Design and Synthesis of Novel Bodipy-Ruthenium(II) Dyads for Light-Driven Oxidation Reactions

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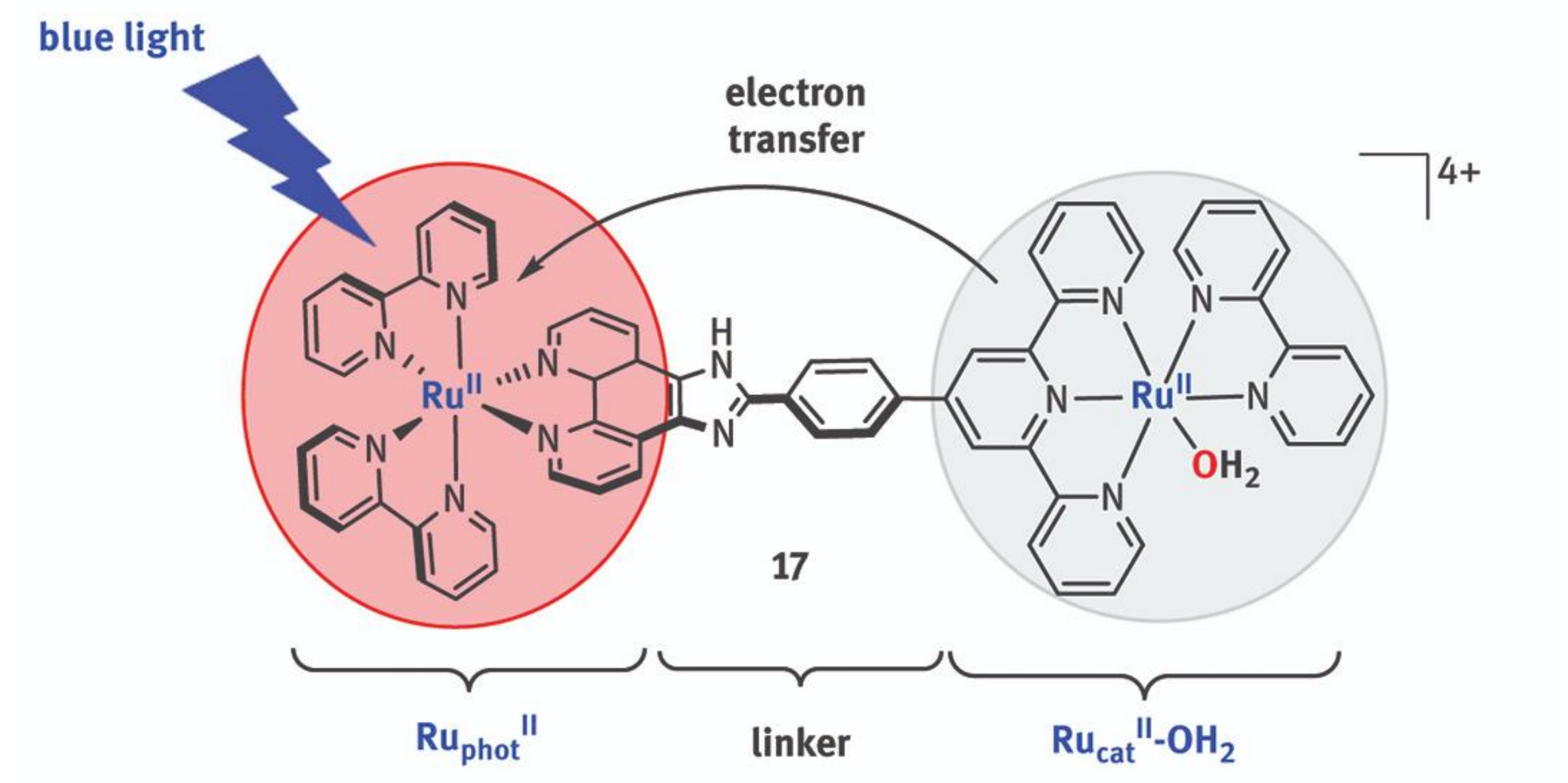
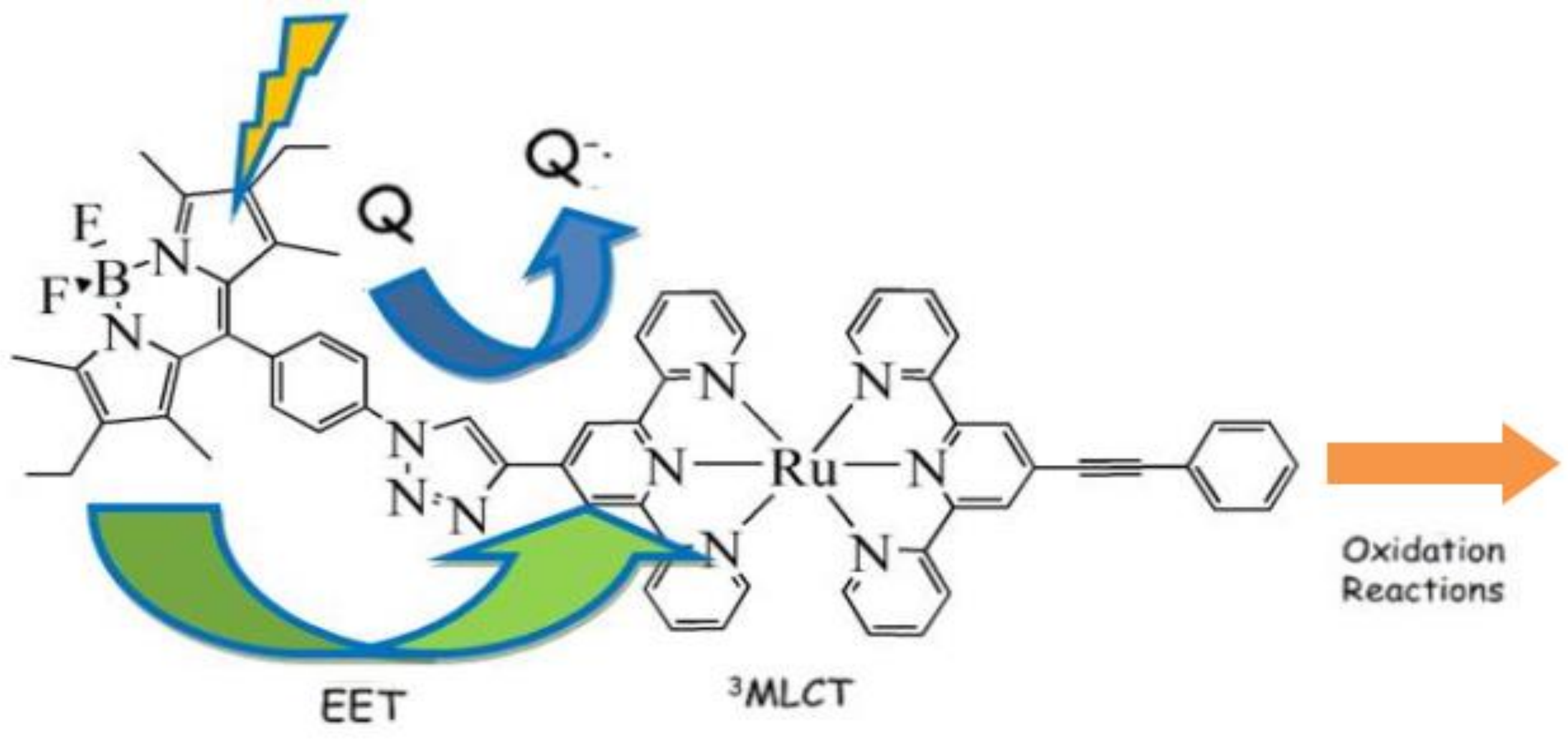
Introduction

Important challenges for the 21st century include topics ranging from energy and artificial intelligence to health [1]. Within the energy arena, solar energy is the only available resource which meets the requirements of being abundant, cheap and clean. However, the main limitations are its intermittent nature and unbalanced availability around the globe. Accordingly, as an example of which is shown below, the design of molecular dyads combining a light-harvesting unit with an electroactive centre is highly demanded in the field of artificial photosynthesis.

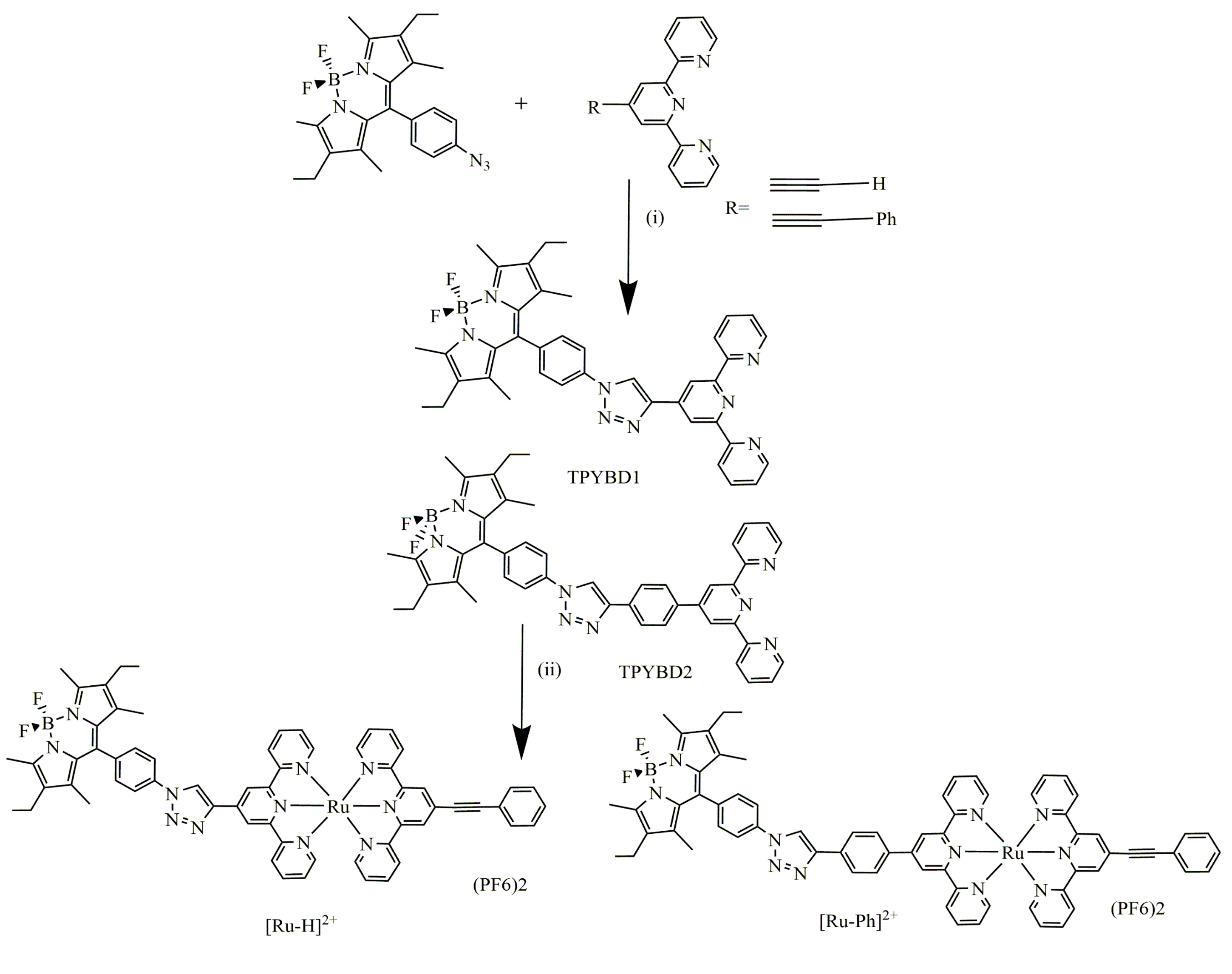


For a widespread use of solar energy, there is the need for a cost-effective solution for its storage. The combination of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (Bodipy) as a photosensitizer having exceptional optical properties, photostability, ease of preparation and purification and a ruthenium complex as a water oxidation catalyst (WOC) is promising to exploit highly efficient molecular artificial photosynthetic systems [2]. Hence, during this study, novel Bodipy-ruthenium(II) tris-bipyridyl dyads have been prepared, purified, and isolated. Both subunits are bridged by a triazole linker to avoid coupling between the Bodipy and the ruthenium complex. Schematic representation of the targeted molecule is shown below.



New terpyridyl Ligand Synthesis

The synthetic strategy involved the use of a simple ‘click’ CuAAC reaction to link a Bodipy subunit with an organometallic ruthenium(III) terpyridine complex. The linking triazole bridge is used to minimize electronic coupling between the two subunits. In addition, ruthenium complexes were prepared in good yields using a common alcohol-based reflux with a PF$_6$ stabilizing anion. These complexes were characterized using NMR, UV-Vis, MS and CV analysis.

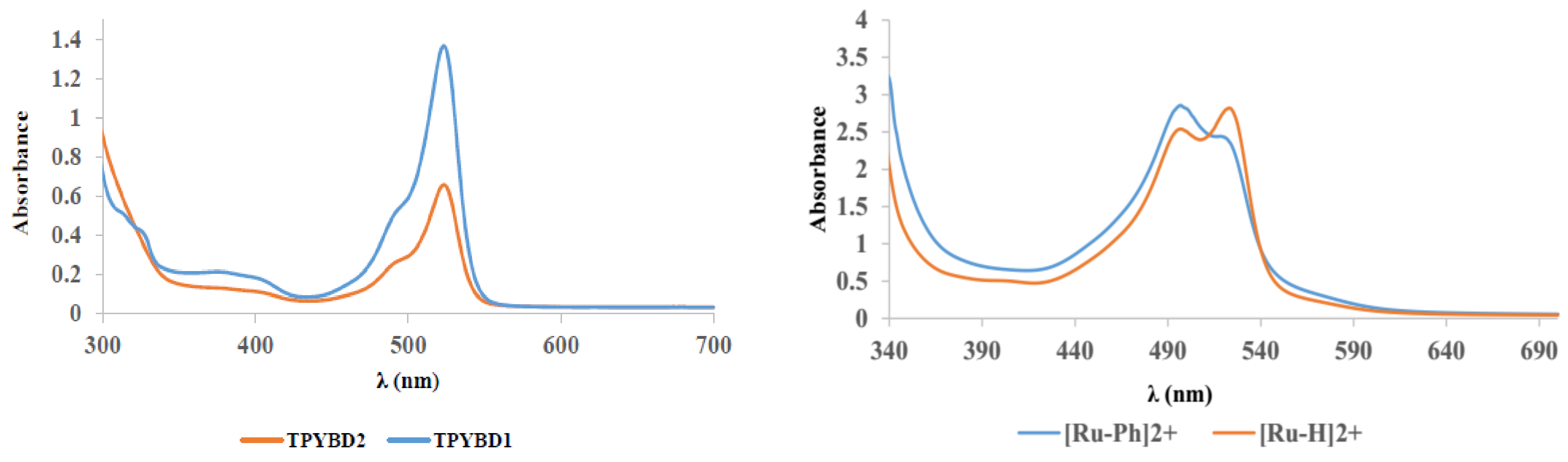


Reagents and conditions: (i) CuSO$_4$, sodium ascorbate, CH$_3$CN/H$_2$O, 40 ºC, 18 h; (ii) EtOH, reflux 18 h, KPF6(aq).

Results

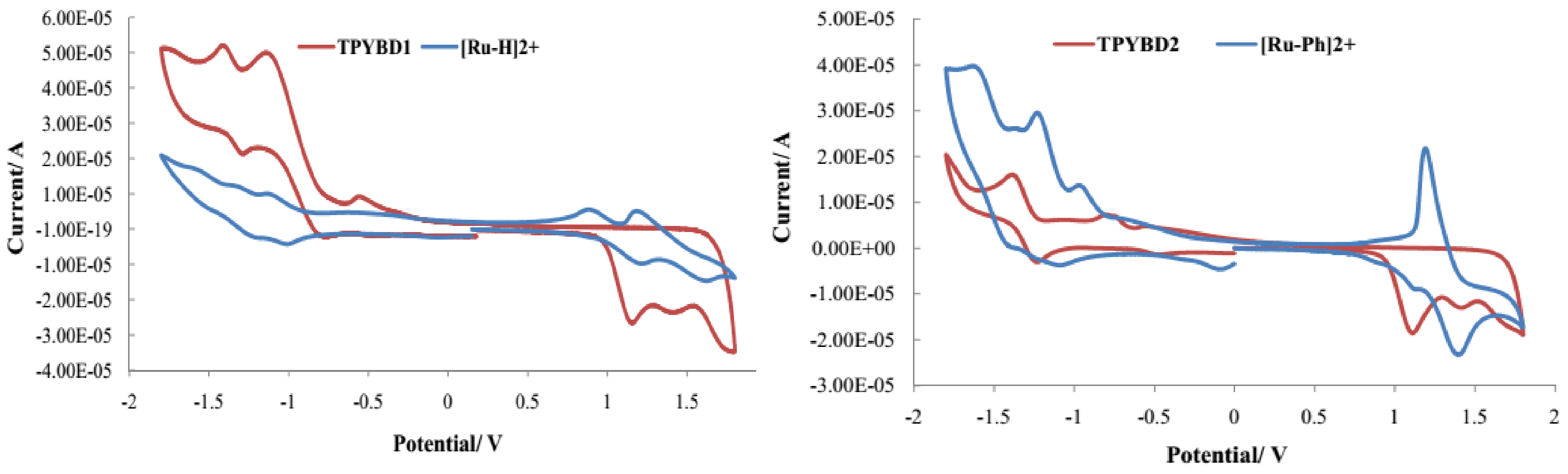
All ligands and complexes were isolated by column chromatography and recrystallization from suitable solvents. Their molecular structures were assigned by using ^{1}HNMR spectroscopy and elemental analysis.

The UV/visible absorption bands of the free ligand and dyad complexes were collected in CH$_3$CN.



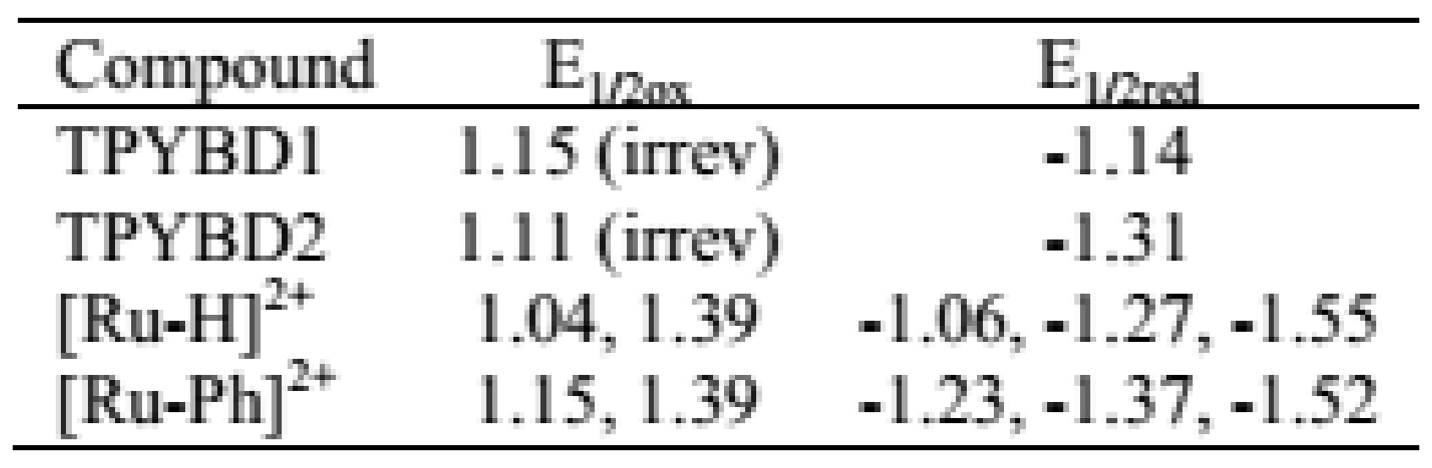
UV-vis spectra of TPYBD1 and TPYBD2 (left) and Ru-complexes (right)

The electronic absorption spectra for TPYBD1 and TPYBD2 are dominated by a sharp band centred at 523 nm which is assigned to the lowest-energy spin-allowed π–π* transitions involving the Bodipy moiety. For [Ru-H]$^{2+}$ and [Ru-Ph]$^{2+}$ dyads, the presence of the metal centre transition is seen by the appearance of bands between 450 and 500 nm. These new bands correspond to the MLCT transitions between the Ru(II) centre and the corresponding tpy ligand.



Redox properties of TPYBD1 and TPYBD2 and the corresponding Ru(II) dyads

Electrochemical experiments were carried out by cyclic voltammetry in dry CH$_3$CN containing 0.1 M TBAH as a supporting electrolyte. The recorded redox potentials for the two ligands and their Ru dyads versus SSCE are presented in Table 1.



Compound	E$_{1/2ox}$	E$_{1/2red}$
TPYBD1	1.15 (irrev)	-1.14
TPYBD2	1.11 (irrev)	-1.31
[Ru-H]$^{2+}$	1.04, 1.39	-1.06, -1.27, -1.55
[Ru-Ph]$^{2+}$	1.15, 1.39	-1.23, -1.37, -1.52

Table 1.

The results confirm that the Ru and BD subunits are isolated and only minor, if any, electronic communication takes place through the bridge in the ground state .

Conclusions

- We have shown that Bodipy subunits can be readily incorporated within Ru(bpy)-like sensitizers for photochemical oxidation reactions.
- The azidophenyl-Bodipy proved to be a promising starting material for incorporating Bodipy subunits within donor–acceptor dyads by formation of the triazole bridge.
- In continuation of this study the capacity to behave as photosensitizer in visible light-driven water oxidation catalysis will be tested to ensure high activity and recyclability of the photocatalysts.
- Also, we expect that the present systems can be modified with anchoring groups via the Bodipy or ruthenium complex site for their attachment to semiconducting metal oxides.

References

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[2] Farràs, P.; C. Benniston, A.; Bodipy-ruthenium(II) tris-bipyridyl dyads for homogeneous photochemical oxidations. **2014**, 55, 7011.

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