Visible-light Augmented Lithium Storage Capacity in a Ruthenium(II) Photosensitizer Conjugated with a dione-catechol Redox Couple

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Abstract

Controlling redox activity of judiciously appended redox units on a photo-sensitive molecular core is an effective strategy for visible light energy harvesting and storage. The first example of a photosensitizer - electron donor coordination compound in which the photoinduced electron transfer step is used for light to electrical energy conversion and storage is reported. A photo-responsive Rudiimine module conjugated with redox-active catechol groups in [Ru(II)(phenanthroline-5,6-diolate)3]4- photosensitizer can mediate photoinduced catechol to dione oxidation in the presence of a sacrificial electron acceptor or at the surface of an electrode. Under potentiostatic condition, visible light triggered current density enhancement confirmed the light harvesting ability of this photosensitizer. Upon implementation in galvanostatic charged discharge of a Li battery configuration, the storage capacity was found to be increased by 100%, under 470 nm illumination with output power of 4.0 mW/cm^2. This proof-of-concept molecular system marks an important milestone towards new generation of molecular photorechargeable materials.

Keywords: Photo-batteries • Photosynthesis • Energy Storage • Photo-induced • Electron Transfer

Introduction

Simple, direct and efficient harvesting of solar energy and storing it to perform useful work is a key technology in fighting climate change.[1] This has fuelled the quest for artificial solar energy conversion and storage mechanisms that can materialize into practical and efficient devices.[2] Recent leaps of effort towards affordable solar energy storage solutions has led to so-called photo-assisted or photo-rechargeable batteries. However, considering these as alternatives for next-generation sustainable energy harvesting and conversion systems remains a distant dream because of the non-availability of suitable materials and energy conversion mechanisms.[3] Among these, simple twoelectrode prototypes based on a photocathode remain poorly explored with only a handful of notable advances made thus far (see discussion in Supporting Information, Section - Overview of Photo-rechargeable Batteries).[4] Development of single bifunctional photoelectrode material that can perform direct light harvesting/conversion and storage of solar energy has emerged recently as probably the most innovative strategy for practical solar-rechargeable batteries.[5] Despite efforts towards efficient photocathodes, the range of materials that can perform simultaneously both the photo-harvesting and the energy storage processes are limited.

Natural photosynthesis is arguably one of the most accurate and productive light harvesting and energy conversion process known so far.[6] In photosystem (PSII), photon absorption by the primary electron donor unit (P_{680} dimer) generates an excited state that undergoes oxidative quenching by pheophytin to yield $^{+}P_{680}$. Being a powerful oxidant, $^{+}P_{680}$ is then able to oxidize a nearby tyrosine residue. The initial excited-state electron transfer step is pivotal for PSII and forms the basis of light harvesting. However, despite a variety of artificial molecular systems being developed to emulate the oxidative quenching and electron recapture mechanism, none of these targeted thus far the utilization of similar phenomenon to perform direct light to electrochemical energy conversion and storage, and in particular in a battery configuration.[7] We envisioned that coupling suitable redox functionalities on a photosensitizer would allow synergistic cooperation between the two components, and would be a relevant system to perform synchronised photo-excitation and redox processes, ultimately leading to the development of molecular photo-charging batteries.

Inspired by the operative mechanism of PSII, we propose a new class of photocathode materials that are based on metalloorganic compound where dione/catecholate redox couples are covalently conjugated on a photo-responsive Ru-diimine core within a single molecular system. Under potentiostatic conditions, visible light triggered current density enhancement confirmed the light harvesting, conversion and storage ability of this photosensitizer with 470 nm illumination at an output power of 4.0 mW/cm^2. This characteristic photo-current generation in the complex is translated into a two-fold increase in the storage capacity in a light-rechargeable Li-battery configuration.

Results and Discussion

The synthesis of [Ru(1,10-phenanthroline-5,6-dione)$_3$](Cl)$_2$ (1) was achieved by direct reaction of 1,10-phenanthroline-5,6-dione with Wilkinson’s complex [Ru(DMSO)$_4$Cl$_2$].[8] The reduced form of the photosensitizer with catechol units, i.e. [Ru(5,6-dihydroxy-1,10-phenanthroline)$_3$](Cl)$_2$ (2), was obtained by chemical reduction of 1 using dithiooxamide as reducing agent (Figure 1A, see Supporting Information for full experimental details).[9] As compared to 1, the absence of band assigned to the stretching frequency of C=O groups (1694 cm^{-1}) and the appearance of a broad (O−H) band in the FTIR spectrum of 2 confirmed the reduction of carbonyls to catechols (Figure 1B and Figure S2). NMR spectroscopy confirmed complete conversion of carbonyl to catechol groups where the increased separation between the aromatic peaks accounted for the electron density perturbation on the ligand and decrease in electronegativity of oxygen at C−O group (Figure 1C).

From a comparative 13CNMR analysis, disappearance of ketonic carbons signal further confirmed the quantitative 6-electron reduction of ketonic groups to catechols (Figure 1D). To the best of our knowledge, this is the first report of the synthesis and complete structural characterization of $[Ru(5,6\text{-dihydroxy-1,10-phenanthroline})_3](Cl)_2$ – a photosensitizer conjugated with reversible redox ligands. The photophysical and photochemical properties of the photosensitizers were studied as hexafluorophosphate salts of 1 and 2, i.e. $[Ru(1,10\text{-phenanthroline-5,6-dione})_3](PF6)_2$ (1.PF6) and $[Ru(5,6\text{-dihydroxy-1,10-phenanthroline})_3](PF6)_2$ (2.PF6). Both 1.PF6 and 2.PF6 revealed intense metal-to-ligand charge transfer (MLCT) transitions centered around 450 nm (Figure 2A).[7e, 10] Upon excitation at 420 nm in de-aerated acetonitrile (ACN), 2.PF6 displayed intense and broad photoluminescence with max located at 612 nm (Figure 2A-inset). Interestingly, 1.PF6 was completely non-photoluminescent in the entire visible region which provided a convenient handle to follow the photochemical conversion of 2.PF6 to 1.PF6.

The ability of 2.PF6 to undergo excited-state electron release and photo-oxidation to 1.PF6 was demonstrated by monitoring the photoluminescence intensity upon continuous illumination at 470 nm in the presence of electron acceptors.[11] With N-methyl-4,4- bipyridinium iodide (MQI) as electron acceptor, a greater than 90% decrease in photoluminescence intensity was observed following 3 hours of illumination (Figure S9). However, such long reaction times suggested slow reaction kinetics between the excited state of the photosensitizer and MQ+ or a favorable thermal back-electron transfer reaction between reduced analogues of MQ+ (e.g. $MQH^{\cdot}$) and the oxidized photosensitizer.[12] Aiming to improve the efficiency of the process, we hypothesized that smaller sacrificial electron acceptor cations might lead to faster reaction times.[13] When MQI was replaced by CuI, the reaction was indeed significantly accelerated, with a greater than 90% decay in photoluminescence intensity observed within 20 minutes (Figure 2B). To gain further mechanistic insight, the absorption profile of
the illuminated reaction mixture was also monitored at 1-minute intervals (Figure 2C). The MLCT absorption band gradually blueshifted and a small increase was observed around 575 nm.
These changes and the position of isosbestic points are consistent with the one-to-one photochemical oxidation of 2.PF6 to 1.PF6 (Figure 2C, inset). Other alternative mechanisms, such as the accumulation of Ru(III) species or deprotonation of 2.PF6 were refuted, as no bleach or red-shift of the MLCT band were observed.[14] Moreover, deposition of metallic copper powder during the photochemical reaction supported the formation of 1 and Cu(0) as the photo-products.

The efficiency of the light-induced electron transfer from 2* to Cu+ and MQ+ was quantified by Stern-Volmer quenching experiments (Figure 2D). A linear Stern-Volmer plot, indicative of dynamic quenching, was obtained when MQPF6 was used as a quencher (Figure 2D, inset). A quenching rate constant of 7×10^9 $M^{-1}s^{-1}$ was determined when the 6 ns excited-state lifetime of 2.PF6 was accounted for. Interestingly, Stern-Volmer plots with upward curvature, indicative of a combination of dynamic (collisiondriven) and static quenching, was obtained with $Cu(ACN)_4PF_6$ as quencher. This additional static quenching mechanism due to the formation of close-lying fluorophore-quencher pair is probably

the main contributor to the faster reaction rates observed with Cu(I) as compared to MQ+. Finally, the role of iodide was also investigated. Stern-Volmer experiments showed an increase in photoluminescence when tetrabutylammonium iodide (TBAI) was added (Figure S10 and discussion therein). This observation is most consistent with the formation of an ion-pair between 2.PF6 and iodide via hydrogen bond.[15] As a result, non-radiative deactivation through these O-H vibrators is decreased, leading to the experimentally observed photoluminescence enhancement.

Thermodynamically, the intermolecular electron transfer from 2* to Cu+ is more exergonic by ca. 0.4 eV than to MQ+ (Figures S9, S10 and associated discussion therein), consistent with the faster reaction kinetics for the photo-oxidation of 2.PF6 with CuI than with MQI. The visible light-mediated formation of Ru(III) species, which is a powerful oxidant, enables the intramolecular oxidation of the conjugated catechol to regenerate the Ru(II) center.[11a, 14a] We propose that proton loss to form the final dione

is facilitated by the hydrogen-bonded iodide ions (Figure 2E). The peculiar photophysical and photochemical properties of 1.PF6 and 2.PF6 provided background to investigate the possibility of electrochemical energy conversion and storage in these redox-units conjugated Ru photosensitizers. In cyclic voltammetry, 1.PF6 is known to display two reversible redox processes at E1/2 value of –0.75 and –1.45 V (vs Ag/Ag+) which can be attributed to one electron reduction of quinone to semiquinone followed by reduction to the fully reduced catecholate form (2.PF6), respectively.[16] Under potentiostatic conditions (at –1.50 V vs Ag/Ag+, as determined from cyclic voltammetry analysis), the solution of 1.PF6 in ACN displayed a constant (steady) current as a result of electrochemical reduction

of the dione groups on the 1.PF6 molecules to the corresponding catecholates. At this stage, when the solution was subjected to 470 nm radiation for a duration of 1 minute, a sharp increase in steady state current intensity was observed reaching maximum value in 2 seconds (Figure 3A-3B). The photocurrent remained stable and dropped to the initial value upon light removal. This gain in photocurrent accounted for photo-oxidation of the potentiostatically generated catecholate form from 1.PF6 following the similar excited-state reactivity pathway explained in the previous section. Fast response time (within 2 seconds of irradiation onset) and reversibility (tested over 20 cycles) of the photo-current generation during dark cycles consolidates the photo-redox stability and light-harvesting ability of 2.

To implement the photoredox properties of these photosensitizers in a photo-functional energy storage system, the catechol units in 2.PF6 were deprotonated and lithiated (to yield $[\mathrm{Ru(II)(phenanthroline\text{-}5,6\text{-}diolate)_3}]^{4-}$. $4\mathrm{Li}^{+}$, noted as $2.\mathrm{Li}_4$) and employed as active cathode material in a Li-cell assembly (see Supporting Information for details and Figure S11). To establish the photo-battery effect, a photo-cathode composition of 85% active material, 10% reduced graphene oxide and 5% polyvinylidene fluoride (PVDF) binder was tested in 5M LiTFSi in Tetraglyme (see Supporting Information for details). The influence of light on solid-state electrochemistry was first tested by cyclic voltammetry which displayed one prominent reversible redox process (~3.04 V) attributed to the two-electron oxidation of each of the phenanthroline-5,6-diolate units to the corresponding phenanthroline-5,6-dione (Figure 3C and Figure S13).[16b, 17] When the potential scan was performed under illumination, the current density was found to be increased considerably. Overall, a >100% increment was estimated in the swept CV area for four cycles (scan rate = 0.1 mV/s, ~ 455 nm, intensity ~ 12 mWcm^{-2}). In galvanostatic measurements under identical illumination condition (Figure 3D and S12), the characteristic light-induced current density enhancement was also observed in the form of increase in charge-discharge capacity by nearly two-folds. The extra capacity is a result of photo-induced oxidation of the $2.\mathrm{Li}_4$ (active cathode material) thereby enhancing the active material utilization. These observations directly point towards faster redox kinetics in the presence of light and corroborate the solution-based photochemistry experiments. As photocathode materials, the Ru-diimine core acts as an antenna system to absorb photons and transfers the energy to the redox-active functional groups to carry out electrochemical oxidation and release of electrons. This allows photo-assisted augmentation of Li-ion storage.

Conclusion

In summary, in this work we address the challenging question of how excited-state reactivity can be integrated with a redoxcouple in a molecular system to both harvest visible light and store the energy in a concerted event. A photochemical energy storage mechanism is proposed, wherein the catecholate units in [Ru(phenanthroline-5,6-diolate)$_3$]$^{4-}$ are oxidized via photoexcitation of the Ru(II) center in the presence of an electron acceptor and reduced back electrochemically. Conjugated coupling of a redox-couple on photo-active Ru-diimine core resulted in seamless synchronization of photo-excitation and redox chemistry to perform light to electrochemical energy conversion. As a result of this bifunctionality, the photocathodes containing [Ru(II)(phenanthroline-5,6-diolate)$_3$]$^{4-}$ .4Li$^+$ as active material achieved a two-fold capacity enhancement under visible light illumination. This proof-of-concept metallo-organic molecular system is beyond the boundaries of conventional purely inorganic and composite-based photo-cathode materials and is a major stepping-stone towards practical and efficient photoelectrochemical energy storage systems.

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References

[1] a) D. G. Nocera, Acc. Chem. Res. 2012, 45, 767-776; b) V. Balzani, A. Credi, M. Venturi, ChemSusChem 2008, 1, 26-58; c) V. Balzani, G. Bergamini, P. Ceroni, Angew. Chem. Int. Ed. 2015, 54, 11320-11337.

[2] a) Q. Zeng, Y. Lai, L. Jiang, F. Liu, X. Hao, L. Wang, M. A. Green, Adv. Energy Mater. 2020, 10, 1903930; b) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, Inorg. Chem. 2005, 44, 6802-6827; c) B. Shan, S. Vanka, T.-T. Li, L. Troian-Gautier, M. K. Brennaman, Z. Mi, T. J. Meyer, Nat. Energy 2019, 4, 290-299; d) B. Shan, M. K. Brennaman, L. Troian-Gautier, Y. Liu, A. Nayak, C. M. Klug, T.-T. Li, R. M. Bullock, T. J. Meyer, J. Am. Chem. Soc. 2019, 141, 10390-10398.

[3] D. Schmidt, M. D. Hager, U. S. Schubert, Adv. Energy Mater. 2016, 6, 1500369.

[4] a) M. Yu, W. D. McCulloch, Z. Huang, B. B. Trang, J. Lu, K. Amine, Y. Wu, J. Mater. Chem. A 2016, 4, 2766-2782; b) Z. Fang, X. Hu, D. Yu, ChemPlusChem 2020, 85, 600-612.

[5] a) S. Ahmad, C. George, D. J. Beesley, J. J. Baumberg, M. De Volder, Nano Lett. 2018, 18, 1856-1862; b) B. D. Boruah, A. Mathieson, B. Wen, S. Feldmann, W. M. Dose, M. De Volder, Energ. Environ. Sci. 2020, 13, 2414-2421; c) B. D. Boruah, B. Wen, M. De Volder, Nano Lett. 2021, 21, 3527-3532; d) B. Deka Boruah, A. Mathieson, S. K. Park, X. Zhang, B. Wen, L. Tan, A. Boies, M. De Volder, Adv. Energy Mater. 2021, 11, 2100115.

[6] C. Tommos, G. T. Babcock, Acc. Chem. Res. 1998, 31, 18-25.

[7] a) T. J. Meyer, Acc. Chem. Res. 1989, 22, 163-170; b) R. L. House, N. Y. M. Iha, R. L. Coppo, L. Alibabaei, B. D. Sherman, P. Kang, M. K. Brennaman, P. G. Hoertz, T. J. Meyer, J. Photoch. Photobio. C 2015, 25, 32-45; c) S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll, A. Llobet, Chem. Soc. Rev. 2014, 43, 7501-7519; d) M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, Chem. Rev. 2014, 114, 11863-12001; e) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani in Photochemistry and Photophysics of Coordination Compounds: Ruthenium, Eds.: V. Balzani, S. Campagna, Springer Berlin Heidelberg, Berlin, Heidelberg, 2007, pp. 117-214; f) A. Paolella, A. Vijh, A. Guerfi, K. Zaghib, C. Faure, J. Electrochem. Soc. 2020, 167, 120545.

[8] A. E. Wendlandt, S. S. Stahl, J. Am. Chem. Soc. 2014, 136, 11910-11913.

[9] W. Paw, R. Eisenberg, Inorg. Chem. 1997, 36, 2287-2293.

[10] a) N. Sutin, J. Photochem. 1979, 10, 19-40; b) K. Kalyanasundaram, Coord. Chem. Rev. 1982, 46, 159-244; c) B. Elias, A. Kirsch-De Mesmaeker, Coord. Chem. Rev. 2006, 250, 1627-1641; d) P. Dongare, B. D. B. Myron, L. Wang, D. W. Thompson, T. J. Meyer, Coord. Chem. Rev. 2017, 345, 86-107; e) L. Troian-Gautier, C. Moucheron, Molecules 2014, 19, 5028-5087.

[11] a) C. J. Gagliardi, B. C. Westlake, C. A. Kent, J. J. Paul, J. M. Papanikolas, T. J. Meyer, Coord. Chem. Rev. 2010, 254, 2459-2471; b) O. S. Wenger, Coord. Chem. Rev. 2015, 282-283, 150-158; c) K. M. Lancaster, J. B. Gerken, A. C. Durrell, J. H. Palmer, H. B. Gray, Coord. Chem. Rev. 2010, 254, 1803-1811.

[12] A. Pannwitz, O. S. Wenger, Phys. Chem. Chem. Phys. 2016, 18, 11374-11382.

[13] M. A. Hoselton, C. T. Lin, H. A. Schwarz, N. Sutin, J. Am. Chem. Soc. 1978, 100, 2383-2388.

[14] a) P. J. Giordano, C. R. Bock, M. S. Wrighton, J. Am. Chem. Soc. 1978, 100, 6960-6965; b) K. Martinez, K. Benson, J. Paul, R. H. Schmehl, Polyhedron 2021, 207, 115376; c) K. R. Benson, J. Stash, K. L. Moffa, R. H. Schmehl, T. J. Dudley, J. J. Paul, Polyhedron 2021, 205, 115300.

[15] a) L. Troian-Gautier, M. D. Turlington, S. A. M. Wehlin, A. B. Maurer, M. D. Brady, W. B. Swords, G. J. Meyer, Chem. Rev. 2019, 119, 4628- 4683; b) L. Troian-Gautier, W. B. Swords, G. J. Meyer, Acc. Chem. Res. 2019, 52, 170-179; c) M. D. Turlington, L. Troian-Gautier, R. N. Sampaio, E. E. Beauvilliers, G. J. Meyer, Inorg. Chem. 2018, 57, 5624-5631; d) L. Troian-Gautier, E. E. Beauvilliers, W. B. Swords, G. J. Meyer, J. Am. Chem. Soc. 2016, 138, 16815-16826.

[16] a) A. E. Lakraychi, S. De Kreijger, D. Gupta, B. Elias, A. Vlad, ChemSusChem 2020, 13, 2225-2231; b) C. A. Goss, H. D. Abruna, Inorg. Chem. 1985, 24, 4263-4267.

[17] G. Hilt, T. Jarbawi, W. R. Heineman, E. Steckhan, Chem-Eur. J. 1997, 3, 79-88.

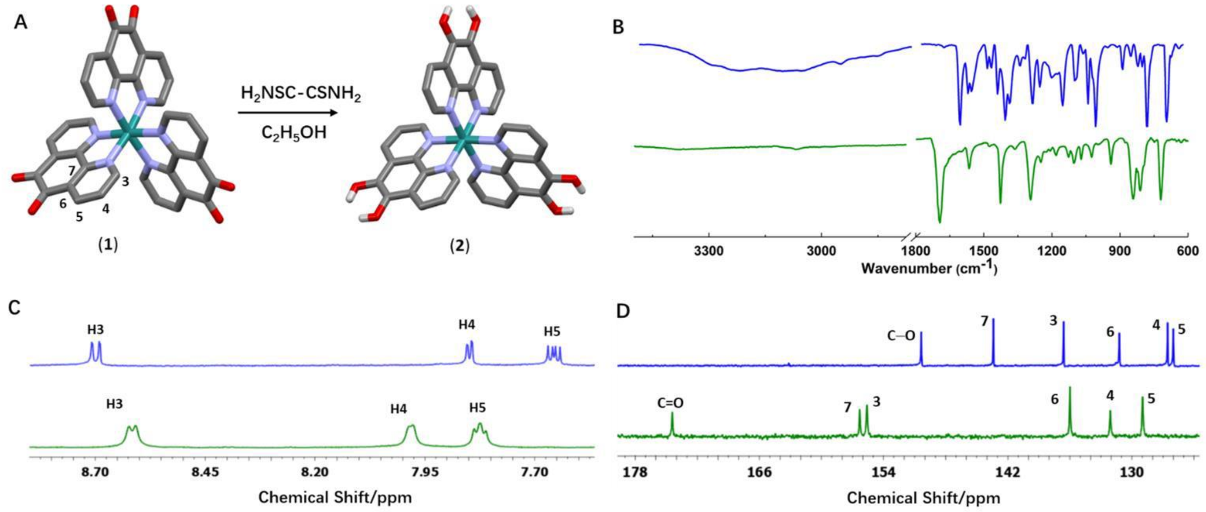

Figure 1: (A) Synthesis scheme for the reduction of 1 to 2. Overlaid FTIR spectra (B), partial ^{1}H NMR spectra in DMSO-d_6 (C) and partial ^{13}C NMR spectra in DMSOd_6 (D) of 1 (green) and 2 (blue).

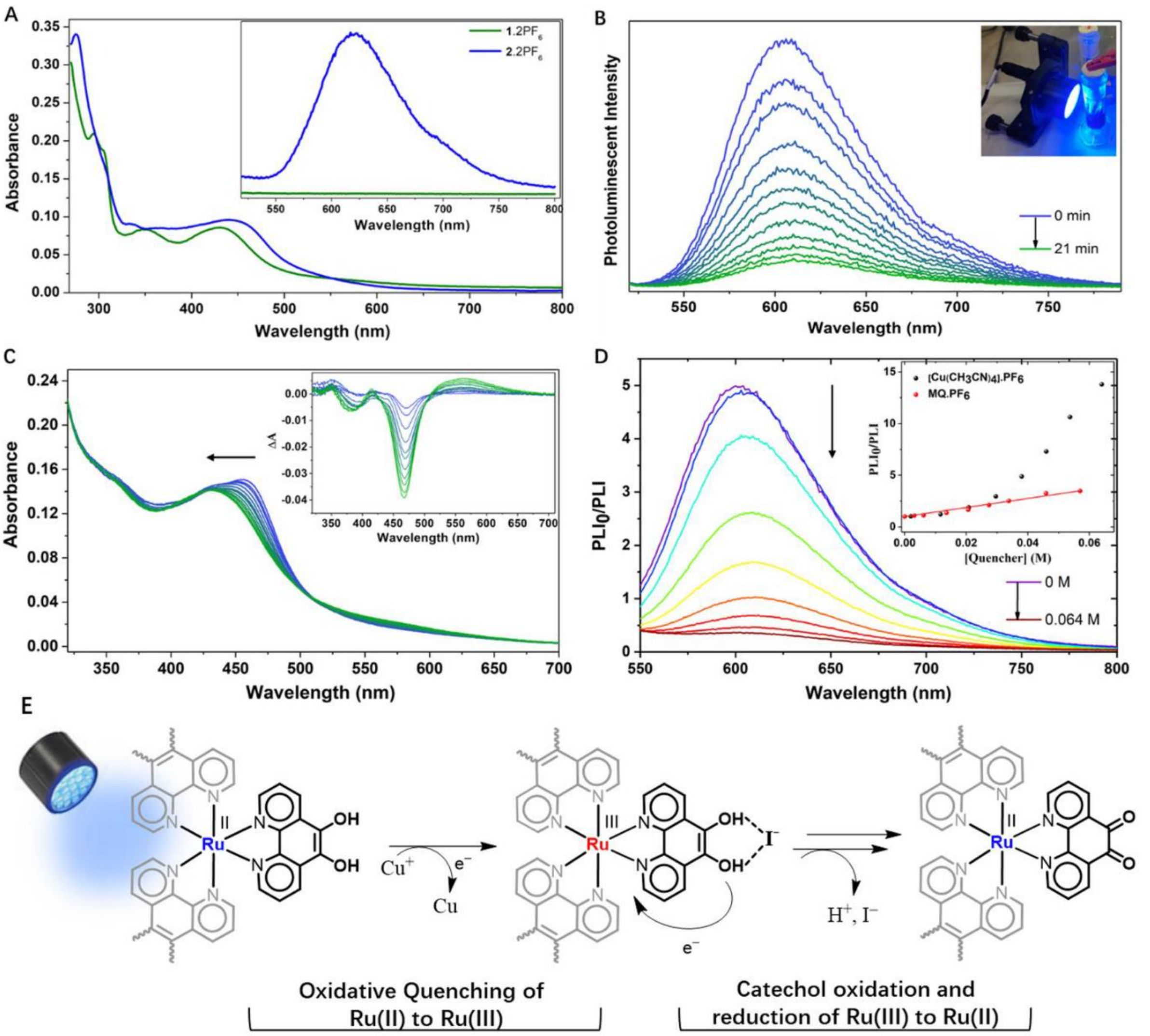

Figure 2: A) Absorption and photoluminescence (inset) (excitation wavelength = 420 nm) spectra of 1.PF$_6$ and 2.PF$_6$ in ACN. Photoluminescence intensity (PLI) (B) and absorption (C) changes (C) of 2.PF$_6$ (200 µM) in the presence of 12 mM CuI in ACN upon illumination at 470 nm (intensity: 4.0 mW/cm^2; total output power: 253 mW). The inset of (C) shows the difference absorption spectra. D) Photoluminescence quenching of 2.PF6 (200 µM) with increasing concentration of [Cu(CH3CN)$_4$]PF$_6$. The inset shows the Stern-Volmer plot ([Cu(CH3CN)$_4$]PF$_6$: black circles; MQPF$_6$: red circles). E) Proposed mechanism for the photochemical oxidation of 2.PF$_6$ to 1.PF$_6$.

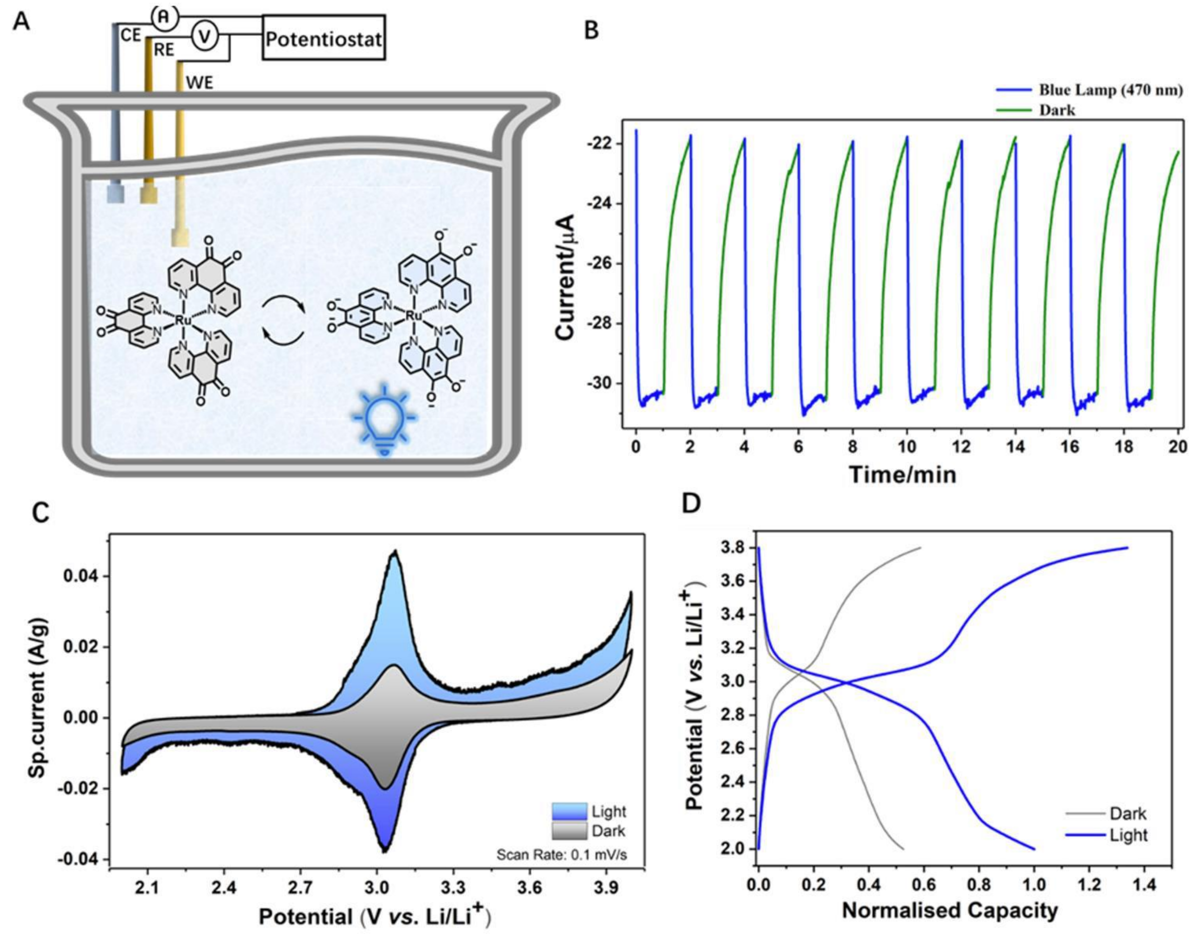

Figure 3: A) Schematic representation of potentiostatic photo-oxidation setup (concentration of 1.PF6: 1 mM; WE: Glassy carbon, CE: Pt wire, RE: Ag/Ag$^+$, electrolyte: 0.1M Tetrabutylammonium perchlorate in ACN). B) Photocurrent response to on/off irradiation conditions ($\lambda = 470$ nm, intensity ~ 4.0 mW cm^{-2}). C) Solid state cyclic voltametric response (at 0.1 mV/s) and D) galvanostatic charge-discharge profiles of 2.Li$_4$ (D) at 5 mA g^{-1} of the photo-batteries under dark and illumination (λ ~ 455 nm, intensity ~ 12 mW cm^{-2}) conditions, where capacities are normalized by absolute discharged capacity obtained under light.