

Fluorene- and Xanthene-Based Redox Mediators for Li–O₂ Batteries: From Spiro-Linkage to Solo Moieties

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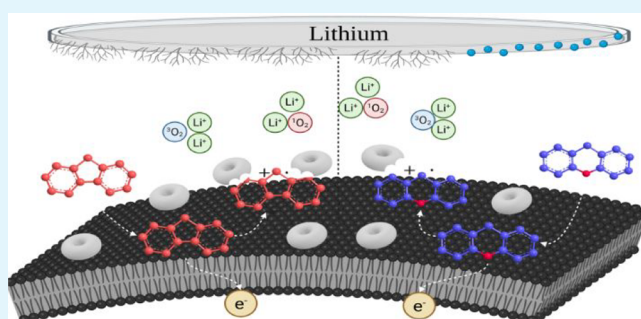
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Supporting Information

ABSTRACT: Soluble charge redox mediators (RMs) are key to improving the reversibility and efficiency of lithium–oxygen (Li–O₂) batteries by facilitating the oxidation of discharge products and reducing charge overpotentials. In this work, we report on two prospective RMs, F-OMeTAD and X-OMeTAD, based on fluorene and xanthene cores, respectively. These compounds model the molecular halves of recently introduced spiro-configured RMs, where two fluorenes, or a fluorene and a xanthene unit, are connected through a sp³ carbon atom. Electrochemical studies revealed that F-OMeTAD exhibits better electronic delocalization and faster redox kinetics with respect to X-OMeTAD, which is also oxidized at a higher potential due to a localized disruption of π -conjugation resulting from the bridging oxygen heteroatom. Spectroscopic and photochemical analyses confirmed the stability of both compounds toward reactive oxygen species such as singlet oxygen, although, compared to their spiro counterparts, some degradation was observed under forcing conditions. When tested in Li–O₂ prototype cells, both proposed RMs successfully reduced the charge overpotential and promoted the oxidation of the oxygen reduction reaction (ORR) deposits over the electrode surface. F-OMeTAD effectively reduced the charge overpotential even at low concentrations, extending battery life, whereas X-OMeTAD did not show a comparable mediation effect but instead primarily contributed to improved solid electrolyte interphase (SEI) formation on lithium metal. This comparative study, combined with DFT modeling, allowed a better understanding of the functioning mode of the parent spiro-configured RMs and offers valuable insights into structure–function relationships that can guide the future design of efficient, stable redox mediators for high-performance Li–O₂ batteries.

KEYWORDS: singlet oxygen, redox mediators, spectroelectrochemistry, charge overpotential, lithium–oxygen batteries, electrochemistry



INTRODUCTION

The growing demand for sustainable energy solutions and high-performance electric vehicles has spurred extensive research into next-generation energy storage systems. Among these, lithium–oxygen batteries are particularly attractive because of their remarkable theoretical energy density of 3550 W·h·kg^{−1}, combined with their potential for lower cost and reduced environmental footprint.^{1–3} However, their practical implementation is limited by the insulating nature of discharge products such as Li₂O₂, which leads to high overpotentials for oxidation and poor cycling stability, as well as by the detrimental impact of parasitic side reactions.^{1,4,5} The incorporation of soluble organic redox mediators (RMs) into the electrolyte is an effective strategy to address these challenges. In this approach, the dissolved RM is electrochemically oxidized at the cathode; the RM^{ox} species thus generated, subsequently diffuse and react with the discharge products, which are oxidized back to Li⁺ and O₂, while the mediator itself is brought back to its RM form.^{2,6–9} In this way, RMs function as electron carriers, promoting the oxygen

evolution reaction (OER) and thereby reducing the charging overpotential.

The effectiveness of a RM is critically dependent on its redox potential and on its ability to interact with the discharge products according to the electron-transfer kinetics described by Marcus theory.^{10,11} The recharge rate, defined by Li₂O₂ oxidation, follows a non-linear relationship resembling a bell curve, with a maximum near 3.4 V vs Li⁺/Li. Potentials above this value fall into the Marcus inverted region, which paradoxically leads to a decrease in the oxidation rate. Concurrently, potentials exceeding ~3.5 V accelerates secondary reactions, driving

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the formation of singlet oxygen ($\text{O}_2(^1\Delta_g)$), a highly reactive species that degrades the electrolyte. Therefore, the optimal performance of RMs is found in the narrow potential range that maximizes kinetics without compromising the system's chemical stability. In $\text{Li}-\text{O}_2$ batteries, the typical potential window for efficient redox mediation typically lies between 3.0 and 3.8 V vs Li^+/Li , providing a broad set of candidate mediators for performance enhancement.¹²

A wide variety of redox-active species have been investigated to fulfill this function, as summarized and discussed in relevant literature reviews.^{7,13–15} Examples include organic quinones, such as 2,5-di-*tert*-butyl-1,4-benzoquinone (DBBQ), that have been employed to catalyze discharge reactions through the formation of soluble intermediate complexes that facilitate Li_2O_2 nucleation with enhanced morphology and capacity retention.^{16,17} Vitamin K_1 has also been shown to enable high discharge capacities by modulating the Li_2O_2 formation mechanism in a solution-phase pathway.¹⁸ On the charging side, nitroxyl radicals like TEMPO are widely studied due to their ability to oxidize Li_2O_2 efficiently while maintaining chemical stability within the electrochemical window of the cell.¹⁹

Combined mediator systems integrating both discharge and charge-active species, such as DBBQ with TEMPO, have demonstrated excellent synergies, enabling decoupled growth and removal of Li_2O_2 while reducing overpotentials and limiting side reactions.²⁰ Recent efforts have explored more complex architectures to enhance mediator performance further. Hybrid molecular systems, such as TEMPO-perylene diimide conjugates, provide simultaneous redox mediation and scavenging of reactive oxygen species (ROS) such as ($\text{O}_2(^1\Delta_g)$), thus offering high-capacity retention over extended cycling.²¹ Inorganic redox mediators such as molybdenum pentachloride (MoCl_5) have also shown promise, serving as bifunctional agents that modulate Li_2O_2 morphology and enable low-overpotential charging with high coulombic efficiency.²² Additionally, halide-based systems like LiBr , when combined with single-atom Co catalysts, have enabled ultralow charging overpotentials (~ 0.69 V) and remarkable cycling performance by coupling soluble mediation with solid-state catalysis.^{23,24}

Recently, a new class of organic molecules characterized by a rigid spiro-configuration has emerged as particularly effective. This was the case for electron-donor-substituted molecules with either spiro-bifluorene or spiro[fluorene-9,9'-xanthene] (SFX) core, such as Spiro-OMeTAD and *p*-SFX-OMeTAD (Chart 1, see Supporting Information for synthesis details and molecular characterization) that exhibit outstanding performance as RMs in $\text{Li}-\text{O}_2$ batteries.^{25,26} These molecules not only effectively reduce charge overpotentials, but also function as powerful scavengers of damaging ROS, specifically $\text{O}_2(^1\Delta_g)$, leading to a significant enhancement in battery cyclability. In particular, we found that Spiro-OMeTAD can increase the cycling life by over 50% with the use of a lithium anode passivator, while SFX derivatives provided a cost-effective alternative with improved electrode surface passivation.²⁵ Although these spiro-based RMs have proven their efficacy, a deeper understanding of the intrinsic contributions of their individual structural components is still lacking. Their unique, three-dimensional cruciform configuration prevents a clear deconvolution of the electrochemical and photochemical properties of the separate fluorene and xanthene moieties.^{25,26} To address this knowledge gap, we have now systematically deconstructed the RM effect of Spiro-OMeTAD and *p*-SFX-OMeTAD by evaluating and comparing

the behavior of two analogues of their isolated fluorene and xanthene components, namely the model compounds F-OMeTAD and X-OMeTAD (Chart 1). We have explored their electrochemical and photochemical properties and investigated how their structural differences influenced redox potential, reversibility, ROS tolerance, and mediation efficiency in $\text{Li}-\text{O}_2$ battery operation. Through a combination of electrochemical testing, spectroelectrochemical characterization, DFT modeling, and long-term cycling evaluation, we aimed to establish structure–property relationships that can inform the rational design of next-generation spiro RMs for high-performance $\text{Li}-\text{O}_2$ batteries.

■ EXPERIMENTAL SECTION

Materials and Chemical Reagents

Acetonitrile (ACN, >99%, Sigma-Aldrich) was kept over 3 Å molecular sieves to preserve its anhydrous condition. Dichloroethane (DCE, >99%, Anedra) was initially dried for 12 h over activated alumina at 300 °C, filtered, and subsequently treated with calcium hydride under argon for an additional 12 h. The solvent was then distilled under reflux for 6 h and stored over 3 Å molecular sieves. Anhydrous diethylene glycol dimethyl ether (DEGDME, >99%, Gelon) was handled and stored inside an argon-filled glovebox in the presence of 3 Å molecular sieves. Dimethyl sulfoxide (DMSO, >99%, Anedra) was dried for 12 h over calcium hydride under argon, vacuum-distilled, and kept over 3 Å molecular sieves prior to use.

Tetrabutylammonium hexafluorophosphate (TBAPF₆, >99%, Fluka) was recrystallized from hot ethanol and dried under vacuum at 80 °C for 48 h. Tetrabutylammonium triflate (TBAOTf, BLDpharm, >99%) was dried under vacuum at 80 °C for 48 h. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, >99%, Sigma-Aldrich) was used as received. Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$, >98%, Sigma-Aldrich, sublimed), Spiro-OMeTAD (>99%, Sigma-Aldrich), 9,9-dimethyl-9H-fluorene (>98%, TCI), 9H-xanthene-9-one (98%, Fluorochem), and Rose Bengal (RB, >99%, Merck) were also employed without further purification. Compounds X-OMeTAD and F-OMeTAD were prepared as described in detail in the Supporting Information (Schemes S1 and S2). The identity and purity of the unprecedented F-OMeTAD compound were confirmed by NMR spectrometry and elemental analysis. The electrochemical configuration consisted of a glassy carbon disk electrode (CHI104, $\phi = 3$ mm), a lithium metal disk (Gelon, $\phi = 5$ mm, >99%), a mesoporous carbon-coated cloth (Gelon, 6×6 mm), and a glass fiber separator (Whatman, $\phi = 1.5$ μm). Platinum mesh (No. 20), platinum wire (0.2 mm diameter), and silver wire (0.5 mm diameter) served as counter and reference electrodes, respectively. Optical experiments were carried out in standard quartz cuvettes (10 $\times$ 10 mm) or reduced-pathlength cuvettes (10 $\times$ 10 $\times$ 1 mm). To prevent moisture contamination, all reagents were vacuum-sealed and stored in a silica gel desiccator. Electrolyte solutions for cell assembly were prepared inside an argon-filled glovebox using DEGDME as solvent. Water content was quantified by coulometric Karl Fischer titration (831 KF Coulometer, Metrohm). Solutions prepared in the glovebox contained 10–20 ppm of water, while those used in electrochemical and photochemical experiments outside the glovebox exhibited higher values: 50–80 ppm for DCE, 700–800 ppm for DMSO, and 400–450 ppm for ACN. No unexpected or unusually high safety hazards were encountered during experimental work.

Electrochemical Characterization Techniques

The electrochemical behavior of F-OMeTAD and X-OMeTAD was investigated using cyclic voltammetry (CV) and chronoamperometry (CA), conducted on an Autolab PGSTAT30 potentiostat equipped with N.O.V.A software (version 2.1). Measurements were performed in a conventional three-electrode glass cell fitted with a Teflon airtight

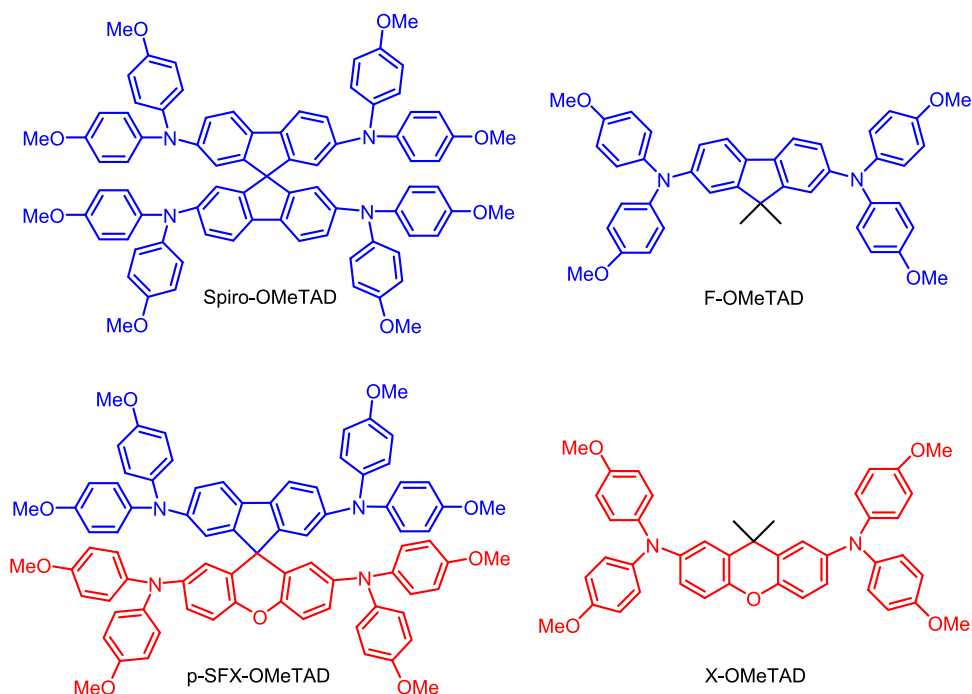


Chart 1. Fluorene- and Xanthene-Based Redox Mediators

seal. A glassy carbon disk electrode (CHI104, $\phi = 3$ mm) was employed as the working electrode. Prior to each measurement, the electrode surface was polished on a felt pad with a 0.03 μm alumina slurry, rinsed with Milli-Q water, sonicated, and immersed in the working solvent. A silver wire (Ag) was used as the quasi-reference electrode, while a platinum wire (Pt) served as the counter electrode. The Pt wire was flame-annealed using a Bunsen burner, electrochemically cleaned in 1 M H_2SO_4 , sonicated in Milli-Q water for 5 min, and conditioned in the working solvent prior to use.

To assess the response of F-OMeTAD and X-OMeTAD under inert and oxygenated conditions, a continuous flow of either argon (Ar) or oxygen (O_2) was passed through the electrochemical cell. Supporting electrolyte solutions were prepared with 0.1 M of either TBAPF₆, TBAOTf or LiTFSI and 1 mM of the compound under investigation, dissolved in DCE, DEGDME, or DMSO.

All CV data were normalized to the geometric surface area of the working electrode and corrected for ohmic drop (IR compensation). The experimental potentials were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple and subsequently converted to the Li⁺/Li scale to standardize the potential reference framework.²⁷ Unless otherwise specified, all potentials are referenced to Li⁺/Li.

Photophysical and Photochemical Analyses

All photophysical and photochemical experiments were conducted in ACN as solvent under an oxygen-saturated atmosphere. UV-Vis-NIR absorption spectra were recorded using a UV-3600i Plus spectrophotometer (Shimadzu), which operates across the UV, visible, and near-infrared regions up to 3300 nm. Fluorescence emission spectra were obtained with a FluoroMax Plus spectrofluorometer (Horiba, Spex), using solutions with an absorbance of approximately 0.05 a.u. (≈ 3 μM) to ensure linearity and avoid inner-filter effects. Both absorption and emission measurements were performed in 10 $\times$ 10 mm quartz cuvettes. To study the stability of F-OMeTAD and X-OMeTAD towards $\text{O}_2(^1\Delta_g)$, a homemade photoirradiation setup was employed, consisting of two green light-emitting diodes (LEDs, 3 W each), coupled to the spectrophotometer. RB was used as a photosensitizer due to its high quantum yield for $\text{O}_2(^1\Delta_g)$ generation in ACN ($\Phi = 0.7$). An absorbance of 0.35 (corresponding to 5.6 μM)

at 557 nm was used for RB to ensure continuous $\text{O}_2(^1\Delta_g)$ production throughout the kinetic experiments. The concentrations of F-OMeTAD and X-OMeTAD were adjusted to give an absorbance of 0.75 at 305 nm with values of concentration of 48 and 44 μM respectively. Photochemical kinetics were monitored by irradiating the solutions containing RB and the investigated compounds with green LEDs ($\lambda_{\text{max}} = 560$ nm), and spectral changes were recorded over 120 min. It is important to note that F-OMeTAD and X-OMeTAD do not absorb light above 450 nm, ensuring that they are not directly affected by LED irradiation. Likewise, RB does not absorb significantly at 305 nm. The kinetics of O_2^- resistance were evaluated by dissolving KO_2 in DMSO at a concentration of 2 mM in the presence of the RM, adjusted to an absorbance of 0.75 at 305 nm. Therefore, any spectral variations observed at these wavelengths can be attributed solely to the photochemical behavior of the compound of interest.

Computational Modelling of the Fluorene and Xanthene RMs

The two Fluorene- and Xanthene-based RMs have been investigated by methods based on Density Functional Theory (DFT),²⁸ as implemented in Gaussian09 (G09).²⁹ Unconstrained geometry optimizations were performed by using B3LYP as the exchange–correlation functional,^{30–32} and 6-31g** as the basis set.^{33,34} Molecular geometries were optimized in dichloroethane, the solvent used in the electrochemical characterization, including the solvation effects by means of the conductor-like polarizable continuum model C-PCM,^{35–37} as implemented in G09. The Electronic Density (ED) and the Molecular Electrostatic Potential (MEP) maps were computed on the optimized geometries of the two neutral RMs, and both the ED maps have been plotted by using the corresponding MEP maps colors (Figure S6). The oxidation potentials of the two RMs have been computed (see Tables S2 and S3): (a) by using the Koopmans theorem, for which $-E_{\text{HOMO}}$ provides a good estimation of the oxidation potentials; (b) as the energy difference between the optimized mono-cationic species and the neutral species and the di-cationic species and the mono-cationic species in solution. These values have then been converted by adding -4.44 eV that refers to the absolute potential of the standard hydrogen electrode (SHE/NHE) relative to the vacuum level.

Moreover, the absorption spectra have been simulated by means of Time-Dependent DFT TDDFT calculations by using B3LYP//6-31G**//CPCM(DCE solvent) level of theory (see Figures S7 and S11, for F-OMeTAD and X-OMeTAD simulated spectra, respectively). The density difference between the excited states and the ground state for the most intense transitions (higher oscillator strengths) of all the neutral and oxidized forms of both F-OMeTAD and X-OMeTAD have been plotted to show where the electron density starts and where it ends in the excitations, see Figures S8–S10 for F-OMeTAD, and Figures S12–S14 for X-OMeTAD.

Battery Characterization

The electrochemical cell was custom-designed based on the Giessen-type battery architecture, using a Teflon body and high-vacuum-compatible components to ensure uniform pressure distribution, efficient oxygen flow around the electrodes, and sufficient internal oxygen volume. The anode consisted of a polished lithium metal disk (area: 0.8 cm²; thickness: 0.45 mm), while the cathode comprised a cloth substrate coated with mesoporous carbon. The electrolyte solution was composed of 1 M LiTFSI in DEGDME, containing either F-OMeTAD or X-OMeTAD at the desired concentration. A glass fiber separator was soaked with 0.1 mL of this solution. Stainless steel mesh and disks were used as current collectors for the cathode and anode, respectively. Cell assembly was carried out inside an argon-filled glovebox (MBraun Unilab Pro SP), maintaining oxygen and moisture levels below 0.1 and 1 ppm, respectively. Electrochemical measurements were performed using a Bio-Logic multi-channel VMP potentiostat. Initially, all measurements were conducted under an argon atmosphere, followed by the introduction of a controlled oxygen stream for 60 s prior to the onset of electrochemical testing. All experiments were conducted at room temperature (20–25 °C). Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 1 MHz to 10 mHz. The open-circuit voltage (OCV) was recorded at the starting point of each experiment to establish the equilibrium potential. For both charge and discharge processes, the OCV was held for 5 min before initiating impedance measurements at the final potential, again using the aforementioned frequency range.

RESULTS AND DISCUSSION

Electrochemical Characterization

The viability of F-OMeTAD and X-OMeTAD as RMs was assessed by studying their redox processes in a conventional electrochemical cell containing a standard electrolyte for Li–O₂ batteries (Lithium bis(trifluoromethanesulfonyl)imide, LiTFSI, in anhydrous diethylene glycol dimethyl ether, DEGDME). The voltammetric responses of both molecules were first recorded in the absence of oxygen, under an inert argon atmosphere (Figure 1aI, bI). No faradaic features attributable to reduction processes are observed within the working potential window of a Li–O₂ battery. This characteristic is essential to prevent interference with O₂^{•−} generation, thereby enabling an accurate assessment of the reactivity of the prospective RMs toward this species. During the subsequent anodic sweep, distinct and reversible oxidation features are observed for both F-OMeTAD and X-OMeTAD. For F-OMeTAD, two well-defined peaks are evident at approximately 3.5 and 4.0 V. In contrast, X-OMeTAD exhibits a shoulder at 3.72 V and a clear anodic peak at 4.0 V. The reversibility of these oxidation processes is corroborated by the appearance of the corresponding cathodic responses in the reverse scan. The first peak in the electrochemical oxidation of F-OMeTAD is associated with the oxidation of one of the molecule's peripheral amines, leading to the formation of a radical cation. This radical cation is stabilized

through resonance delocalization (electronic coupling) and by Coulombic interactions between the two amino groups. The second redox process appears at a higher potential and corresponds to the oxidation of the second amino group, which produces a dication. In this species, the positive charges are localized on the amino groups connected by the fluorene bridge. This behavior is consistent with previous reports on similar molecular structures,³⁸ and it also mirrors the behavior observed for spiro-OMeTAD, thus confirming the minimal electronic interactions existing between the two molecular halves of the latter.^{25,26,38}

For X-OMeTAD, the formation of the radical cation requires a higher overpotential (3.75 V) when compared to F-OMeTAD. This is due to the incorporation of the oxygen atom into the xanthene-bridged structure which moves its oxidation potential to higher.³⁹ In contrast, the formation potential for the dication species is not as significantly affected because both charges are localized on the amino groups.^{38,40} As a consequence of this greater potential shift for the first oxidation with respect to the second, the voltammetric wave fails to clearly resolve the two processes. However, this was made possible by performing the corresponding electrochemical measurements in dichloroethane (DCE), which serves as a suitable medium for oxidative studies (see Figure S1 in the Supporting Information).⁴¹ The clearer definition of the successive redox processes thus obtained supports the identification of both the radical cation and dication species, as well as previous observations made for SFX derivatives, for which a similar behavior was reported.²⁵ Table S1 reports the experimental oxidation potential along with their diffusion coefficients.

The voltammetric responses of F-OMeTAD and X-OMeTAD were next recorded in the presence of oxygen, while replacing LiTFSI with tetrabutylammonium triflate (TBAOTf) as the electrolyte (Figure 1aII, bII). Cyclic voltammetry experiments were initiated from open circuit voltage (OCV), toward reductive potentials. In this case, a cathodic current characteristic of oxygen reduction reaction (ORR) is observed, with a partially reversible redox process between 2.5 and 2.0 V associated with the formation of O₂^{•−}. As we continue toward positive potentials, the oxidation peaks corresponding to both molecules are recovered. In both cases, no significant changes are recorded with respect to the measurement in an inert atmosphere. This behavior suggests that the presence of O₂^{•−} does not appreciably modify the redox processes of the molecules.

The same experiments under oxygen atmosphere were repeated in the presence of LiTFSI as the electrolyte (Figure 1aIII, bIII). As seen in the figures, the ORR is also observed between 2.5 and 2.0 V. However, unlike the previous experiments with TBA⁺, where Li⁺ ions were absent, the anodic sweep does not show a comparable reversibility of the O₂ redox process. This difference can be attributed to the chemical dismutation of the LiO₂ intermediate, leading to the formation of Li₂O₂, which requires higher overpotentials for its oxidation. Upon the reverse scan, a broad oxidation peak of Li₂O₂ appears close to 3.0 V.^{42,43} This broad band, which overlaps the oxidation signal of the molecules under study, generates an increase in the currents associated with their redox processes. This increase indicates the catalytic regeneration of the reduced species near the electrode surface. Since the oxidation of Li₂O₂ occurs around 3.0 V vs Li⁺/Li and the first oxidation of the F-OMeTAD and X-OMeTAD occur at higher potentials (see Table S1), we can conclude that the mediation process is

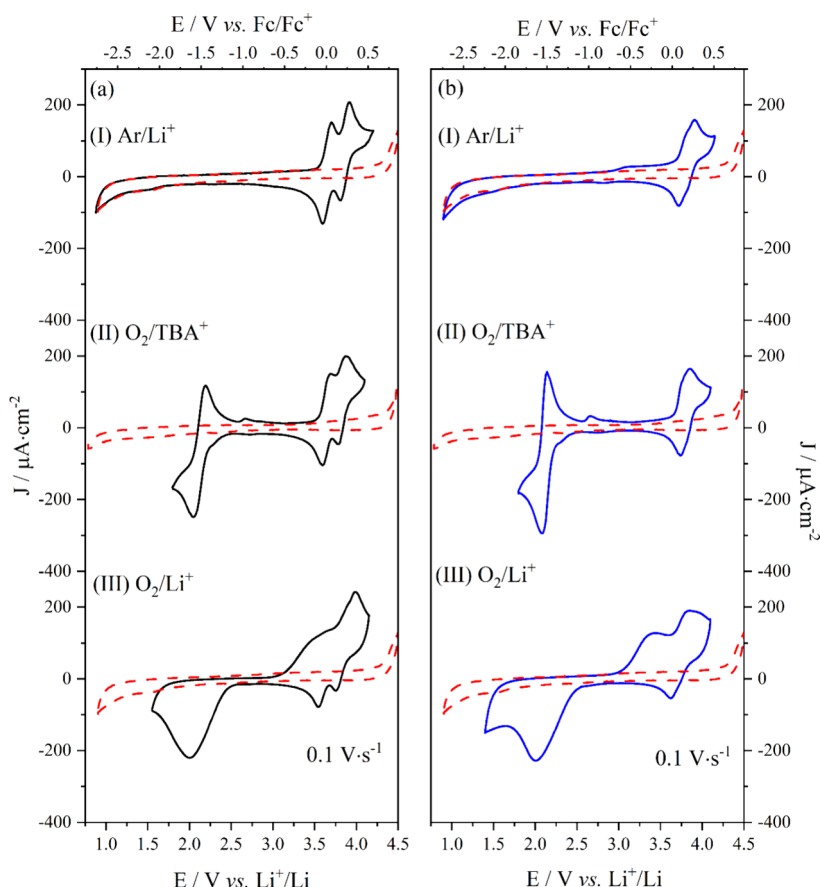


Figure 1. Cyclic voltammograms recorded on a glassy carbon electrode in two different electrolyte solutions: 0.1 M LiTFSI or 0.1 M TBAOTf in DEGDME, under either Ar or O₂ atmospheres as detailed in the main text. Red traces correspond to the background response of the supporting electrolyte. (a) 1 mM F-OMeTAD (black traces) and (b) 1 mM X-OMeTAD (blue traces), measured at a scan rate of 0.1 V·s⁻¹.

thermodynamically favorable and could help to reduce the charge overpotentials in Li–O₂ batteries. Consequently, the two compounds under study will be referred to as RMs.

To obtain a more quantitative analysis of the interaction of the ORR products with the RMs, chronoamperometry experiments were performed (Figure 2). Chronoamperometry was preferred here because the applied potential-step protocol allows a more direct separation of charge contributions than cyclic voltammetry, where the dynamic potential scan can increase the overlap of kinetically coupled processes. DMSO was used as the solvent, to leverage its high Donor Number (DN) for a more efficient solvation of anions, specifically superoxide (O₂⁻) thereby extending their lifetime in solution.^{43–46} The potentials used were established based on the mid-wave potential values derived from the CVs shown in Figure 1. First, experiments were conducted under an Ar atmosphere, by applying a potential step to generate the first radical cation of the RMs. A second experiment was then performed in the presence of O₂, applying a potentiostatic step from the OCV to the ORR potential (held for 60 s), followed by a step to the oxidation potential of the RMs for an additional 60 s. These measurements were carried out both with and without the RMs in the electrolyte. The applied electrochemical perturbation and the corresponding current–time responses obtained for each RM are shown in Figure 2aI,bI, respectively. To quantify the results, the charges were obtained by integrating the

current overtime and the relative charge contributions of each process are shown in bar chart format in Figure 2aII,bII. The charge recorded during the ORR was normalized by defining this stage as 100% of the process (See light blue bar), whereas the charge required for RM oxidation under an Ar atmosphere accounted for approximately 8% relative to the ORR (see grey bar for F-OMeTAD and blue bar for X-OMeTAD). In the absence of RMs, after holding the potential at the ORR for 60 s and then applying the oxidation potentials of F-OMeTAD and X-OMeTAD, the resulting Li₂O₂ oxidation charges were 20 and 25% (see red bar), respectively. Conversely, when F-OMeTAD and X-OMeTAD were present in the electrolyte, the total charge passed increased to 42 and 46% (black bar). After subtraction of the contributions arising from direct RM oxidation and from Li₂O₂ oxidation in the absence of mediator, the remaining additional charge, 14% for F-OMeTAD and 13% for X-OMeTAD (green bar), was assigned to the mediated oxidation process. Thus, under the selected potential-step protocol, the increase in charge at the oxidation potential of the mediators provides direct electrochemical evidence that both molecules participate in the removal of ORR products.

Stability of Redox Mediators toward Reactive Oxygen Species: Photophysical and Photochemical Analysis

The absorption and fluorescence spectra of F-OMeTAD and X-OMeTAD are shown in Figure 3a,b. Both RMs exhibit an

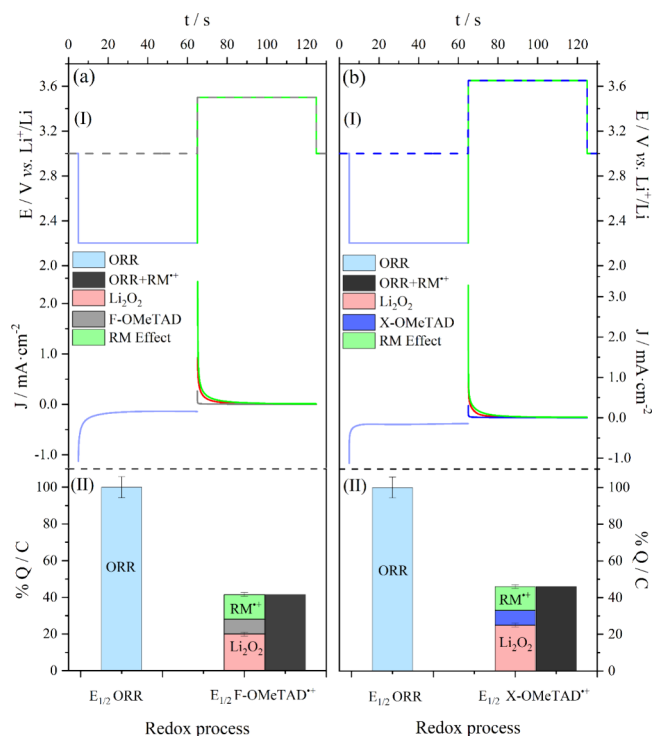


Figure 2. Quantification of the charges involved, based on ORR reaction obtained through chronoamperometry. (a) F-OMeTAD and (b) X-OMeTAD. Gray = ORR and Li₂O₂ formation; red = Li₂O₂ oxidation region; blue = Ar atmosphere; and green = ORR + oxidation of molecules under study.

absorption band at 305 nm, attributed to the $\pi \rightarrow \pi^*$ transition of the diarylamine group. Additionally, F-OMeTAD displays a second well-defined band at 382 nm, corresponding to a charge-transfer (CT) transition.^{38,40} whereas X-OMeTAD shows only a shoulder near 380 nm. This indicates that the presence of the bridging oxygen atom affects the conjugation of the system, almost completely suppressing the intensity of the CT band. Regarding fluorescence emission, F-OMeTAD shows a maximum at 423 nm, whereas X-OMeTAD emits with a maximum at 400 nm (see Figure 3a,b), demonstrating that oxygen incorporation also influences the excited state.

The highly reactive $O_2(^1\Delta_g)$ species generated in the operation of Li–O₂ batteries can degrade internal battery components, including most soluble RMs currently in use.^{47–50} This issue must be taken into account in the design of new RM candidates. Therefore, the chemical stability of F-OMeTAD and X-OMeTAD against $O_2(^1\Delta_g)$, generated using Rose Bengal (RB) as photosensitizer, was investigated in detail. RB efficiently produces $O_2(^1\Delta_g)$ upon green light (~ 515 nm) irradiation in an oxygen atmosphere.^{25,26} Moreover, its absorption spectrum does not overlap with that of the two investigated compounds (see panel (a) in Figure S2), enabling the reliable spectrophotometric quantification of RM degradation in solution. Acetonitrile (ACN) was chosen as the solvent because the appreciable lifetime of $O_2(^1\Delta_g)$ in this medium (~ 70 μ s) maximizes the exposure of the RMs to the oxidizing agent. Figure 3c shows the absorbance evolution (305 nm) of F-OMeTAD and X-OMeTAD in solutions containing RB after 120 min of exposure to $O_2(^1\Delta_g)$. A progressive decrease in the absorption band intensity of both RMs is observed, indicating

chemical degradation of the same order of magnitude (approximately 30% for X-OMeTAD and 22% for F-OMeTAD, see inset Figure 3c). Noteworthy, it was previously found that under the same experimental conditions both Spiro-OMeTAD and its SFX analogues do not undergo significant degradation as exemplified by the Spiro-OMeTAD data shown in Figure 3c.^{25,26} It becomes then clear that the orthogonal spiro junction between the molecular halves is a key factor when it comes to stability against $O_2(^1\Delta_g)$.

The orthogonal arrangement of π -systems around the spiro carbon electronically decouples the conjugated fragments and shields the otherwise reactive 9-positions of fluorene and xanthene. This geometric isolation limits oxygen accessibility and reduces intermolecular interactions that promote oxidative degradation.^{51,52} As a result, spiro-based systems exhibit markedly enhanced photochemical and electrochemical robustness toward $O_2(^1\Delta_g)$. This improved molecular stability not only preserves the structural integrity of the mediator under reactive oxygen environments but also translates into superior durability and reversibility during the redox mediation process in Li–O₂ batteries, where exposure to $O_2(^1\Delta_g)$ is a critical degradation pathway.^{25,26,53} The stability of F-OMeTAD and X-OMeTAD against $O_2(^1\Delta_g)$ was further evaluated in DEGDME solutions (see Figure S3) to better mimic the conditions that these RMs would encounter in Li–O₂ batteries. In this medium, a much lower degree of chemical degradation (approximately 5%) was observed compared with ACN, likely because the lifetime of $O_2(^1\Delta_g)$ in DEGDME is considerably shorter and insufficient to induce significant RM degradation within the experimental timescale.

Besides $O_2(^1\Delta_g)$, other reactive oxygen species are generated under the working conditions of Li–O₂ batteries. In particular, superoxide anions (O_2^-) are generated during battery discharge. To evaluate the stability of the RMs against this reactive oxygen species, kinetic experiments were conducted exposing F-OMeTAD and X-OMeTAD to KO₂ as an O_2^- source in DMSO, a solvent chosen due to its high donor number, which prolongs the lifetime of the superoxide anion in solution.^{54,55} UV–Vis spectrophotometry was well-suited to monitor the variation of RM content in solution, since KO₂ does not absorb in the spectral region of the RMs (see panels d and e in Figure S2). Thus, both compounds showed approximately 4% degradation after 120 min of exposure to O_2^- (Figure 3d). This stability is consistent with the results observed in the electrochemical experiments (Figure 1aII,bII), even considering that this medium is considerably more aggressive than the electrolyte typically used in Li–O₂ batteries.

Spectroelectrochemical Characterization of RMs

To better correlate the structural and electronic properties of F-OMeTAD and X-OMeTAD with their efficiency as RMs, the evolution of their UV–Vis–NIR absorption spectra in solution upon application of different oxidation potentials was investigated. As shown in Figure 4a,b a total of six potentials were evaluated for each molecule, represented schematically as points on their CV diagrams, corresponding to different oxidation states. In the case of F-OMeTAD (Figure 4a) for absorption spectra recorded at potentials corresponding to the formation of the radical cation (F-OMeTAD)^{•+} (red and blue lines) two characteristic spectral regions stand out. The first, between 5000 and 9000 cm^{−1} (2000–1100 nm), is assigned to an intervalence charge transfer (IVCT) band, associated with

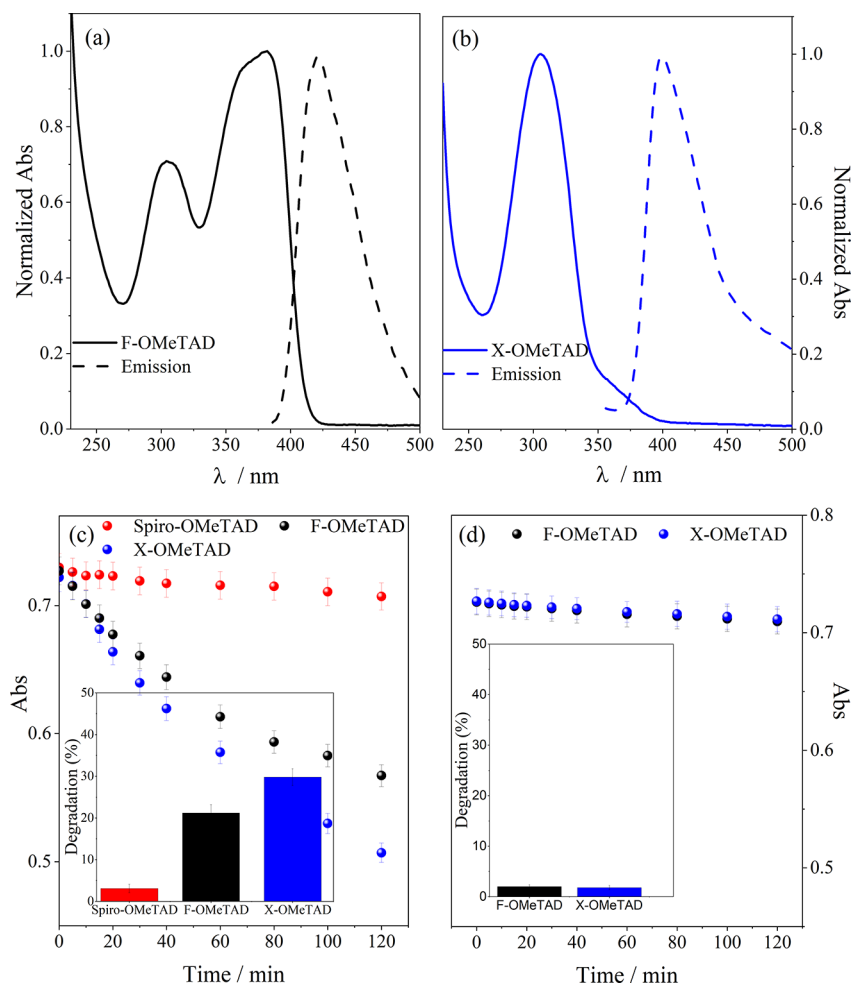


Figure 3. Normalized absorption spectra (solid lines) and fluorescence spectra (dotted lines) of F-OMeTAD (a) and X-OMeTAD (b) in ACN. (c) Kinetics profiles of the RMs during 120 min of irradiation in the presence of abs 0.35 (5.6 μM) RB in ACN. Inset: percentage of RM degradation. (d) Kinetics profiles of the RMs over 120 min in presence of 2 mM KO₂ in DMSO. Inset: percentage of RM degradation.

optically induced hole transfer from an oxidized arylamine unit to another in its neutral state, typical of D- π -D⁺ systems. The second region, between 20,000 and 26,300 cm⁻¹ (500–380 nm), corresponds to a long-range charge transfer (LRCT) band, ascribed to the process of electronic excitation from the donor to the acceptor through the π -conjugated bridge.^{38,40} Upon moving the oxidation potential to higher values (green, orange, and magenta lines), the absorbance shows a significant increase in intensity between 10,500 and 13,000 cm⁻¹ (952–769 nm). This signal is attributed to the transfer of holes from the oxidized arylamine units to the π -bridge of the fluorene. Additionally, an extra band assigned to characteristic $\pi \rightarrow \pi^*$ transitions appears in the interval between 13,000 and 16,000 cm⁻¹ (769–625 nm). Although this region has poorly defined bands due to spectral overlap, the presence of these two features confirms the formation of the (F-OMeTAD)²⁺ dication generated in the second electrochemical oxidation.^{38,40} On the other hand, when X-OMeTAD is oxidized to the corresponding radical cation, a well-defined band is observed between 7000 and 10,300 cm⁻¹ (1428–970 nm) (see the red line in Figure 4b). This band is assigned to hole transfer processes from the diarylamine units to the xanthene bridge. Upon reaching the potentials associated with the second oxidation current peak of

the X-OMeTAD, the presence of an additional band is detected at 10,650 cm⁻¹ (938 nm), attributed to $\pi \rightarrow \pi^*$ transitions characteristic of the dication. Due to the proximity of the first and second oxidation potentials, this band also partially manifests itself at the potential corresponding to the first oxidation, where the radical cation and the onset of dication formation (X-OMeTAD)²⁺ coexist (see the blue line in Figure 4b). The absence of signals attributable to IVCT and LRCT transitions relative to those observed in the (F-OMeTAD)⁺ spectrum suggests that the introduction of oxygen in the central xanthene bridge partially interrupts the electronic conjugation of the molecule, decreasing the electronic coupling between the arylamine units. This disruption limits charge delocalization through the π -conjugated system, which is reflected in the suppression of IVCT and LRCT electronic transitions in the spectrum. Such behavior is also consistent with results observed in the electrochemical analysis, where a higher oxidation potential was observed for the radical cation formation of X-OMeTAD compared to F-OMeTAD.

To further substantiate this interpretation, DFT and TD-DFT calculations were performed on both mediators, as highlighted in the Supporting Information where quantitative electronic-structure schemes for F-OMeTAD and X-OMeTAD in their

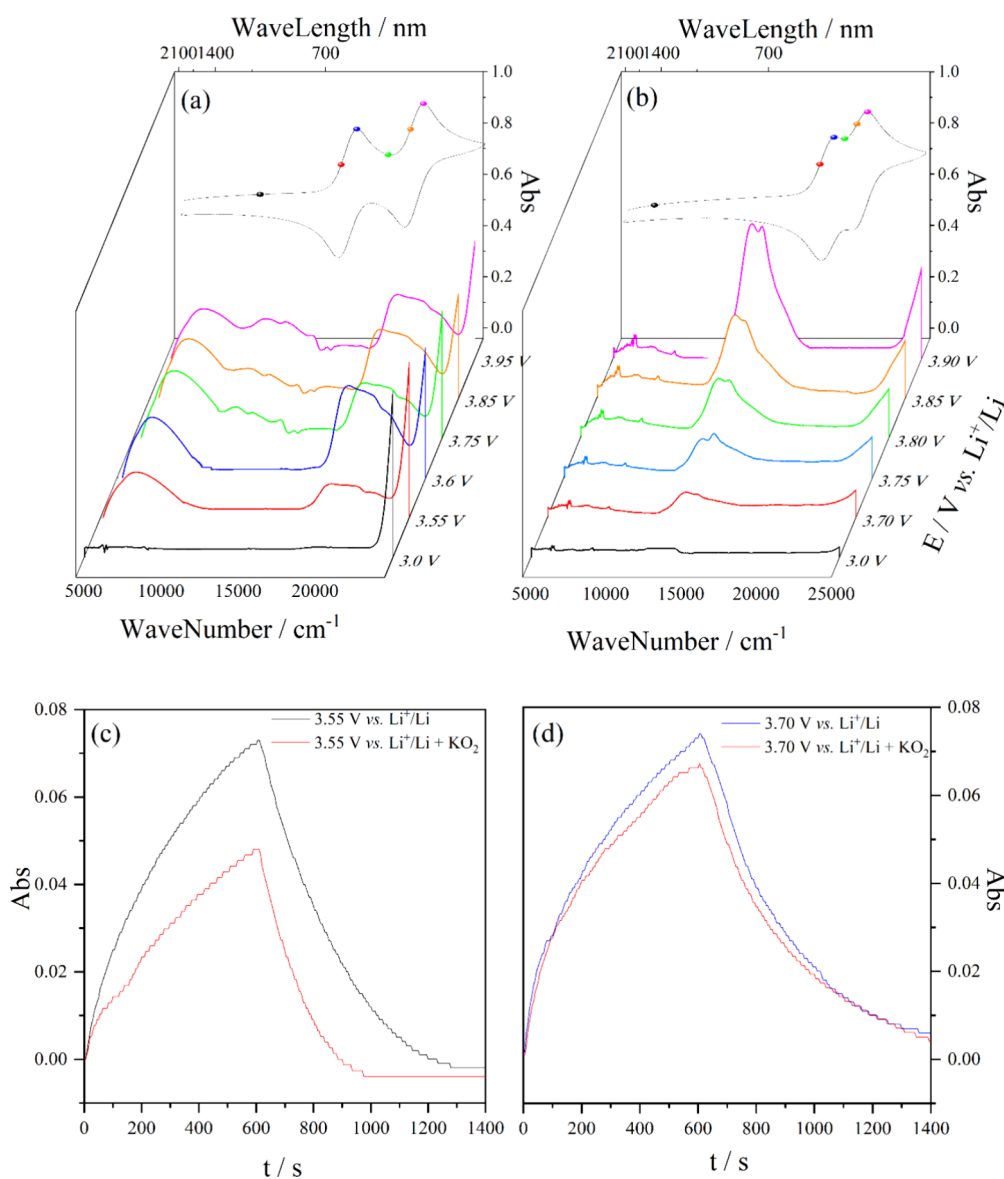


Figure 4. Spectroelectrochemistry of (a) F-OMeTAD 0.5 mM and (b) X-OMeTAD 0.5 mM, in the presence of 0.1 M TBAPF₆ in DCE; (c) Kinetics of radical cation formation of F-OMeTAD at 7000 cm⁻¹ (1450 nm) at 3.55 V and (d) X-OMeTAD at 13,750 cm⁻¹ (730 nm) 3.70 V, in the presence of 1 M LiClO₄ in DMSO. Red lines = evolution of the radical cation in the presence of 2 mM KO₂.

neutral and oxidized forms (Figures S4 and S5), simulated electronic spectra together with the corresponding excited-state/ground-state electron-density-difference plots for the most relevant transitions (Figures S6–S13), and the resulting electronic density (ED), molecular electrostatic potential (MEP), and spin-density-difference (SDD) maps (Figure S14) are reported. These calculations are consistent with the experimental evidence and indicate that in F-OMeTAD, the central π -framework preserves a more continuous electronically delocalized pathway, whereas in X-OMeTAD the oxygen-containing xanthene bridge introduces a clear discontinuity across the molecular core. In the ED maps plotted with the corresponding MEP color scale (Figure S6a,b), the more negative regions are shown in red and the more positive ones in blue; notably, F-OMeTAD exhibits a more extended and continuous red/orange distribution across the central conjugated scaffold, while in X-OMeTAD this pattern becomes less continuous around the O-containing bridge,

consistent with attenuated through-bridge electronic communication. In agreement with this picture, the SDD maps of the radical cations (Figure S6c,d) show that, although the unpaired spin remains distributed over both mediators, its delocalization across the molecular core is less effective in X-OMeTAD than in F-OMeTAD. This weaker through-bridge coupling provides a molecular basis for the suppression of the IVCT/LRCT features observed experimentally (Figure 4) and for the higher potential required to generate the X-OMeTAD radical cation (Figure 2).

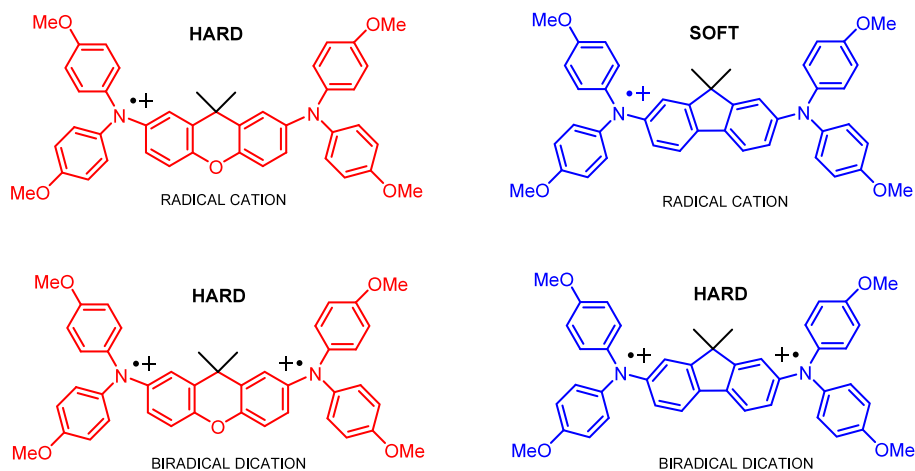
In Li–O₂ cells containing RMs, radical cations species RM^{•+} are actually responsible for the oxidation of Li₂O₂. Therefore, kinetic experiments were performed in order to evaluate the behavior of (F-OMeTAD)^{•+} and (X-OMeTAD)^{•+} both in the absence and in the presence of Li₂O₂ (Figure 4c,d). At first, the absorbance of a 0.5 mM solution of RM dissolved in DMSO in the presence of 1 M LiClO₄ was monitored at a wavelength previously identified as associated with the

formation of the corresponding radical cation species (7000 cm^{-1} (1450 nm) for F-OMeTAD, and $13,750\text{ cm}^{-1}$ (730 nm) for X-OMeTAD) while applying the medium-wave oxidation potential for 600 s, followed by 800 s at open-circuit potential (OCP). Under these conditions, the absorbance traces (blue lines in Figure 4c,d) of both RMs under study, reached a maximum of ~ 0.070 and exhibited a similar decay profile under OCP conditions, with an estimated half-life of the $\text{RM}^{\cdot+}$ species of $\sim 250\text{ s}$ at OCP. These experiments were repeated in the presence of Li_2O_2 , generated in situ by adding KO_2 (2 mM) to the DMSO solutions of RM containing LiClO_4 . After application of the medium-wave oxidation potential for 600 s the absorbance trace for F-OMeTAD (red line in Figure 4c) reached a maximum value of 0.049, with a decrease of 28% with respect to the value observed in the absence of Li_2O_2 . Moreover, the absorbance decayed faster under OCP conditions, with an estimated half-life of the $\text{RM}^{\cdot+}$ species of $\sim 100\text{ s}$ at OCP. In the case of X-OMeTAD the reduction of the observed absorbance maximum (0.065) was much more contained (6%), with a half-life of $\sim 180\text{ s}$ at OCP (Figure 4d). These data clearly indicate a faster regeneration kinetics of $(\text{F-OMeTAD})^{\cdot+}$ in the presence of Li_2O_2 compared to $(\text{X-OMeTAD})^{\cdot+}$. This difference is primarily determined by the distinct oxidation potentials of the two mediators, analyzed under the framework of the Marcus theory.¹⁰ X-OMeTAD exhibits a higher oxidation potential than F-OMeTAD. Assuming the optimal thermodynamic driving force for Li_2O_2 oxidation occurs near 3.4 V, the RM with the higher potential (X-OMeTAD) would be further into the Marcus inverted region. In this region, an excessive thermodynamic driving force paradoxically leads to a slower electron transfer rate, significantly hindering the overall regeneration kinetics of X-OMeTAD.¹⁰ Also, this difference is likely related to the nature of the π -bridge in each molecule, since in F-OMeTAD, the fluorene unit acts as a rigid and strongly conjugated connector that delocalizes the positive charge, facilitating more efficient electron transfer between the radical cation $\text{F-OMeTAD}^{\cdot+}$ and Li_2O_2 . In contrast, in X-OMeTAD, the oxygen atom in the xanthene bridge partially disrupts π -conjugation, localizing the charge on the amine groups, thereby reducing electronic

coupling and hindering charge transfer. The structural difference is reflected in the UV–Vis–NIR absorption spectra, where F-OMeTAD exhibits a more pronounced response, while X-OMeTAD lacks a characteristic intervalence charge transfer (IVCT) band. The same effect can also be rationalized within the hard and soft acids and bases (HSAB) framework, where the degree of charge delocalization in the radical cation defines its Lewis softness.^{56,57} The X-OMeTAD radical cation, with charge localized on the amine groups, behaves as a harder Lewis acid, whereas $\text{F-OMeTAD}^{\cdot+}$, whose charge is delocalized through the fluorene bridge, acts as a softer one. Additional insight is provided by the computational analysis of the doubly oxidized states. As summarized in Scheme 1, the dications of both mediators are better described as open-shell biradical dications rather than as closed-shell dications. Although the first oxidation step occurs at different potentials for F-OMeTAD and X-OMeTAD, the second oxidation takes place in a much more similar potential region for both molecules and leads to electronically analogous doubly oxidized states. Accordingly, the main distinction between the two mediators appears to be established primarily at the radical-cation level, where charge/spin delocalization and through-bridge electronic communication differ substantially (see Figure S6). Therefore, the superior mediation behavior of F-OMeTAD appears to reflect the combined influence of its redox potential and the greater delocalization and softer character of its radical cation.

Although the peroxide anion (O_2^{2-}) is formally a hard base in redox mediation processes,⁵⁸ the reaction pathway can proceed either through *inner-sphere* or *outer-sphere* electron transfer, as discussed by Bruce and co-workers.⁵⁹ Softer, more delocalized radical cations are expected to favor *outer-sphere* charge transfer, minimizing strong coordination to the Li_2O_2 surface and lowering the reorganization energy associated with electron (or hole) exchange. In this sense, the improved kinetic regeneration observed for F-OMeTAD can be rationalized by its enhanced charge delocalization and molecular softness, which promote more efficient *outer-sphere* mediation. From both the Marcus and HSAB perspectives, charge delocalization and softness thus emerge as key descriptors governing redox mediator performance in Li-O_2 batteries.

Scheme 1. Proposed Electronic Description of the Oxidized States of X-OMeTAD and F-OMeTAD, Highlighting the Different Radical-Cation Character and the Analogous Open-Shell Biradical Dication States



Characterization in Prototype Li–O₂ Batteries

Figure 5 shows CV experiments performed with F-OMeTAD and X-OMeTAD in the absence and presence of O₂ in prototype Li–O₂ batteries (see Materials and Methods section). In Ar (Figure 5a), the voltamperometry behavior of both molecules is consistent with what was observed previously, although certain variations are observed. In the case of X-OMeTAD, instead of observing two oxidation peaks as registered in the flat electrode, only one is identified. This fusion of signals is attributed to the effect of the high surface area, which makes it difficult to resolve redox processes that are close in potential values. However, the oxidation potentials fall within the same potential window observed for both DCE and DEGDME on flat electrodes. In presence of O₂, (Figure 5b), in the reduction region, between 2.7 and 2.0 V, ORR takes place, leading to the formation of discharge products. At potentials above 3.1 V, the oxidation of these products is observed, corresponding to the OER. This is reflected in the deformation of the redox peaks observed above 3.5 V for F-OMeTAD and 3.7 V for X-OMeTAD (similar behavior to that observed previously in Figure 1aIII,bIII). Figure 5c,d show the behavior of the battery in full discharge/charge conditions, in the presence and absence of the molecules under study. The concentration of F-OMeTAD was fixed at 2 mM due to its lower solubility, while X-OMeTAD was studied across a broader range of concentrations (2 and 18 mM). In the absence of the RMs, the main processes can be observed: ORR at 2.7 V and OER ~4.3 V. The high resistance of ORR non-conductive products (mainly Li₂O₂) generates a large overpotential in the charging stage, with a total difference between discharge and charge of 1.6 V. To further verify that the first charging plateau is associated with mediated oxidation of discharge products rather than with the intrinsic oxidation of the dissolved RM, a control experiment was performed in which the Li–O₂ cell was charged without a prior discharge

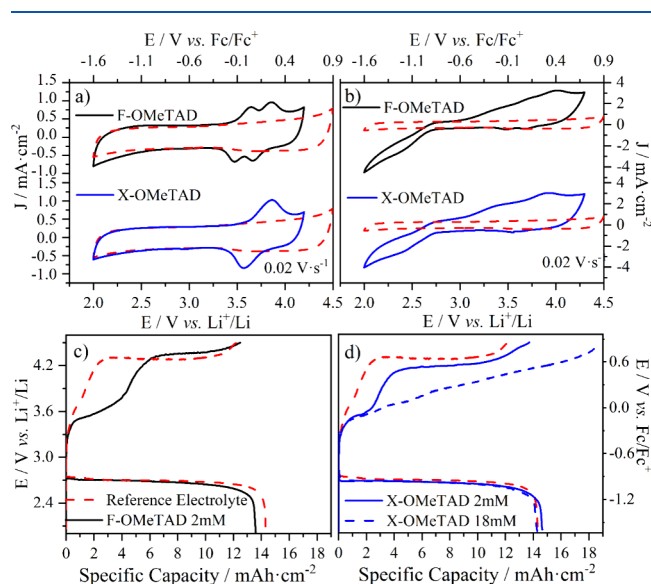


Figure 5. Cyclic voltammetry at 0.02 V·s⁻¹. 1 M LiTFSI in DEGDME (dotted red line); 2 mM F-OMeTAD (black line); 2 mM X-OMeTAD (blue line) (a) Under Ar atmosphere. (b) Under O₂. (c) Galvanostatic charge and discharge curves at 0.05 mA·cm⁻². Dotted red lines = reference. Black lines = F-OMeTAD 2mM; (d) blue line = X-OMeTAD 2 mM; dotted blue lines X-OMeTAD 18 mM.

(Figure S15). Under these conditions, the plateau at the RM potential was negligible and the cell rapidly reached the cutoff voltage, indicating that the direct oxidation of the mediator alone makes only a minor contribution to the charging profile. In contrast, when the cell was first discharged and then charged, a clear low-overpotential plateau was observed, consistent with the redox-mediated oxidation of the ORR products generated during discharge. With the incorporation of the RMs proposed, it is observed that the ORR potential and discharge capacity are unchanged with respect to the reference electrolyte. Similarly, the discharge traces appear essentially unaltered for both F-OMeTAD and X-OMeTAD. This observation is consistent with the previous electrochemical and photochemical analysis, which shows that the RMs do not interact with the reduction intermediates during the discharge process. However, during the charging process, there is a significant decrease in the overpotential value in the early stages, with the appearance of a plateau around 3.6 V. This decrease represents a gap of approximately 0.8 V compared to the battery without RM. In addition, at the start of charge, an extension of the plateau was observed from 0.048 to 4.5 mA·cm⁻², which is attributed to the molecule acting as an RM and enabling the decomposition of the discharge products. In the case of F-OMeTAD, this mediation extends to a capacity of approximately 5 mA·cm⁻², while for X-OMeTAD the mediated plateau is limited to 3 mA·cm⁻². The greater redox efficiency of the fluorene derivative compared to the xanthene derivative is evident at the same concentration. This agrees with the analysis of the spectroelectrochemistry shown in Figure 4c. Once this plateau, attributed to redox-mediated oxidation finished, the potential rises quickly until reaching values close to 4.3 V. This stage is associated with the direct oxidation of discharge products that were not completely removed by the action of the RM. Conversely, at the maximum concentration of X-OMeTAD (18mM), both the potential and the discharge capacity remain constant when compared to results obtained at lower concentrations. However, during the charge, significant overcharging was observed and a great decreasing of the coulombic efficiency. This phenomenon suggests that, at this concentration, the mediator has limited efficiency in oxidizing these products.

The discharge/charge experiments showed that the proposed molecules improved battery reversibility compared to the reference electrolyte. SEM images were performed to confirm the interaction between the RMs and discharge products and their role in helping removal from the electrode surface. In Figures 6 and S16, the images in group I show the electrode surface after the full discharge process. In these images, both for the support electrolyte and for the batteries containing F-OMeTAD and X-OMeTAD, toroidal structures are observed, typically associated with Li₂O₂, the main product of discharge in this type of system. The insert shows the particle size distribution (average of 50 structures analyzed), with a diameter of 1.2 ± 0.4 μm, with no significant differences between the different conditions evaluated. On the other hand, the images in group II show the cathodes after charging. No visible residues of the previously formed discharge products are identified in these images, suggesting that the products were efficiently removed during recharging.

The obtained plateaus at low overpotential in the full discharge/charge profiles showed that with F-OMeTAD a capacity of 5 mA·cm⁻² was achieved, while with X-OMeTAD the capacity depended on its concentration. Based on this, two

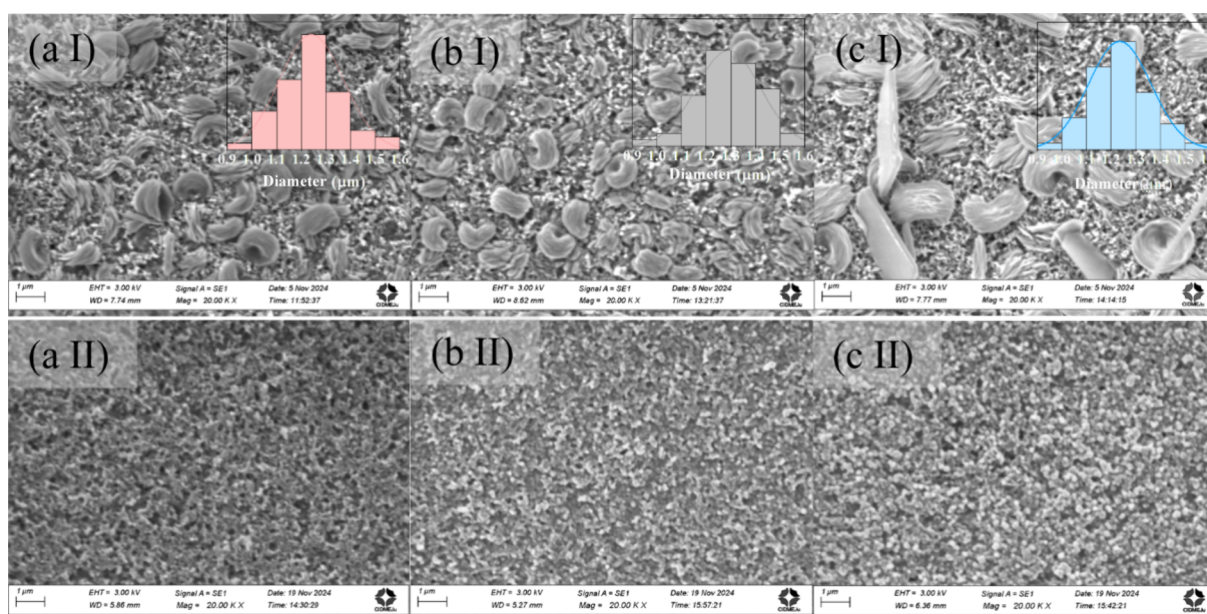


Figure 6. Scanning electron microscope images of cathodes after discharge (group I) and charging (group II) processes: (a) reference electrolyte, (b) F-OMeTAD at 2 mM, and (c) X-OMeTAD at 2 mM. Insets: particle size distribution.

conditions were defined to evaluate cyclability: capacities limited to 0.5 and 1.2 $\text{mAh}\cdot\text{cm}^{-2}$ (Figure 7). Usually, a battery failure was defined as the cycle at which the coulombic discharge efficiency dropped below 80%. The reported cycle number corresponds to the last cycle prior to reaching this threshold. Working with limited capacity to 0.5 $\text{mAh}\cdot\text{cm}^{-2}$, the reference electrolyte reached a maximum of 101 cycles. In the case of F-OMeTAD, 189 cycles were obtained, while for X-OMeTAD concentrations of 2 and 18 mM, the maximums were 105 and 93 cycles, respectively (see Figures S17 and S18). These values are considered comparable to the reference electrolyte, as they are within the typical error (less than 15%). On the other hand, experiments with the capacity limited to 1.2 $\text{mAh}\cdot\text{cm}^{-2}$, the same trend is observed, reaching a maximum of 48 cycles with the reference electrolyte. In the case of F-OMeTAD, 84 cycles were obtained, while for X-OMeTAD concentrations of 2 and 18 mM, the maximums were 59 and 42 cycles, respectively.

The results suggest that 2 mM of F-OMeTAD significantly improves the removal of discharge products, which translates into a longer battery life. This is reflected in an increase of up to 80% in the number of cycles achieved, both for the 0.5 and 1.2 $\text{mAh}\cdot\text{cm}^{-2}$ conditions. In contrast, X-OMeTAD, evaluated at two different concentrations, did not produce a substantial increase in battery life, presenting cyclability values similar to the reference electrolyte. These results are consistent with the analysis presented in the spectroelectrochemistry section, which suggested that the extended conjugation in F-OMeTAD enables a more efficient removal of discharge products, whereas its interruption in X-OMeTAD reduces the mediator's effectiveness. EIS experiments were conducted to analyze the degree of cathode passivation (estimation of the amount of non-conductive products remaining on the surface) after charge and discharge cycles, both in the presence and absence of the proposed RMs. From these spectra, the charge transfer resistance (R_{ct}) was determined following the procedure described in Figure S19. This approach allows the interfacial processes

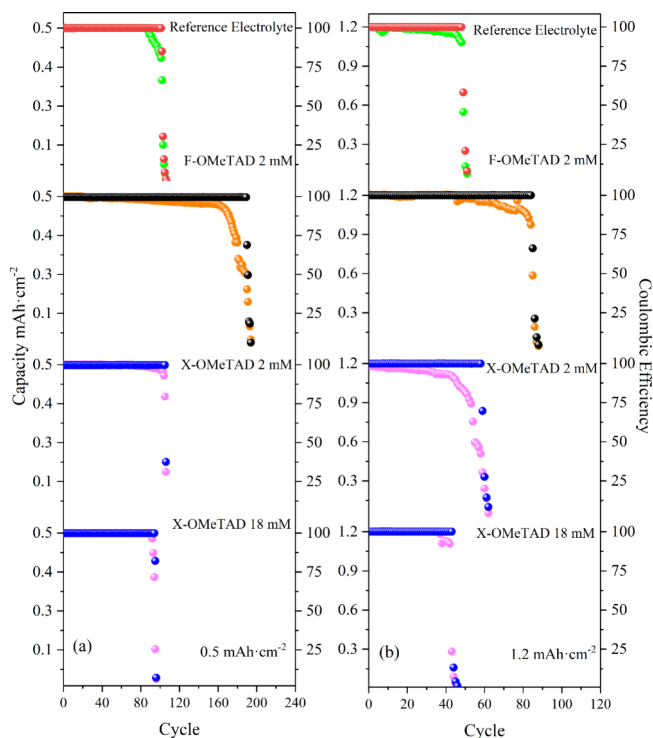


Figure 7. Cycling of prototype battery cells. Red dots = reference electrolyte; black dots = F-OMeTAD; blue dots = X-OMeTAD (a) capacity limited to 0.5 $\text{mAh}\cdot\text{cm}^{-2}$ (b) capacity limited to 1.2 $\text{mAh}\cdot\text{cm}^{-2}$. Current density of 0.05 $\text{mA}\cdot\text{cm}^{-2}$.

between the electrode and the solution to be evaluated by fitting to equivalent circuits.^{47,60} Figure 8a shows the evolution of R_{ct} at the end of each discharge and charge cycle. Cycle 0 corresponds to the initial state of the newly assembled cell. In the case of 2 mM F-OMeTAD, a significant decrease in R_{ct} is

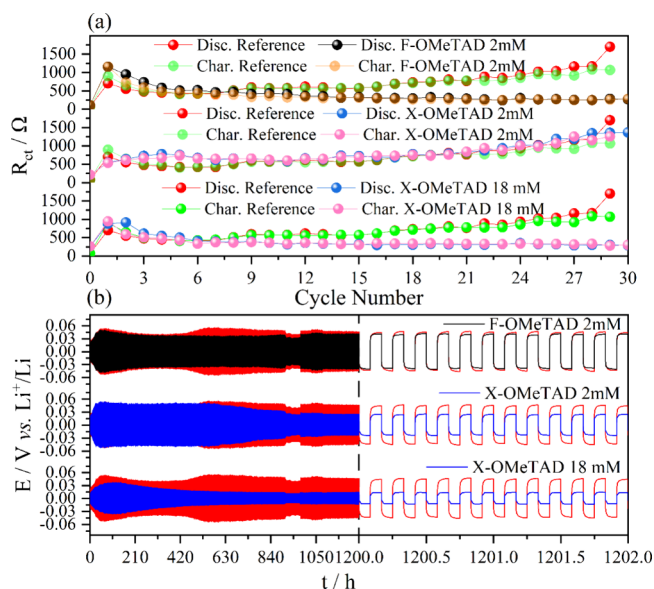


Figure 8. (a) Charge transfer resistance as a function of discharge and charge cycles in the presence and absence of the molecules under study. Red dots = reference electrolyte; black lines = F-OMeTAD; blue lines = X-OMeTAD. Capacity limited to $0.5 \text{ mAh}\cdot\text{cm}^{-2}$. Current density = $0.05 \text{ mA}\cdot\text{cm}^{-2}$. (b) Potential response of symmetrical Li/electrolyte/Li cells during 1200 h of cycling. Current density = $0.1 \text{ mA}\cdot\text{cm}^{-2}$. Red line = Reference electrolyte only. Black line = F-OMeTAD 2mM, blue line = X-OMeTAD (2 and 18 mM).

observed starting from cycle 10, indicating a better interaction at the electrode/electrolyte interface (less cathode passivation). In contrast, X-OMeTAD at the same concentration shows R_{ct} values similar to those of the reference electrolyte, suggesting lower efficiency in the removal of discharged products. These results, together with the data on cyclability under conditions of limited capacity, indicate that X-OMeTAD does not achieve the same effectiveness as F-OMeTAD as a RM. However, when the concentration of X-OMeTAD is increased to 18 mM, a progressive reduction in R_{ct} is observed, reaching values comparable to those obtained with 2 mM F-OMeTAD. This behavior suggests that the increase in concentration improves the ability of this molecule to facilitate the removal of ORR deposits. Nevertheless, cyclability tests performed at limited capacities of 0.5 and $1.2 \text{ mAh}\cdot\text{cm}^{-2}$ indicate that these increases in concentration are not sufficient to substantially improve the battery's life.

In addition, complementary tests were carried out on the lithium metal anodes in order to evaluate the possible impact of these molecules on their stability. To this end, symmetrical Li/separator/Li cells were made, in which oxidation and reduction cycles were performed. Figure 8b shows the potential response when applying a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ during 9000 oxidation-reduction cycles. Since the reactions at both electrodes (of the same dimensions) are identical ($Li^0 \rightleftharpoons Li^+ + e^-$), the cell potential remains close to 0 V, and the differences between charging and discharging mainly reflect the resistance of the electrolyte and the formation of the solid electrolyte interface (SEI). These cells allow us to evaluate whether the proposed neutral RMs react with metallic lithium, thus affecting the stability of this interface and, consequently, the electrochemical response. In experiments lasting 1200 h (equivalent

to the cycling tests performed on Li- O_2 batteries), the response of the reference electrolyte showed a potential difference between discharge and charge of 0.090 V. When F-OMeTAD was introduced, no significant changes were observed, with a slightly smaller gap of 0.081 V, suggesting little interaction with metallic lithium. In contrast, when X-OMeTAD was used at 2 mM, greater stabilization was observed, with a gap of only 0.048 V, and when its concentration was increased to 10 and 18 mM, it decreased further to 0.040 and 0.026 V, respectively. These results suggest that X-OMeTAD interacts more strongly with metallic lithium, probably favoring the formation of a more stable SEI. In contrast, F-OMeTAD does not appear to form a significant SEI, maintaining a response more similar to that of the electrolyte without mediator. This difference could have important implications for the stability and service life of Li- O_2 batteries, where an adequate SEI can protect the anode and improve the overall efficiency of the system.

Finally, Figure S20 shows the metallic lithium electrodes of the symmetrical cell, from which the characteristic marks of the surface cleaning process are visible. Figure S20b shows the lithium electrode after cycling in the reference electrolyte. A rough surface with irregular formations can be observed, attributable to uncontrolled lithium growth. Figure S20c,d, corresponding to cells with F-OMeTAD and X-OMeTAD at 2 mM respectively, show morphologies similar to those in Figure S20a. These formations are characteristic of the heterogeneous growth of metallic lithium during reduction processes (oxidation in the operating Li- O_2 battery), where deposition occurs preferentially on surface discontinuities or defects. These sites act as active nucleation centers due to their lower surface energy, favoring localized and branched lithium formation rather than homogeneous coverage. This type of growth negatively affects the stability of the anode and can promote the formation of non-uniform SEI or even internal short circuits over time. In contrast, at higher concentrations of X-OMeTAD (18 mM, Figure S20e), a clear change in morphology is observed: the surface becomes less homogeneous and rougher. Although this effect was not an initial focus of the present study and no additional surface-sensitive characterization of the lithium anode is available at this stage, the morphological changes observed for the lithium electrode in the presence of X-OMeTAD suggest an interesting anode-side effect that deserves further investigation. A more systematic correlation between molecular structure and lithium surface morphology/interfacial chemistry, however, lies beyond the scope of the present work.

These results are consistent with previous reports on SFX and Spiro-OMeTAD systems, underscoring the crucial role of the spiro configuration in governing redox mediator performance.^{25,26} The rigid orthogonal linkage efficiently decouples the fluorene and xanthene π -systems, preserving their intrinsic electrochemical and photochemical characteristics while minimizing charge delocalization and aggregation. This electronic isolation enhances stability and promotes selective interaction with Li_2O_2 , enabling more efficient mediation and reducing parasitic reactions during cycling. Comparison of the individual non-spiro analogues reveals that the OMeTAD-fluorene unit exhibits superior redox-mediation efficiency due to its extended conjugation and faster charge-transfer kinetics, whereas the xanthene counterpart shows higher solubility and a more favorable interaction with the lithium anode, likely related to its oxygen bridge and interfacial stabilization. At 2 mM concentration, F-OMeTAD nearly doubles the number of galvanostatic cycles

compared with the reference electrolyte, while X-OMeTAD displays only a slight decrease in overpotential during early cycles (Figures S17 and S18). The higher solubility of X-OMeTAD, however, enables concentrations up to 18 mM. Table S4 provides a comparative summary of the electrochemical performance of the redox mediators investigated in this work alongside selected literature-reported systems. Key parameters such as capacity, cycle reaches, current density and charge potential are included, allowing for a contextual evaluation of the advantages and limitations of F-OMeTAD and X-OMeTAD relative to other known mediators in Li–O₂ batteries. Compared with previously reported systems (see Table S4), the redox mediators proposed in this work show a favorable compromise between cycling stability, charge potential, and mediator efficiency. TEMPO- and TDPA-based mediators have demonstrated relevant improvements in Li–O₂ battery cycling performance, whereas halide-based systems such as LiBr and LiI are particularly effective in lowering the charge potential. In this context, F-OMeTAD stands out by providing a clear improvement in cycle life while maintaining a competitive charge potential under relatively low mediator loading. X-OMeTAD also shows a positive effect on the cycling response, although to a lesser extent. On the whole, the present results indicate that the proposed mediators, particularly F-OMeTAD, offer an efficient performance profile in comparison with representative literature redox mediators, especially when considering the balance between electrochemical efficiency and cycling enhancement.

CONCLUSIONS

This work presents a comparative study on the structure–function relationship of two π -conjugated molecules, F-OMeTAD and X-OMeTAD, designed for its application in Li–O₂ batteries as redox mediators. Through comprehensive electrochemical, spectroelectrochemical, and photochemical analyses, we demonstrate that molecular architecture, specifically the degree of π -conjugation, has a critical influence on redox kinetics, electronic delocalization, and interaction with discharge products.

The greater charge delocalization and resulting Lewis softness of F-OMeTAD favor outer-sphere electron transfer, reducing strong interactions with Li₂O₂ and lowering reorganization energy. In contrast, the more localized (harder) X-OMeTAD radical cation is less effective in this role. Thus, charge delocalization and molecular softness emerge as key descriptors governing redox mediator performance in Li–O₂ batteries.

This leads F-OMeTAD to exhibit superior redox reversibility and lower oxidation potential, enabling more efficient redox mediation during the charging process. Its extended π -conjugation translating into lower overpotentials and extended cycle life. Notably, F-OMeTAD enabled up to 80% improvement in cycle life under limited-capacity operation without compromising anode integrity and keeping lower R_{ct} values. On the contrary, X-OMeTAD showed lower redox efficiency even at high concentrations but induced a stabilizing effect on the lithium surface, improving interfacial stability through the formation of a better SEI on the lithium metal anode. Although these results were not entirely favorable, it provides valuable insight and motivates further investigation in forthcoming studies. While neither molecule achieved the outstanding stability of Spiro-OMeTAD, both retained appreciable chemical stability under Li–O₂ battery–relevant conditions, even in the presence

of O₂(¹ Δ_g) and superoxide species. These results confirm that the orthogonal spiro junction between the two molecular halves plays a decisive role in enhancing stability against O₂(¹ Δ_g). Overall, this study highlights the critical role of molecular design in tuning redox mediator performance, offering valuable insights for the development of advanced, stable, and efficient materials for next-generation Li–O₂ batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.6c01433>.

Synthesis procedure and chemical characterization of X-OMeTAD and additional electrochemical; photophysical and electrode morphology details; electron density (ED) and spin density difference (SDD) maps for F-OMeTAD and X-OMeTAD; and the corresponding radical cations (DOCX)

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