

Accepted Article

Title: A "π-Conjugation Extended Viologen" as Novel Two-Electron Storage Anolyte for Total Organic Aqueous Redox Flow Battery

Authors: Jian Luo, Bo Hu, Camden Debruler, and Tianbiao Leo Liu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201710517 Angew. Chem. 10.1002/ange.201710517

Link to VoR: http://dx.doi.org/10.1002/anie.201710517 http://dx.doi.org/10.1002/ange.201710517

WILEY-VCH

WILEY-VCH

A "π-Conjugation Extended Viologen" as Novel Two-Electron Storage Anolyte for Total Organic Aqueous Redox Flow Battery

Jian Luo, Bo Hu, Camden Debruler, T. Leo Liu*

Dedicated to Professor Mei Wang on the occasion of her 62nd birthday

Abstract: Extending the conjugation of viologen by a planar thiazolo[5,4-d]thiazole (TTz) framework and functionalizing the pyridinium with hydrophilic ammonium group yielded a highly water-soluble " π -conjugation extended viologen", 4,4'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(1-(3-(trimethylammonio)propyl)pyridin-1-ium) tetrachloride, **[(NPr)**₂TTz]Cl₄, as a novel two-electron storage anolyte for AORFB applications. Its physical and electrochemical properties were systematically investigated. The **[(NPr)**₂TTz]Cl₄ / N^{Me}-TEMPO AORFB enables a 1.44 V battery voltage with 53.7 Wh/L theoretical energy density and delivered 70 % EE and 99.97 % capacity retention per cycle battery stability.

With the advantages of decoupled energy and power, high current and power performance, non-flammable and low cost aqueous supporting electrolytes, as well as the tunable redox potentials of the organic active materials, aqueous organic redox flow batteries (AORFBs) have attracted increasing research and technology development for large scale and dispatchable storage (up to MW/MWh) of the intermittent renewable energy including solar and wind energy.^[1] In AORFBs, water-soluble organic redox active materials or compounds were applied as electrolyte materials. In the charge process, energy is stored by the reduction of anolyte and oxidation of catholyte; in the discharge process, the energy is outputted by the re-oxidation of anolyte and re-reduction of catholyte. Organic compounds have been used as electrolytes in AORFBs and non-aqueous organic redox flow batteries (NAORFBs).^[2] We and others have utilized water-soluble viologen (anolyte),^[2b, 2f-h, 2j] ferrocene (catholyte),^{[2g,} ^{2h, 2j]} and TEMPO (catholyte)^[2b, 2f] compounds to demonstrate high performance neutral AORFBs. Among the reported organic compounds, only quinone or alloxazine based (anolyte) compounds are capable of storing two electrons in AORFBs, however, they have been applied in strong acidic or basic AORFBs.^[2a, 2c, 3] There is not a two-electron storage compound that is applied in a neutral aqueous system. In addition, very few total organic aqueous redox flow batteries with redox active organic electrolytes in both anode and cathode sides were reported.^[2b, 2f, 2g, 2j, 3e]

Methyl viologen (MV²⁺) exhibits two single-electron reductions at -0.45 V and -0.76 V (vs. NHE). However, only the reversible MV^{2+/++} redox couple was utilized in the battery charge/discharge process, which is due to the insolubility of the charge-neutral MV⁰ state in aqueous solution.^[2b, 2f-h, 2] Meanwhile, the reduced states of MV (MV⁺⁺ and MV⁰) are highly

 [a] Dr. Jian Luo, Bo Hu, Camden Debruler, Dr. and Prof. Tianbiao Leo Liu
Chemistry and Biochemistry
Utah State University
0300 Old Main Hill, Logan, Utah
E-mail: leo.liu@usu.edu

Supporting information for this article is given via a link at the end of the document.

air sensitive, which may affect the stability and energy efficiency of battery.^[4] The "extended viologens" are conjugation-extended viologens in which two pyridinium moieties are linked by a central π-conjugated framework.^[5] With the extension of the skeletal structure of 4,4'-bipyridinium of viologen, the reductive potential gap between the 1st and 2nd electron reduction can be reduced due to a larger π-conjugated system,^[6] which would enable the viologen-based batteries to deliver more uniform battery voltages. More importantly, the stability of the reduced species can be enhanced by the strategy of "π-conjugated extension".[5a] The thiazolo[5,4-d]thiazole (TTz) is a rigid aromatic bicyclic framework that was widely applied in the organic semiconductor, and it can be simply synthesized by double condensation of aromatic aldehyde with dithiooxamide.^[7] The TTz backbone is a good extending framework for the viologen due to its planar structure that is beneficial for the electronic communication of a conjugated system. The "extended viologens", N,N'-disubstituted dipyridinium thiazolo[5,4-d]thiazole (TTz²⁺), were recently reported as long life-time blue photo-luminescent materials.^[8] Herein, we functionalize the 2,5-di(pyridin-4-yl)thiazolo[5,4-d]thiazole (Py₂TTz) through rational molecular engineering to yield a new water-soluble two-electron storage anolyte compound, 4,4'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(1-(3-

In our previous research, the N,N'-dimethylated 4,4'bipyridinium (MV2+) showed reliable performance in AORFBs application.^[2b, 2g] So we first synthesized the N,N'-dimethylated dipyridinium thiazolo[5,4-d]thiazole dichloride ((Me2TTz)Cl2) as shown in Scheme 1. Unfortunately, due to the high rigidity and hydrophobicity of the Py₂TTz skeleton, (Me₂TTz)Cl₂ is poorly water-soluble (< 10 mM in water). Functionality of highly hydrophilic groups, such as ammonium, sulfonate, and phosphate groups, has been suggested as an efficient strategy to improve the water solubility of hydrophobic compounds.^[2g, 9] Herein, a highly hydrophilic functional group was applied to functionalize the N atoms of the pyridine to overcome the solubility issue of the TTz²⁺. Specifically, the Py₂TTz was functionalized with hydrophilic 3-(trimethylaminium)propyl (NPr) pendant arms to get the water-soluble 4,4'-(thiazolo[5,4dlthiazole-2,5-diyl)bis(1-(3-(trimethylammonio)propyl)pyridin-1-

ium) tetrachloride (**[(NPr)₂TTz]Cl**₄). As displayed in Scheme 1, Py₂TTz was refluxed with (3-bromopropyl)trimethylammonium bromide in DMF to precipitate the 4,4'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(1-(3-(trimethylammonio)propyl)pyridin-1-ium)

tetrabromide ([(NPr)₂TTz]Br₄). Then, anion exchange was conducted to quantitatively convert [(NPr)₂TTz]Br₄ to the chloride version [(NPr)₂TTz]Cl₄ to avoid the effect of redox active bromine in the battery test. The synthesis of

WILEY-VCH



Scheme 1. Synthesis of the "π-conjugation extended viologen" compounds, (Me₂TTz)Cl₂ and [(NPr)₂TTz]Cl₄.

[(NPr)₂**TTz]CI**₄ was demonstrated up to a 20 g scale through a three-step synthetic route with 63% overall isolated yield. The product was characterized by ¹H-, ¹³C-NMR, and elemental analysis. In comparison to inorganic Vanadium ARFBs, the estimated cost of **[(NPr)**₂**TTz]CI**₄ (ca. \$2.3/kg, see Supporting Information) is only one tenth of the V₂O₅ (ca. 24/kg).

As expected, the highly charged ionic $[(NPr)_2TTz]Cl_4$ exhibited a high solubility in aqueous solution, 1.3 M in H₂O (69.7 Ah/L) or 1.1 M in 2.0 M NaCl (60.0 Ah/L). The cyclic voltammogram (CV) of $[(NPr)_2TTz]Cl_4$ shows two reversible redox waves at -0.38 V vs NHE for $E_{1/2}([(NPr)_2TTz]^{4+/3+})$ and -0.50 V vs NHE for $E_{1/2}([(NPr)_2TTz]^{3+/2+})$ (Figures 1A and S1), respectively. Under different scan rate, the peak currents of the two reductions of $[(NPr)_2TTz]Cl_4$ show linear relationship with the square root of scan rate ($v^{1/2}$, Figure S2), which indicates both redox couples of $[(NPr)_2TTz]^{4+/3+}$ and $[(NPr)_2TTz]^{3+/2+}$ are reversible and are diffusion controlled.

To further qualify the [(NPr)2TTZ]Cl4 as an anolyte candidate for AORFB, the diffusion coefficient (D) was investigated using linear sweep voltammetry (LSV) with a glassy carbon rotating disk electrode. LSV plots, and derived Levich plot for [(NPr)2TTz]Cl4 are shown in Figure S3. Due to the near redox potentials of the two single-electron reductions (-0.38 V for the 1st electron and -0.50 V for the 2nd electron), there was only one plateau observed in the LSV curves (Figure S3A). The linear Levich plot (Figure S3B) was constructed for the single-electron reduction of [(NPr)2TTz]4+ and [(NPr)2TTz]3+ using limiting currents (i) and the square root of rotation speeds ($\omega^{1/2}$). The corresponding slope from the linear relationship was transformed using the Levich equation (Equation S1, all equations are given in the experimental section in the supporting information) to calculate the average diffusion coefficient for $[(NPr)_2TTz]^{4+}$ and $[(NPr)_2TTz]^{3+}$ as 3.15 x 10⁻⁶ cm²/s. Furthermore, the rate constants (k^0) for the electron transfers of [(NPr)₂TTz]⁴⁺ and [(NPr)₂TTz]³⁺ were estimated using Nicholson's method. The k⁰ for [(NPr)₂TTz]⁴⁺ and [(NPr)₂TTz]³⁺ were both greater than 0.28 cm/s, which indicates fast electron transfer Regarding the high water-solubility, hoop electrochemical reversibility, and fast electron transfer, the [(NPr)2TTz]Cl4 is a promising anolyte candidate for AORFBs using a Cl⁻ exchange mechanism.

To demonstrate the proof of concept of the two-electron storage capability of $[(NPr)_2TTz]Cl_4$, it was paired with highly water-soluble 4-trimethylammoinium-TEMPO (abbreviated as N^{Me}-TEMPO, 3.0 M solubility in water) for a redox flow battery

test.^[21] As shown in Figure 1A, in a neutral NaCl solution, **[(NPr)**₂**TTz]Cl**₄ exhibited two single-electron reductions with average redox potential at -0.44 V (vs. NHE) and N^{Me}-TEMPO undergoes a single-electron oxidation at +1.0 V (vs. NHE). Both of these potentials are within the water splitting window (the potential gap between HER at -1.0 V and OER at +1.5 V in a



Figure 1. (A) Cyclic voltammograms of 4.0 mM [(NPr)₂TTz]Cl₄ and 4.0 mM N^{Me}-TEMPO in 0.5 M NaCl solution. The gray dash curve is the cyclic voltammogram of only the 0.5 M NaCl electrolyte, with labels for the onset potentials for the hydrogen evolution reaction (HER, -1.00 V) and oxygen evolution reaction (OER, +1.50 V). The red and green dash curves are the fitted redox waves for the 1st and 2nd electron reduction, respectively. (B) Schematic representation of the [(NPr)₂TTz]⁴⁺/N^{Me}-TEMPO AORFB and its anodic and cathodic half-cell reactions.

neutral NaCl supporting electrolyte), which ensures their application in AORFBs. The combination of $[(NPr)_2TTz]Cl_4$ and N^{Me}-TEMPO enables a 1.44 V battery voltage with a 53.7 Wh/L theoretical energy density, which is higher than most of reported AORFBs. Equations in Figure 1B give the anodic and cathodic half-cell reactions for the flow battery. In the anolyte side, the yellow $[(NPr)_2TTz]^{4+}$ was first reduced to the cation radical, $[(NPr)_2TTz]^{3+}$, at -0.38 V, and then further reduced to purple

WILEY-VCH

 $[(NPr)_2TTz]^{2+}$ with a neutral Py₂TTz skeleton at -0.50 V. The two electron reduced state, $[(NPr)_2TTz]^{2+}$, was synthetically prepared and characterized by ¹H- and ¹³C-NMR spectrum. Compared with the ground state $[(Nr)_2TTz]^{4+}$, both ¹H-and ¹³C-NMR signals of $[(NPr)_2TTz]^{2+}$ were upfield shifted due to its higher electron density of the reduced state. It is worth noting that the $[(NPr)_2TTz]^{2+}$ was oxygen insensitive (Figure S5), which (EE) and voltage efficiencies (VE), for example, 70% EE and VE at 40 mA/cm² operational current density, and they decreased linearly with the increasing of the operational current density (Figure 2C). The long term cycling performance of the **[(NPr)**₂**TTz]Cl**₄ / N^{Me}-TEMPO AORFB was measured at 40 mA/cm² for 300 cycles. As shown in Figure 2D, the flow battery delivered rather stable cycling performance, i.e. more than 90%



Figure 2. (A) Plot of battery capacity versus cycling numbers of the **[(NPr)**₂**TTz]Cl**₄ / N^{Me}-TEMPO AORFB at current densities from 40 mA/cm² to 100 mA/cm²; (B) Representative charge and discharge curves at current densities from 40 mA/cm² to 100 mA/cm² for the AORFB; (C) Plots of average Coulombic efficiency (CE), energy efficiency (EE), and voltage efficiency (VE) at different operational current densities; (D) Extended 300 cycle data of the AORFB showing charge capacity, discharge capacity, and Coulombic efficiency versus cycle number at 40 mA/cm² current density. Inset: Representative charge and discharge curve from the experiment. Conditions: anolyte: 0.1 M **[(NPr)**₂**TTz]Cl**₄ in 2 M NaCl; catholyte: 0.2 M N^{Me}-TEMPO in 2.0 M NaCl; AMV anion-exchange membrane, 25 °C.

confirms the stabilization of the reduced state species by extending the conjugation of viologen molecules and would make the TTz-based RFBs more tolerant. In the cathode side, N^{Me}-TEMPO was oxidized to the oxoammonium in the charge state and recovered to the nitroxyl radical in the discharged state through a single-electron redox process.

A flow battery was constructed using 0.1 M [(NPr)2TTz]Cl4 and 0.2 M N^{Me}-TEMPO in 2.0 M NaCl supporting electrolyte for anolyte and catholyte (a charge capacity of 5.36 Ah/L and an energy density of 3.86 Wh/L), respectively. Using a Selemion AMV anion-exchange membrane as the separator, the battery delivered outstanding performance as shown in Figure 2. The current rate performance was investigated from 40 to 100 mA/cm² with increments of 20 mA/cm² with cutoff voltages at 1.8 V for the charge process and 0.2 V for the discharge process. In five continuous cycles, stable capacity retention was observed at each current density (Figure 2A). Upon increasing the current density from 40 to 60, 80, and 100 mA/cm², capacity retention gradually decreased, which is due to the increased ohmic loss and is also consistent with the increased voltage gap of the charge/discharge curves (Figure 2B). The Coulombic efficiency (CE) of the battery under each current density was nearly 100%. Furthermore, the battery showed reasonable energy efficiencies total capacity retention after 300 cycles, equivalent to 99.97% capacity retention per cycle. It is worth noting that there are two almost merged plateaus in the charge and discharge curve, corresponding to the two single-electron redox processes (Figure 2D inset, also see Figure S6 for a zoom-in image). The CV post analysis showed no active material crossover in both anolyte and catholyte (Figure S7).

As shown in Figure S8, at higher concentrations of electrolytes, i.e. 0.25 M [(NPr)₂TTz]CI₄ and 0.5 M N^{Me}-TEMPO as catholyte (equivalent to 0.5 M electrons), the RFB (13.4 Ah/L and 9.65 Wh/L) delivered similar rate performance and slightly lower energy efficiency (68.6% EE at 40 mA/cm²) than the 0.1 M [(NPr)₂TTz]CI₄ and 0.2 M N^{Me}-TEMPO bdtery. Same as the previously reported viologen-based RFBs,^[2b, 2f, 2g, 2j] the [(NPr)₂TTz]CI₄ / N^{Me}-TEMPO AORFB displayed concentration dependent long-term cycling stability. Specifically, the 0.5 M electron RFB delivered 99.94% capacity retention per cycle. A mechanistic understanding of the AORFB is needed to elucidate the concentration dependent battery performance.

In summary, we reported a " π -conjugation extended viologen" compound, **[(NPr)₂TTz]Cl**₄, as a novel two-electron storage anolyte for total organic neutral AORFB applications. Through the rational molecular engineering, planar TTz

WILEY-VCH

framework was inserted into the two pyridinium moieties to adjust the electrochemistry of viologen while a highly hydrophilic 3-(trimethylaminium)propyl group was introduced to the hydrophobic Py2TTz skeleton to improve solubility in water. The synthesis of [(NPr)2TTz]Cl4 was demonstrated through a straightforward reaction route from the commercially available reagents with a satisfactory isolated yield. [(NPr)2TTZ]Cl4 exhibits a high solubility in water, reversible electrochemical behaviors, and fast electron transfer rate constants. Paired with the cathodic compound, NMe-TEMPO, the [(NPr)2TTz]Cl4 / NMe-TEMPO flow battery enables a 1.44 V battery voltage with a theoretical energy density of 53.7 Wh/L. The demonstration of [(NPr)2TTz]Cl4 / NMe-TEMPO cell delivered outstanding battery performance, specifically, 70 % energy efficiency and 99.97 % capacity retention per cycle. The results confirm the reliability of the strategy of extending the π -conjugation of viologen molecules to obtain new redox active compounds for the AORFB application. It is anticipated that the concept of "mconjugation extension" can be also applied with other redox active molecules and lead to the discovery of novel RFB chemistry.

Supporting Information contains experimental details and additional figures and tables. Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements We thank Utah State University for providing faculty startup funds to the PI (T. Leo Liu) and the Utah Science Technology and Research initiative (USTAR) UTAG award for supporting this study. Bo Hu is grateful for China CSC Abroad Studying Fellowship and Utah Energy Triangle Student Award supported by the Office of Energy of the Utah State government, respectively. Camden DeBruler is grateful for his USU Presidential Doctoral Research Fellowship (PDRF) supported by USU.

Keywords: "Extended viologen" • Redox flow battery • Molecular engineering • TEMPO

 (a) Z. Yang, J. Zhang, M. C. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem Rev* 2011, *111*, 3577-3613; (b) W. Wang, Q. Luo, B. Li, X. Wei, L. Li, Z. Yang, *Adv. Funct. Mater.* 2013, *23*, 970-986; (c) G. L. Soloveichik, *Chem Rev* 2015, *115*, 11533-11558; (d) Q. Huang, Q. Wang, *ChemPlusChem* 2015, *80*, 312-322; (e) P. Leung, A. A. Shah, L. Sanz, C. Flox, J. R. Morante, Q. Xu, M. R. Mohamed, C. Ponce de León, F. C. Walsh, *J. Power Sources* 2017, *360*, 243-283; (f) X. Wei, W. Pan, W. Duan, A. Hollas, Z. Yang, B. Li, Z. Nie, J. Liu, D. Reed, W. Wang, V. Sprenkle, *ACS Energy Lett.* 2017, 2187-2204; (g) J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager, U. S. Schubert, *Angew. Chem. Int. Ed.* **2016**, *56*, 686-711.

- (a) B. Huskinson, M. P. Marshak, C. Suh, S. Er, [2] M. R. Gerhardt, C. J. Galvin, X. Chen, A. Aspuru-Guzik, R. G. Gordon, M. J. Aziz, Nature 2014, 505, 195-198; (b) T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, Adv. Energy Mater. 2016, 6, 1501449; (c) K. Lin, R. Gómez-Bombarelli, E. S. Beh, L. Tong, Q. Chen, A. Valle, A. Aspuru-Guzik, M. J. Aziz, R. G. Gordon, *Nat. Energy* **2016**, *1*, 16102; (d) Y. Ding, Y. Li, G. Yu, *Chem* **2016**, *1*, 790-801; (e) T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager, U. S. Schubert, *Nature* **2015**, *527*, 78-81; (f) T. Janoschka, N. Martin, M. D. Hager, U. S. Schubert, Angew. Chem. Int. Ed. 2016, 55, 14427-14430; (g) D. Rueda-García, D. P. Dubal, F. Huguenin, P. Gómez-Romero, J. Power Sources 2017, 350, 9-17; (h) B. Hu, C. Seefeldt, C. DeBruler, T. Liu, J. Mater. Chem. A 2017, 5, 22137-22145. ; (i) J. Luo, A. Sam, B. Hu, C. DeBruler, X. Wei, W. Wang, T. L. Liu, Nano Energy 2017, 42, 215-221; (j) E. S. Beh, D. De Porcellinis, R. L. Gracia, K. T. Xia, R. G. Gordon, M. J. Aziz, ACS Energy Lett. 2017, 2, 639-644; (k) X. Wei, W. Xu, M. Vijayakumar, L. Cosimbescu, T. Liu, V. Sprenkle, W. Wang, *Adv. Mater.* **2014**, *26*, 7649-7653; (I) X. Wei, W. Xu, J. Huang, L. Zhang, E. Walter, C. Lawrence, M. Vijayakumar, W. A. Henderson, T. Liu, L. Cosimbescu, B. Li, V. Sprenkle, W. Wang, Angew. Chem. Int. Ed. 2015, 54, 8684-8687; (m) J. Huang, L. Cheng, R. S. Assary, P. Wang, Z. Xue, A. K. Burrell, L. A. Curtiss, L. Zhang, Adv. Energy Mater. 2015, 5, 1401782; (n) C. S. Sevov, D. P. Hickey, M. E. Cook, S. G. Robinson, S. Barnett, S. D. Minteer, M. S. Sigman, M. S. Sanford, J. Am. Chem. Soc. 2017, 139, 2924-2927; (o) Y. G. Zhu, Y. Du, C. Jia, M. Zhou, L. Fan, X. Wang, Q. Wang, J. Am. Chem. Soc. 2017, 139, 6286-6289; (p) G. Cong, Y. Zhou, Z. Li, Y.-C. Lu, ACS Energy Lett. 2017, 2, 869-875.
- [3] (a) E. J. Son, J. H. Kim, K. Kim, C. B. Park, *J Mater Chem A* 2016, *4*, 11179-11202; (b) K. Lin, Q. Chen, M. R. Gerhardt, L. Tong, S. B. Kim, L. Eisenach, A. W. Valle, D. Hardee, R. G. Gordon, M. J. Aziz, M. P. Marshak, *Science* 2015, *349*, 1529-1532; (c) A. Orita, M. G. Verde, M. Sakai, Y. S. Meng, *Nat Commun* 2016, *7*, 13230; (d) M. R. Gerhardt, L. Tong, R. Gómez-Bombarelli, Q. Chen, M. P. Marshak, C. J. Galvin, A. Aspuru-Guzik, R. G. Gordon, M. J. Aziz, *Adv. Energy Mater.* 2017, *7*, 1601488-n/a; (e) B. Yang, L. Hoober-Burkhardt, S. Krishnamoorthy, A. Murali, G. K. S. Prakash, S. R. Narayanan, *J. Electrochem. Soc.* 2016, *163*, A1442-A1449.
- [4] C. L. Bird, A. T. Kuhn, *Chem. Soc. Rev.* **1981**, *10*, 49-82.
- (a) Kazuko Takahashi, Takayasu Nihira, Kimio Akiyama, Yusaku Ikegami, E. Fukuyo, *J. Chem. Soc., Chem. Commun.* **1992**, 620-622; (b) William W. Porter III, Thomas P. Vaid, A. L. Rheingold, *J. Am. Chem. Soc.* **2005**, 16559-16566.
- [6] Masato Nanasawa, Makio Miwa, Michiko Hirai, T. Kuwabara, *J. Org. Chem.* **2000**, 593-595.
- [7] Gianna Reginato, Alessandro Mordini, Lorenzo Zani, Massimo Calamante, A. Dessì, *Eur. J. Org. Chem.* **2016**, 233–251.
- [8] A. N. Woodward, J. M. Kolesar, S. R. Hall, N.-A. Saleh, D. S. Jones, M. G. Walter, J. Am. Chem. Soc. 2017, 139, 8467-8473.
- [9] S. Er, C. Suh, M. P. Marshak, A. Aspuru-Guzik, *Chem. Sci.* 2015, 6, 885-893.



WILEY-VCH

Entry for the Table of Contents

A highly water-soluble " π -conjugation extended viologen" is designed as a novel two-electron storage analyte to enable a 1.44 V total organic neutral aqueous redox flow battery.

COMMUNICATION



Jian Luo, Bo Hu, Camden Debruler,

and T. Leo Liu*

Page No. – Page No.

A "π-Conjugation Extended Viologen" as Novel Two-Electron Storage Anolyte for Total Organic Aqueous Redox Flow Battery

This article is protected by copyright. All rights reserved.