



Synthesis and assessment of new cyclopenta-2,4-dienone derivatives for energy storage applications



Zheng Bang Lim^a, Kim Seng Tan^{a,b,c}, Andrey V. Lunchev^a, Hairong Li^a, Sung Ju Cho^a, Andrew C. Grimsdale^{a,b,*}, Rachid Yazami^{a,b,c}

^a Nanyang Technological University, School of Materials Science and Engineering, 50 Nanyang Avenue, Singapore 639798, Singapore

^b Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, X-Frontier Blk. 50 Nanyang Drive, Singapore 637553, Singapore

^c TUM CREATE, 1CREATE Way #10-02 CREATE Tower, Singapore 138602, Singapore

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ABSTRACT

A series of tetraphenylcyclopenta-2,4-dienones with various substituents including hydrogen, thiophene and methoxy groups were prepared to compare their suitability as materials for forming alkali metal-based (Li or Na) solvated electron solutions (SEs) for potential use as anode materials for flow Li-Air (or Na) batteries at ambient temperature condition. The materials are amorphous, not luminescent and have moderate $E_{g, opt}$ in range 1.84–1.91 eV. They also possess good thermal stability (stable above 200 °C), exhibit quasi-reversible reduction and oxidation reactions. It was also found that the type of substituent can influence the ability of the cyclopentadienones to form SEs with alkali metals, where the derivatives with hydrogen or methoxy units were found to form SEs with lithium, but the thienyl derivative did not. Parallel studies also indicated that our big π -systems were thermodynamically more favorably to solvate the electrons than small and simple aromatic or polar aprotic solvent molecules such as benzene, toluene, xylene, tetrahydrofuran, solvate acetone, etc.

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1. Introduction

There is an ongoing urgent demand for new charge storage materials and devices – including batteries, supercapacitors, and memory devices – with significantly improved performance over existing technology. In the field of rechargeable Li batteries, current research mainly focuses on solid state electrode materials. In recent years, efforts have been made to incorporate both the advantages of the LIBs' high energy density as well as the redox flow batteries' (RFB) dual refueling/recharging options. Such efforts have yielded the alkali-metals (Li or Na) and semi-solid rechargeable lithium flow cells [1–5]. Unfortunately, such cells have their disadvantages which can limit their practical applications. Alkali-metals flow cells contain metallic lithium as the solid anode material which poses a safety concern and also has to be manually replaced when depleted. Semi-solid flow batteries circulate viscous slurry suspensions from external storage tanks through the cells during operation. These suspensions comprise of non-conducting lithium-based oxide materials (LiFePO₄, LiCoO₂, etc.,) which requires a large quantity of additives to improve their

conductivity. Also, there is a possibility of solid particles agglomerating and clogging the circulatory system during operation.

One novel concept for use in secondary batteries is the use of solvated electron solutions (SES) [6–8] as liquid anodes, in which alkali metals such as lithium or sodium give up electrons which are delocalized around an acceptor such as an aromatic system. Solvated electron solutions have shown promise in a variety of applications and research fields [6–14]. An attempt was made in the 1980s to develop a liquid-based refuelable Li/Air battery using lithium solvated electron solution (LiSES) made by dissolving metallic lithium in liquid ammonia [6–8]. The advantage of using a liquid anode is the added option of replacing the spent battery anolyte besides electrical recharging which drastically reduces the “refueling” time to several minutes. However, during the discharge of such cells, liquid ammonia becomes a gas which raises a safety issue. We have recently shown that such solutions generated from lithium plus biphenyl in THF exhibit metallic behavior in that their conductivity decreases with temperature. This behavior is unlike that of conjugated polymers (pure, donor-doped or acceptor-doped) [15–18], semiconductors and solutions or liquids containing ions. For these materials, their conductivity increases with increasing temperature. Hence when SES is formed, conductivity in the solution is controlled mostly by solvated electrons and not by

* Corresponding author. Tel.: +65 6790 6728.

E-mail address: acgrimsdale@ntu.edu.sg (A.C. Grimsdale).

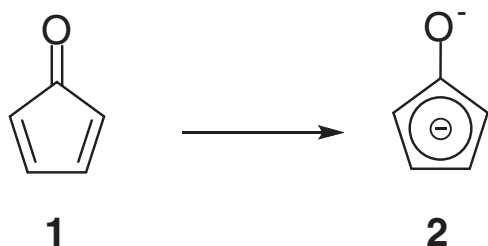


Fig. 1. Reduction of a cyclopentadienone ring to form a dianion.

ions, thus having great potential as liquid anode in LiSES/Air cell at ambient temperature condition [19,20].

However there is still considerable scope for improvement in the performance of SESs in such applications and the search continues for materials which can display better performance. One possibility is to use expanded aromatic systems such as polycyclic aromatic hydrocarbons (PAHs), which can delocalize electrons over large areas due to their extended π -systems. These have already attracted considerable interest as materials for a variety of applications, including as electrodes in lithium ion batteries, due to their unique electronic properties and propensity to form self-assembled graphitic nanostructures or columnar assemblies [21]. Another possibility is to use hetero-atoms to help stabilize the anions due to their high electronegativity. A system that appealed to us was the cyclopenta-2,4-dienone system **1** as this can accept 2 electrons to form a dianion **2** (Fig. 1) in which one negative charge would be delocalized round the aromatic cyclopentadienyl ring, while the other would be localized on the oxygen.

The anion might be further stabilized by the presence of aromatic substituents on the ring as are found in tetraphenylcyclopenta-2,4-dienones which are readily produced by condensation of 1,3-diphenylacetone and benzyl derivatives. Hence we investigated the ability of the compounds **3–5** (Fig. 2) bearing different functionality on the phenyl groups to form SESs. Then we investigated the effect of incorporating such units into a macrocycle. Conjugated macrocycles are interesting molecules that are highly challenging synthetic targets due to the inherent loss of entropy in ring formation which makes ring closure of large rings potentially unfavorable. Macrocycles thus tend to be hard to produce in high yield. Conjugated macrocycles with nanometre dimensions consist of a relatively rigid and planar, or nearly planar, π -electron-rich core and exhibit liquid crystallinity (LC) when properly decorated with flexible aliphatic substituents that additionally enhance their solubility [22,23]. Therefore, we synthesized the macrocycle **6** (Fig. 3) by reductive coupling of the dibromo-molecule **8**, as we hypothesized that there might be a difference in behavior between the outside and inside of the rings which could produce interesting electronic properties. Alkyl rings were incorporated into the design of **6** to enhance its solubility.

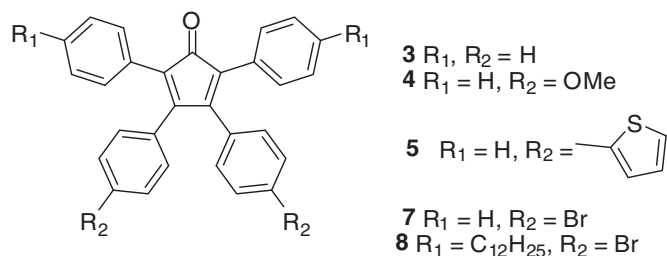


Fig. 2. Tetraphenylcyclopenta-2,4-dienones with varying functionalities attached.

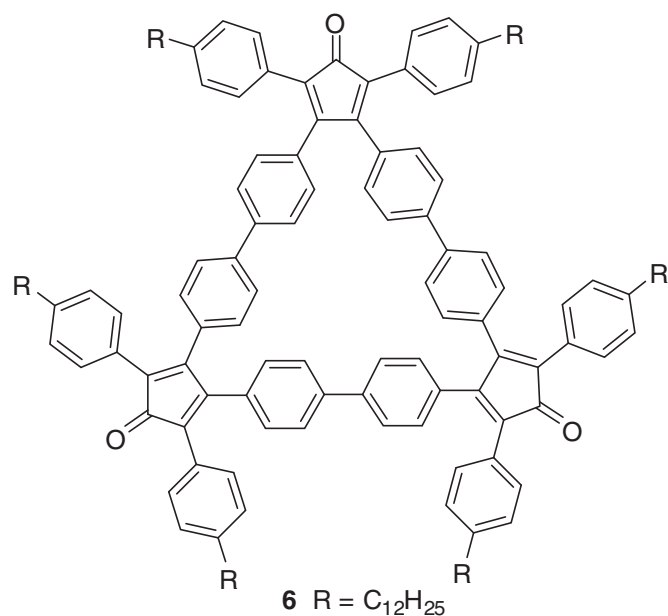


Fig. 3. Proposed macrocyclic cyclopentadienones.

2. Experimental

2.1. Synthesis procedures and analysis of molecules

Details of synthetic procedures for synthesis of the molecules shown in this paper are described in detail in the Supporting Information. The structures of synthesized molecules shown in this paper were confirmed and described in detail in the ESI by ^1H NMR, ^{13}C NMR, MALDI-TOF mass spectra, Elemental Analysis and HRMS.

2.2. Preparation of Li-SES from molecules and OCV measurements

In order to check whether compounds **3–5** can form solvated electron solutions with lithium metal, the samples were each dissolved in 0.50 MLiI in THF. The mixtures are stirred for about an hour to give dark brown solutions after which lithium foils are added to each mixture in the mole ratio of Li: PAH = 4:1.

Undissolved lithium metal fragments are observed in all three samples after overnight stirring. The undissolved lithium fragments are separated from each solution. For each sample solution, OCV was measured between a metallic lithium sheet electrode and a nickel mesh electrode, both of which are immersed in the solution. A schematic drawing of the OCV measurement cell is shown in Fig. 4. OCV measurements were also taken from a blank solution of 0.50 M LiI in THF and a Li-saturated Li-SES formed from dissolving an excess of Li metal in a solution consisting of 0.40 M Biphenyl and 0.50 M LiI in THF [8].

3. Results and discussion

3.1. Synthesis of cyclopentadienones

The unsubstituted cyclopentadienone **3** was obtained in 83% yield by the Knoevenagel condensation of commercially available benzil **9** and 1,3-diphenylacetone **10**. Reaction of **10** with commercially available dimethoxy- (**11**) and dibromobenzil (**12**) respectively under the same conditions gave the substituted dienones **4** and **7** in 78 and 88% yields Scheme 1 (Fig. 5). Suzuki coupling [24] of **7** with thiophene-2-boronic acid produced the

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