Electronic Supplementary Information

Six-Electron Organic Redoxmers for Aqueous Redox Flow Batteries

Xiaoting Fang,[a,b,c] Andres Cavazos,[a] Zhiguang Li,[a,b,c] Chenzhao Li,[a,b] Jian Xie,[a] Stephen R. Wassall,[a] Lu Zhang,[c]* and Xiaoliang Wei [a]*

[a.] *Indiana University-Purdue University Indianapolis, 723 West Michigan Street, Indianapolis, IN 46202, USA.*

[b.] *Purdue University, 585 Purdue Mall, West Lafayette, IN 47907, USA.*

[c] *Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439, USA.*

Corresponding authors:

Lu Zhang: luzhang@anl.gov;

Xiaoliang Wei: xwei18@iupui.edu.

S1. Experimental

S1.1 Materials

Hexaketocyclohexane hydrate (99%), 4-diaminobenzenesulfonic acid, and 4-hydroxy-2-nitroaniline (98%) were purchased from AmBeed. 2-[2-(2-chloroethoxy)ethoxy]ethanol (96%), palladium on activated carbon (10% Pd), and all the solvents were purchased from Fisher. These chemicals were used as received.

S1.2 Characterizations

^{1}H and ^{13}C NMR spectra were collected on an AVANCE III HD 400 MHz spectrometer (Bruker, Germany). The radical state of **TPz-1** was determined by continuous wave X band EPR spectroscopy using a Bruker ESP-300 EPR spectrometer.

S1.3 Electrochemical measurement

Cyclic voltammetry (CV) was performed using a CHI760D potentiostat (CH Instruments) with a three-electrode configuration that consisted of a glassy carbon working electrode (3 mm diameter), a carbon felt counter electrode and an Ag/AgCl reference electrode. The samples were 3 mM redoxmer in 1 M NaOH electrolyte. The CV data were obtained at a

series of specified scan rates (Figure S7a and S8a), which were used to calculate the kinetic parameters of redoxmers described in Section S3.

S1.4 Flow cell test

The 5 mM flow cells were assembled with stacked layers of ELAT carbon cloth electrodes (Nuvant) sandwiching a Nafion 212 membrane with an active area of 10 cm^2. The electrolytes were pumped through the carbon cloth electrodes using a peristaltic pump at a flow rate of 20 $mLmin^{-1}$. The flow cell tests were conducted at room temperature on a Neware CT-4008 battery tester in an argon filled glove box with the O_2 level less than 1 ppm. The anolyte was 5 mM **TPZ-2** in 1 M NaOH (10 mL) and the catholyte was 0.2 M $K_4Fe(CN)_6$ in 1 M NaOH (15 mL).

A different cell was used to test the 1 mM **TPz-2** flow cells, consisting of 2.5mm-thick GFD graphite felt electrodes (SGL Carbon, Germany) with an active area of 2.4 cm^2. The anolyte was 1 mM **TPZ-2** in 1 M NaOH (10 mL) and the catholyte was 0.04 M $K_4Fe(CN)_6$/0.02 M $K_3Fe(CN)_6$ (15 mL), both in 1 M NaOH.

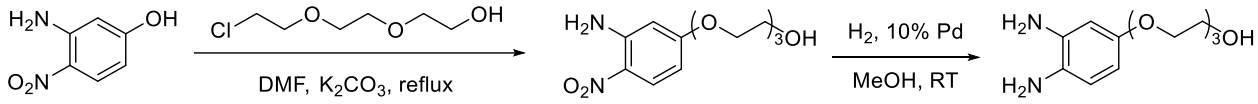
S2. Synthesis of Redoxmers

1) Synthesis of TPz-1

Hexaketocyclohexane (2 mmol, 0.37 g) and 3,4-diaminobenzenesulfonic acid (6.6 mmol, 1.24 g) were dissolved in a mixture solvent of glacial acetic acid/ethanol (1:1 v/v, totally 50 mL) in a nitrogen atmosphere. The solution was maintained at 118 ℃ for 16 hours with vigorous stirring. The resulting dark green precipitate was filtered, washed with acetone and ethanol, and dried in vacuum to yield a dark green solid (0.98 g, 80%). ^{1}H NMR (400 MHz, D_2O): δ (ppm) 7.83 (s, 3H), 7.63 (d, 3H), 7.58 (d, 3H).

2) Synthesis of TPz-2

a) Synthesis of the modified diaminobenzene



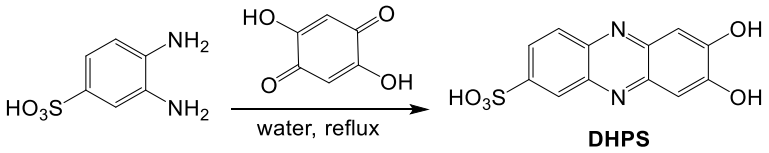
To a solution of 4-hydroxy-2-nitroaniline (25 mmol, 3.85 g) in anhydrous DMF (60 mL) were added K_2CO_3 (62.5 mmol, 8.63 g) and 2-[2-(2-chloroethoxy)ethoxy]ethanol (30 mmol, 5.04 g) under a nitrogen atmosphere. The reaction mixture was stirred under reflux at 130 ℃ overnight. After cooling down, deionized water (100 mL) and CH_2Cl_2 (100 mL) were added to the reaction. The organic phase was separated and washed with a large amount of deionized water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude residue was purified using silica gel column chromatography with ethyl acetate/n-hexane (1:1 v/v) as an eluent to give an oily red compound, 4-tri(ethylene glycol)-2-nitroaniline (6.00 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56~7.57 (d, 1H), 7.10~7.11 (d, 1H), 6.75~6.78 (d, 1H), 5.93 (s ,2H), 4.10~4.13 (t, 2H), 3.85~3.88 (t, 2H), 3.73~3.74 (t, 6H), 3.63 (t, 2H).

The 4-tri(ethylene glycol)-2-nitroaniline (8 mmol, 2.3 g) was dissolved in MeOH (80 mL) and mixed with 10% Pd-C (0.5 g) under a nitrogen atmosphere. A hydrogen balloon was connected to the reaction mixture and vigorous stirring was continued overnight at room temperature. The catalyst was filtered through Celite and the solvent was evaporated to yield a brown solid, 4-tri(ethylene glycol)-1,2-diaminobenzene (1.96 g, 96%), which was used immediately in the next step without further purification due to its air sensitivity.

b) Synthesis of TPz-2

Synthesis of **TPz-2** followed a similar procedure for **TPz-1**. Hexaketocyclohexane (2 mmol, 0.372 g) and 4-tri(ethylene glycol)-1,2-diaminobenzene (6.6 mmol, 1.68 g) were dissolved in a mixture solvent of glacial acetic acid/ethanol (1:1 v/v, totally 50 mL) in a nitrogen atmosphere. The solution was maintained at 118 ℃ for 16 hours with vigorous stirring. The resulting dark green precipitate was filtered and purified by silica gel column chromatography with CH_2Cl_2/MeOH/Et_3N (100:10:1 v/v/v) as an eluent to give a dark green solid (1.18 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (d, 3H), 7.74 (s, 3H), 7.62(d, 3H), 4.40 (t, 6H), 4.03 (t, 6H), 3.83~3.81 (m, 18H), 3.68 (t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 161.57, 161.36, 145.19, 145.54, 144.94, 144.89, 143.56, 143.28, 143.09, 142.85, 141.34, 141.18, 141.09, 140.93, 140.72, 140.21, 139.91, 131.55, 131.42, 126.80, 126.75, 126.54, 126.49, 107.40, 72.59, 70.95, 70.44, 69.39, 68.26, 61.76.

3) Synthesis of DHPS



DHPS

2,5-Dihydroxy-1,4-benzoquinone (1.4 g, 10 mmol) was added to 50 mL water in a round-bottomed flask pre-heated to 100 ℃. After stirring for 5 minutes, solid 3,4-diaminobenzenesulfonic acid (1.89 g, 10 mmol) was slowly added in a few portions. The reaction mixture was refluxed overnight and then cooled down to room temperature under vigorous stirring. 30 ml of acetone was added to dilute the reaction mixture, yielding a gold solid. The solid was filtered, washed with water and acetone, and dried under vacuum for several days to give the product (2.82 g, 97%). NMR (400 MHz, DMSO): δ (ppm) 8.23 (s, 1H), 8.07(d, 1H), 7.98 (d, 1H), 7.30 (s, 1H), 7.29 (d, 1H).

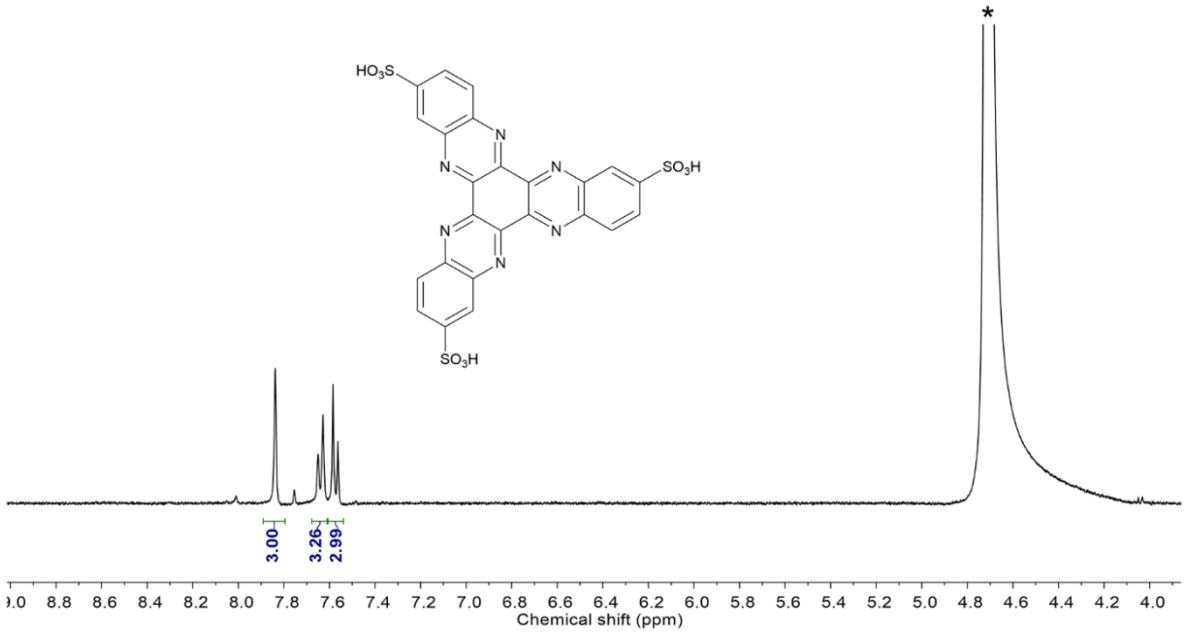


Figure S1. ^{1}H NMR spectrum of **TPz-1** in D_2O. The asterisk represents the NMR solvent (H_2O).

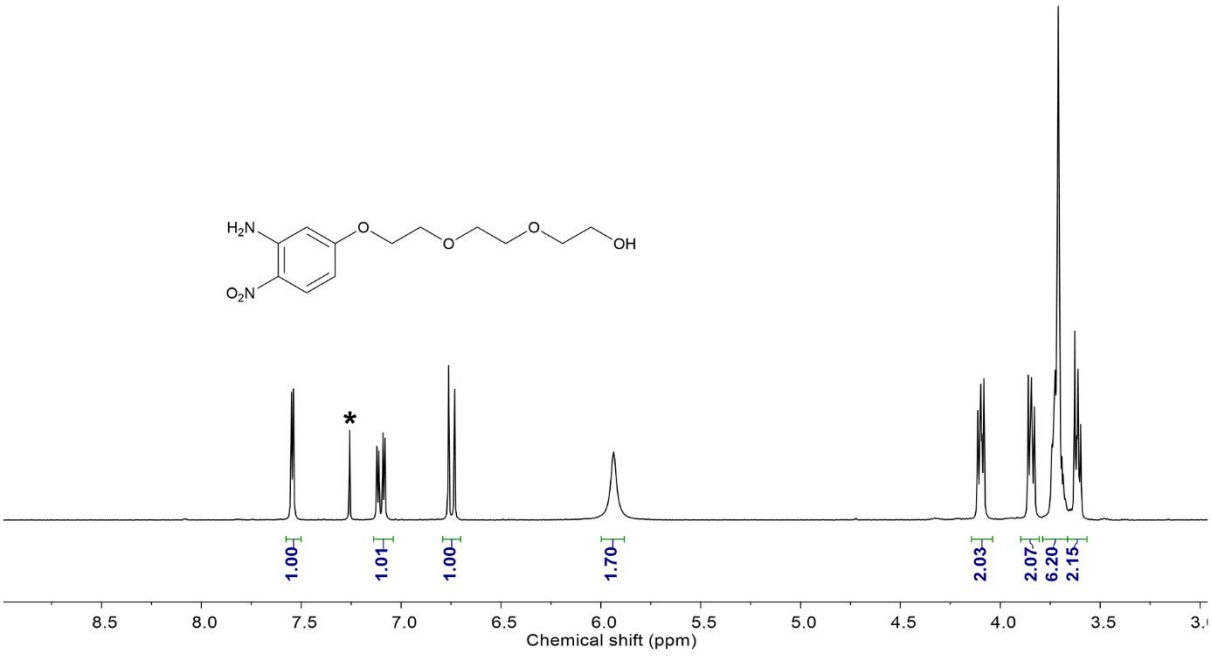


Figure S2. ^{1}H NMR spectrum of 4-tri(ethylene glycol)-2-nitroaniline in $CDCl_3$. The asterisk represents the NMR solvent ($CHCl_3$).

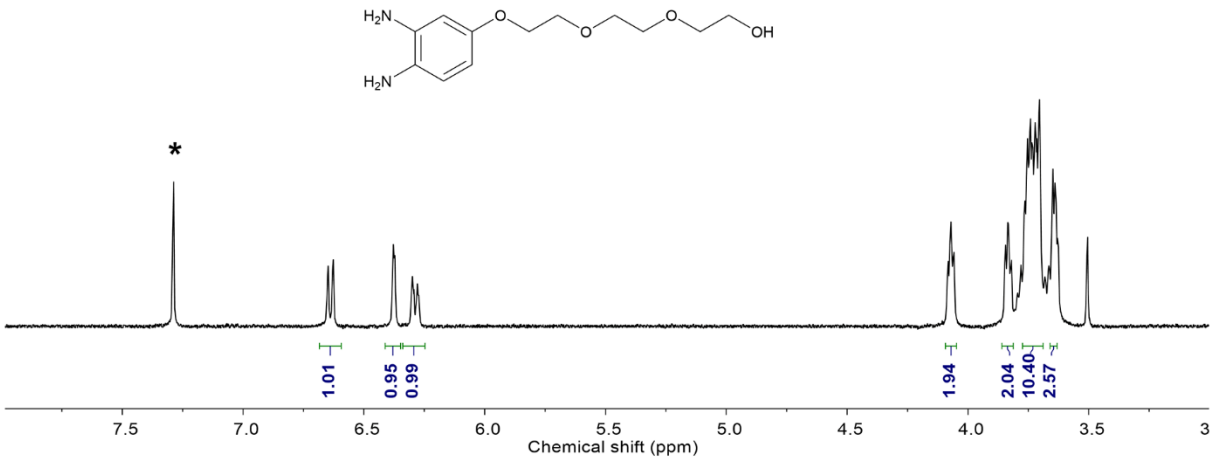


Figure S3. ^{1}H NMR spectrum of 4-tri(ethylene glycol)-1,2-diaminobenzene. The asterisk represents the NMR solvent ($CHCl_3$).

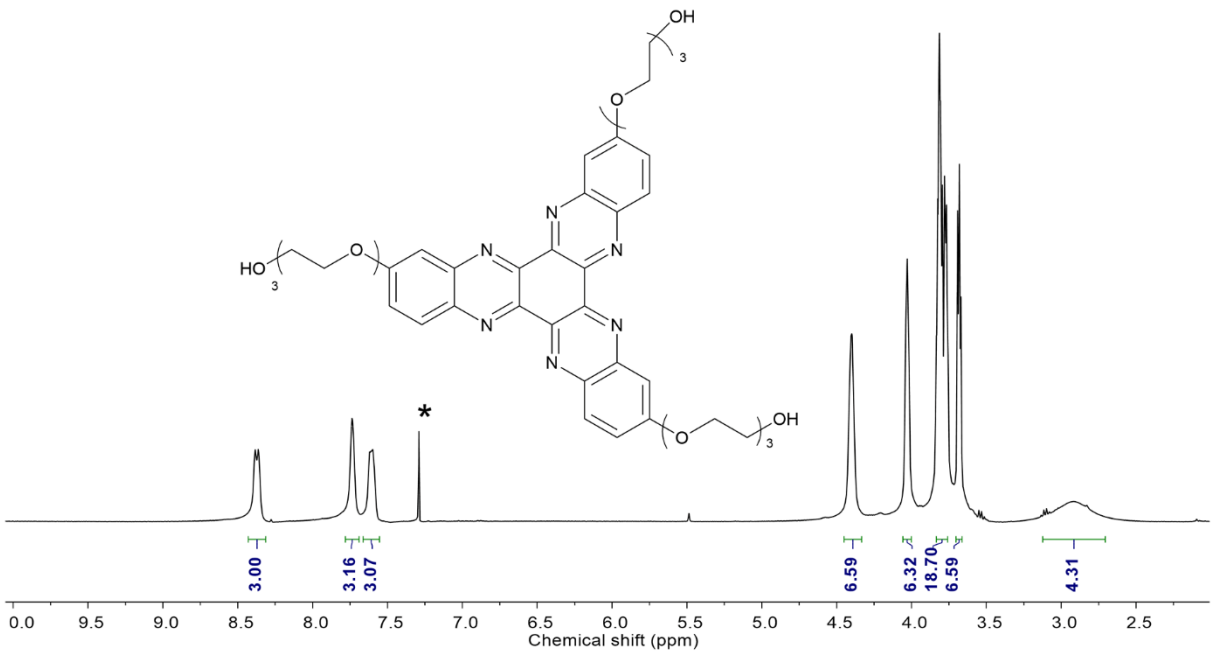


Figure S4. ^{1}H NMR spectrum of **TPz-2** in $CDCl_3$. The asterisk represents the NMR solvent ($CHCl_3$).

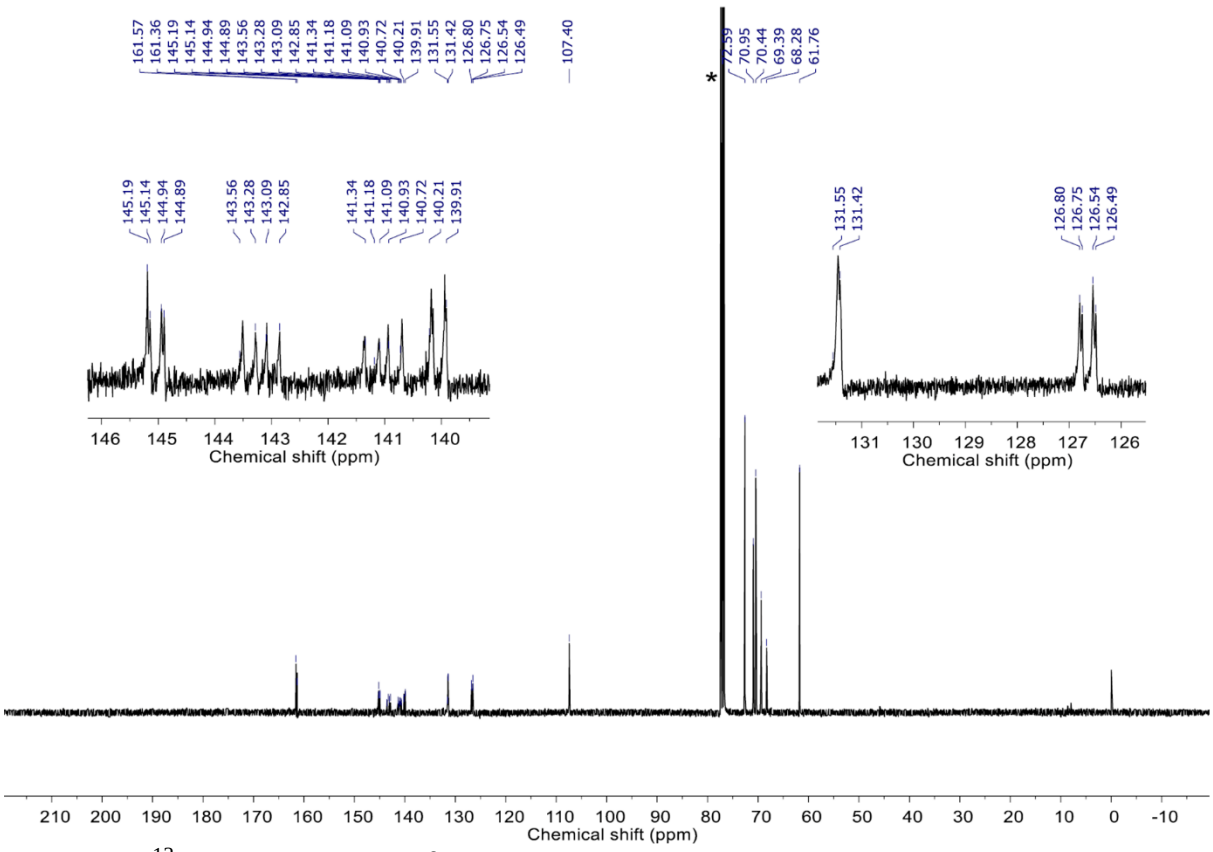


Figure S5. ^{13}C NMR spectrum of **TPz-2** in $CDCl_3$. The asterisk represents the NMR solvent ($CHCl_3$).

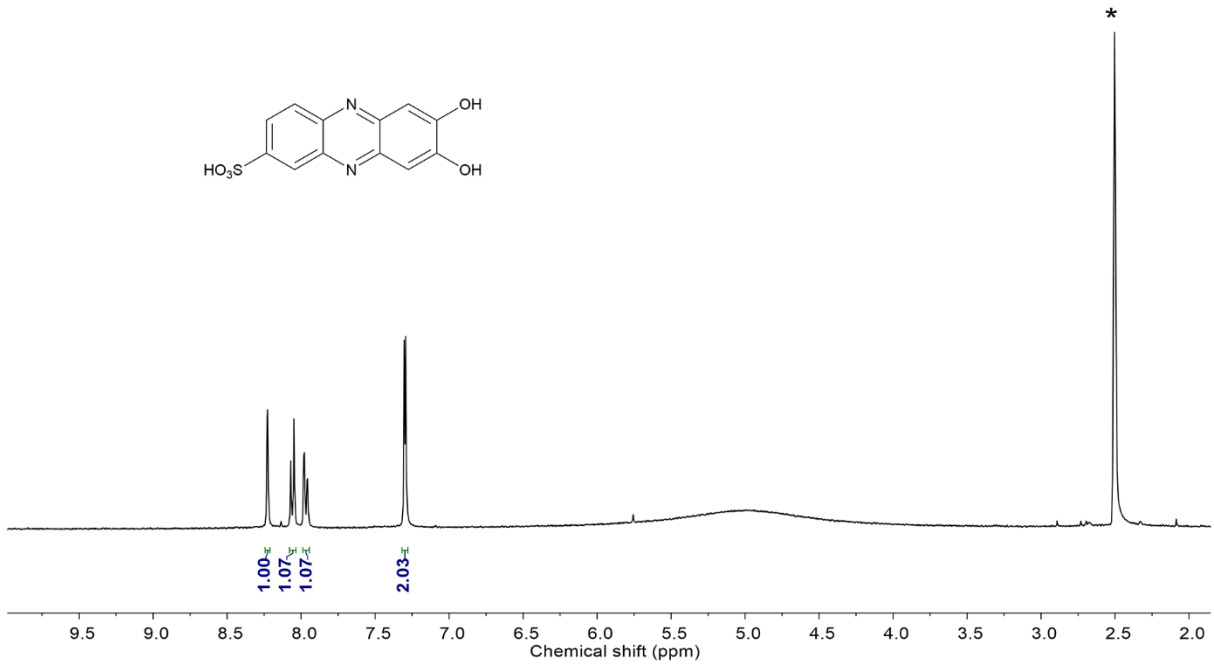


Figure S6. ^{1}H NMR spectrum of **DHPS** in DMSO. The asterisk represents the NMR solvent (DMSO).

S3. Kinetic Parameter Determination

Calculations of the diffusion coefficients (D) and charge transfer rate constants (k^0) followed a reported method.[1] Normally, Randles-Sevcik Eq. 1 is used to calculate D for a reversible redox reaction. Here, "reversible" is determined by the oxidation-reduction peak separation $\Delta E_p \leq (57/n)$ mV.[2]

$$i_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}} \quad (1)$$

where i_p is the peak current, n is the number of transferred electrons, F is the Faraday constant (96485 C mol^{-1}), A is the surface area of the electrode (A = 0.0707 cm^2), C is the bulk concentration of redoxmers (3 mM), v is the scan rate and T is the room temperature (298 K). D is obtained from the slope of the linearly fitted $i_p - v^{1/2}$ plot, that is $2.69\times10^5 n^{3/2}ACD^{1/2}$.

For an irreversible redox reaction (determined by $\Delta E_p >$ (200/n) mV, a correction factor α was introduced to obtain Eq. 2:

$$i_p = 0.4463nFAC\left(\frac{n\alpha FvD}{RT}\right)^{\frac{1}{2}} \quad (2)$$

Here, α is defined by Eq. 3:

$$\left|\boldsymbol{E_p - E_{p/2}}\right| = \left(\frac{\mathbf{48}}{\boldsymbol{\alpha n}}\right)\boldsymbol{mV} \quad (\mathbf{3})$$

where E_p and $E_{p/2}$ are the potentials at the peak current and half of the peak current, respectively. For **DHPS**, α=0.51. For **TPz-2**, α=0.52 for first redox peak and α=0.56 for second redox peak. Using Eq. 2, the Ds for the anodic and cathodic peaks (D_O and D_R) were calculated (Figure S7b and S8b). D is the average value of D_O and D_R.

Based on the CV curves at different scan rates, the straight relationship of ln(i_p) and the overpotential (E_p -$E^{0'}$), expressed in Eq. 4, was used to determine k^0:[1]

$$\ln(i_p) = \ln(0.227nFAk^0\,C^*) - \left(\frac{\alpha F}{RT}\right)\left(E_P - E^{0'}\right) \quad (4)$$

Here, $E^{0'}$ is the formal potential and is determined from Eq. 5:[3]

$$E^{0'} = \frac{\sum_{i=1}^{j}\frac{E_{pa_i} + E_{pc_i}}{2}}{j} \quad (5)$$

where j is the total number of CV scans, E_{pa} and E_{pc} represent the anodic and cathodic peak potentials, respectively. The linearly fitted plot of ln(i_p) vs (E_p – $E^{0'}$) gives an intercept that is a function of k^0, as shown in Figure S7c, d and S8c, d.

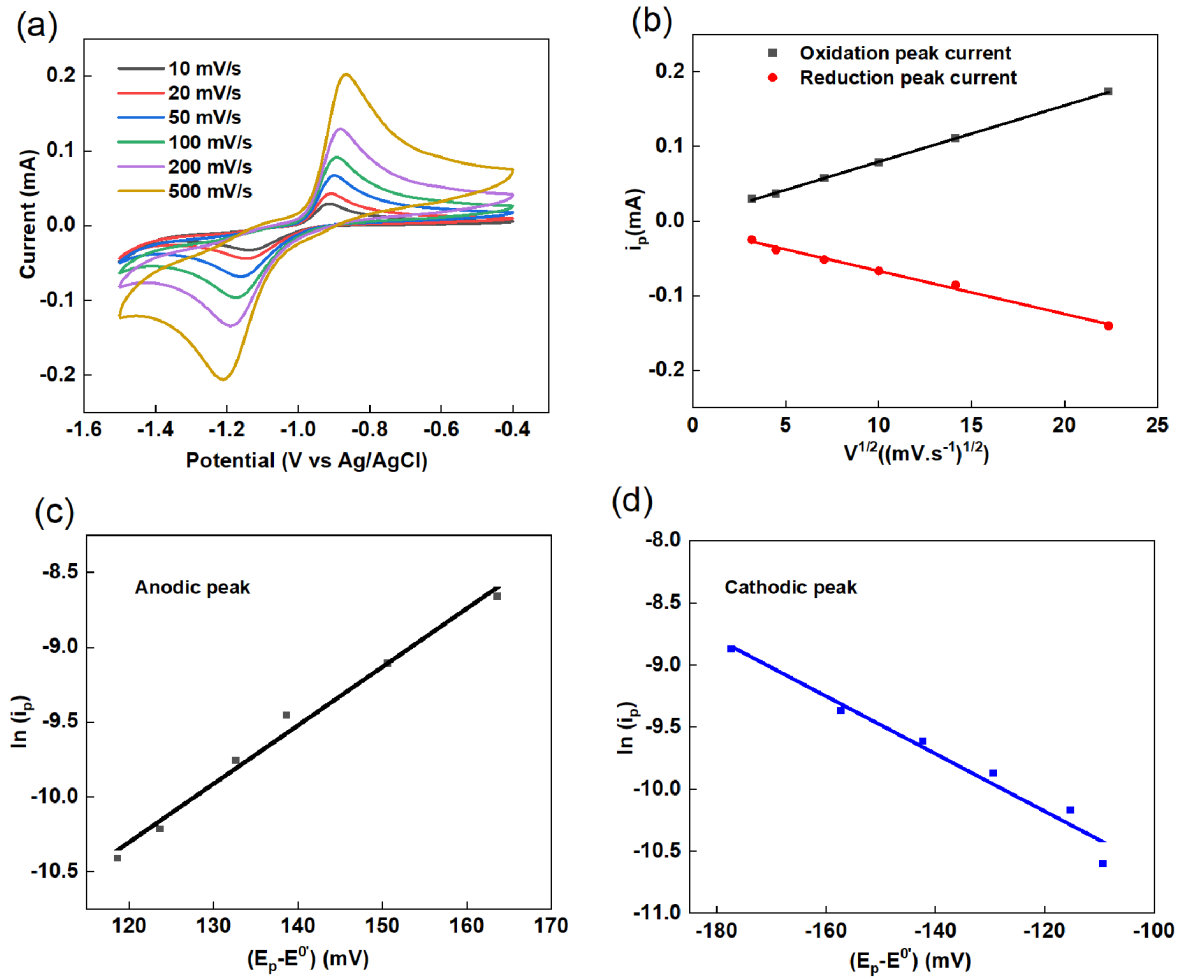


Figure S7. Kinetic performance of 3 mM **DHPS** in 1 M NaOH: (a) CV curves at different scan rates; (b) linearly fitted $i_p - \upsilon^{1/2}$ plot; (c,d) linearly fitted $\ln(i_p) - (E_p\text{-}E^{0'})$ plot for both anodic and cathodic peaks.

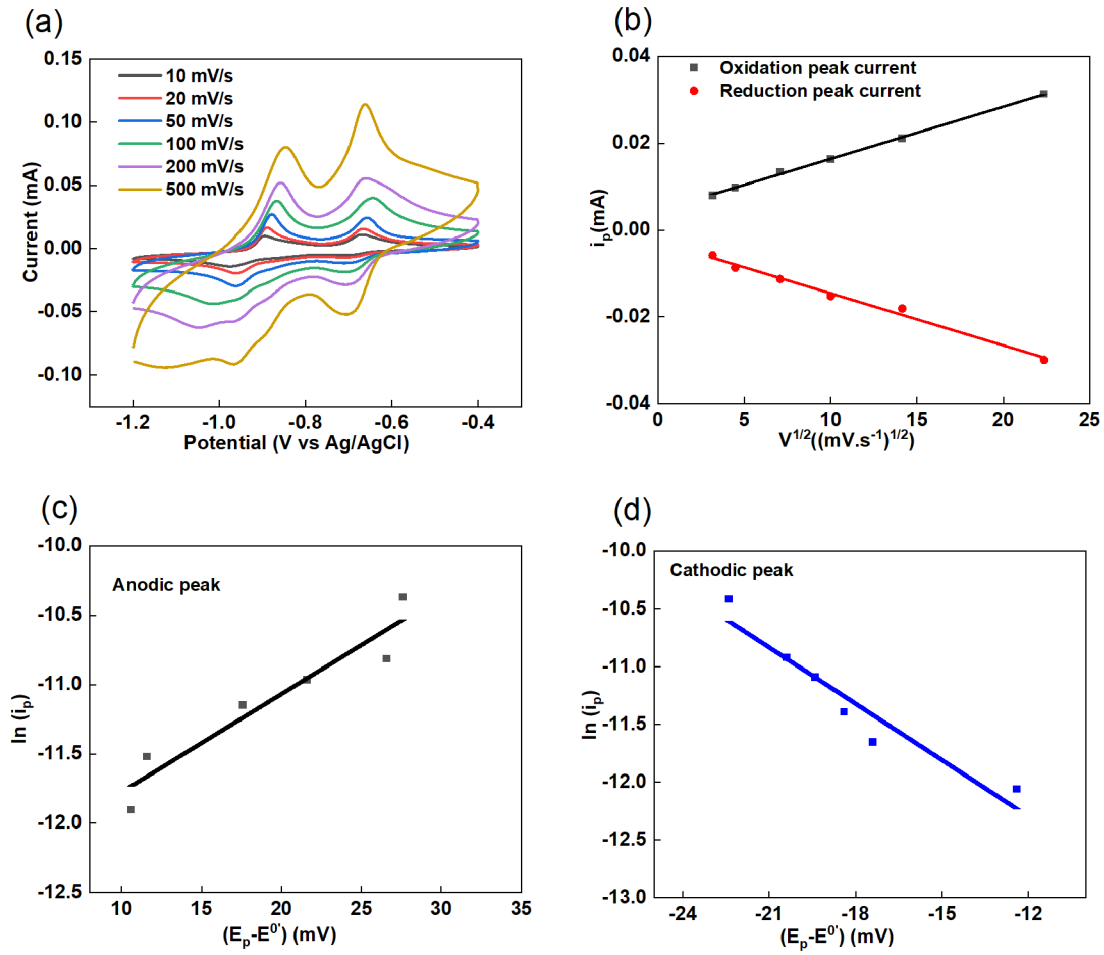


Figure S8. Kinetic performance of 3 mM **TPz-2** in 1 M NaOH (first redox peak): (a) CV curves at different scan rates; (b) linearly fitted $i_p - \upsilon^{1/2}$ plot; (c,d) linearly fitted $\ln(i_p) - (E_p\text{-}E^{0'})$ plot for both anodic and cathodic peaks.

S4. Supporting Figures for Flow Cells

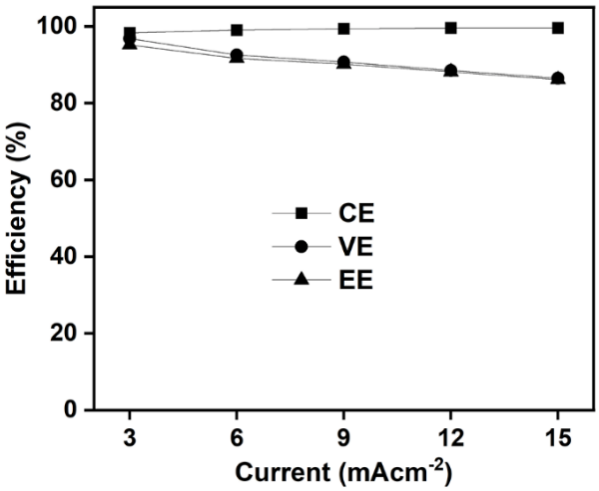


Figure S9. Rate capability of a 5 mM **DHPS** flow cell under the same conditions as **TPz-2** based flow cells.

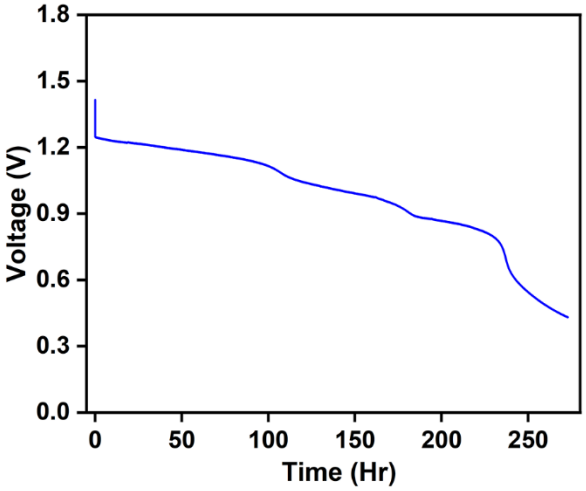


Figure S10. Self-discharge open-circuit voltage curve of the fully charged 1 mM **TPz-2** flow cell shown in Figure 1b.

References

1. H. Wang, S. Y. Sayed, E. J. Luber, B. C. Olsen, S. M. Shirurkar, S. Venkatakrishnan, U. M. Tefashe, A. K. Farquhar, E. S. Smotkin, R. L. McCreery and J. M. Buriak, *Acs Nano*, 2020, **14**, 2575-2584.
2. N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, *J Chem Educ*, 2018, **95**, 197-206.
3. W. J. Wang, X. Z. Fan, J. G. Liu, C. W. Yan and C. L. Zeng, *Rsc Adv*, 2014, **4**, 32405-32411.