

Artificial Photosynthesis a Brief Literature Review

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ABSTRACT: Dye Sensitized Photoelectrochemical Cells (DS-PEC) are a promising development for artificial photosynthesis. Currently however photoinduced conversion of water to hydrogen and oxygen remains limited by desorption, alternative processes and charge accumulation. This brief literature review will primarily focus on transition metal complex chromophore catalyst dyads, for water oxidation catalysis (WOC) as well as hydrogen evolution catalysis (HEC). Assessing the dyads individual charge separation, electron transfer and catalytic photoelectrochemical properties. Comparing and contrasting the techniques employed by Dye Sensitized Photoelectrochemical Cells (DS-PEC) dyads in addition to collectively evaluating their current limiting factors and suggesting potential developments for further work.

1. INTRODUCTIONS

1.1 Dye-Sensitized Photoelectrochemical Cell

Solar panels generate electricity, but fuels account for most energy consumption, photocatalytic fuel production should thus expand renewable energies scope.¹ In 1972 Fujishima and Honda first verified UV water splitting, eventually evolving into dye-sensitized photoelectrochemical cells, illustrated in figure 1, a form of artificial photosynthesis.²

Artificial photosynthesis is a promising development for photoconversion of water into hydrogen a fuel with one of the highest energy densities.

1.2 Photosynthesis & Artificial Photosynthesis

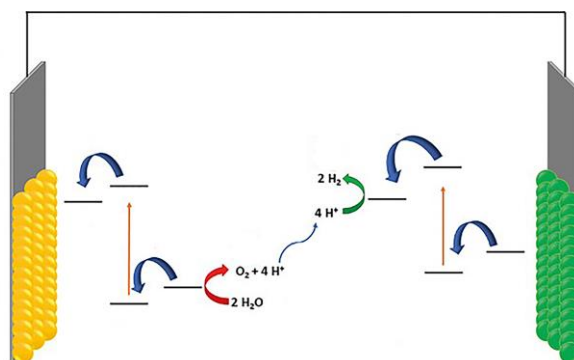


Figure 1. Simplified diagram showing the energy conversion of dye-sensitized photoelectrochemical cells

Photosynthesis converts light into chemical-energy. Artificial photosynthesis aims to mimic photosynthesis, converting electromagnetic energy into fuel. During photosynthesis chlorophyll-P680 absorbs photons causing electron photoexcitation, excited electrons transfer to pheophytin then the chloroplast electron transport chain, separating the oxidised chlorophyll-P680 and free electron.³ Oxidised chlorophyll-P680s undergo the Kok Cycle and free electrons produce NADPH. Artificial photosynthesis encompasses similar processes but typically utilises more broadly absorbing chromophore and Donor-Chromophore-Acceptor setups comprising versatile functional groups promoting charge separation, demonstrated in figure 2.

Pushing and pulling excited electron/hole to acceptor/donor respectively, forming donor⁽⁺⁾-chromophore-acceptor⁽⁻⁾, allows favourable rates and electron transfer.⁴

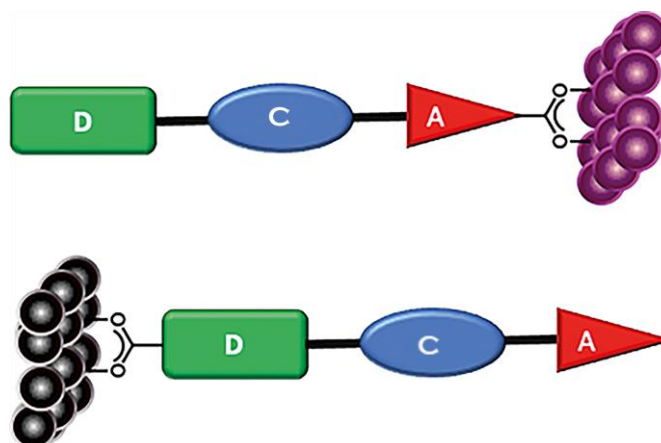


Figure 2. simplified diagram of Donor-Chromophore-Acceptor for WOC and HEC setups.

1.3 Kok Cycle & Water Oxidation Catalysis_(WOC)

Oxidised chlorophyll-P680 undergoes the Kok Cycle. Oxidised chlorophyll-P680 remove an electron from a surrounding tyrosine, reforming chlorophyll-P680 and generating a tyrosine radical.⁵ The radical will oxidise a surrounding Manganese active site, removing an electron from absorbed oxygen atoms. This process, repeats 4 times until completion of the Kok cycle, producing O₂, H⁺ plus free electrons.

Artificial photosynthesis water oxidation catalysis mimics this via various less well understood water oxidation mechanisms. The basic processes are essentially identical the hole will transfer from the oxidised donor to the catalyst where absorbed water is oxidised.⁶ Oxidation is often thermodynamically unfavourable, unpaired valence electron ruthenium catalysts with good energy overlap for faster rates and hole stabilising electron donating substituents mitigate this.

1.4 NADPH Production & Hydrogen Evolution Catalysis_(WOC)

The free electron produces NADPH.⁵ Free excited state electrons, transport through the chloroplast electron transport chain and ultimately accumulate at chlorophyll-P700. The chlorophyll-P700 again absorbs light for electron photoexcitation, allowing the excited state electron to reduce NADP⁺ to NADPH in Ferredoxin-NADP(+) reductase.³ The oxidised chlorophyll-P700 are reduced via accumulated electrons.

Artificial photosynthesis hydrogen evolution catalysis mimics this basic processes. WOC excited electron transferring to the counter electrode, where the free electron will reach accumulated donor⁺-chromophore-acceptor⁻ (D⁺-C-A⁻) reducing the acceptor hole. First the acceptor-chromophore-donor setup chromophore undergoes electron photoexcitation causing charge separation, eventually reaching the catalyst to reduce absorbed H⁺.⁷ Similar to water oxidation catalysis the process is often thermodynamically unfavourable so also utilise unpaired valence electron cobalt catalysts and favourable substituents.

2. MAIN BODY

2.1 Dye-Sensitized Photoelectrochemical Dyads_(DS-PEC)

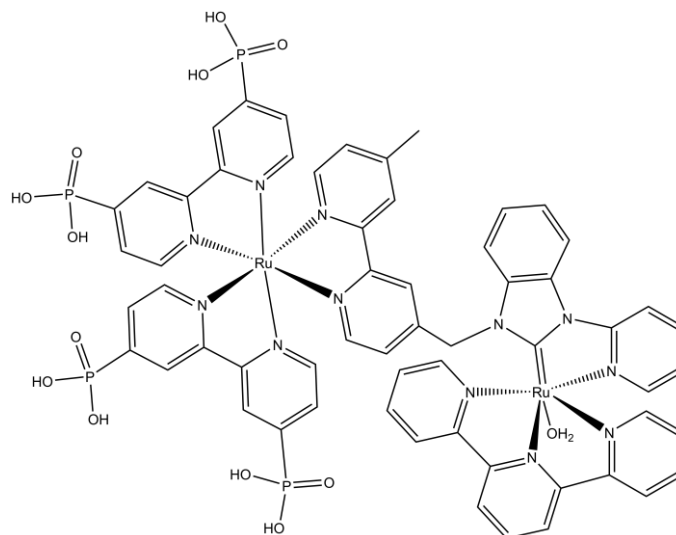
Dye-sensitized photoelectrochemical cells are promising developments towards photocatalytic hydrogen production but remain limited by re-combination processes and desorption.¹ Improvements focus on maximising chromophore absorbance, charge separation, catalyst efficiency and driving forces. Typically, heterogeneous transition metal complexes are studied as they offer greater electronic and structural tunability plus affable analysis but encompass many metal-to-ligand charge transfers potentially increasing non-productive alternative processes. The chromophore and catalyst are typically individual semiconductor surface assemblies, but one growing strategy is linking both Chromophore and catalyst into one dyad.⁸⁻¹³ This mini-review provides recent literature examples illustrating principles and challenges facing artificial photosynthesis, primarily focusing on transition metal complex chromophore-catalyst-dyads.

2.2 Water Oxidation Catalysis Dyad_(WOC)

2.2.1 Water Oxidation Catalysis Mechanism

The purpose of the WOC is to reduce the chromophore hole whilst oxidising water into O₂ and 4 H⁺, many catalysts have been proposed for this but most research focuses on Ru^{II}.

The exact mechanism is complex but Brennaman et al investigated this for Ru^{II}-Ru^{II} dyad, seen in figure 3, water oxidation catalysis.⁸ A simplified theorised mechanism:



- 1) $\text{TiO}_2\text{-[Ru}^{\text{II}}\text{-Ru}^{\text{II}}\text{-OH}_2\text{]}^{4+} \rightarrow \text{TiO}_2\text{-[Ru}^{\text{II}}\text{-Ru}^{\text{III}}\text{-OH}_2\text{]}^{5+}$
- 2) $\text{TiO}_2\text{-[Ru}^{\text{II}}\text{-Ru}^{\text{III}}\text{-OH}_2\text{]}^{5+} \rightarrow \text{TiO}_2\text{-[Ru}^{\text{III}}\text{-Ru}^{\text{III}}\text{-OH}_2\text{]}^{6+}$
- 3) $\text{TiO}_2\text{-[Ru}^{\text{III}}\text{-Ru}^{\text{III}}\text{-OH}_2\text{]}^{6+} \rightarrow \text{TiO}_2\text{-[Ru}^{\text{II}}\text{-Ru}^{\text{IV}}\text{=O]}^{4+}$
- 4) $\text{TiO}_2\text{-[Ru}^{\text{II}}\text{-Ru}^{\text{IV}}\text{=O]}^{4+} \rightarrow \text{TiO}_2\text{-[Ru}^{\text{II}}\text{-Ru}^{\text{II}}\text{-OH}_2\text{]}^{4+}$

Transient Absorption Spectroscopy and Spectro-electrochemical data reportedly indicating each species, although dyad metal-to-ligand charge transfer and alternative processes massively increased analytical complexity.⁹ Only investigating 4.6(pH), while catalysis is effected by pH.

2.2.2 Donor-Chromophore-Acceptor (D-C-A)

One of the limiting factors in water oxidation catalysis is alternative processes and unfavourable charge separation, utilising a D-C-A dyad limits this. Wang et al investigated the effects of different D-C-A groups, seen in figure 4, on water splitting with a focus on mimicking photosynthesis processes.¹⁰

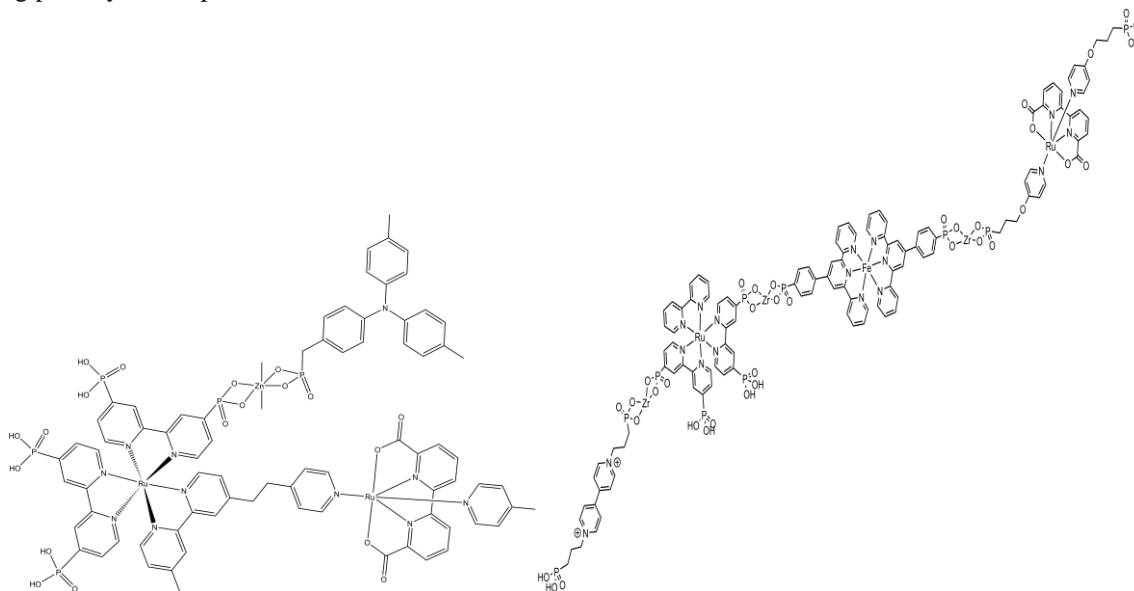


Figure 4. RuP (TPA)(Cat)²⁺ & MV²⁺-S-Fe^{II}-Ru^{II} dyads respectively Wang et al studied

RuP(TPA)(Cat)²⁺ dyad transient absorption, showing catalyst to TPA oxidation ~3.6 ns and radical TPA to chromophore 827ps or competing catalyst directly to Ru-chromophore ~28 ps. Photocurrent comparison of RuP(TPA)(Cat)²⁺ and RuP(Cat)²⁺ control show control initial photocurrent was higher before decreasing ~50 % over minutes but electron donating (TPA) containing photocurrent initially charged slightly before reaching 0.58 mAcm⁻² maximum also seemingly increasing surface stability against control over 16 h.

Investigating MV²⁺-S-Fe^{II}-Ru^{II} spectro-electrochemical and transient absorption data too.¹¹ Notably the electron withdrawing MV²⁺ bridge significantly increased charge separation lifetime and increased oxidation of -Fe^{II}, against control. Water oxidation was

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assessed under 1 sun at 4.65 pH, $\sim 250 \text{ A/cm}^2$ maximum photocurrent at $\sim 30 \text{ s}$ but decreasing over 1 h to $50 \mu\text{A/cm}^2$ and 67 % faradaic efficiency.

Interestingly the electron withdrawing MV^{2+} and electron donating TPA, push-pull techniques work well for charge separation against control but the major decrease in photocurrents over time might suggest desorption is occurring however this would ideally require a more detailed study possibly also investigating the effect to which different substituents effects charge separation rate.

2.3 Hydrogen Evolution Catalysis Dyad

2.3.1 Dyad Charge Accumulation

The purpose of the HEC is to reduce H^+ to H_2 but its typically a slow process relative to light absorption and electron transfer, often leading to a mismatch in dyad rates.

Bold et al investigated the photo-electrochemistry and TON of phosphonate-ruthenium-tris-diimine linked via triazole-bridged to cobalt-diimine-dioxime dyad, seen in figure 5.¹²

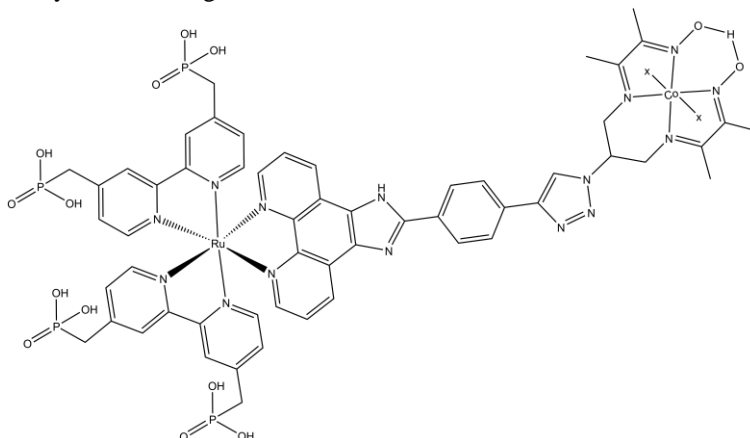


Figure 5. Dyad studied by Bold et al when x characterises a halide

Computational data indicating $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ reduction is thermodynamically unfavourable $\sim +0.36 \text{ eV}$, supported via time-resolved spectroscopy reporting 12 % active Co^{I} formation. Rate data illustrated charge separation is favoured at 45 ps and recombination is disfavoured at $\sim 4 \mu\text{s}$, supporting Co^{I} formation being limiting. Surprisingly, the dyad performed relatively well at AM1.5G, 5.5 pH, 2h with $84 \mu\text{A}\cdot\text{cm}^{-2}$ photocurrent, 26 % faradaic efficiency and 13 TON. Post-operando analysis however indicated, undesirable desorption with a $\sim 80 \%$ UV-Vis absorbance decrease and hydrolysis of the diimine ligand via time-of-flight secondary ion mass spectrometry illustrated via 1224 peak, theorised to result from charge accumulation.

Lyu et al similarly investigated cobaloxime-complex however tried a pyridyl-functionalized axial coordination to ruthenium-diacetylide as illustrated by figure 6.¹³

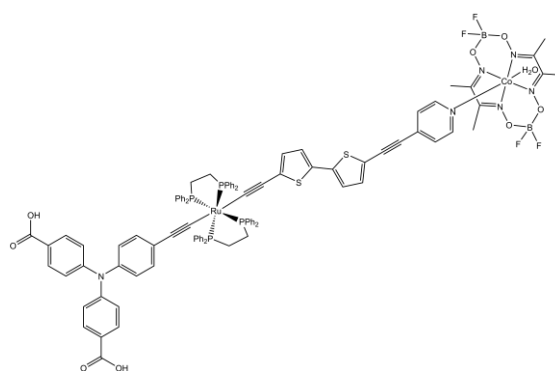


Figure 6. Dyad studied by Lyn et al.

Cyclic voltammetry and computational data indicated the system was more energetically favourable. HOMO spanning the entire π -conjugated system with electron density on the anchoring groups, making electron transfer to dyad hole favourable and LUMO electron density localized on pyridine-Co, making excited electron transfer to the catalyst barrierless. However arguably the system is less efficient under 1 Sun, 4.5 pH with $\sim 5.6 \mu\text{A}\cdot\text{cm}^{-2}$ photocurrent, 27 % faradaic efficiency although different operating condition are utilised.

The lacklustre performance is again theorised to result from slow cobalt centre kinetics causing charge accumulation illustrated via linear sweep voltammogram traces before reaching equilibrium, cathodic photocurrent spikes when the light is switched on and

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small anodic spikes when the light is switched off not observed in control. ~60 % slow photocurrent decrease is observed attributed to leaching.

Against direct bonding, pyridyl coordination substantially reduced photocurrents but decently improved dyad stability although both still appear limited by charge accumulation. Dyad stability and TON are seemingly affected by charge accumulation even when the system is energetically favourable with good orbital overlap and reduced alternative processes, although some of the bond cleavage negatives can seemingly be mitigated utilising coordination systems.

It's not just the catalyst that causes charge accumulation, slow chromophore electron transfer can also cause dyad charge accumulation limiting TON and stability. Charalambidis et al investigated porphyrin-cobalt diimine-dioxime dyads, seen in figure 7, photophysical properties.¹⁴

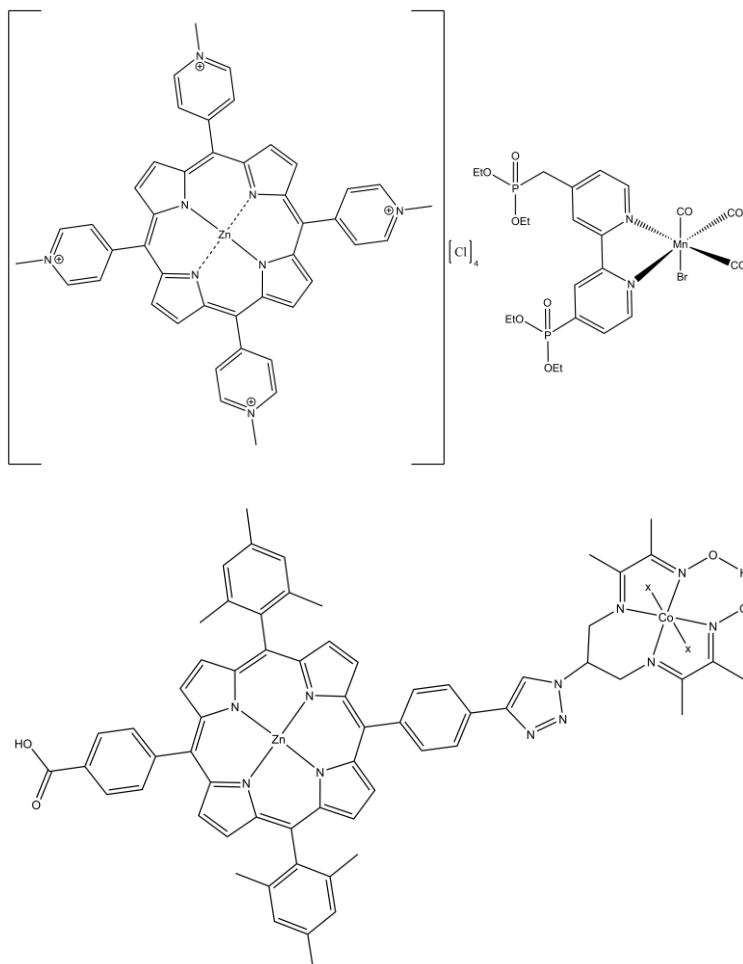


Figure 7. Dyad studied by Shipp and Charalambidis et al when x characterises a halide

Dyad cyclic voltammetry analysis of catalytic couples and porphyrin excitation were used to estimate $-1.13 \Delta G^\circ$ thermodynamic favourability for this electron transfer. Dyad linear sweep voltammograms at 2h, 5.5-7 pH showed a 7 nmolcm^{-2} hydrogen production and 8 % Faradaic Efficiency. Post-operando characterization of the dyad indicated desorption of ~40% and a Q-band indicating possible porphyrin demetallation. Desorption and Q-band are theorised to result from charge accumulation, indicating inefficient electron transfer to the catalyst although thermodynamically favoured, absorption peaks indicated weak interactions in the dyad ground state.

Shipp et al also investigated Zn-Porphyrins, seen in figure 7, electron transfer but for separately absorbed chromophore catalyst species and CO_2 to CO Mn^{I} Catalysis.¹⁵ Finding first and second reductions of catalyst by the photoexcited porphyrin are thermodynamically unfavorable $1.7 \Delta G_{\text{et}}$ and 1.8 V , explaining the observed slow rate of CO_2 reduction. Supporting charge accumulation theory and highlighting these issues aren't exclusive to dyads.¹⁶

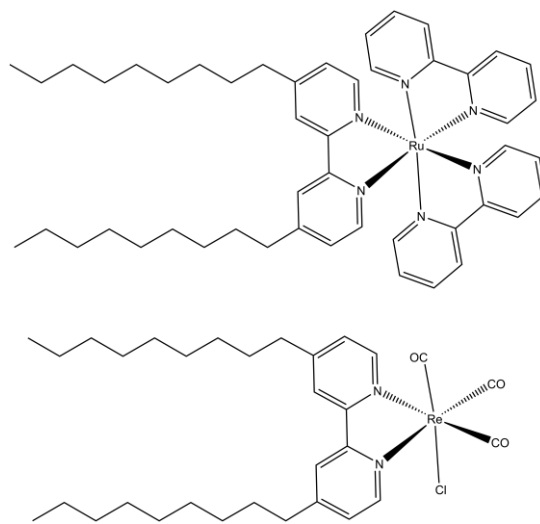


Figure 8. Dyad structure for liposome incorporation

Table 1: Dyad metrics for comparison of TON, FE and Photocurrent.

Dyad	TON	FE(%)	Photocurrent(μAcm^{-2})
Lyu	-	27	~5.6
Bold	5	26	84
Wang	-	83	-
Wang	-	67	50

Comparing the dyads with the data provided in table 1, its clear Dye-sensitized photoelectrochemical cell dyads are still in early development. Almost all dyads photocurrent decreases after 1h, indicating dyad desorption is a major issue, one possible alternative is to utilise a liposome incorporating structure seen in figure 8 although for dyads this isn't as well studied.¹⁷

3. CONCLUSION

This brief literature review has compared different techniques employed by individual dyads. Although it remains clear dye-sensitized photoelectrochemical cells are still in very early development, it's proving to be a promising development for conversion of photons into fuel.

Dyads generally seem to offer swift analysis of chromophore and catalyst photochemical properties but with added analytical complexity. Push-pull techniques have largely been implemented successfully and offer energetically favourable charge transfer at improved rates. For dye Sensitized Photoelectrochemical Cell dyads however this has been indicated as not being enough for sustained high photoconversion, as if the rate of electron donation and catalysis aren't roughly equal charge accumulation will cause dyad cleave and limit catalysis. Almost all dyads indicated some form of desorption was occurring and with in-depth dyad studies this remains unclear but again charge accumulation and pH dependence are suggested as possible reasons. Further work will hopefully aim to illuminate the causes of desorption and implement strategies to limit charge accumulation such as TPA tyrosine bridge and liposome incorporating structure.

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