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Dong Jun Kim, Keith R. Hermann, Aleksandrs Prokofjevs, Michael T. Otley, Cristian Pezzato, Magdalena Owczarek and J. Fraser Stoddart^{*}

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

*E-mail: stoddart@northwestern.edu

MAIN TEXT

*Correspondence Address

Professor J. Fraser Stoddart

Department of Chemistry

Northwestern University

2145 Sheridan Road

Evanston, IL 60208 (USA)

Email: *stoddart@northwestern.edu*

ABSTRACT

Organic rechargeable batteries, composed of redox-active molecules, are emerging as candidates for the next generation of energy storage materials because of their large specific capacities, cost effectiveness, and the abundance of organic precursors, when compared with conventional lithium-ion batteries. Although redox-active molecules often display multiple redox states, precise control of a molecule's redox potential, leading to a single output voltage in a battery, remains a fundamental challenge in this popular field of research. By combining macrocyclic chemistry with density functional theory calculations (DFT), we have identified a structural motif that more effectively delocalizes electrons during lithiation events in battery operations—namely, through-space electron delocalization in triangular macrocyclic molecules that exhibit a single well-defined voltage profile-compared to the discrete multiple voltage plateaus observed for a homologous macrocyclic dimer and an acyclic derivative of pyromellitic diimide (PMDI). The triangular macrocycle, incorporating three PMDI units in close proximity to one another, exhibits a single output voltage at 2.33 V, compared with two peaks at (i) 2.2 and 1.95–1.60 V for reduction and (ii) 1.60–1.95 and 2.37 V for oxidation of the acyclic PMDI derivative. By investigating the two cyclic derivatives with different conformational dispositions of their PMDI units and the acyclic PMDI derivative, we identified noticeable changes in interactions between the PMDI units in the two cyclic derivatives under reducing conditions, as determined by differential pulse voltammetry (DPV), solution-state spectroelectrochemistry, and variable temperature UV-Vis spectra. The numbers and relative geometries of the PMDI units are found to alter the voltage profile of the active materials significantly during galvanostatic measurements, resulting in a desirable single plateau for the triangular macrocycle. The present investigation reveals that understanding and controlling the relative conformational dispositions of redox-active units in macrocycles are key to achieving high energy density and long cycle-life electrodes for organic rechargeable batteries.

INTRODUCTION

Rechargeable batteries impact our everyday lives and play a critical role in meeting modern energy demands, while also holding out promise for a more sustainable future by facilitating the utilization of energy from renewable sources.¹ Amongst many different rechargeable ones, lithium-ion batteries (LIBs) have become ubiquitous in today's world, delivering spectacular performance in applications, ranging from portable electronic devices to electric vehicles.² Nevertheless, conventional materials employed in commercial LIBs rely on non-renewable sources of rare metals, a situation which is not desirable from a long-term environmental perspective.³ Hence, new strategies are needed in order to develop next generation energy storage systems based on more sustainable and low-cost materials.⁴

Organic rechargeable batteries (ORBs) utilizing redox-active small molecules or polymers have received⁵ a significant amount of attention on account of their versatility, sustainability, flexibility, and low environmental impact, all of which reflect the wide availability of electrode materials from abundant natural sources. In order to design an active material for ORBs, the compounds need to satisfy the following criteria. They must (i) display redox reversibility in the solid-state in a wet electrolyte environment, (ii) intercalate cations or anions reversibly, and (iii) exhibit the lack of solubility toward the electrolyte during electrochemical cycling. While recent investigations⁶ into ORBs have greatly improved electrochemical performance, major challenges in organic electrode design have still not been addressed in a wholly satisfactory manner. When compared to their conventional transition-metal based counterparts, cathodes based on redox-active organic molecules featuring numerous redox states often deliver larger capacities, yet they typically exhibit unfavorable voltage profiles. Thus, multiple voltage plateaus originating from discrete redox potentials are typically observed, and substantial voltage decline during discharge cannot be avoided, even when neighboring redox units are forced to interact with each other.⁷ Steadily declining voltage profiles pose a substantial problem for designing full-cell

batteries, where consistent output voltages are desirable. Furthermore, small redox-active organic molecules are often soluble in electrolyte solutions,²⁰ or participate in irreversible side reactions during repeated battery cycling,^{8, 9} causing severe capacity drops over time. Achieving (i) a single well-defined voltage profile, in combination with (ii) practical cyclability characteristics in small molecule-based organic rechargeable batteries, therefore, still present considerable challenges.

In an effort to address these challenges, we chose to explore redox-active macrocycles, which have received much less attention than their corresponding small-molecule and polymer-based counterparts. Rigid macrocycles exhibit unique physical and chemical properties, which result primarily from the presence of enforced cavities, and are tunable through controlling the conformations of the molecules.^{10,} ¹¹ For our part, we have been focusing on gaining a better understanding of the material properties of rigid macrocycles, some of which result from electronic communication between redox-active units within the structure.^{12, 13, 14} Despite the long history¹⁰ of macrocyclic chemistry, direct observation of its

impact on performance of energy storage devices, such as batteries and supercapacitors, has limited precedent.^{14, 15}

Herein, we demonstrate that constraining three redox-active units exhibiting multiple discrete potentials—and thus giving rise to two-plateau voltage profiles in batteries—into a rigid triangular macrocycle has allowed us to access cathode materials which exhibit single well-defined voltage profiles. Our investigation suggests that the intrinsic properties of the redox unit itself and the mutual arrangement of individual redox units within the active material are equally critical to designing organic electrodes for rechargeable batteries.

RESULTS AND DISCUSSION

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Design and Synthesis. In order to probe the macrocyclic effect on battery performance, we synthesized a series of three compounds—namely, bis(cyclohexyl)pyromellitic diimide (**PMDI-Ref**), the cyclic dimeric pyromellitic diimide ((–)-2**PMDI**), and the cyclic trimeric pyromellitic diimide ((–)-3**PMDI-** Δ). The first compound **PMDI-Ref** is a simple pyromellitic diimide featuring one PMDI redox unit (Figure 1a), bearing cyclohexyl rings attached to both nitrogen atoms and so experiences relatively facile rotation around exocyclic C–N bonds. The second compound (–)-2**PMDI** is a strained cyclic dimer (Figure 1b) with two cofacially oriented redox-active PMDI units held in close proximity by two (*RR*)-1,2-diaminocyclohexano linkers. The third compound in the series, (–)-3**PMDI-** Δ , a larger triangular macrocycle (Figure 1c) composed of alternating PMDI and (*RR*)-1,2-diaminocyclohexano units, is less strained than the dimer.

While **PMDI-Ref** and (–)-2**PMDI** were synthesized according to previously reported¹⁶ procedures, the synthesis of (–)-3**PMDI-** Δ has been optimized for multi-gram scale production without the use of column chromatography. X-Ray crystal structures of the PMDI macrocycles exhibit minor differences from those reported¹⁶ in the previous study, apparently reflecting the influence of the solvents used in crystallizations. We also attempted many different crystallizations of the radical anion along with numerous lithium salts – lithium cations from lithium naphthalenide, lithium hexafluorophosphate, lithium bis(trifuoromethane)sulfonimide – but all attempts were unsuccessful. Detailed experimental procedures and full ¹H and ¹³C NMR spectroscopic characterization, as well as single-crystal X-ray diffraction analysis, are described in detail in the Supporting Information.

Redox Properties and UV–Vis–NIR Spectrophotometry. The redox properties of all three compounds were studied in 1 mM solutions in DMF, using 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) as the supporting electrolyte. Since cyclic voltammetry (CV, Figure

S11) did not afford good resolution of individual redox peaks, differential pulse voltammetry (DPV, Figure 2a) was used as the electrochemical technique of choice.

Upon reduction, PMDI-Ref shows two peaks at -0.69 and -1.38 V vs Ag/AgCl, resulting from the formation of [PMDI-Ref]⁻ and [PMDI-Ref]²⁻, respectively. In contrast, the DPV plot of (-)-2PMDI shows four distinct peaks clustered in two well-separated groups (-0.41, -0.70 and -1.73, -1.92 V vs Ag/AgCl), originating from a series of one-electron reduction processes, featuring electronic interactions between the two diimide units. A similar pattern is observed in the case of (-)-3PMDI- Δ , where the total number of reduction steps is six (-0.61, -0.70, -0.77 and -1.33, -1.55, -1.72 V vs Ag/AgCl), confirming the fact that the triangle also allows for some through-space electron delocalization in the reduced state. Spectroelectrochemistry (SEC) experiments were performed (Figure S13) in order to gather additional information about the reduced forms of the PMDI derivatives. At the reducing potential of -1.25 V, all the PMDI derivatives exhibit absorptions around 650 and 720 nm, indicating the formation of radical anionic species. Reduced (-)-2PMDI, however, also showed two broad absorption bands, one around 550–1100 nm, and the other above 1200 nm, qualitatively resembling observations in a closely related naphthalene diimide dimer reported previously,¹³ lending further support for intramolecular interactions between the diimide units in the dimer. The reduced states of all PMDI derivatives were also characterized by temperature- (Figure 3a-c) and concentration-dependent (Figure 3d-f) UV-Vis-NIR spectrophotometry. We employed 1 equiv of cobaltocene (CoCp₂) per PMDI unit in the particular molecule as reducing agent, on account of its reduction potential¹⁸ of $E_o = -1.91$ V vs Fc/Fc⁺, which is sufficient to deliver one electron per PMDI unit in each of the three compounds in this investigation. On increasing the temperature from 20 to 80 °C, the intensity of the peak at 720 nm in the UV-Vis spectrum (Figure 3a) of PMDI-Ref decreases considerably. No new signals appear in the spectrum, and the initial absorption intensity is restored upon returning the sample to 20 °C. While the UV-Vis

spectrum (Figure 3b) of (-)-2PMDI at 20 °C differs considerably from that of PMDI-Ref, the differences become progressively less apparent on increasing the temperature, and at 80 °C, the UV–Vis spectra of the reduced states of all three PMDI derivatives exhibit considerable similarities. The temperature-dependent changes in the UV-Vis spectrum (Figure 3c) of (-)-3PMDI- Δ , reduced on adding 3 equiv CoCp₂ are unremarkable, and are best described as an incremental change in the normalized absorbance with temperature. Concentration-dependent (0.05–0.5 mM) experiments (Figure 3d-f) involving chemically reduced PMDI-Ref and (-)-3PMDI-A did not present any evidence of intermolecular radical-anion pairing.^{13, 18} The interpretation of the concentration-dependent UV-Vis spectrophotometric data (Figure 2e) for the reduced (-)-2PMDI is less straightforward, as changes in the intensity of the 1600 nm peak may potentially indicate some contribution from intermolecular interactions between reduced (-)-2PMDI molecules. The chemical stability of the reduced forms of all three compounds was confirmed by NMR experiments involving reduction of the imides by adding $CoCp_2$ in DMF- d_7 solution, followed by reoxidation with nitrosonium hexafluorophosphate (NOPF₆) after 24 h at ambient temperature. (Figure S5-7) In all cases, proton resonances corresponding to starting imides reappeared upon addition of the oxidant, indicating that the compounds suffered little to no degradation in their reduced states.

Battery Measurements of Macrocyclic Compounds. Since our initial observations indicated a strong dependence of the electronic properties of the cyclic PMDI derivatives on the mutual arrangement of redox-active units within the macrocycle, we have performed galvanostatic measurements on all three compounds in order to elucidate the effect of changes in conformation on LIB performance. Coin-type cells, which were fabricated inside an Ar-filled glovebox, were employed in the galvanostatic measurements. Each PMDI redox unit in these derivatives undergoes two sequential one-electron redox processes. In other words, **PMDI-Ref**, (–)-2PMDI and (–)-3PMDI-Δ are capable of accepting two, four

and six lithium atoms, respectively, as depicted in Figure S12. Hereafter, all of the potentials listed are based on the Li/Li⁺ redox couple, while charging and discharging processes refer to the lithiation (reduction) and delithiation (oxidation), respectively. Current rates were calculated based on the theoretical capacity of each PMDI derivative, and not on the actual charge/discharge cycle durations.

At the current rate of C/20, PMDI-Ref exhibits (Figure 3a) a voltage profile consisting of two plateaus,¹⁹— a distinct one at 2.11 V, followed by a less well-defined one in the range of ca. 1.95–1.60 V, corresponding to the formation of [PMDI-Ref]⁻ and [PMDI-Ref]²⁻, respectively. Similarly, during the discharge process, oxidation of $[PMDI-Ref]^{2-}$ resulted in a distorted plateau in the range of ca. 1.60–1.95 V, while further oxidation of [PMDI-Ref]^{•-} delivered a clear plateau at 2.37 V. The specific capacities observed during the first charge and discharge were 94 and 172 mAh g^{-1} , respectively. The capacity decayed rapidly in the subsequent cycles, resulting in only 52 mAh g^{-1} during the third discharge. The observed low values for both the Coulombic efficiency (CE) and specific capacity of the first cycle are most likely a result of the dissolution of the PMDI-Ref (or its lithiated forms) in the electrolyte.²⁰ A similar voltage profile was also observed (Figure 3b) for (-)-2PMDI, where the reduction to $[(-)-2PMDI]^{2-}$ gives rise to a plateau at around 2.47 V, and the subsequent reductions to [(-)-2PMDI]³⁻ and [(-)-2PMDI]⁴⁻ occurred between 2.22 and 1.60 V. During the discharge process, a sloped voltage profile was observed in the range of 1.60-2.31 V, corresponding to the oxidation of [(-)-2PMDI]⁴⁻, while a more discrete plateau at 2.58 V stems from the oxidation of [(-)-2PMDI]²⁻. The charging profile of (-)-2PMDI also showed some deviation during the first and subsequent cycles. When compared with PMDI-Ref. (-)-2PMDI revealed substantial CE improvement in the first cycle, as well as better capacity retention in the subsequent cycles, demonstrating a specific capacity of 126 mAh g^{-1} after three cycles. Significantly, the voltage profile of (–)-**3PMDI-** Δ (Figure 4c) is substantially different from those of PMDI-Ref and (-)-2PMDI, featuring a single well-defined

plateau at 2.33 V, corresponding to reduction of (-)-**3PMDI**- Δ to [(-)-**3PMDI**- Δ]⁶⁻. This triangular macrocycle also showed a specific capacity of 163 mAh g^{-1} , indicating acceptance of 5.8 Li^+ per molecule.²¹ The highly desirable single-plateau voltage profile and good capacity retention of (-)-3PMDI- Δ were also preserved in galvanostatic rate capability tests (Figure 4e and f) performed at current rates of up to 2C. Both macrocycles demonstrated substantially higher first cycle CE compared to the reference compound. Thus, while the first cycle CEs of (–)-2PMDI and (–)-3PMDI- Δ were found to be 96% and 94%, respectively, that of PMDI-Ref was only 55%. In galvanostatic cycling tests performed at a C/5 current rate, the (-)-3PMDI- Λ showed substantially better capacity retention than the other two compounds, delivering 86 mAh g^{-1} after 50 cycles, a value which corresponds to 64% of the initial capacity. At the same time, both PMDI-Ref and (-)-2PMDI displayed rapid capacity decay, with less than 10 mAh g^{-1} remaining after 50 cycles. High solubility of the neutral state of **PMDI-Ref** in the carbonate-based electrolyte was confirmed experimentally, thus providing a convenient rationale for the unstable cycling behavior of the reference compound. Both (-)-3PMDI- Δ and (-)-2PMDI, however, were found to be insoluble in the electrolyte, and so we performed additional investigations to explain the different cycling performance of these two compounds. Postulating that more prominent differences in the physical properties may be observed for the lithiated states of these compounds, we attempted reducing both macrocycles (Figure S14) with metallic lithium in DMF. Upon reduction, the solution of (-)-3PMDI- Δ was rapidly transformed into a gel, which reverted back to a liquid upon re-oxidation. At the same time, reduction had much less influence on the viscosity of the (-)-2PMDI solution. It is possible that agglomeration via intermolecular O-Li•••O interactions may be more favorable in the case of (-)-**3PMDI**- Δ on account of its triangular geometry, therefore preventing dissolution of the active material during battery operation.⁹

Computational Studies. The marked differences which exist between the three PMDI derivatives explored experimentally motivated us to perform density functional theory (DFT) calculations in order to gain a better understanding of how the molecular structure of these compounds translates into their performance in ORBs. Towards this end, we performed structural optimization of all PMDI derivatives. as well as their respective O-lithiated states containing up to two Li atoms per PMDI unit, at BP-86(D3BJ)/def2-TZVP level of theory. Computational details are described in the Supporting Information. Even although the computational approach employed ignored the condensed phase effects beyond solvation, resulting in the systematic overestimation of absolute values of reduction potentials by ca. 1 V in all cases, nevertheless it was possible to reproduce major trends observed in the experimental studies. Thus, a 0.43 eV separation between two calculated Li⁺-coupled reduction potentials (-3.15 and -2.72 eV) for PMDI-Ref fits (Figure 4a) well within ca. 0.16-0.77 eV range obtained from galvanostatic measurements. For (-)-2PMDI, calculated sequential redox potentials (-3.80, -3.73 and -3.00, -2.96 eV) parallel the marginally distorted two-plateau voltage profile determined experimentally (Figure 4b), while also predicting correctly the higher operational voltages of LIBs based on the cyclic dimer. More importantly, the theoretical studies (Figure 4c) predict that the Li⁺-coupled redox behavior of (-)-3PMDI- Δ differs substantially from those of PMDI-Ref and (-)-2PMDI, mirroring all major features of the experimental data. Thus, the calculated difference between the lowest and the highest reduction potentials of (-)-**3PMDI-A** is only 0.33 eV, a value which is particularly noteworthy in view of the fact that six distinct redox states (-3.53, -3.48, -3.52 and -3.25, -3.26, -3.20 eV) are contained within this narrow region, leading to the unique one-plateau discharge profile.

Atoms in Molecules (AIM) charge and Shannon aromaticity (see the Supporting Information) calculations were used to trace changes occurring during the reduction of different PMDI derivatives. The results (Figure 5 and Figure S15–17) show representative bond lengths, and changes in AIM

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charges of the **PMDI-Ref** core occurring upon reduction with one and two Li atoms, respectively. In good agreement with chemical intuition, reduction of **PMDI-Ref** with 1 equiv of Li results in the formation of *O*-lithiated species (Figure 5b) with substantially decreased AIM charges at the C (by 0.23) and O (by 0.18) atoms of the carbonyl group coordinated to Li⁺. Some electron density is also transferred to the other three carbonyl carbon atoms in the molecule, yet to a substantially smaller extent, while the remaining non-hydrogen atoms play a relatively small role in accommodating the electron density transferred from lithium. The second *O*-lithiation event (Figure 5c) shows little regiochemical preference, although the structure with both Li⁺ coordinating to different carbonyls of the same imide unit is of marginally lower energy. Both lithiated carbonyl groups of the doubly reduced **PMDI-Ref** feature longer C–O distances (1.28 Å vs. 1.25 Å) and lower AIM charges (by 0.22 at O and 0.16 at C, see the Supporting Information) than the non-lithiated carbonyl groups in the same molecule.

In contrast, reduction of the (–)-2PMDI leads to species (Figure 5d–f) in which every Li⁺ cation is simultaneously coordinated by two PMDI units, and each electron transferred from the lithium is accommodated by both participating carbonyl groups in a nearly equal manner. This situation is most apparent in the fully lithiated (–)-2PMDI (Figure 5f), where all carbonyl C and O charges, as well as C–O distances (1.27Å) are nearly equal throughout the molecule. A very similar picture is observed (Figure 5. g–i) in (–)-3PMDI- Δ , where each Li⁺ cation is again bonded to two oxygen atoms belonging to different sides of the (–)-3PMDI- Δ , and both carbonyl groups involved accept roughly equal amounts of electron density, implying that the third side of the (–)-3PMDI- Δ plays no role in the monolithiation event (Figure 5h). In the six-fold lithiated state of (–)-3PMDI- Δ (Figure 5i), atomic charges, as well as C–O distances once again show little spread within the molecule, and are almost equal to the corresponding values in the fully lithiated (–)-2PMDI (Figure 5f). Despite the similarities between charge distribution in both exhaustively lithiated macrocycles, electron repulsion between the reduced

PMDI units is diminished considerably in the case of the molecular triangle on account of larger spacing between the redox units. In particular, while differences in shape between the (–)-2PMDI and the (–)-3PMDI- Δ have relatively little influence on O····O separation within each C–O–Li–O–C subunit (3.02 Å in (–)-2PMDI-Li₄, and 3.15 Å in (–)-3PMDI- Δ -Li₆), and almost no influence on the lengths of Li–O bonds, the carbonyl C···C separations are considerably larger in the latter species, i.e., 3.19 Å in (–)-2PMDI-Li₄, and 3.63 Å in (–)-3PMDI- Δ -Li₆. Therefore, at high levels of the lithiation process, electrons experience more stabilization in the case of (–)-3PMDI- Δ , consequently leading to a substantially less-sloped voltage profile.

The dramatic changes in voltage profiles observed across the series of PMDI derivatives can thus be attributed by interplay of two factors—namely, the size of the delocalization surface involved in each reduction event, as well as spacing between PMDI units in the structure. Specifically, the **PMDI-Ref** produces a more localized reduced state, leading to the familiar two-plateau voltage profile. In turn, both the (–)-**2PMDI** and (–)-**3PMDI-** Δ feature more complete utilization of carbonyl groups in the stabilization of the fully lithiated state. As the degree of lithiation increases, however, so does the electron repulsion between the reduced PMDI units in the (–)-**2PMDI**. In the (–)-**3PMDI-** Δ , the geometrical arrangement of the PMDI units is such that it reduces unfavorable interactions in highly lithiated states, without sacrificing the efficiency of Li⁺ chelation.

CONCLUSIONS

We have synthesized a series of PMDI-based redox-active compounds, including two rigid macrocycles, and measured their performance as active materials in batteries. The macrocycles (–)-2PMDI and (–)-3PMDI- Δ exhibit through-space electron delocalization on account of the forced proximity between redox units. We have also observed substantial differences in the electrochemical

performance between (–)-2PMDI and (–)-3PMDI- Δ , with only the latter compound producing the desired one-plateau voltage profile on account of dense clustering of all six redox potentials of the (–)-3PMDI- Δ within a narrow voltage range. We believe that this difference arises primarily from repulsive interactions between the reduced PMDI units, which are particularly strong in (–)-2PMDI because of their cofacial orientation and the strain present in the cyclic dimer, both of which are lessened substantially in the triangular macrocycle. We conclude that controlling the delocalization of the reduced states and minimizing the electron repulsion between redox-active units are important considerations in designing active materials for organic rechargeable batteries.

EXPERIMENTAL SECTION

Preparation of PMDI derivatives. Bis(cyclohexyl)pyromellitic diimide (**PMDI-Ref**), the cyclic dimeric pyromellitic diimide ((–)-2**PMDI**), and the cyclic trimeric pyromellitic diimide ((–)-3**PMDI-** Δ)) were synthesized as previously described in the literature.¹⁶ The first two compounds were purified using automated column chromatography on a Teledyne Isco Combiflash RF 200 system, while the triangular macrocycle was purified according to the procedures described in Section B without the use of column chromatography.

Material characterization. Degassed *N*,*N*-dimethylformamide- d_7 (DMF- d_7) or DMF was used in all investigations in order to ensure the use of a single solvent for the acquisition of all the experimental data. A three-cycle freeze-pump-thaw method was employed in order to degas DMF- d_7 for the NMR titrations and UV–Vis spectroscopy. Liquid N₂ was used as the coolant, and a 0.1 mtorr vacuum was applied for 30 min in each cycle. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). UV–Vis–NIR spectra were recorded between 20 and 80 °C on a Shimadzu UV-3600 spectrophotometer, equipped with an external temperature controller S1700. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 500 spectrometers, with working frequencies of 500 MHz (¹H nuclei) and 125 MHz (¹³C nuclei). Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ((CD₃)₂NCDO $\delta_{\rm H} = 8.03$,

2.92, 2.75 and $\delta_{\rm C}$ = 163.2, 34.9, 29.8 ppm). Single crystals of (–)-2PMDI and (–)-3PMDI- Δ were grown by slow vapor diffusion of H₂O into a solution of (–)-2PMDI in DMF and (–)-3PMDI- Δ in NMP, respectively. Details of the crystallization procedures are given in Supporting Information.

Electrochemical measurements. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out using a three-electrode beaker cell, with Ag/AgCl as a reference electrode. Glassy carbon and platinum mesh was used for the working and counter electrodes, respectively. Spectroelectrochemistry (SEC) was performed using an EF-1362 BASi spectroelectrochemical cell with Pt mesh as the working electrode. A Gamry Reference 600 potentiostat interfaced to a PC was employed in the collection of CV, DPV and SEC data.

Battery electrode fabrication and testing. Coin-type cells were fabricated inside an Ar-filled glovebox. The battery electrode slurry was prepared by mortar and pestle, mixing each PMDI derivative with carbon black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 60:30:10 using in *N*-methylpyrrolidone (NMP) as the solvent. The mixed slurry was cast onto copper foil using the Doctor-Blade technique and dried in vacuum oven at 70 °C overnight. Lithium hexaflurophosphate (LiPF₆), dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC, 1:1 v/v, Sigma Aldrich), was employed as the electrolyte, while metallic lithium was used as both counter and reference electrodes. Celgard 2320 microporous film was used as a separator. All coin-type cells were subjected to galvanostatic cycling using automated tester with 1.6–3.2 V vs Li/Li⁺ potential limitation condition. The current rates from galvanostatic measurements were calculated based on the theoretical specific capacity of each compound.

Computational details. All geometry optimizations and frequency calculations were performed using the ORCA 3.0.2 suite of computational programs.²² Tight SCF convergence criteria (ORCA: TightSCF) and increased resolution integration grids (ORCA: Grid6) were employed throughout calculations. Geometry optimization was performed at BP-86(D3BJ)/def2-TZVP level of theory using COSMO²³ solvation model. Additionally, resolution of identity (RI-J) approximation²⁴ and D3BJ empirical dispersion correction²⁵ were used. For solution phase calculations, $\varepsilon = 38$ was assumed based on the

dielectric constant estimated²⁶ for the actual solvent mixture used in battery fabrication. The fact that the resulting superstructures represent true minima on the potential energy surface was confirmed by gas phase re-optimization at HF-3c level of theory,²⁷ and subsequent frequency calculations. A large number of lithiated superstructures were explored for the **PMDI-Ref** to identify general patterns in Li⁺ ion binding to the reduced species. It was established that *O*-lithiated superstructures were consistently of lower energy compared to potential alternatives, e.g., superstructures with Li⁺ ion located above the PMDI ring. In the ease of the larger cyclic dimer (–)-2PMDI and triangle (–)-3PMDI-A attention was focused on the systematic evaluation of all conceivable *O*-lithiated superstructures for each reduced state, and only the lowest energy superstructures were considered. AIM and Shannon aromaticity²⁸ (SA) calculations were performed as follows. Starting from optimized geometries, wave function files were generated in single-point gas phase calculations at B3LYP/6-31+G(d,p) level of theory using Gaussian 09W package.²⁹ Subsequently, AIM charges and electron densities at bond critical points were performed using charge densities at all C–C bond critical points within the ring.

ASSOCIATED CONTENT

Supporting Information

Detail experimental details, synthetic procedures, spectroscopic and crystallographic characterization, computational details, and supportive figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*stoddart@northwestern.edu

Notes

The authors declare no competing financial interest.

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(21) Following previously reported work (ref •16), we have synthesized a linear PMDI trimer, linked by 1,2-diaminocyclohexane units and terminated by cyclohexylamine residues. Galvanostatic measurements were conducted. We could not achieve galvanostatic cycling data, however, because of the high solubility of this compound in the electrolyte.

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Captions of Figures

Figure 1. Series of synthesized pyromellitic diimide (PMDI) molecules. The structural formulas, schematic illustration, and space-filling representation of the superstructures of PMDI derivatives. a) Bis(cyclohexyl)pyromellitic diimide (**PMDI-Ref**), b) cyclic dimeric pyromellitic diimide ((–)-2PMDI), and c) cyclic trimeric pyromellitic diimide ((–)-3PMDI-Δ).

Figure 2. Differential pulse voltammetry (DPV) of PMDI derivatives. DPV (10 mV s⁻¹ scan rate / 25 mV pulse / 0.1 msec pulse time / 1 mV step size / 1 sec sample period / 1 mM of PMDI derivatives / DMF / 298 K / 0.1 M *n*-Bu₄NPF₆) results of three PMDI compounds. Peak separations during reduction indicate the presence of through-space electron communication of the PMDI units in the macrocycle.

Figure 3. UV–Vis–NIR spectrophotometry of reduced PMDI derivatives. (a-c) Temperature-dependent UV–Vis spectrophotometry from 20 °C (blue) to 80 °C (red) in 10 °C increments (0.5 mM of PMDI derivatives / DMF / 1 equiv. CoCp₂ per **PMDI** unit). (d-f) Concentration-dependent UV-Vis-NIR spectrophotometry (0.05–0.5 mM of PMDI derivatives / DMF / 1 equiv. CoCp₂ per **PMDI** unit), while the concentration dependent relationship for (–)-2PMDI at 1600 nm is shown in the inset of e) Compound (–)-2PMDI is observed to show a large absorption in the near-IR range, which is indicative of intramolecular interactions. Based on our experiments, (–)-3PMDI-Δ does not appear to have noticeable intramolecular interactions.

Figure 4. Galvanostatic measurements of PMDI derivatives. The galvanostatic voltage profile for the first three cycles of a) **PMDI-Ref** (red), b) (–)-**2PMDI** (green), and c) (–)-**3PMDI-** Δ (blue) at C/20. Calculated voltage profile of each compounds are described (orange) in right axis. d) The cycling performance at the current rate of C/5 and, e) rate capability test of each PMDI derivatives. f) Charge and discharge voltage profiles of (–)-**PMDI-** Δ at different current rates. In all the galvanostatic measurements, the same current rate was applied during both charge and discharge.

Figure 5. Changes of Atoms in Molecules (AIM) and bond lengths during redox process. Illustration of (a-c) **PMDI-ref**, (d-f), (–)-**2PMDI**, and (g-i), (–)-**3PMDI-** Δ at neutral- (a, d, g), mono- (b, e, h) and exhaustive (c, f, i, – two Li atoms per each PMDI in the molecule) lithium redox process. During the lithiation processes of **PMDI-Ref**, major electron density is transferred to the lithiated carbonyl group carbons, producing a more localized reduced state. In case of (–)-**2PMDI** and (–)-**3PMDI-** Δ , lithium-ion is stabilized by each carbonyl oxygens belonging to different sides of the macrocycles. Both carbonyl groups accept approximately equal amounts of electron density, providing higher stabilization of the fully lithiated state. Changes in atomic charges of carbon (black font), oxygen (red font) and selected C–O bond lengths (grey font) are calculated relative to the corresponding neutral (a, d, g – non-lithiated) structures. Atom color code–carbon (black), nitrogen (blue), oxygen (red), and lithium (magenta).



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Figure 5

TOC Image

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