrow \pi^*(b_{2g})$  excitations and the  $\pi^*(b_{3u}) \leftarrow \pi^*(b_{2g})$  excitation, respectively. The Rydberg( $b_{3u}$ ) orbital is diffuse and has a 4f shape (Fig. S8). These excitations below 260 nm are all  ${}^{1}B_{1u} \leftarrow {}^{1}A_{g}$  excitations (Fig. 2a, bottom). There is no peak at ~300 nm, and most importantly, the broad peak of CA<sup>--</sup> at ~415 nm (Fig. S9a) is noticeably blue-shifted to 379 nm in CA<sup>2-</sup> (Fig. 2a, bottom and S9b), as with the experimental spectra (Fig. S5b and S6b–c). Similar to the  ${}^{2}A_{u} \leftarrow {}^{2}B_{2g}$  excitation of CA<sup>+-</sup> at 406 nm which, in part, causes the broad peak at ~415 nm, the  ${}^{1}B_{2u} \leftarrow {}^{1}A_{g}$  excitation of CA<sup>2-</sup> that causes the broad peak at 379 nm (the black stick at 381 nm, Fig. 2a, bottom) is attributed to the  $\pi^*(a_u) \leftarrow \pi^*(b_{2g})$  excitation (LUMO+1  $\leftarrow$  HOMO excitation in CA<sup>2-</sup>, Fig. 2c). We summarized the peak assignment in Table 1.

#### The peak shifts of CA<sup>2-</sup> at 379 nm in the TD-DFT calculation

Our calculations show that the EtOH solvation around the O atoms of  $CA^{2-}$  (specifically, out-of-plane contact of the OH group(s) to  $CA^{2-}$ ) causes the blue shift of the broad peak at 379 nm ( ${}^{1}B_{2u} \leftarrow {}^{1}A_{g}$ , Fig. 2a and 2c). Even if pure EtOH solvation is considered within the PCM framework, a similar blue shift does not appear (Fig. S9b, gray curve). This is partly because the PCM model does not explicitly consider hydrogen bonding and partly because the permittivity (dielectric constant) of EtOH is not very different from that of acetonitrile. In addition, the EtOH solvation around the O atoms of  $CA^{*-}$  and around the Cl atoms of  $CA^{*-/2-}$  does not cause a similar blue shift (Fig. S9–S14). These results confirm that the hydrogen bonding between EtOH and the O atoms of  $CA^{2-}$  plays a major role in the blue shift.

## 4. The Derivation of the Theoretical Model Equations on Square Wave Voltammetry

#### Redox potential shift of CA by adding an H-bonding donor

The redox potentials from neutral CA to CA<sup>-</sup>  $(E_{1/2}^{I})$  and from CA<sup>-</sup> to CA<sup>2-</sup>  $(E_{1/2}^{II})$  are expressed by the Nernst equation as below:

$$E_{1/2}^{I} = E_{0}^{I} + \frac{RT}{nF} \ln\left(\frac{[CA]}{[CA^{\bullet^{-}}]}\right)$$
(Eq. S1)  
$$E_{1/2}^{II} = E_{0}^{II} + \frac{RT}{nF} \ln\left(\frac{[CA^{\bullet^{-}}]}{[CA^{2^{-}}]}\right)$$
(Eq. S2)

where  $E_0^I$  and  $E_0^{II}$  are the standard potentials of CA<sup>0/--</sup> and CA<sup>--/2-</sup>, respectively, R is the gas constant, T is the absolute temperature, n is the number of electrons, and F is Faraday constant. When  $CA^{-}$  and  $CA^{2-}$  are bound with the number of *i* and *j* of H-bonding donor molecules, respectively, the association reactions are shown in Eq. S3 and S4.

$$CA^{\bullet-} + iD \rightleftharpoons CA^{\bullet-} - D_i$$
 (Eq. S3)  
 $CA^{2-} + jD \rightleftharpoons CA^{2-} - D_j$  (Eq. S4)

The binding constants of the H-bonding donor with CA<sup>--</sup> ( $K_{i}^{I}$ , the number of the donor molecules is *i*) and CA<sup>2-</sup> ( $K_{j}^{II}$ , the number of the donor molecules is *j*) are represented by Eq. S5 and S6, respectively.

$$K_{i}^{I} = \frac{[CA^{\bullet -} - D_{i}]}{[CA^{\bullet -}]_{free}[D]^{i}}$$
(Eq. S5)  
$$K_{j}^{II} = \frac{[CA^{2 -} - D_{j}]}{[CA^{2 -}]_{free}[D]^{j}}$$
(Eq. S6)

The total concentration of free CA<sup>--</sup> and the one binding with the donor molecules ( $[CA^{--}]_{total}$ ) is expressed in Eq. S7. and the total concentration of  $CA^{2-}([CA^{2-}]_{total})$  is also expressed in Eq. S8.

$$[CA^{\bullet^{-}}]_{total} = [CA^{\bullet^{-}}]_{free} + [CA^{\bullet^{-}} - D] + [CA^{\bullet^{-}} - D_2] + \dots + [CA^{\bullet^{-}} - D_i]$$
(Eq. S7)  
$$[CA^{2^{-}}]_{total} = [CA^{2^{-}}]_{free} + [CA^{2^{-}} - D] + [CA^{2^{-}} - D_2] + \dots + [CA^{2^{-}} - D_j]$$
(Eq. S8)

Previous reports assumed that only free CA species (H-bonding is not formed) undergo the redox reaction and that an Hbonding donor can bind with only CA<sup>-</sup> and CA<sup>2-</sup>, but not with neutral CA.<sup>18-23</sup> Consequently, Eq. S1 and S2 can be transformed by using Eq. S5 and S7, and Eq. S6 and S8, respectively.

(Eq. S8)

$$E_{1/2}^{\ I} = E_0^{\ I} + \frac{RT}{nF} \ln \left[ \frac{[CA]_{total}}{[CA^{\bullet -}]_{total}} (1 + K_1^{\ I}[D] + K_2^{\ I}[D]^2 + \dots + K_i^{\ I}[D]^i) \right]$$
(Eq. S9)

$$E_{1/2}^{II} = E_0^{II} + \frac{RT}{nF} \ln \left( \frac{[CA^{2^-}]_{total} 1 + K_1^{I}[D] + K_2^{I}[D]^2 + \dots + K_j^{I}[D]'}{[CA^{2^-}]_{total} 1 + K_1^{I}[D] + K_2^{I}[D]^2 + \dots + K_i^{I}[D]^i} \right)$$
(Eq. S10)

In the absence of an H-bonding donor ([D] = 0), the total concentration of CA<sup>--</sup> is equal to the concentration of free CA<sup>--</sup>. The difference ( $\Delta E_{1/2}^{l}$ ) between the  $E_{1/2}^{l}$  without the H-bonding donor and with the donor is represented as Eq. S11. Note [CA]<sub>total</sub>

that this operation deletes the terms,  $E_0^I$  and  $[CA^{\bullet -}]_{total}$ .

$$\Delta E_{1/2}^{\ I} = \frac{RT}{nF} \ln \left( 1 + K_1^I[D] + K_2^I[D]^2 + \dots + K_i^I[D]^i \right)$$
(Eq. S11)

By performing the same operation for CA<sup>2–</sup> as Eq. S11, the difference between the  $E_{1/2}^{II}$  with and without the H-bonding donor ( $\Delta E_{1/2}^{II}$ ) is represented as Eq. S12.

$$\Delta E_{1/2}^{II} = \frac{RT}{nF} \ln \left( \frac{1 + K_1^{II}[D] + K_2^{II}[D]^2 + \dots + K_j^{II}[D]^j}{1 + K_1^{I}[D] + K_2^{I}[D]^2 + \dots + K_i^{I}[D]^i} \right)$$
(Eq. S12)

EtOH concentration and the binding constants generate the positive shifts of the CA redox potentials.

We fitted the experimental  $\Delta E_{1/2}^{I}$  values with Eq. S11, which revealed that one or two EtOH molecules are bound to CA<sup>--</sup> anion, as shown in Fig. S18 and Table S1. In  $\Delta E_{1/2}^{II}$ , the number of EtOH molecules bound to the CA<sup>2-</sup> anion was set to two or four, because CA<sup>2-</sup> has a symmetric structure. TD-DFT calculation also showed four H-bond-accepting sites per a CA<sup>2-</sup> anion (Fig. 2c). From this simplification, Eq. S12 can be transformed as Eq. S13.

$$\Delta E_{1/2}^{II} = \frac{RT}{nF} \ln \left( \frac{1 + K_2^{II}[D]^2 + K_4^{II}[D]^4}{1 + K_1^{I}[D] + K_2^{I}[D]^2} \right)$$
(Eq. S13)

We then fitted the experimental values of  $\Delta E_{1/2}^{ll}$  with Eq. S13 by using the values of binding constants  $K_1^l$  and  $K_2^l$  (yielded from the theoretical fitting of  $\Delta E_{1/2}^{ll}$ ). Fig. S18 shows the result of the theoretical fitting at various temperatures (288–308 K). The obtained binding constants are listed in Table S1.

#### The molar fraction of the number of bound EtOH molecules

The molar fraction of CA<sup>--</sup> binding with the number *i* of the donor molecules  $(\varphi_i^l)$  is expressed in Eq. S14 by transforming Eq. S7.

$$\varphi_{i}^{l} = \frac{\left[CA^{\bullet^{-}} - D_{i}\right]}{\left[CA^{\bullet^{-}}\right]_{free} + \left[CA^{\bullet^{-}} - D\right] + \left[CA^{\bullet^{-}} - D_{2}\right] + \dots + \left[CA^{\bullet^{-}} - D_{i}\right]}$$
(Eq. S14)

Eq. S14 can be transformed by using the binding constant,  $K_i^l$  (Eq. S5) into Eq. S15. Then, we performed the same operation for CA<sup>2-</sup> and obtained the molar fraction of CA<sup>2-</sup> binding with the number *j* of the donor molecules ( $\varphi_j^{II}$ ) as Eq. S16.

$$\varphi_i^I = \frac{K_i^I[D]^i}{1 + K_1^I[D] + K_2^I[D]^2 + \dots + K_i^I[D]^i}$$
(Eq. S15)

$$\varphi_j^{II} = \frac{K_j^{II}[D]^j}{1 + K_1^{II}[D] + K_2^{II}[D]^2 + \dots + K_j^{II}[D]^j}$$
(Eq. S16)

The  $\varphi_i^l$  and  $\varphi_j^{ll}$  at various temperatures (288–308 K) are summarized in Fig. S19.

#### The enthalpy and entropy of the association of various numbers of EtOH

Table S1 shows the binding constants between CA species and various numbers of EtOH at various temperatures. The binding constants are plotted as a function of the reciprocal of temperature (Fig. S20). The plots were fitted with the van't Hoff equation (Eq. S17), and we can obtain the enthalpy ( $\Delta H_{as}$ ) and entropy ( $\Delta S_{as}$ ) of the association between CA species and various numbers of EtOH (Table 2).

$$\ln K = -\frac{\Delta H_{as1}}{R} + \frac{\Delta S_{as}}{R}$$
(Eq. S17)

where *K* is a binding constant, *R* is the gas constant, and *T* is a measured temperature. The van't Hoff plots on the association of EtOH in Fig. S20 show a goodness of fit close to unity ( $r^2 > 0.998$ ), and the assumption that  $\Delta S_{as}$  and  $\Delta H_{as}$  is independent of temperature is valid in EtOH–CA<sup>-/2–</sup> mixed system.

#### Simulation of the entropy change in the redox reaction of $CA^{-/2-}$ ( $\Delta S_{rc}$ ) at various EtOH concentrations

The entropy change in the redox reaction  $(\Delta S_{\rm rc})$  can be simulated by the sum of the original  $\Delta S_{\rm rc}$  (the redox entropy of CA<sup>-/2-</sup> in acetonitrile electrolyte in the absence of EtOH,  $\Delta S_{\rm rc,0}$ ) and the difference of  $\Delta S_{\rm as}$  between CA<sup>2-</sup> and CA<sup>-</sup>. Since the number of bound EtOH molecules is distributed according to Eq. S14 and S15, the total association entropy of EtOH molecules with CA<sup>-</sup> ( $\Delta S_{as,total}^{l}$ ) can be represented as the expected value of the association entropy for each number of EtOH molecules and formulated as Eq. S18.

$$\Delta S_{as,total}^{I} = \sum_{i=1,2} (\varphi_i^{I} \Delta S_{as,i}^{I})$$
(Eq. S18)

The total association entropy of EtOH molecules with  $CA^{2-} (\Delta S_{as,total}^{II})$  can be represented as Eq. S19 by the same operation as Eq. S18.

$$\Delta S_{as,total}^{II} = \sum_{j=2,4} (\varphi_j^{II} \Delta S_{as,j}^{II})$$
(Eq. S19)

Since both values of  $\varphi_i^l$  and  $\varphi_j^{II}$  depends on the concentration of an H-bonding donor, the values of  $\Delta S_{as,total}^{I}$  and  $\Delta S_{as,total}^{II}$  change with EtOH concentration and are shown in Fig. S22.

As written above, the  $\Delta S_{\rm rc}$  can be simulated with the sum of  $\Delta S_{rc, 0}$  and  $\Delta S_{as,total}^{II} - \Delta S_{as,total}^{I}$ , as shown in Eq. S20.

$$\Delta S_{rc} = \Delta S_{rc, 0} + \left(\Delta S_{as, total}^{II} - \Delta S_{as, total}^{I}\right) = \Delta S_{rc, 0} + \left[\sum_{j=2,4} (\varphi_j^{II} \Delta S_{as, j}^{II}) - \sum_{i=1,2} (\varphi_i^{I} \Delta S_{as, i}^{I})\right]$$
(Eq. S20)

The simulated values of  $\Delta S_{\rm rc}$  with EtOH concentration by Eq. S20 are shown in Fig. 3e, and we compared the simulated and experimental values of the  $\Delta S_{\rm rc}$  of CA<sup>+-/2-</sup> redox pair. To evaluate the experimental  $\Delta S_{\rm rc}$ , we measured the square wave voltammograms of CA<sup>+-/2-</sup> at various temperatures. When increasing temperature, the redox potential ( $E_{1/2}^{II}$ ) of CA<sup>+-/2-</sup> without EtOH shifted negatively, and the addition of EtOH caused the larger negative potential shift with elevated temperature. The potential shifts were plotted versus the temperature change from an initial measured temperature (Fig. S21). The slope of the graph shows the  $\Delta E/\Delta T$  value, which can be converted to the  $\Delta S_{\rm rc}$  value by using Eq. 1. The experimental  $\Delta S_{\rm rc}$  values at various concentrations of EtOH are shown in Fig. 3e (black circles) and listed in Table S2. The simulated  $\Delta S_{\rm rc}$  values agree with the experimental values, and this result supports that the increment of  $\Delta S_{\rm rc}$  by adding EtOH is associated with the reorganization of the EtOH solvation with CA<sup>+-/2-</sup>.

## 5. Supporting Figures and Tables



**Fig. S1** (a) H-shape glass cell used in measuring the Seebeck coefficient and the current–voltage curve. Diameter of the Pt electrode is 1.0 mm, and the distance between the electrodes is 9.5 cm. (b) Three-electrode cell for SWV and EIS measurements. (c) The top view of (b). GC and CE electrodes are separated by 1.5 cm. (d) Glassy carbon electrodes. Diameter of the active area is 3.0 mm.



**Fig. S2 (a)** Time-course of the bulk electrolysis. (**b**, **c**) Experimental setup (**b**) for thermoelectric measurement and current-voltage measurement (**c**) for the continuous power generation. The electrolyte consists of 0.5 mM of CA<sup>--</sup> and CA<sup>2-</sup> and 0.1 M of TBAPF<sub>6</sub> in acetonitrile. The electrolyte was put into an H-shape glass cell. One side of the cell was heated by (**b**) a ribbon heater and (**c**) a hot plate, and the other side was cooled by a water circulator. (**b**, **c**) Two electrodes (**b** = Pt, **c** = GC) and thermocouples were immersed into both sides of the electrolyte, and the output current and the temperature were monitored.

(a) The constant potentials were set to -0.5 and -1.1 V vs Ag pseudo electrode for the reduction reactions from neutral CA to CA<sup>--</sup> and from CA<sup>--</sup> to CA<sup>2-</sup>, respectively. The acetonitrile electrolyte before the reduction was comprised of 1.0 mM of neutral CA and 0.1 M of TBAPF<sub>6</sub>. [CA] = 1.0 mM, [TBAPF<sub>6</sub>] = 0.1 M in acetonitrile



**Fig. S3** The thermoelectrical voltage of  $Fe(CN)_6^{3-/4-}$  aqueous electrolyte against the temperature difference. [ $Fe(CN)_6^{3-/4-}$ ] = 0.5 mM, [KCl] = 0.1 M in water



**Fig. S4** The current-voltage plots of the CA<sup> $\cdot$ -/2-</sup> in ACN electrolyte and aqueous Fe(CN)<sub>6</sub><sup>3-/4-</sup> electrolyte. [CA<sup> $\cdot$ -/2-</sup>] = 0.5 mM, [TBAPF<sub>6</sub>] = 100 mM, [EtOH] = 0, 0.040, 0.25, or 1.3 M in acetonitrile. [Fe(CN)<sub>6</sub><sup>3-/4-</sup>] = 0.5 mM, [KCl] = 0.1 M in water.

The temperature difference between the hot and cold sides of the thermocells ( $\Delta T$ ) is 4.6–5.9 K.





(a) The cyclic voltammogram of CA in acetonitrile electrolyte without EtOH. Glassy carbon, Ag/Ag<sup>+</sup>, and Pt coil were used as working, reference, and counter electrodes, respectively. [CA] = 1.0 mM,  $[TBAPF_6] = 0.1 \text{ M}$  in acetonitrile. (b) The UV-vis spectra of CA species in acetonitrile. CA<sup>--</sup> and CA<sup>2-</sup> were prepared by electrochemical reduction at -0.7 and -1.4 V vs Ag/Ag<sup>+</sup>, respectively. [CAs] = 0.5 mM,  $[TBAPF_6] = 0.1 \text{ M}$  in acetonitrile.

(a) Neutral CA



Fig. S6 UV-vis spectra of (a) neutral CA, (b) CA<sup>--</sup>, and (c) CA<sup>2-</sup> in acetonitrile with various EtOH concentrations.  $[CAs] = 0.5 \text{ mM}, [TBAPF_6] = 0.1 \text{ M}, [EtOH] = 0, 0.0025, 0.016, 0.040, 0.10, 0.16, 0.25, 0.63, 1.3, 1.6, or 5.0 \text{ M} in acetonitrile.}$ 



 $\sigma^{*}(a_{g}), -1.22 \text{ eV}$ 



 $\pi^*(b_{2g})$ , LUMO, -4.37 eV



 $\pi(b_{3u})$ , -8.39 eV



 $\pi^*(b_{3u})$ , -0.81 eV



 $\pi^*(a_u)$ , -1.65 eV



π(b<sub>1g</sub>), HOMO, -7.71 eV



n(b<sub>3g</sub>), -8.52 eV

Fig. S7 Kohn–Sham frontier orbitals (from HOMO-2 to LUMO+3) of electroneutral CA.

The orbital energies are shown in eV. The equilibrium geometry belongs to the  $D_{2h}$  point group.



**Fig. S8** Rydberg( $b_{3u}$ ) orbital (LUMO+18) of CA<sup>2-</sup>. The orbital energy is 2.51 eV.



Fig. S9 Theoretical UV-Vis absorption spectra of  $CA^{-/2-}$  and  $CA^{-/2-}$  (nO) $\cdots nEtOH$  (n = 1, 2).

The black stick spectra in panels (a) and (b) indicate the oscillator strengths f of the X  $\leftarrow$  <sup>2</sup>B<sub>2g</sub> excitations in CA<sup>-</sup> and the X  $\leftarrow$  <sup>1</sup>A<sub>g</sub> excitations in CA<sup>2-</sup>, respectively. The term symbols, X, of the final electronic states of excitations with f > 0.05 are shown to indicate the excitation characteristics. The spectra (curves) were obtained by convolution of the stick spectra with a Gaussian function (HWHM = 0.333 eV). Acetonitrile solvation effects were considered in all the spectrum calculations. Acetonitrile solvation effects were considered in all the calculation of CA<sup>-/2-</sup> in EtOH, in which the ethanol solvation was modeled as a polarizable continuum.



Fig. S10 Theoretical UV-Vis absorption spectra of CA<sup> $\cdot$ -/2-</sup> and CA<sup> $\cdot$ -/2-</sup>(*m*Cl) $\cdots$ *n*EtOH (*m*, *n* = 1 or 2).

The black stick spectra in panels (a) and (b) indicate the oscillator strengths f of the X  $\leftarrow$   $^{2}B_{2g}$  excitations in CA<sup>-</sup> and the X  $\leftarrow$   $^{1}A_{g}$  excitations in CA<sup>2-</sup>, respectively. The term symbols, X, of the final electronic states of excitations with f > 0.05 are shown to indicate the excitation characteristics. The spectra (curves) were obtained by convolution of the stick spectra with a Gaussian function (HWHM = 0.333 eV). Acetonitrile solvation effects were considered in all the spectrum calculations.

(a) CA•-(b) CA<sup>--</sup> in EtOH Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup>cm<sup>-1</sup>) 3.5 3.5 0.8 0.8 3.0 3.0 0.7 0.7 Oscillator strength Oscillator strength 2.5 2.5 0.6 0.6 0.5 0.5 2.0 2.0 0.4 0.3 0.4 1.5 1.5 0.3 1.0 1.0 0.2 0.2 0.5 0.5 0.1 0.1 0.0<del>1 -</del> 200 0.0<del>1 .</del> 200 250 300 350 300 350 400 250 400 Wavelength (nm) Wavelength (nm) (c) CA<sup>•–</sup>(O)····EtOH (d) CA•-(2O)···2EtOH Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup>cm<sup>-1</sup>) 3.5 3.5 0.8 0.8 3.0 3.0 0.7 0.7 Oscillator strength Oscillator strength 2.5 2.5 0.6 0.6 2.0 0.5 0.5 2.0 0.4 0.4 1.5 1.5 0.3 0.3 1.0 1.0 0.2 0.2 0.5 0.5 0.1 0.1 0.0<del>]</del> 200 0.0 250 300 350 400 250 300 350 400 Wavelength (nm) Wavelength (nm)

Fig. S11 Theoretical UV-Vis absorption spectra of (a) CA<sup>--</sup> and (b–d) CA<sup>--</sup>(nO)···*n*EtOH (n = 1, 2).

The black sticks indicate the oscillator strength, while the cyan curves, given as convolution with a Gaussian function with a half width at half maximum (HWHM) of 0.333 eV, indicate molar absorbance. Using the PCM theory, we considered acetonitrile solvation effects for all the spectra; an exception is the spectrum of  $CA^{-}$  in EtOH, in which we modeled the ethanol solvation as a polarizable continuum.

(a) CA<sup>2-</sup> (b) CA<sup>2-</sup> in EtOH Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup>cm<sup>-1</sup>) Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) 3.5 3.5 0.8 0.8 3.0 3.0 0.7 0.7 Oscillator strength Oscillator strength 2.5 2.5 0.6 0.6 0.5 0.5 2.0 2.0 0.4 0.4 1.5 1.5 0.3 0.2 0.3 0.2 1.0 1.0 0.5 0.5 0.1 0.1 -10.0 450 니<sub>0.0</sub> 450 0.0<del>1 -</del> 200 0 .0<del>1 '.</del> 200 300 350 400 300 350 400 250 250 Wavelength (nm) Wavelength (nm) (d) CA<sup>2–</sup>(2O)····2EtOH (c) CA<sup>2-</sup>(O)···EtOH Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup>cm<sup>-1</sup>) Molar absorbance (10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) 3.5 3.5 0.8 0.8 3.0 3.0 0.7 0.7 Oscillator strength Oscillator strength 2.5 2.5 0.6 0.6 2.0 0.5 2.0 0.5 0.4 0.4 1.5 1.5 0.3 0.3 1.0 1.0 0.2 0.2 0.5 0.5 0.1 0.1 0.0<sup>3</sup>---200 - 10.0 450 250 300 350 400 250 300 350 400 Wavelength (nm) Wavelength (nm)

Fig. S12 Theoretical UV-Vis absorption spectra of  $CA^{2-}$  and  $CA^{2-}(nO)\cdots nEtOH$  (n = 1, 2).

The black sticks indicate the oscillator strength, while the cyan curves, given as convolution with a Gaussian function with a half width at half maximum (HWHM) of 0.333 eV, indicate molar absorbance. Using the PCM theory, we considered acetonitrile solvation effects for all the spectra; an exception is the spectrum of  $CA^{2-}$  in EtOH, in which we modeled the ethanol solvation as a polarizable continuum.

(a) CA•-



Fig. S13 Theoretical UV-Vis absorption spectra of CA<sup>--</sup> and CA<sup>--</sup>(mCl) $\cdots$ nEtOH (m, n = 1 or 2).

The black sticks indicate the oscillator strength, while the cyan curves, given as convolution with a Gaussian function with a half width at half maximum (HWHM) of 0.333 eV, indicate molar absorbance. We considered acetonitrile solvation effects using the PCM theory.



Fig. S14 Theoretical UV-Vis absorption spectra of  $CA^{2-}$  and  $CA^{2-}(mCl)\cdots nEtOH$  (m, n = 1 or 2).

The black sticks indicate the oscillator strength, while the cyan curves, given as convolution with a Gaussian function with a half width at half maximum (HWHM) of 0.333 eV, indicate molar absorbance. We considered acetonitrile solvation effects using the PCM theory.

(a) CA<sup>•-</sup> with and without EtOH molecules

(b) CA<sup>2-</sup> with and without EtOH molecules



**Fig. S15** Potential energies and geometries of CA<sup>•-/2-</sup> and CA<sup>•-/2-</sup>(nO) $\cdots nEtOH$  (n = 1, 2).

All the energies are relative to the reference energy of CA<sup>-/2-</sup> and two EtOH molecules at infinite separation in the acetonitrile solvent, and the geometries of any free EtOH molecules are not shown. The equilibrium geometries were obtained at the B3LYP/cc-pVDZ level (black solid circles). Single-point calculations were performed at the B3LYP/aug-cc-pVTZ level with and without the D3BJ dispersion correction (green diamonds and orange squares, respectively).



(b) CA<sup>2-</sup> with and without EtOH molecules



**Fig. S16** Potential energies and geometries of CA<sup>•-/2-</sup> and CA<sup>•-/2-</sup>(nO)···nEtOH (n = 1, ..., 4).

All the energies are relative to the reference energy of  $CA^{-/2-}$  and four EtOH molecules at infinite separation in the acetonitrile solvent, and the geometries of any free EtOH molecules are not shown. The equilibrium geometries were obtained at the B3LYP/cc-pVDZ level (black solid circles). Single-point calculations were performed at the B3LYP/aug-cc-pVTZ level with and without the D3BJ dispersion correction (green diamonds and orange squares, respectively).



(a) CA<sup>--</sup> with and without EtOH molecules

(b) CA<sup>2–</sup> with and without EtOH molecules



Fig. S17 Potential energies and geometries of CA<sup>-/2-</sup> and CA<sup>-/2-</sup>(*m*Cl)···*n*EtOH (m, n = 1 or 2).

All the energies are relative to the reference energy of  $CA^{-/2-}$  and two EtOH molecules at infinite separation in the acetonitrile solvent, and the geometries of any free EtOH molecules are not shown. The equilibrium geometries were obtained at the B3LYP/cc-pVDZ level (black solid circles). Single-point calculations were performed at the B3LYP/aug-cc-pVTZ level with and without the D3BJ dispersion correction (green diamonds and orange squares, respectively).



**Fig. S18** The redox potential shifts of  $CA^{0/-}$  and  $CA^{-/2-}$  by adding EtOH at various temperatures (288–308 K). [CA] = 1.0 mM, [TBAPF<sub>6</sub>] = 0.1 M, and [EtOH] = 0.0010, 0.0025, 0.0063, 0.016, 0.04, 0.10, 0.16, 0.25, 0.40, 0.63, 0.79, 1.0, 1.3, 1.6, 2.0, 3.2, 5.0, or 7.9 M. Glassy carbon, Ag/Ag<sup>+</sup>, and Pt coil were used as working, reference, and counter electrodes. The black and red lines derive from the theoretical model fitting using Eq. S11 and S13, respectively, and the binding constants at 288–308 K are summarized in Table S1.

		<i>T</i> = 288 K	<i>T</i> = 293 K	<i>T</i> = 298 K	<i>T</i> = 303 K	T = 308  K
CA•-	$K_1^l (10^{-1} \mathrm{M}^{-1})$	$3.9\pm 0.1$	$3.7\pm 0.1$	$3.5\pm 0.5$	$3.3\pm 0.4$	$3.1\pm0.4$
	$K_2^I (10^{-2} \mathrm{M}^{-2})$	$4.8\pm1.4$	$4.4\pm1.2$	$4.0 \pm 1.1$	$3.8\pm1.0$	$3.5\pm 0.9$
CA <sup>2-</sup>	$K_{2}^{II}$ (10 <sup>2</sup> M <sup>-2</sup> )	$15\pm5$	$12 \pm 3$	$10 \pm 2$	$7.5\pm1.6$	$5.9\pm1.1$
	$K_{4}^{II}$ (10 <sup>3</sup> M <sup>-4</sup> )	$35\pm5$	$21 \pm 3$	$12 \pm 1$	$7.2\pm0.8$	$4.4\pm0.5$

(c) 298 K

**Table S1.** Binding constants of EtOH with CA<sup>--</sup>  $({}^{K_i^I})$  and CA<sup>2-</sup>  $({}^{K_j^{II}})$  at various temperatures.



(b) 293 K



**Fig. S19** The molar fraction of the number of bound EtOH molecules with  $CA^{-}$  and  $CA^{2-}$  at various temperatures. The molar fractions are calculated from Eq. S15 and S16.



**Fig. S20** Van't Hoff plots showing the temperature dependence of the binding constants of EtOH molecules associating with CA<sup>--</sup> or CA<sup>2-</sup> (the subscript shows the number of EtOH). The results showed good agreement with the linear fitting ( $r^2 > 0.998$ ).

 $K_i^l$  is the binding constant of EtOH molecules (the number of *i*) with CA<sup>-</sup>, and  $K_j^{ll}$  is the binding constant of EtOH molecules (the number of *j*) with CA<sup>2-</sup>.



**Fig. S21** Shift of redox potential of CA<sup> $-/2^-$ </sup> in the SWV measurement versus the temperature change of the electrolyte at various concentrations of EtOH: (a) 0–0.0025 M; (b) 0.0063–0.016 M (the first and second measurements); (c) 0.040–0.16 M; (d) 0.25–0.63 M; (e) 0.79–1.3 M; (f) 1.6–3.2 M; and (g) 5.0–7.9 M

Glassy carbon, Ag/Ag<sup>+</sup>, and Pt coil were used as working, reference, and counter electrodes. The plots were given by the

current peaks of SWV measurement at various temperatures. The slope of the graph shows a  $\Delta E/\Delta T$  value. [CA] = 1.0 mM, [TBAPF<sub>6</sub>] = 0.1 M, and [EtOH] = 0, 0.0010, 0.0025, 0.0063, 0.016, 0.040, 0.10, 0.16, 0.25, 0.40, 0.63, 0.79, 1.0, 1.3, 1.6, 2.0, 3.2, 5.0, or 7.9 M

Considering the  $\Delta E/\Delta T$  of Ag/Ag<sup>+</sup> reference electrode is ca. +0.2 mV/K,<sup>1</sup> the *S*<sub>e</sub> can be estimated by adding 0.2 mV K<sup>-1</sup> to the value of  $\Delta E/\Delta T$ . The estimated *S*<sub>e</sub> values can be converted into the values of redox entropy ( $\Delta S_{rc}$ ) by using Eq. 1. In Regions 1 and 2 (low concentration region of EtOH), the experimental values of  $\Delta S_{rc}$  of CA<sup>\*-/2-</sup> deviate from the theoretical values (Fig. 3e). One possible reason could be a gradual loss of EtOH from the electrolyte due to vaporization of EtOH during the SWV measurement. We compared the goodness of fit (*r*<sup>2</sup>) of the plot of  $\Delta E$  vs.  $\Delta T$  at each concentration of EtOH studied (Fig. S21). The *r*<sup>2</sup> values are 0.999 in most of the plot, showing a good linearity of the experimental values. However, lower *r*<sup>2</sup> values less than 0.997 were observed when the concentration of EtOH is low, such as at 0.0025, 0.016, 0.10, and 0.16 M. The deviation from the linearity is likely caused by the vaporization of EtOH at high temperature, and especially when the concentration of EtOH is low, the effect of losing the EtOH from the electrolyte can induce a larger shift in the redox potential and reduce the *r*<sup>2</sup> values.

EtOH concentration (M)	$\Delta S_{\rm rc}$ value (J mol <sup>-1</sup> K <sup>-1</sup> )
0	-130
0.001	-130
0.0025	-140
0.0063	-170
0.016	-170
0.040	-180
0.063	-210
0.10	-230
0.16	-250
0.25	-260
0.40	-270
0.63	-270
0.79	-270
1.0	-270
1.3	-290
1.6	-280
2.0	-280
3.2	-270
5.0	-280
7.9	-250

**Table S2.** Experimental  $\Delta S_{rc}$  values of CA<sup>-/2-</sup> with various EtOH concentrations obtained from Fig. S21.

Glassy carbon, Ag/Ag<sup>+</sup>, and Pt coil were used as working, reference, and counter electrodes. The slope of the graph shows a  $\Delta E/\Delta T$  value. [CA] = 1.0 mM, [TBAPF<sub>6</sub>] = 0.1 M, and [EtOH] = 0, 0.0010, 0.0025, 0.0063, 0.016, 0.040, 0.10, 0.16, 0.25, 0.40, 0.63, 0.79, 1.0, 1.3, 1.6, 2.0, 3.2, 5.0, or 7.9 M

Considering the  $\Delta E/\Delta T$  of Ag/Ag<sup>+</sup> reference electrode is ca. +0.2 mV K<sup>-1</sup>,<sup>1</sup> the S<sub>e</sub> can be estimated by adding 0.2 mV K<sup>-1</sup> into the value of  $\Delta E/\Delta T$ . The estimated S<sub>e</sub> values can be converted into the values of redox entropy ( $\Delta S_{rc}$ ) by using Eq. 1. The change in the experimental values of  $\Delta S_{rc}$  with increasing EtOH concentration is shown in Fig. 3e.



Fig. S22 The entropy changes in the association of various numbers of EtOH molecules with (top)  $CA^{2-}$  and (bottom)  $CA^{-}$ .

 $\phi_i^I$  is the molar fraction of the number (*i*) of bound EtOH molecules with CA<sup>--</sup>,  $\phi_j^{II}$  is the molar fraction of the number of (*j*) of bound EtOH molecules with CA<sup>2-</sup>,  $\Delta S_{as,i}^{I}$  is the association entropy between *i* of EtOH molecules and CA<sup>--</sup>,  $\Delta S_{as,j}^{II}$  is the association entropy between *j* of EtOH molecules and CA<sup>2-</sup>, and  $\Delta S_{as,total}^{I}$  and  $\Delta S_{as,total}^{II}$  are the total values of the association entropy of CA<sup>--</sup> and CA<sup>2-</sup>, respectively. The simulated  $\Delta S_{rc}$  curve can be obtained from Eq. S20 by using  $\Delta S_{as,total}^{II}$  and  $\Delta S_{as,total}^{II}$ .



**Fig. S23** The Nyquist plot for the acetonitrile electrolyte containing neutral CA and TBAPF<sub>6</sub> at the potential of +0.1 V vs Ag/Ag<sup>+</sup>, where no redox reaction is observed.

 $[CA] = 1.0 \text{ mM}, [TBAPF_6] = 0.1 \text{ M}$  in acetonitrile solvent. The glassy carbon,  $Ag/Ag^+$ , and Pt coil electrodes were used as working, reference, and counter electrodes, respectively.

The Nyquist plot in Fig. S23 was measured at the potential of +0.1 V vs Ag/Ag<sup>+</sup>, and a semi-circle was observed at the high-frequency side. At the potential of +0.1 V, no redox reaction was observed (Fig. S5a), suggesting that the semi-circle is attributed not to the charge transfer resistance of CA species but to the solution resistance ( $R_s$ ) and the electrical double layer formation ( $C_d$ ).

The Nyquist plot in Fig. 4a (-0.277 V vs Ag/Ag<sup>+</sup>) shows a similar semi-circle to Fig. S23. The semi-circle in Fig. 4a is followed by a 45°-degree line at the low-frequency side, which is attributed mainly to the diffusion process of the redox reaction (the Warburg impedance) and confirms the redox reaction of CA<sup>0/-</sup>.

Thus, we conclude that the redox reaction of  $CA^{0'-}$  is so fast (the  $R_{ct}$  of  $CA^{0'-}$  is so small) that the semi-circle derived from the  $R_{ct}$  in Fig. 4a merges with a semi-circle derived from  $R_s$  and  $C_d$ . In light of this result, we show the total resistances of the  $R_s$  and  $R_{ct}$  of the electrolytes in Fig. 4c to investigate the clear effect of EtOH on the redox kinetics of CA species.

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